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**Study of Semiconductor Valence Plasmon Line
Shapes via Electron Energy-Loss Spectroscopy
in the Transmission Electron Microscope**

M.K. Kundmann
(Ph.D. Thesis)

November 1988

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Department of Physics
University of California at Berkeley

and

National Center for Electron Microscopy
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory

Berkeley, CA 94720

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Study of Semiconductor Valence Plasmon Line Shapes via Electron Energy-Loss Spectroscopy in the Transmission Electron Microscope

Michael Karl Kundmann

Abstract

Electron energy-loss spectra of the semiconductors Si, AlAs, GaAs, InAs, InP, and Ge are examined in detail in the regime of outer-shell and plasmon energy losses (0-100eV). Particular emphasis is placed on modeling and analyzing the shapes of the bulk valence plasmon lines. A line shape model based on early work by Fröhlich is derived and compared to single-scattering probability distributions extracted from the measured spectra. Model and data are found to be in excellent agreement, thus pointing the way to systematic characterization of the plasmon component of EELS spectra. The model is applied to three separate investigations.

First, variations in the Si plasmon line shape are detected and quantified via least-squares analysis of measured plasmon lines based on the derived model. Broadening of the plasmon line with decreasing specimen thickness is found. The broadening becomes particularly pronounced at thicknesses less than 30nm. Significant broadening is also found in amorphous versus crystalline silicon. No change in the plasmon energy or in the functional form of the plasmon line is observed in association with the line broadening.

Next, the line shape analysis technique is employed in the detailed measurement and comparison of the plasmon line shapes of the semiconductors listed above. By comparing the measured plasmon energy with the free-electron plasmon energy of the valence electrons in each case, it is found that, in all but the In semiconductors, the upward shift of the plasmon energy due to coupling with lower-energy interband transitions is dominant over a downward shift due to the polarizability of the ion cores near the plasma frequency. These two effects seem to balance out in the In semiconductors due to the presence of the relatively weakly bound (19eV) In $4f$ electrons, which enhance the core

polarizability at the plasma frequency ($14.8\text{eV}/\hbar$).

Finally, since the power-law background model (used to extract ionization edge intensities for EELS elemental analysis) breaks down in the low-loss (20-50eV) regime, the suitability of the plasmon model as a replacement for the power law in this particular case is examined. Indications are that low-energy ionization edges, such as Ga $M_{4,5}$ or In $N_{4,5}$, can indeed be extracted from the strong plasmon background upon which they ride.

To the zeroth-order terms of my interaction Hamiltonian

*Mom and Dad,
Marc, Tom, and Tony,
and
Roseann*

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CHAPTER 1

Introduction

This dissertation describes experimental studies of semiconductor electron energy-loss spectra in the bulk valence plasmon excitation regime. Specifically, the energy-loss spectra of 100keV electrons transmitted by thin ($\leq 100\text{nm}$) Si, InP, InAs, GaAs, AlAs, and Ge samples have been measured and analyzed in detail in the 0-100eV (*low-loss*) range. Particular attention has been directed towards precise characterization of the dominant feature of these spectra, the bulk plasmon peak. This important component of energy-loss spectra represents the probability distribution for the excitation of collective valence electron oscillations, a quantum of which is denoted by the term *plasmon*. The shape and energy of the plasmon peak are characteristic of the plasmon excitations of a solid, and these in turn are a function of the solid's atomic-scale properties. The overall goal of this work is to achieve refined measurements of plasmon line shapes and energies for various semiconductor samples and to correlate the results with the other known properties of these materials. The hope is to develop the potential of plasmon spectroscopy as a tool for materials characterization and thereby further the microanalytical capabilities of electron energy-loss spectroscopy (EELS).

The motivations for such a study are two-fold. From a fundamental perspective, it is of interest to determine and understand precisely how plasmons are influenced by changes in specimen structure or composition. Although the basic properties of plasma-mode excitations in solids have been well-understood since the 1950's, theoretical considerations alone cannot, at the present time, predict precise plasmon energy shifts, changes in damping, or other alterations of the overall plasmon line shape associated with

particular modifications of a solid. Thus experimental investigation of these effects is in order. Semiconductors of diamond and zinc blende structure have been chosen for this study as they represent a set of related materials which are particularly amenable to plasmon line shape analysis. Due to the nature of their band structures and the associated partial localization of their valence electrons into covalent bonds, the plasmons of these semiconductors display many interesting energy shift and damping effects on account of their interactions with the single-electron band and core-level states and their transitions. This is in contrast to the simple free-electron-gas behavior of plasmons in simple metals. On the other hand, unlike the strongly damped plasmons of ionic and insulating solids, semiconductor plasma modes, as a result of the disparity between the plasmon and band-gap energies, are sufficiently well-defined to conform to a relatively simple theoretical description.

On the practical side, additional motivation for a detailed understanding of the connection between the plasmon line shape and other specimen properties arises out of the potential materials characterization applications of plasmon spectroscopy. Recently, EELS has been the subject of a great deal of technical development primarily because of its ability to provide chemical composition information with $\sim 1\text{nm}$ spatial resolution when combined with the latest generation of transmission electron microscopes. Although the plasmon-regime signal is by far the strongest in EELS spectra, it is generally ignored due to the difficulty of interpreting this part of the spectrum. The present work seeks to establish methods for analyzing plasmon EELS data for the particular case of semiconductors and to shed some light on what may be gained from it.

1.1. Background

Since electron energy-loss spectroscopy and plasmons are the central topics of this dissertation, a brief review of these subjects follows in order to provide background for the discussion and to establish the context of the present work.

1.1.1. *Transmission EELS and Plasmons*

For the purposes of the present study, energy-loss spectroscopy has been carried out in conjunction with transmission electron microscopy (TEM). Besides providing a ready-made probe for EELS, working in the TEM instrument has the added advantage of providing a well-resolved (better than 1nm resolution) image of the specimen area under study, allowing accurate targeting of the beam. With currently available TEM microscopes, stable monoenergetic electron beams with energies from 20keV to 1MeV and beyond are readily achieved. In general practice, beam energies of 100-200keV are standard. At such energies, normally incident electrons pass through as much as 100-200nm of material without being absorbed appreciably. Although not absorbed, these high energy electrons do interact with the sample, giving up energy to various kinds of excitations along the way. In EELS, the transmitted electrons are collected and their energy losses are measured to yield an energy-loss spectrum related to the excitation spectrum of the solid. Note that unlike the well-known surfac. EELS technique, in which electrons of much lower energy are reflected from sample surfaces, TEM EELS probes *bulk* material.

A typical setup for TEM EELS is illustrated schematically in figure 1.1. Electrons are accelerated at the top of the microscope column, impinge upon the specimen mounted near the middle of the column, and form either a specimen image or diffraction pattern (scattering-angle distribution) on a viewing screen at the bottom. This screen can be lifted to pass a selected portion of the projected electrons to a magnetic prism

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Figure 1.1 - Schematic view of TEM EELS apparatus and experimental configuration.

spectrometer below. The EELS spectrum is acquired electronically by sweeping the prism current and measuring, versus time, the electron intensity passing through a slit near the exit-face focus of the prism. A typical EELS spectrum obtained in this way is shown in figure 1.2.

Bulk valence plasmons (hereafter simply denoted *plasmons*) are the excitations most often induced by the electron probe in TEM EELS of most materials. Plasmons are responsible for the strong peak near 15eV in the sample spectrum of figure 1.2. In order to visualize what plasmons are, one can begin by thinking of a solid as a neutral plasma, its valence electrons forming a mobile, negatively-charged component which is balanced by its fixed, positively-charged ion-core component. Displacement of valence electron density from its equilibrium position relative to the ionic cores gives rise to a restoring force due to the electric field brought about by the associated polarization of charge. As a consequence, the valence electrons undergo oscillatory motion. When this motion at a particular core site of the solid has a definite phase relationship with that at other sites (as is likely to be the case when significant valence-electron wavefunction overlap occurs from site to site), oscillatory modes of the polarization completely analogous to true plasma waves result. The characteristic frequency of these plasma modes is called the plasma frequency, ω_p , of the solid. In the free-electron model, ω_p of the long-wavelength ($q \approx 0$) modes is given by

$$\omega_p = \left(\frac{4\pi n e^2}{m} \right)^{1/2}$$

where n is the valence electron density, e is the electron charge, and m is the electron mass. As in any microscopic system, the excitations of these collective, plasma-like modes of the solid are necessarily quantized, each quantum having energy $E_p = \hbar \omega_p$. It is precisely these quanta which are denoted by the term *plasmons*. Figure 1.3 gives a

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Figure 1.2 - Typical TEM EELS spectrum of a crystalline silicon specimen.

schematic illustration of a plasmon mode in a covalently bonded solid.

1.1.2. Historical Survey

Historically, progress in the understanding of plasmon excitations in solids and development of the EELS technique have been intertwined. Because the EELS spectra of most solids are almost completely dominated by plasmon-excitation events, energy-loss experiments first led to the discovery of plasmons and to an understanding of their nature. On the other hand, since plasmons are most easily generated and studied via energy-loss experiments with electron probes, the desire to study plasmons in greater detail spurred refinement of the EELS technique. The earliest electron energy-loss experiments were carried out in 1929 by Rudberg [1]. Further work by Ruthemann in 1941 [2] ultimately led to the discovery of plasmons. Ruthemann's observation of very pronounced loss peaks at integer multiples of 15eV in the spectrum of 3-8keV electrons transmitted by thin (~ 10 's of nm) aluminum films spurred theoretical efforts to determine the energy-loss mechanism which gave rise to them. At the time, the well-defined peaks were puzzling because it was not clear why one particular transition or excitation was so strongly favored or why the excitation energy deduced from the spacing of the energy-loss peaks did not match that of any known atomic transitions of aluminum.

The solution to the puzzle came with the introduction of the solid-state plasma model of metals. This model was first proposed by Kronig and Korringa [3] in 1943, and was developed by Pines and coworkers [4] into a successful theory of the characteristic energy-loss spectra of solids during the 1950's. Within this well-known *jellium* model, a metallic solid is viewed as a neutral plasma consisting of a mobile valence electron "sea" and a charge-compensating ionic background which is stationary and uniformly distributed. With this simple model, the characteristic energy losses observed in EELS could

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Figure 1.3 - Schematic picture of a plasmon mode in a covalent solid. Note that it may be viewed as both a density-fluctuation (compressional) wave of the valence electrons and as a polarization wave of the complete solid.

be explained and even their energies could be reasonably accounted for.

The 1950's saw considerable theoretical development of the plasmon concept and significant improvements in the data provided by EELS experiments. In 1952, Pines and Bohm [5] first proposed that, in addition to single-particle transitions or ionizations, collective plasmon excitations contributed to the energy losses measured in EELS experiments and that these excitations accounted for the characteristic loss peaks observed by Ruthemann. In support of this proposition, they were able to show that energy losses to these collective excitations should occur in units of $\hbar\omega_p$, and that calculated values of this quantity closely matched the energies of the observed characteristic loss peaks. For example, taking the case of Al with three valence electrons, the expression for the plasmon energy given in section 1.1.1 yields $E_p=15.8\text{eV}$, fairly close to the observed 15eV. Besides this quantitative agreement, the uniqueness of the plasmon excitation explained the dominance of a single, strong excitation in the spectrum.

This success spurred a flurry of EELS experiments with refined instruments on a wider range of materials to test the general validity of the plasmon theory [6]. From the point of view of the EELS technique, two significant improvements were introduced at this point. First, new spectrometer and electron source designs brought spectrum energy resolution down to .0015-.0030% or 1-2eV. Second, some of the spectrometers were incorporated into electron microscopes to facilitate positioning and monitoring of the sample area under study. With the higher energy resolution, deficiencies of the simple valence plasmon excitation model began to appear, while the expanded results from other metals showed that strong, sharply-defined characteristic peaks such as those of Al are not a universal phenomenon. The new results gave peak positions and, especially, inherent peak widths which did not appear to be consistent with the plasmon loss theory.

Further work by Wolff [7] and Nozieres and Pines [8], however, demonstrated that the majority of the characteristic loss peaks were still consistent with plasmon excitations. Apparent discrepancies in plasmon energy could be attributed to plasma frequency shifts resulting from interaction between the plasma mode and the periodic lattice potential and core-electron polarizability, while inherently broad plasmon lines were found to be the result of plasmon damping or decay into single-particle intra- and interband transitions. Furthermore, the possibility of plasma oscillations beyond the free-electron approximation was established, thus explaining why EELS detects pronounced plasmon peaks not only from nearly-free-electron metals, but from other materials (eg. semiconductors), as well.

Another important theoretical development at this time was the elucidation of the role played by the complex dielectric function, $\epsilon(\omega, \mathbf{q})$, in characteristic energy loss experiments and its connection to plasmon properties and dispersion. In 1954, Fröhlich and Pelzer [9] first derived an expression for the energy-loss probability distribution using a macroscopic, phenomenological approach. They showed that the energy-loss spectrum is directly proportional to $\text{Im}\{\epsilon^{-1}\}$ and that the zeroes of ϵ (and therefore the peaks in $\text{Im}\{\epsilon^{-1}\}$) give the frequencies of free oscillations of longitudinal electric fields in a solid. Since precisely such fields are set up by plasma-mode charge density oscillations, this provided an alternate path to the determination of plasmon energies and established the intimate link between plasmons and the dielectric function.

Ultimately, a quantum-mechanical many-body treatment of electron motion in solids by Nozieres and Pines [10,11] provided expressions for $\epsilon(\omega, \mathbf{q})$ from microscopic considerations of the electronic structure and in turn provided a first-principles theory of plasmon properties such as frequency shifts, damping, and dispersion. This work also elu-

culated the role of screening, showing that individual valence electrons of a solid are screened from the EELS probe electrons by the collective plasma motion, at least for small momentum transfer, q . This explained why the EELS spectra of many materials were found to be dominated by the plasmon excitation peak and did not show any of the characteristic structure one might expect from interband transitions.

The 1960's brought further refinements in the understanding and measurement of EELS spectra. On the theoretical side, additional energy-loss mechanisms were proposed to account for more of the fine structure observed in the spectra. Among the most important are various plasma oscillation modes associated strictly with surfaces and interfaces, and Čerenkov radiation losses. On the experimental side, efforts to improve EELS measurements continued, the efforts being driven by the desire to resolve inconsistencies and deficiencies in the experimental data available at that time. The need for more accurate energy-loss measurements with higher resolution shifted focus from electron microscope-based systems to specialized EELS set-ups with deceleration as well as acceleration stages and pre-specimen energy filters. The former reduced errors due to instabilities in beam energy and allowed for higher energy dispersion, while the latter improved resolution by reducing the spread in the incident beam energy. The bulk of the experimental work was directed at testing the theoretical predictions of surface plasmon and Čerenkov losses and exploring the connection between optical and energy-loss experiments via $\epsilon(\omega, q)$ [12-14].

In the late 1960's and early 1970's, the EELS technique once again became strongly associated with transmission electron microscopy as focus shifted to development of EELS for chemical microanalysis to supplement the structural characterization of samples in TEM instruments [15, 16]. For this application, the low-probability loss events above 100eV involving ionizations of core electrons became of interest. Due to the tight binding

of core electrons (particularly K- and L-shell electrons), these ionization events give rise to "edge" features in the EELS spectrum that are not strongly affected by the solid state. Hence, core edges are characteristic purely of the atomic species present in the sample and their intensities reflect the elemental composition of the probed specimen. Since the EELS spectrum has very low intensity above 100eV and includes significant background from valence excitations, a number of technical improvements were required to access core-edge information. Detection systems based on photographic emulsions were replaced by more sensitive electronic systems capable of single-electron counting and having an expanded dynamic range. Digitization of the data, combined with the need for mathematical processing to extract composition information, led naturally to the incorporation of computers into TEM EELS systems [17-19]. This development was greatly facilitated by the small-computer revolution of the late 1970's so that computer-controlled collection, storage and on-line analysis of spectra are now standard features of TEM EELS instrumentation.

Although the major efforts in EELS during the 1970's focussed on technical improvements related to ionization edge detection and analysis, fundamental work relevant to plasmons continued. On the theoretical side, improvements in band structure calculations led to detailed calculations of $\epsilon(\omega, \mathbf{q})$ including so-called local-field effects [20, 21]. Basically, local-field effects give rise to a directional dependence of ϵ on a microscopic scale and are a result of the non-uniform, anisotropic valence electron density associated with directional bonds in a solid, such as the covalent bonds of semiconductors. Inclusion of these effects yielded the first theoretical calculations of plasmon line shapes beyond the jellium model. In response, several experimental studies of such directional effects on plasmon EELS spectra were carried out by measuring the plasmon peak and width dispersions along different crystallographic directions in a number of tetrahedral

semiconductors. Although the data are limited, small but significant differences between the plasmon peak dispersions along $\langle 100 \rangle$ and $\langle 111 \rangle$ were observed in Si, GaAs, and InSb for $|\mathbf{q}|$ (plasmon momentum) greater than about 9nm^{-1} [22,23]. In addition, the first practical plasmon line shape models were developed and tested for accuracy in connection with the above dispersion studies [24], as these required precise measurements of the plasmon energy and half-width.

1.1.3. Present Status

Work towards a detailed understanding of plasmon line shapes and properties continues (eg. see review by Sturm [25] or recent theoretical work by Egri [26]). Although much is now known about plasmons and about the correlation between the electronic structure of a material and its plasmon excitations, it is not yet possible to calculate either the plasmon EELS spectrum or even simply the plasmon energy and linewidth to the accuracy to which they can be measured. As a consequence, the information provided by the plasmon EELS spectrum of a given material cannot be directly interpreted in terms of its physical properties by theory alone.

This fact is reflected in the current state of electron energy-loss spectroscopy. Although EELS core-edge analysis for determination of specimen chemical composition is a highly developed and fairly routine technique, extraction of electronic structure information from plasmon-regime EELS is still a highly specialized topic addressed in only a few research labs around the world. This is unfortunate in light of the rapid technological development and refinement of EELS over the past decade as a result of its close association with transmission electron microscopy. This development has made EELS the best candidate for spatially-resolved spectroscopy of materials with sub-nanometer resolution. For example, currently available scanning TEM (STEM) microscopes, which use

high-quality *pre*-specimen optics to focus the incident electron beam to a small spot, are capable of 0.5nm probes, while presently available high-resolution TEM instruments, which use high-quality *post*-specimen optics to collect and project scattered electrons to a phosphor screen, achieve better than 0.2nm lateral resolution in images. A number of reports on new applications of EELS made possible by these technical advances have appeared in the literature [27,28].

Several factors have contributed to the neglect of plasmon-regime EELS information. One factor is that the features of low-loss EELS spectra are often indistinct since they can comprise overlapping collective and single-particle excitations as well as convolutions of the two due to multiple scattering. As yet, there has been no standard approach to unraveling these various spectrum components. Another factor is that, in general, analytical microscopists have tended to ignore low-loss EELS because of their greater concern for chemical composition information. Finally, it is often thought that, since plasmons are fairly well described by the results of the free-electron model, the only information they can provide is the valence electron density, which is usually not a particularly interesting piece of information about a material.

In light of the latest theoretical work on semiconductor plasmons, however, it is clear that the plasmon peak can be sensitive to electronic structure effects beyond the free-electron and jellium models. Interactions of the plasma mode oscillation with single-particle transitions among the valence and conduction bands and with the core-electron polarization leads to shifts in the plasmon energy. Plasmon decay via band transitions leads to plasmon broadening. Additional effects of the periodic potential of the solid, such as local-field effects, give rise to variation of the plasmon energy and half-width with both the magnitude and direction of the plasmon momentum. Presently, it is known that a

combination of the above has subtle but observable influences on the plasmon line shape. The relative importance of the various effects, however, is not known. With the improvements in EELS instrumentation that have occurred over the past decade, these subtle effects are becoming easier to detect and measure accurately with readily available apparatus. The time is therefore ripe for expanding and updating the body of experimental plasmon data so that more detailed comparisons of experimental and theoretical results can be made and ultimately a clearer picture of the plasmon excitation in non-jellium solids is achieved. In addition, it is likely that such an endeavor will provide the fundamental understanding and practical techniques needed to develop the materials characterization potential of plasmon-regime EELS.

1.2. Contributions of this Thesis

The work described in the chapters to follow makes a number of contributions within the context established above:

- Since there are no generally established procedures for handling plasmon-regime EELS data, a method for analyzing the low-loss spectra of semiconductors into their essential component signals is proposed. The most significant aspects of the method are that the effects of multiple scattering are removed and that the plasmon peak is isolated by least-squares fitting a theoretically-based line shape model to the single-scattering EELS spectrum. The multiple scattering correction is achieved by working with angle-integrated data and applying Fourier-log deconvolution. The line shape model is derived from the theory of electron energy loss in solids based on the complex dielectric function and is an angle-integrated version of the model proposed by Hinz and Raether [24]. It will be shown that this approach provides a systematic and precise means for detecting subtle distinctions between the plasmon energies and linewidths of different samples. Furthermore, since the line shape model used in the analysis involves fundamental parameters, rather than being strictly empirical, this method provides a connection between the observed plasmon EELS spectrum and more basic physical properties of a material.

- Using the above method in conjunction with the spatially resolved capabilities of TEM EELS, subtle variations in the Si plasmon line shape with specimen characteristics have been explored. Specifically, variations in plasmon energy and linewidth were measured as a function of specimen thickness and proximity of morphological features such as bounding free surfaces and an internal grain boundary.

- In a further application of the technique, refined plasmon line shape measurements have been carried out on crystalline samples of Ge, AlAs, GaAs, InAs, and InP. Although

the plasmon *energies* for some of these materials have been reported previously in the literature [29], this is the first time complete single-scattering plasmon-regime spectra have been measured for all of them on a single experimental set-up and analyzed with a consistent, well-defined procedure. As a consequence, the spectra could be compared directly to a high level of precision in order to meaningfully assess the subtle differences between the plasmons of these related materials. An attempt has been made to correlate these distinctions with known differences in the electronic energy-level structures of these semiconductors.

- Finally, the possibility of using plasmon line shape modeling techniques to improve background models for EELS microanalysis has been considered. It has been found that the plasmon component of low-loss spectra can indeed be removed by fitting and subtracting the plasmon line shape model, thus overcoming one barrier to the application of the relatively high cross-section ionization edges of low-loss EELS to composition analysis.

1.3. Outline of the Dissertation

The main body of this thesis is organized into five chapters. Chapter 2 discusses experimental details such as instrumentation, specimens, and optimized data collection techniques. Chapter 3 describes the procedure developed to analyze the data, its theoretical basis and specific implementation. Chapters 4-6 comprise the heart of the experimental work. Chapter 4 reports on spatially-resolved line shape variation studies in Si, chapter 5 discusses the measurement and comparison of the plasmon line shapes of other semiconductors, and chapter 6 treats the applicability of plasmon line shape modeling to the background subtraction problem in low-loss EELS quantitative analysis. A concluding chapter summarizes and integrates the findings.

CHAPTER 2

Experimental Setup and Procedures

Electron energy-loss spectroscopy, particularly in conjunction with transmission electron microscopy, is a well-established technique. There is a considerable literature describing TEM EELS in general terms as well as providing technical details of its application. It is treated thoroughly in selected chapters of several general analytical TEM books [30,31] and the recent book by Egerton [32] serves as an excellent reference text for the technique. Nevertheless, there are many adjustable parameters in any TEM EELS setup and in order to obtain the best results for a given purpose, the conditions under which the data are collected must be considered carefully. In addition, a delineation of the setup is important to the subsequent interpretation and evaluation of results. The present chapter gives details of the instrumentation and experimental conditions used in this study. Since some effort was expended to optimize the collection of plasmon EELS spectra and since the optimized procedures were followed fairly consistently throughout the experimental work, discussion of this topic has been relegated to a separate chapter. Besides allowing a more coherent treatment of the experimental details, covering this material at the outset will make for smoother, digression-free discussion in later chapters.

2.1. Apparatus

At the core of the experimental setup is a transmission electron microscope with an appended 90° magnetic prism for electron energy analysis. The TEM instrument is ideally suited for transmission EELS experiments. It provides a ready-made, monoenergetic beam of electrons, electron optics for shaping and manipulating the beam both before and after interaction with the target, a convenient specimen stage, and various apertures to apply selection criteria to the events collected by the spectrometer. A fairly realistic cross-sectional view of the system used here is given in figure 2.1. Further details about the system components are given in the subsections below.

2.1.1. Electron-Optical Column

The electron optical column is that of the Philips EM400 transmission electron microscope, comprising an electron source, pre-specimen optics, specimen stage, post-specimen optics and a viewing screen. In the EM400, the source is a heated LaB_6 crystal within the cathode. A large negative voltage applied to the cathode with respect to the grounded anode accelerates the thermally emitted electrons to near-relativistic kinetic energy. The accelerating voltage (and thus the incident beam energy) can be varied within the 20-120kV range ($\beta=v/c=0.3-0.6$). Despite the high beam energy, the FWHM energy spread of the beam is only about 1eV or .001%.

The pre-specimen optics or *condenser* system, consists of apertures and magnetic solenoid lenses and deflectors which permit shaping, focusing, and manipulating the incident beam or *probe*. The focal lengths of the condenser lenses (as well as all the other lenses along the column) are continuously variable and allow a range of incident beam conditions to be achieved. At one extreme, a large area (up to .2mm in diameter) of the specimen is illuminated by forming an image of the source at a considerable distance from

Figure 2.1 - Cross-sectional view of microscope/spectrometer system used for the TEM EELS experiments.

the specimen plane, as shown in the left half of figure 2.2. This mode achieves approximate plane-wave illumination (angular divergence $\sim 0.05\text{mrad}$) at the specimen and is useful for experiments requiring good angular resolution. At the other extreme, illustrated on the right of figure 2.2, a demagnified source image is formed precisely at the specimen plane to probe the smallest possible area (down to 40nm). This mode is often applied to spatially resolved studies of a specimen. Augmenting the action of the lenses, the condenser aperture further prepares the beam by restricting the incident angular range. Insertion of a sufficiently small aperture while operating in probe mode allows good spatial and angular resolution to be achieved simultaneously (see dotted rays in right half of figure 2.2), although at great cost in beam intensity. Finally, dipole deflectors allow the beam to be precisely positioned onto a particular region of interest.

The specimen stage resides at the end of a rod inserted through the side of the microscope column (see figure 2.1). The specimen itself, in the form of a 3mm disk or grid with regions of interest thinned to 100nm or less, is mounted in the stage so as to intersect the optic axis of the microscope. Micrometer drives coupled to the specimen rod facilitate fine positioning of the specimen within the column.

The post-specimen optics collect the electrons scattered by the specimen and project a specimen image or diffraction pattern onto the phosphor viewing screen. This critical part of the electron-optical column is comprised of three main sections. First and foremost is the objective lens and its associated *objective* (angle-selecting) and *intermediate* (area-selecting) apertures (see figure 2.1). The objective lens is operated with a very short focal length ($2\text{--}3\text{mm}$) in order to achieve a number of desired ends. It permits the largest possible range of scattering angles to be collected from the target region, it provides a large first stage magnification by forming a specimen image at the relatively dis-

Figure 2.2 - Condenser system configuration for wide-area illumination (left) and for probe formation (right). Horizontal dimensions exaggerated by $\sim 50\times$ relative to vertical.

tant area-selecting aperture plane, and it provides a large angular *de*-magnification to facilitate subsequent beam transport. As an additional consequence, not necessarily desirable, the focal length of the objective is comparable to the physical extent of its magnetic field. Thus the specimen, necessarily placed near the front focal plane of the lens for high magnification, is actually immersed in a magnetic field of several kGauss. Furthermore, the Fraunhofer diffraction pattern, which appears at the back focal plane of the lens and provides a spatial map of scattering angles, is also in the lens field so that the angle-selecting aperture must reside within the lens, in close proximity to the specimen. Figure 2.3 gives a detailed illustration. Due to their placement at the first diffraction pattern and image planes, respectively, the objective and intermediate apertures apply additional selection criteria to the scattering events represented at the viewing screen and consequently influence the subset of energy-loss events ultimately included in the measured EELS spectrum.

The final two sections of the microscope column include the intermediate and projector lenses, which give several stages of magnification and yield the electron intensity pattern seen on the viewing screen. When the intermediate aperture plane serves as the object to the magnifying system, an enlarged specimen image appears at the viewing screen. Alternatively, when the objective aperture plane serves as the object, a magnified Fraunhofer diffraction pattern results. These two distinct modes of operation are called *image* and *diffraction* mode, respectively. In either case, the beam has a very small crossover (local minimum in its lateral dimension) near the back focal plane of the last lens of the magnifying system, a typical crossover dimension being a few μm . This gives rise to a very large depth of focus for the final projected image and the small crossover dimension is also important for the energy resolution of the EELS system, as discussed below.

Figure 2.3 - Detail of specimen and aperture placement within the objective lens system with illustrative ray diagram. Actual specimen to objective aperture distance is a few mm's. Horizontal dimensions exaggerated $\sim 50\times$ relative to vertical.

2.1.2. Spectrometer

The spectrometer system is attached immediately following the viewing chamber of the microscope column. Energy analysis of the transmitted (both scattered and unscattered) beam electrons is achieved by bending their mean trajectory through 90° in a uniform magnetic field, as shown in figure 2.4. Energy dispersion at the plane of the energy-selecting slit is $1.8\mu\text{m}/\text{eV}$ for 100keV beam energy. Pre-magnet lenses, in conjunction with the magnet fringe fields, act to focus a $\times 4$ demagnified image of the final beam crossover (mentioned above) onto the slit plane. Typically, the crossover image at the slit is $1\mu\text{m}$ or less in lateral dimension so that the limit it and the $1.8\mu\text{m}/\text{eV}$ dispersion impose upon the system energy resolution is considerably smaller than 1eV. As a result, the actual energy resolution achieved in acquired spectra is predominantly determined by the width of the slit (adjustable) and the $\sim 1\text{eV}$ energy spread of the incident beam.

Due to the large depth of image focus in the viewing area, a well-focused version of the viewing-screen image also appears at the spectrometer aperture plane. The only effect of the additional drift distance is a small enlargement (about $1.3\times$) of the image. The spectrometer aperture can therefore be used to apply one final selection criterion on the collected EELS events by passing only a small portion of the viewing screen image or diffraction pattern to the spectrometer. For example, if a specimen image with $15,000\times$ magnification is projected onto the viewing screen, an image with $\sim 20,000\times$ magnification appears at the aperture plane. Thus, neglecting aberrations, a 1mm diameter aperture restricts the energy loss spectrum to a specimen region 50nm ($1\text{mm}/20,000$) across. If on the other hand a diffraction pattern with 150mm camera length appears on the screen, a 1mm aperture selects events within a 5mrad ($1\text{mm}/200\text{mm}$) range of scattering angles.

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Figure 2.4 - Illustration of combined crossover-imaging and energy-dispersing properties of magnetic prism. Only dispersion direction is shown. Focus in non-dispersion direction does not necessarily occur at slit.

2.1.3. Spectrum Acquisition Electronics

Spectra are acquired via an electronic signal chain which ultimately yields digitized energy-loss spectra suitable for computerized analysis. Initial detection and pulse processing electronics are part of the Gatan 607 EELS system. Its output is fed to a Kevex 7000 multichannel analyzer which in turn is interfaced to an LSI 11/2 microcomputer for computer-controlled acquisition, storage, and some processing of spectra (see figure 2.5).

The above system produces EELS spectra by measuring the electron flux as a function of position along the energy dispersion direction (vertical in figure 2.4) at the energy-selecting slit plane. Specifically, electron flux through the slit is measured by means of a scintillator/photomultiplier assembly which sends a pulse to a multichannel analyzer (MCA) for each electron passing through the slit. The analyzer counts the pulses for a fixed time interval to obtain a number directly proportional to the electron flux. The flux at different energy losses is sampled by changing the bending magnet current to position different parts of the dispersed beam over the slit. The MCA measures the energy-loss distribution by ramping the current to the bending magnet in fixed steps and counting electrons for a fixed time interval at each step. The resulting list of counts is precisely the desired EELS spectrum. A sample spectrum obtained in this way from crystalline Si can be found in the introductory chapter.

Calibration of the energy-loss scale is achieved through the use of a standard. A commonly used standard in TEM EELS and the one used to calibrate the data to be presented here is the π^* peak at the threshold of the K-shell ionization edge of evaporated amorphous carbon. The energy of this peak, reflecting single-electron transitions between the $1s$ and π^* orbitals of this material, is known from early EELS experiments and has a generally accepted value of 285eV. Assuming linear dispersion, taking the peak MCA

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Figure 2.5 - Schematic diagram of electronic spectrum acquisition signal chain.

channel of the elastic scattering (zero-loss) distribution to represent 0eV energy loss and determining the channel number of the π^* peak yields a calibration of the spectrum energy scale. Absolute accuracy of the calibration is dependent upon that of the standard, the latter being better than 1%. Reproducibility trials show the stability of the calibration in the course of an experimental run spanning several hours to be $\pm 2\%$ or better. Spectra are collected with 1024 channels of MCA resolution so that the finite channel width does not seriously affect the precision of the calibration. Over the range of energies of interest for plasmon line shape studies (0-100eV), nonlinearity of the energy scale is less than .1% and is completely negligible [33].

2.2. Specimens

In general, the specimens examined were taken from bulk crystalline samples and prepared using standard techniques for TEM specimen preparation. Many were courteously provided by other investigators in prepared form. Preparation procedures include initial mechanical cutting (via diamond saw or ultrasonic cutter) followed by grinding (using metallographic grits and polishing techniques) to yield a disk 2-3mm in diameter and less than 100 μ m in thickness. Final thinning to obtain electron transparent regions is achieved with either a chemical polishing solution or an ion mill (sputterer) trained on the center of the disk. The thinning procedures form a bowl-shaped depression in the middle of the disk and ultimately result in perforation, the hole being kept as small as possible. A schematic view of the "ideal" TEM specimen appears in figure 2.6. In principle, the specimen thickness goes continuously to zero at the perforation. In practice, perhaps $\sim$ 5nm at the perforation is more realistic. In any case, 50nm-thickness is readily obtained over sufficiently large specimen regions and yields reasonable electron transparency and good TEM EELS spectra. During experiments, specimen and beam are manipulated so that only the thinnest specimen areas are intersected by the beam.

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Figure 2.6 - The "ideal" TEM specimen, actual diameter 3mm.

2.3. Spectrum Acquisition Conditions and Procedures

As the experimental work here focussed on accurate and precise measurement of plasmon line shapes, the acquire-time conditions and data collection procedure were optimized accordingly. The flexibility of the TEM instrument makes it possible to control many parameters of the EELS scattering experiment. Among them are the intensity, angular range, and degree of localization of the incident beam, the incident beam energy, the range of scattering angles over which energy-loss events are collected, and the lateral size and thickness of the specimen area represented in the acquired EELS spectrum. Many of these have significant influence on the quality of acquired plasmon EELS data and are of particular concern in the present work.

For example, a very important factor is the average number of times a single beam electron undergoes inelastic scattering while traversing the sample. Multiple scattering gives rise to undesired sum features in the energy-loss spectrum which obscure the true shape of the plasmon line (see discussion of section 3.1.3). The amount of multiple scattering can be minimized by probing only the thinnest possible specimen areas and by using the highest possible incident beam energy in order to reduce the probability of repeated energy loss events. However, the probability of individual energy-loss events are also thereby reduced, leading to low count rates and associated problems with statistical noise and instrumental drift. As will be shown in chapter 3, multiple scattering can instead be mathematically removed from measured spectra, but this places yet other constraints on the data acquisition. Another concern relevant to accurate line shape measurement is the energy resolution achieved with the EELS system. Since the natural plasmon linewidth of semiconductors is usually 3-4eV, instrumental energy resolution better than 1eV is highly desirable. This can be achieved via appropriate adjustment of

the electron source and the spectrometer aperture and focusing, however, the overall spectrum count rate and, consequently, the quality of spectral data are thereby reduced.

In short, the optimization of experimental conditions for precision plasmon line shape measurement involves the simultaneous optimization of several inter-related parameters. Although any one parameter can quite easily be set for best results, the simultaneous optimization problem is considerably more complex and does not permit a clear-cut solution. The conditions and procedures ultimately settled upon here were arrived at empirically through several iterative stages, until the data obtained were suitable for the purposes of this study. The remainder of this chapter describes the specific conditions and procedures used to acquire EELS data for the present work and some of the considerations relevant to each choice of operating conditions.

2.3.1. Incident Beam

The most significant experimental parameters adjustable at the source are the intensity, energy, and energy half-width of the beam. The choice of beam energy is unambiguous, since TEM instruments are generally optimized to give best performance, specifically, highest imaging resolution and beam intensity, at the highest accelerating voltage. In addition, maximizing the beam energy yields the greatest penetration of a given specimen thickness, thereby keeping multiple scattering effects to a minimum. Although the Philips EM400 has a maximum accelerating voltage of 120kV, the particular instrument available for the present work unfortunately suffered from stability and discharge problems at this voltage. This made it impractical to collect large numbers of comparable spectra or to collect spectra with good counting statistics as conditions effectively changed too frequently. As a consequence, the next best choice, 100kV, was used instead throughout this study. The remaining two source parameters, intensity and energy half-

width, are unfortunately tied in an inverse relationship. It was deemed more important to minimize the latter than to maximize the former at this stage since low intensity can to some degree always be compensated by longer collection times. Thus, filament heating was kept below saturation and the bias voltage between filament and cathode was set to minimize broadening of the source energy distribution due to interactions between beam electrons.

The condenser system permits selection of the size of the illuminated specimen region, the incident angular range of the illumination, and again, indirectly, the incident intensity. Due to the low source intensity, the predominant concern in setting the condenser system was to transfer the greatest possible incident flux to the specimen. Although intuitively, it would seem best to demagnify (and thereby concentrate) the source as much as possible in order to achieve the highest flux, in practice, it was found that large spot size (low source demagnification) gave the best results. This is because a large fraction of beam electrons is lost to fixed beam stops as a result of the increase in trajectory angles at the demagnified source image within the two-lens condenser system. In addition, spreading high intensity illumination over a larger specimen area (1-2 μ m diameter) reduced the rate of contamination build-up on many of the specimens, thereby permitting longer useful collection times. The range of incident angles was not an important concern in these experiments, thus the beam was very nearly focussed onto the region of interest and the largest available condenser aperture (300 μ m) was selected to pass the greatest possible beam current. As estimated from the width of the transmitted beam in diffraction patterns, the convergence semi-angle of the incident illumination was always in the 4-7mrad range.

2.9.2. Selection of Scattered Events

A number of criteria guided the selection of scattered events. One requirement was that the data be amenable to multiple scattering correction to permit extraction of the true plasmon line shape from measured spectra. As will be discussed in chapter 3, Fourier-log deconvolution is a very simple and effective mathematical method for achieving this, but it imposes two criteria on the selection of scattered events. Number one, spectra must be collected over the largest possible range of scattering angles and, number two, they must be obtained from as uniform a specimen thickness as possible. Both of these measures serve to validate the basic premise of Fourier-log deconvolution, that the probability of n -fold inelastic scattering follows the Poisson distribution.

Large collection (semi-)angle($\equiv\beta$) can be achieved in two ways. One possibility is to operate in diffraction mode with a small camera length in order to pass as much of the diffraction pattern through the spectrometer aperture as possible. Operating in this mode, however, the spatial resolution is limited by the $1\text{-}2\mu\text{m}$ size of the incident probe (see preceding section) making it difficult to satisfy the second requirement of uniform specimen thickness. The thickness profiles of the available specimens were generally irregular, the thickness varying considerably within a $1\mu\text{m}$ area. In order to avoid this problem, spatial resolution significantly better than $0.1\mu\text{m}$ was needed. In addition to the thickness variation problem, poor spatial resolution indirectly limits the spectrum energy resolution achieved in diffraction mode. Because the projector crossover, which the spectrometer images onto the energy selecting slit, contains an image of the probed sample area, the size of this crossover image determines the image size at the slit and therefore the spectrum energy resolution (see discussion in section 2.1.2). As a specific example consider that to achieve collection angle $\beta=25\text{mrad}$, camera length 20mm in conjunction

with a 1mm spectrometer aperture ($\frac{1}{2}(1\text{mm}/20\text{mm})=25\text{mrad}$) are required. With a projector crossover to spectrometer aperture distance of 50cm, the magnification of the crossover image will thus be $50\text{cm}/2\text{cm}=25\times$. Hence a $1\mu\text{m}$ probed specimen area leads to a $25\mu\text{m}$ projector crossover and a $6.25\mu\text{m}$ image of the crossover at the energy selecting slit. The end result is an unacceptable $6.25\mu\text{m}/1.8\mu\text{m}/\text{eV}=3.5\text{eV}$ energy resolution.

The other way to achieve large β is to operate in image mode with a large (or no) objective aperture. This approach avoids the problems described above and was found to give the best results for the present work. In this mode, the spatial resolution needed to ensure approximately uniform sample thickness within the probed volume is achieved by working at high image magnification and using the 1mm spectrometer aperture to select scattered events from a particular specimen area. For example, events passed by the 1mm aperture from a $100,000\times$ magnified image originate from an area $1\text{mm}/100,000=10\text{nm}$ across. Loss of energy resolution is no longer of concern in this case as the projector crossover now comprises a diffraction pattern of very short camera length ($50\text{cm}/100,000=5\mu\text{m}$) so that its size is very small and independent of the dimensions of the probed specimen region.

The simple relationship between specimen area probed and image magnification used above only holds in the absence of aberrations. In reality, aberrations are inherent to the system and their effects must be considered carefully. One important effect is that of objective-lens chromatic aberration on the area selecting function of the spectrometer aperture. Although electrons which do not scatter inelastically within the sample give rise to an image with better than 0.5nm resolution, those that do experience energy losses will not be focussed at the same plane. The corresponding loss of resolution is related to the chromatic aberration coefficient, C_c , the scattering angle, θ , and the energy loss, ΔE ,

via $\Delta x_c = C_c \theta \Delta E / E_0$. Since the concern here is with plasmon-regime data, the largest energy loss of any consequence is about 100eV. The angular distribution of the inelastic scattering is characterized by the loss angle $\theta_E \equiv \Delta E / 2E_0$, 94% of losses ΔE scattering within $10\theta_E$ of the forward direction [34]. Hence the corresponding largest scattering angle of concern is $10(100\text{eV}/100,000\text{eV})/2 = 5\text{mrad}$. For the Philips EM400, C_c is roughly 3mm, hence $\Delta x_c = 15\text{nm}$. In other words, although a 1mm aperture at 100,000 $\times$ magnification would appear to restrict events to a 10nm area, in the worst case, 100eV-loss scattering events in surrounding regions as far as 15nm away will contribute to the spectrum. More typically, for inelastic events contributing to the main plasmon peak at around 15eV, the loss of resolution is less than 1nm. Thus, chromatic aberration effects are not of great concern in the present context.

Of far greater importance is the effect of large-angle elastic (Bragg) scattering and the spherical aberration of the objective lens. The loss of resolution in this case is related to the spherical aberration coefficient (again $\sim 3\text{mm}$), C_s , and θ via $\Delta x_s = C_s \theta^3$. The strong Bragg scattering in the crystalline samples studied here sends a significant fraction of the beam intensity out beyond 30mrad, thus the corresponding Δx_s is about 80nm. The obvious remedy, particularly in light of the relatively small angular width of the inelastic scattering of interest here, is to use an objective aperture small enough to restrict spherical aberration effects to an acceptable level but large enough to include enough of the inelastic scattering distribution to ensure the Poisson form of the n -fold scattering probabilities. A 7mrad objective aperture was found to satisfy these requirements quite nicely, as it is roughly $100\theta_E$ for simple plasmon-loss scattering, yet gives Δx_s of around 1nm.

The conclusions of the preceding arguments were checked experimentally with two test samples. The first sample was of an Al:Ag alloy extensively studied and characterized by J. Howe [35]. The specimen consisted of an Al matrix with plate-like γ' precipitates of composition Ag_2Al scattered throughout. These precipitates have the following useful features: they have well-defined boundaries, plate-like morphology (typical dimensions $20\text{nm} \times 100\text{nm} \times 3\mu\text{m}$), and a composition that is quite distinct from that of the matrix. When oriented edge-on to the incident beam, they provide a very convenient means for checking the spatial resolution achieved in EELS spectra with the setup described above. The bright-field micrograph shown in figure 2.7 shows two of the precipitates embedded in the Al matrix and viewed at right angles to their smallest dimension. The small circle drawn on the image illustrates the size of the area selected by the spectrometer aperture. An overall feeling for the size, shape, and distribution of the precipitates is given by the lower-magnification stereo pair in figure 2.8.

Very different EELS spectra are expected from the matrix and precipitate regions since the former is purely Al, which has a very strong plasmon excitation, whereas the latter is mostly Ag, which does not have a well-defined plasmon excitation due to damping and other complexities inherent to its electronic structure. Figure 2.9 shows the results obtained from matrix and precipitate regions positioned over the spectrometer aperture. The top spectra were obtained with large collection angle (no objective aperture) while the bottom correspond to a 6mrad collection angle ($20\mu\text{m}$ objective aperture). The clear difference between the EELS results in the latter case demonstrates that scattering events can indeed be localized to an area as small as 15nm in lateral dimension as long as the resolution degrading effects of large-angle scattering are avoided.

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Figure 2.7 - Bright-field micrograph of Ag_2Al plate-like precipitates in Al matrix, viewed edge-on. Circle indicates effective size of spectrometer aperture projected onto image.

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Figure 2.8 - Lower magnification bright-field stereo pair of Ag_2Al precipitates in Al matrix.

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Figure 2.9 - Plasmon-regime EELS spectra collected in image mode using spectrometer aperture to select events from either matrix or precipitate regions. Top, collection angle $> 50 \text{ mrad}$, bottom, collection angle $= 6 \text{ mrad}$.

The importance of good spatial resolution for accurate Fourier-log deconvolution was demonstrated with a second test sample taken from a bulk mono-crystalline Si wafer. The measured spectra and extracted single-scattering distributions (SSD's) are shown in figure 2.10. Again, the top results were obtained with a large collection angle (no objective aperture) and the bottom with a 6mrad collection angle. Note that large collection angle leads to an artifact (negative energy-loss probability) near twice the plasmon peak energy upon Fourier-log deconvolution of the single-scattering profile. By restricting the collection angle, and thereby improving the spatial resolution and thickness uniformity of the sampled area, this artifact is removed and a physically reasonable single-scattering distribution is obtained.

2.3.3. Recording Spectra

Having optimized experimental conditions to give the best possible EELS data for extracting plasmon line shapes as described above, the final step was actually recording spectra. In order to keep spectrum statistical noise due to Poisson counting statistics to an acceptable level, it was desirable to collect several thousand counts per channel, at least in the vicinity of the plasmon peak. In order to achieve this, a total acquisition time on the order of 10min was required for each spectrum. Due to this long acquisition time, a number of instrumental instabilities had to be monitored and their effects on recorded data eliminated.

The most noticeable instability was the drift of the zero of the energy-loss scale. Drift of the zero-loss peak over a 2eV range within the 10min acquisition period was not uncommon. This led to either unacceptable smearing of the energy resolution or to distortion of the energy scale, depending upon whether a spectrum was acquired in multiple sweeps or in a single slow scan of the energy range. Occasionally, large transient shifts of

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Figure 2.10 - Effects of collection angle on Fourier-log deconvolution of single-scattering distribution (SSD) from measured EELS spectra of crystalline silicon. Top, $\beta > 50 \text{ mrad}$, bottom $\beta = 6 \text{ mrad}$.

the zero-loss peak would occur during an acquisition run, rendering that run useless. Mechanical instability of the specimen also proved to be a significant factor as the desired specimen region often drifted entirely out of the field of view of the spectrometer during the acquisition period. As the viewing screen must be raised during acquisition, this drift could not be observed until *after* the erroneous data had already been collected.

The above difficulties were circumvented by placing the data acquisition under the control of a computer program designed to collect the desired EELS spectrum in multiple quick ($\sim 10\text{-}20\text{sec}$) sweeps of the energy-loss range (rather than in a single, slow 10min scan) and to monitor several key parameters between sweeps. This approach provided several advantages. First, it gave the opportunity to check incoming data against data already collected in a given run for changes signaling an alteration in the set-up. If such a change was detected, purity of the data could be maintained by discarding just the current sweep (rather than aborting the entire run) and temporarily halting acquisition until the setup was returned to its initial settings. For example, the program monitored the maximum value of the cross-correlation between current sweep and previous data as a function of relative energy shift. If the maximum cross-correlation coefficient was found to be significantly less than one, a major disruption in the set-up, such as a transient or a loss of beam, was indicated and acquisition was temporarily halted for corrective measures. The program also monitored the intensity of the zero-loss peak, a very sensitive measure of specimen thickness. If the specimen drifted and an area of different thickness moved into view of the spectrometer, a change in zero-loss intensity was detected and acquisition again paused to allow specimen repositioning.

Secondly, the monitoring approach allowed certain instabilities to be corrected automatically. For example, the relative energy shift corresponding to the maximum

cross-correlation described above was applied to each sweep before adding it to the rest of the data, thereby eliminating zero-loss drift.

Finally, multi-sweep acquisition in itself provided two bonuses: 1) it helped avoid overflow of the 24-bit channels of the MCA as only a fraction of the total counts were ever stored there, the sum spectrum being stored as 32-bit values in the computer memory and 2) it helped average out non-statistical noise, particularly when a dwell time of 16.7msec (one 60Hz cycle) per channel was used. Unavoidable stray fields at 60Hz-harmonic frequencies are always present (usually due to thyristor-controlled power supplies) and these lead to oscillation of the energetic electron beam and "jitter" in the position of the EELS spectrum on the MCA. This jitter is averaged out by the multi-sweep acquisition.

A listing of a FORTRAN program written to carry out the above procedures on a Kevex 8000 MCA is given in appendix A.

CHAPTER 3

Theory and Analysis of Plasmon-Regime EELS Spectra

Although energy losses to plasmon excitations are the most prominent feature of semiconductor EELS spectra, a correct picture of the plasmon line shape is not immediately provided by the raw data. Often, the bulk plasmon peak is obscured by features associated with other excitations occurring within the low-loss (0-100eV) regime, such as surface plasmons, interband transitions, and core-electron ionizations. In addition, since a single beam electron will frequently transfer energy to several excitations during its traversal of the sample, the measured spectrum is further complicated by self-convolution due to multiple scattering. Figure 3.1, a typical plasmon-regime EELS spectrum from GaAs, illustrates these effects. Despite these difficulties, it is possible to isolate and analyze the bulk plasmon line of such spectra with good precision by applying a few simple results from the established theoretical literature on the energy-loss spectrum and multiple scattering. The present chapter briefly reviews the physics and theory of electron energy loss in solids and describes in detail the procedures developed to accurately extract and analyze plasmon line shape data from measured EELS spectra for the studies of the following chapters.

Since the characteristics of the plasmon line are largely determined by the overall valence electron density and only the coarser features of the electronic band structure, the differences between plasmons of related materials, such as semiconductors, tend to be subtle. Changes in the plasmon line shape associated with imperfections in a particular material, examined in chapter 4, are also not very pronounced. Detailed mathematical analysis of the data is therefore necessary to measure these subtle effects.

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Figure 3.1 - Typical EELS spectrum measured from crystalline GaAs demonstrating obfuscation of bulk plasmon line shape by other features.

3.1. Physics of Electron Energy Loss in Solids

The physics of EELS, as applied here, is fairly straightforward. However, the interaction between an energetic ($>20\text{keV}$) electron and a solid has unique features which differentiate EELS from other spectroscopic techniques and give EELS spectra their characteristic structure. The special properties of electrons as probes of solids are described below within the context of a qualitative, physical picture of electron energy loss in solids.

3.1.1. Nature of the Electron Probe

At first thought, one might expect the EELS spectrum of a solid to be analogous to its photon absorption spectrum since both probe the electron energy level structure of the solid. This, however, is not the case, as illustrated by the comparison of the energy-dependent absorption coefficient [36] and EELS spectrum of silicon in figure 3.2. They appear to have nothing in common. The source of this difference can be traced to the nature of the electromagnetic field associated with the probe particle in each of these techniques. A given Fourier component, $\mathbf{E}_0(\omega, \mathbf{q})e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$, of the electron field (before entering the solid) is longitudinal, $\mathbf{E}_0$ being along the direction of propagation. The photon field, on the other hand, is transverse. Thus, electrons excite longitudinal modes of the solid, such as the bulk valence plasmon at $\sim 15\text{eV}$, while photons excite transverse modes, such as the interband transitions occurring below about 5eV . This distinction can be stated more concretely with reference to figure 3.3. Due to the boundary condition on electric fields in dielectric media, the transverse photon field, being tangential to the boundary, propagates unchanged into the sample, while the longitudinal electron field, being normal to the boundary, is reduced by a factor of $1/\epsilon$, where ϵ is the (frequency-dependent) dielectric constant of the solid. Hence these probes have very different net

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Figure 3.2 - Comparison of spectral dependences of optical absorption (top) and electron energy loss (bottom) in low-energy regime for Si.

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Figure 3.3 - Distinction between electron and photon fields propagated into dielectric medium at normal incidence.

effects within the sample.

Insight into the nature of the energy-loss process can be obtained by focusing on the physical mechanism which gives rise to ϵ , ie. the polarization of the solid in response to the electron or photon probe. This dielectric response results in a net macroscopic electric field, $\mathbf{E}_{\text{in}}$, inside the solid which is related to the polarization, $\mathbf{P}$, and applied field, $\mathbf{D}$, via the usual constitutive relation $\mathbf{E}_{\text{in}} + 4\pi\mathbf{P} = \mathbf{D} = \epsilon\mathbf{E}_{\text{in}}$. In addition, specific frequency components of these quantities, $\mathbf{E}_{\text{in}}(\omega)e^{-i\omega t}$, $\mathbf{P}(\omega)e^{-i\omega t}$, and $\mathbf{D}(\omega)e^{-i\omega t}$, will generally display phase shifts between $\mathbf{E}_{\text{in}}$ and both $\mathbf{P}$ and $\mathbf{D}$. It is the periodic motion of the solid's constituent charges, represented by $\mathbf{P}$, within the field $\mathbf{E}_{\text{in}}$ that is responsible for the transfer of energy from the incident beam to the solid. In analogy with the driven harmonic oscillator, that part of the polarization charge motion $\pm\pi/2$ out of phase with $\mathbf{E}_{\text{in}}$, will absorb energy from beam.

In quantitative terms, the power, $\frac{dW}{dt}$, transferred from beam to solid via the macroscopic field varies according to (see section 3.2)

$$\frac{dW}{dt} \propto \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t}$$

In the usual complex formalism for periodic fields, components of $\mathbf{E}_{\text{in}}$, $\mathbf{P}$, and $\mathbf{D}$ at frequency ω are expressed as $\text{Re}\{\mathbf{E}_{\text{in}}(\omega)e^{-i\omega t}\}$, $\text{Re}\{\mathbf{P}(\omega)e^{-i\omega t}\}$, and $\text{Re}\{\mathbf{D}(\omega)e^{-i\omega t}\}$. The phase shifts of $\mathbf{P}$ and $\mathbf{D}$ are included by allowing their amplitudes to be complex, ie. $\mathbf{P}(\omega) = \mathbf{P}_1(\omega) + i\mathbf{P}_2(\omega)$ and $\mathbf{D}(\omega) = \mathbf{D}_1(\omega) + i\mathbf{D}_2(\omega)$. To preserve the relation $\mathbf{D} = \epsilon\mathbf{E}_{\text{in}}$, ϵ is also taken to have real and imaginary parts so that $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, yielding $\mathbf{D}_1 = \epsilon_1\mathbf{E}_{\text{in}}$ and $\mathbf{D}_2 = \epsilon_2\mathbf{E}_{\text{in}}$. Hence, for field components at frequency ω , the power transfer goes as

$$\begin{aligned}\frac{dW}{dt} &\propto \text{Re}\{\mathbf{E}_{\text{in}}(\omega)e^{-i\omega t}\} \cdot \frac{\partial}{\partial t} \text{Re}\{\mathbf{D}(\omega)e^{-i\omega t}\} \\ &\propto \mathbf{E}_{\text{in}}(\omega)\cos\omega t \cdot (-\omega\mathbf{D}_1(\omega)\sin\omega t + \omega\mathbf{D}_2(\omega)\cos\omega t)\end{aligned}$$

and time-averaging over one cycle yields

$$\begin{aligned}\frac{dW}{dt} &\propto \omega\mathbf{E}_{\text{in}}(\omega) \cdot \mathbf{D}_2(\omega) = \omega\mathbf{E}_{\text{in}}(\omega) \cdot \epsilon_2(\omega)\mathbf{E}_{\text{in}}(\omega) \\ &= \omega\epsilon_2|\mathbf{E}_{\text{in}}|^2\end{aligned}$$

By incorporating the relationship between the modified probe field inside the solid $\mathbf{E}_{\text{in}}$ and its initial value $\mathbf{E}_0$, the distinction between a longitudinal probe and a transverse probe can be made explicit. In the longitudinal case, $|\mathbf{E}_{\text{in}}|^2 = |\mathbf{E}_0|^2/\epsilon^2$ so that

$$\left(\frac{dW}{dt}\right)_{\text{long}} \propto \omega\epsilon_2|\mathbf{E}_0|^2/\epsilon^2 = \omega\text{Im}\{-1/\epsilon\}|\mathbf{E}_0|^2$$

This is the well-known result that the structure of the EELS spectrum is described by $\text{Im}\{-1/\epsilon\}$. For comparison, note that in the case of a photon probe, $|\mathbf{E}_{\text{in}}|^2 = |\mathbf{E}_0|^2$ and

$$\left(\frac{dW}{dt}\right)_{\text{trans}} \propto \omega\epsilon_2|\mathbf{E}_0|^2 = \omega\text{Im}\{\epsilon\}|\mathbf{E}_0|^2$$

An assumption of the preceding discussion is that the same $\epsilon(\omega)$ applies to both the longitudinal and transverse cases. Detailed theoretical treatments [37] have shown that $\epsilon_{\text{long}} = \epsilon_{\text{trans}}$ if correlations between the valence electrons are negligible (random phase approximation or RPA). Furthermore, the validity of the RPA in semiconductors has, to some extent, been tested experimentally by comparing the observed plasmon dispersion with that obtained from the Lindhard (RPA) ϵ [13], and by direct comparison of $\epsilon(\omega)$ determined by EELS and optical methods [14,38]. The results show that the RPA gives a reasonable account of the observations in many cases (eg. Si, Ge, GaAs, InAs, and InSb).

To the extent that ϵ_{long} and ϵ_{trans} are the same, the above results show the EELS spectrum differs from its optical analog only in that it is multiplied by $1/k^2$. For semiconductors, the electronic contribution to the polarizability, α , is very high at optical frequencies and below, due to the onset of valence electron interband transitions at these frequencies, but becomes very small at ultraviolet frequencies and beyond. This gives magnitude $\epsilon (=1+4\pi n\alpha)$ the characteristic frequency (energy) dependence shown schematically in figure 3.4. The $1/k^2$ factor plays a major role in determining the overall shape of the EELS spectrum, accounting for its very low intensity at or below optical transition frequencies, its dominant peak between 10 and 20eV, and its ionization edge structure at higher energies which matches that of X-ray absorption edges (since $\text{Im}\{-1/\epsilon\} = \epsilon_2/k^2 \approx \epsilon_2 = \text{Im}\{\epsilon\}$ at UV energies and above). Stated in physical terms, the $1/k^2$ dependence of EELS reflects the fact that the longitudinal field of the electron probe is strongly screened by the polarization response of the solid at frequencies below the plasma frequency, ω_p , resonates with it at ω_p , and ceases to be screened at higher frequencies.

3.1.2. EELS Kinematics

Another unique aspect of the electron probe is that it can be used to measure the momentum-transfer dependence of the excitation spectrum, or in other words, the complete $\epsilon(\omega, \mathbf{q})$. This is because the momentum transferred to an excitation in EELS is determined by the kinematics of the scattering event rather than by the energy of the probe. By contrast, photon absorption at energy $\hbar\omega$ always transfers momentum $\hbar\mathbf{q} = \hbar\omega/c$ to the sample. Furthermore, since q of photons with energies up through the UV is negligible on the scale of the Brillouin zone, photons can be thought of as probing $\epsilon(\omega, 0)$ only. The kinematics of an EELS event is illustrated in figure 3.5. The relationships between the energy loss $E (= \hbar\omega)$, momentum transfer $\hbar\mathbf{q}$, and scattering angle θ are

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Figure 3.4 - Schematic energy ($= \hbar\omega$) dependence of $|\epsilon|$ in semiconductors.

given by

$$\begin{aligned} q_t &= k_0 \tan \theta & q_l &= k_0 [1 - (1 - 2\theta_E)^{1/2} \cos \theta] \\ q^2 &= k_0^2 [2(1 - \theta_E) - 2(1 - 2\theta_E)^{1/2} \cos \theta] \end{aligned}$$

where $\theta_E \equiv \frac{E}{2E_0} = \frac{1}{2}(1 - k_f^2/k_0^2)$.

The range of scattering angles over which energy-loss events are collected directly determines the momentum transfers contributing to the measured spectrum. If the spectral features have dispersive behavior (energy shifts or other changes with q), then the collection semi-angle, β , has an important influence on the observed spectral structure and must be taken into consideration. Fortunately, the beam energies used in TEM EELS greatly simplify the discussion, particularly in the low-loss (0-100eV) regime. The experiments to be described here were generally carried out with an initial beam energy $E_0=100\text{keV}$ so that losses as large as 100eV are virtually negligible in comparison. Furthermore, as the angular distribution of inelastic scattering has a $(\theta^2 + \theta_E^2)^{-1}$ dependence [34], its full width at half maximum (FWHM) is $2\theta_E = E/E_0$, which amounts to only 1 mrad for $E=100\text{eV}$ and $E_0=100\text{keV}$. Under these conditions, $\beta=5\text{mrad}$ will include almost 94% of the events at 100eV loss and 99% of the plasmon-loss events. Thus both the energy loss and the scattering angle may be approximated as being very small ($E \ll E_0, \theta \ll 1$) and the relationships between E , q , and θ given above simplify to

$$\begin{aligned} q_t &= k_0 \theta & q_l &= k_0 \theta_E \\ q^2 &= k_0^2 (\theta^2 + \theta_E^2) \end{aligned}$$

Note that under these conditions the component of $\mathbf{q}$ along the beam direction, q_l , is determined solely by the energy loss, whereas that transverse to the beam, q_t , is fixed by the scattering angle. If $\mathbf{v}_0$ is the initial velocity of a beam electron, then the above rela-

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Figure 3.5 - Kinematics of an EELS scattering event.

tionships imply

$$\mathbf{q} \cdot \mathbf{v}_0 = q_l \frac{\hbar k_0}{m} = \frac{\hbar k_0^2 E}{2mE_0} = \frac{E}{\hbar} = \omega$$

Although relativistic effects have been neglected in the above discussion, the results are substantially the same if they are included, the only change being that θ_E becomes

$$\theta_E = \left(\frac{E_0 + mc^2}{E_0 + 2mc^2} \right) \frac{E}{E_0}$$

As a result of the small θ and fractional energy losses, $E/E_0 = 2\theta_E$, of TEM EELS, over 90% of plasmon-regime events involve q smaller than 1.7nm^{-1} , which is less than 0.1 of the (111) Brillouin zone wave vector in most semiconductors. Hence, in many cases, even if non-zero momentum transfer changes the excitation spectrum, this effect is often not apparent in angle-integrated EELS spectra which include the forward scattering direction, as events with $\mathbf{q} \approx 0$ dominate. Thus, angle-integrated TEM EELS at high beam energies ($\geq 100\text{keV}$) also basically measures only $\epsilon(\omega, 0)$ (as in optical spectroscopy).

3.1.3. Multiple Scattering

A final noteworthy feature of the electron probe in EELS is its ability to participate in several inelastic scattering events while traversing the sample rather than being absorbed in a single event like a photon. Due to this multiple scattering, any measured EELS spectrum will actually be the superposition of several different energy-loss probability distributions. First, there is the energy distribution of electrons that pass through the specimen without scattering. This is simply the zero-loss peak which appears at $E=0$ and reflects the energy resolution of the EELS system. Added to that is the distribution of electrons which have scattered only once within the specimen. This is the single-scattering distribution (SSD) and the only component which can be meaningfully

compared to a theoretical calculation of the energy-loss probability distribution. As indicated in section 3.1.1, the SSD is proportional to $\text{Im}\{-1/\epsilon\}$. The next addition to the spectrum is the 2-fold scattering distribution which is comprised of electrons whose energies were first "assigned" according to the SSD and then redistributed in the same way, with each energy channel spread out according to the SSD. It follows that the 2-fold distribution is a convolution of the SSD with itself. Similarly, 3-fold and higher scattering also contribute to the spectrum, each n -fold contribution proportional to the n -fold convolution product of the SSD. Broadened peaks at multiples of the plasmon-loss energy are the clearest manifestation of multiple scattering in the measured spectrum.

As the thickness of the probed specimen region increases, the relative contribution of each of the n -fold energy-loss distributions will change, the higher n contributions growing at the expense of the lower. Assuming each inelastic event is localized, involves the loss of a negligible fraction of the initial beam energy, and is independent of the previous one, the scattering can be modeled as a Poisson process characterized by a mean free path, λ_{inel} , between inelastic events [39]. Consequently, the probability for n -fold scattering (integrated over energy-loss and scattering angle), and thus the relative contribution of each n -fold distribution, can be determined from the Poisson distribution

$$p(n) = \frac{\tau^n}{n!} e^{-\tau}, \quad \tau = \frac{t}{\lambda_{\text{inel}}}$$

where t is the sample thickness.

It is important to emphasize that the Poisson distribution strictly applies only to spectra collected over all scattering angles, as the scattering-angle distributions of the various n -fold contributions are not the same. Since each of the n -fold components represents a convolution of the SSD with the $(n-1)$ -fold component in both energy and scattering angle, the width of the angular distribution increases with n . Depending upon

the thickness of the specimen, this restriction on the applicability of Poisson statistics is not as severe as it might seem. For thicknesses of about one λ_{inel} or less, the contributions of the n -fold scattering components for $n > 3$ are very small. Any effect on the total spectrum resulting from truncation of these contributions by a finite collection angle is likely to go unnoticed. Furthermore, since θ_E (half the angular FWHM of the SSD) is significantly less than 1 mrad in the plasmon regime, collection angles of a few mrad are sufficient to ensure a Poisson probability distribution for the n -fold scattering collected in EELS spectra from such thin specimens. This fact has been used to advantage for the data collection and analysis in this work.

3.2. Basic Theory of the EELS Spectrum

The physical description of EELS given in the preceding section has been given a firm mathematical basis in various theoretical treatments. The present section describes the specific theoretical results that permit quantitative modeling and analysis of the EELS spectrum in the plasmon-loss regime. The relevant literature on this topic is extensive and well-established. The earliest explanations of observed EELS spectra are due to Fröhlich, Platzman, and Pelzer, who developed a macroscopic classical theory [40,41,9], and to Pines, Bohm, and Nozieres, who carried out a microscopic quantum-mechanical treatment of valence excitations and the energy-loss spectrum [42, 43,37]. Additional theoretical contributions have been made by Platzman and Wolff [44], and advances and increased interest in the EELS technique over the past decade have recently spurred further development of the theory of electron energy-loss spectra and plasmons by Sturm [25] and Egri [26]. Useful reviews for experimentalists have been given by Schnatterly [45], Raether [29], and Egerton [32]. The multiple scattering problem in EELS has been given specific treatment by Misell and Jones [46], Johnson and Spence [47], and Leapman and Swyt [48].

3.2.1. The Energy-Loss Probability Distribution

The first step in arriving at a model of the EELS spectrum is to determine the probability (per unit time) that an energy loss $\hbar\omega$ occurs as an electron passes through the sample. This represents the single-scattering energy-loss probability distribution, or SSD, mentioned in section 3.1.3. As indicated above, the theoretical calculation of the SSD has been approached both classically, focusing on the energy transferred via the macroscopic fields within the solid, and quantum-mechanically, focusing on the solid's collective valence electron states and their interaction with the incident beam electron. Using the

former approach, Fröhlich and coworkers derived the SSD from the rate of electromagnetic energy transfer (over all frequencies or energy-loss channels) from beam to solid via [49]

$$\frac{dW}{dt} = \frac{1}{4\pi} \int_V \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} d\mathbf{r}$$

where V is the probed sample volume. The contributions of individual frequency components can be shown explicitly by substituting the Fourier expansions of $\mathbf{E}$ and $\mathbf{D}$

$$\begin{aligned} \frac{dW}{dt} &= \frac{1}{4\pi} \int_V d\mathbf{r} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \sum_{\mathbf{q}_1} \sum_{\mathbf{q}_2} -i\omega_2 \mathbf{E}(\omega_1, \mathbf{q}_1) \cdot \mathbf{D}(\omega_2, \mathbf{q}_2) e^{i(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{r}} e^{-(\omega_1 + \omega_2)t} \\ &= \frac{1}{4\pi} \int_V d\mathbf{r} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \sum_{\mathbf{q}_1} \sum_{\mathbf{q}_2} -i\omega_2 \epsilon^{-1}(\omega_1, \mathbf{q}_1) \mathbf{D}(\omega_1, \mathbf{q}_1) \cdot \mathbf{D}(\omega_2, \mathbf{q}_2) e^{i(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{r}} e^{-(\omega_1 + \omega_2)t} \end{aligned}$$

In the quantum mechanical approach of Nozieres and Pines, the starting point is the application of time-dependent perturbation theory (Fermi's golden rule) to a many-body description of the beam specimen interaction to yield the rate of energy loss via transitions characterized by momentum transfer $\hbar\mathbf{q}$ and energy loss $\hbar\omega$ [37]

$$\left(\frac{dW}{dt} \right)_{\omega, \mathbf{q}} = \frac{2\pi}{\hbar^2} \left(\frac{4\pi e^2}{q^2} \right)^2 \hbar\omega \sum_n |\langle \rho_{\mathbf{q}} \rangle_{n0}|^2 \delta(\omega_{n0} - \omega)$$

Here, $(\rho_{\mathbf{q}})_{n0}$ is the matrix element of the electron density-fluctuation operator at wave vector $\mathbf{q}$ between many-body states Ψ_n and Ψ_0 comprised of a suitable combination of plasmon and screened single-particle states. Both of the above theoretical approaches lead to the basic result that the probability per unit time that the beam induces an excitation with momentum $\hbar\mathbf{q}$ and energy $\hbar\omega$ is

$$p(\omega, \mathbf{q}) = \frac{8\pi e^2}{\hbar q^2 V} \text{Im} \left\{ \frac{-1}{\epsilon(\omega, \mathbf{q})} \right\} \delta(\omega - \mathbf{q} \cdot \mathbf{v}_0)$$

where the δ function explicitly includes the kinematic constraint discussed in section 3.1.2.

It should be noted that the above only strictly applies in isotropic solids, ie. those in which $\epsilon(\omega, \mathbf{q})$ is a scalar. Experimentally [22,23], it has been found that the anisotropy of

ϵ in semiconductors is actually rather weak, particularly within the range of $\mathbf{q}$'s relevant to TEM EELS. Thus the expression above is a satisfactory starting point for modeling semiconductor plasmon EELS spectra.

For spectra collected in angle-integrated mode with a collection solid angle Ω , the measured energy-loss distribution is the sum of the energy-loss probabilities for all momentum transfers, $\mathbf{q}$, consistent with Ω . This sum of $p(\omega, \mathbf{q})$ can be carried out by taking $\mathbf{q}$ to be a continuous variable and replacing $\sum_{\mathbf{q}}$ with $\frac{V}{(2\pi)^3} \int d\mathbf{q}$, to yield

$$P(\omega) = \int p(\omega, \mathbf{q}) d\mathbf{q} = \int \frac{e^2}{\pi^2 \hbar q^2} \text{Im} \left\{ \frac{-1}{\epsilon(\omega, \mathbf{q})} \right\} \delta(\omega - \mathbf{q} \cdot \mathbf{v}_0) d\omega d\mathbf{q}$$

In general, this integral is difficult to carry out in closed form for arbitrary Ω due to the unknown $\mathbf{q}$ -dependence of $\text{Im}\{-1/\epsilon\}$. However, due to the kinematics of TEM EELS, a number of simplifying approximations can be made and the integral evaluated, yielding an expression useful for analyzing angle-integrated plasmon spectra. The key point is that angle-integrated spectra centered on $\theta=0$ are dominated by $\mathbf{q} \approx 0$ events so that $\epsilon(\omega, \mathbf{q}) \approx \epsilon(\omega, 0)$ and $\text{Im}\{-1/\epsilon\}$ can be factored out of the integral. Furthermore, since θ_E is so small in the low-loss regime, even the relatively small β used in the present experiments ($\sim 6-7\text{mrad}$) is sufficient to yield a spectrum equivalent to that integrated over all angles (neglecting the effects of elastic Bragg scatter which simply reduce the total counts collected in an EELS spectrum but not their energy distribution). With these points in mind, the integral over $\mathbf{q}$ is carried out to the maximum momentum transfer allowed by kinematics to yield [49,51]

$$P(\omega) = \frac{2e^2}{\pi \hbar v_0} \text{Im} \left\{ \frac{-1}{\epsilon(\omega)} \right\} \ln \left(\frac{2E_0}{\hbar \omega} \right)$$

This is the basic result used for analysis of the spectra.

A complete model of the spectrum now simply requires an appropriate expression for $\epsilon(\omega)$. The macroscopic theory cannot provide such an expression, since it takes ϵ to be a given, fundamental parameter of the solid. The detailed microscopic theory can be used to obtain a first-principles expression for ϵ , but this is in general a very difficult task and not very practical for the present application. Nevertheless, in the course of the current study [52], it has been found that the following simple form for ϵ suggested by Fröhlich [49], based on a damped-harmonic-oscillator model of the atomic polarizability, is quite useful for modeling semiconductor plasmon spectra:

$$\epsilon(\omega) = \epsilon(E/\hbar) = \epsilon_c + \frac{E_p^2}{(E_p^2 - E^2) - i\Gamma E}$$

where ϵ_c is the core electron contribution to the dielectric constant, E_p ($=\hbar\omega_p$) is the free-electron-equivalent plasmon energy of the valence electrons, E_g is an "average" $\mathbf{q}=0$ band gap of the semiconductor, and Γ is a phenomenological parameter which accounts for plasmon damping.

Substitution of $\epsilon(\omega)$ into the expression for $P(\omega)$ yields the functional form of the semiconductor plasmon EELS spectrum

$$I(E) \propto P(E/\hbar) = \frac{2e^2\Gamma E_p^2}{\pi\hbar v_0 \epsilon_c^2} \frac{E \ln(2E_0/E)}{(E_p^2 + E_p^2/\epsilon_c - E^2)^2 + \Gamma^2 E^2} = \frac{CE \ln(2E_0/E)}{(E_p'^2 - E^2)^2 + \Gamma^2 E^2}$$

This model, evaluated for $E_p'=16.70\text{eV}$ and $\Gamma=3.50\text{eV}$, is illustrated in figure 3.6 and compared with a measured EELS spectrum from silicon. It should be noted that E_p' and Γ are directly related to the plasmon peak position and FWHM, respectively. The precise relationship between the fit parameters and the plasmon peak parameters can be determined by analyzing the above functional form to find the values of E corresponding to its maximum and half-maximum values. Taking advantage of the fact that the $\ln(2E_0/E)$ factor varies very slowly in the vicinity of the plasmon peak and replacing it with a

Figure 3.6 - Sample plot of theoretically based plasmon peak model (top) compared to actual EELS spectrum from Si (bottom). Note that model does not include surface plasmons (feature below main peak) and double scattering (feature above main peak).

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constant, it can be shown that if $\Gamma^2 \ll E_p'^2$ then

$$\text{Peak Position} \approx E_p'(1 - \Gamma^2/8E_p'^2)$$

$$\text{FWHM} \approx \Gamma(1 - \Gamma^2/16E_p'^2)$$

Thus, in the case above, the peak occurs at 16.61eV and its FWHM is 3.49eV.

It is important to emphasize that the above spectrum model is principally one of the (angle-integrated) bulk plasmon line shape and does not include other potential contributions to the plasmon-regime EELS spectrum. The reason for this lies in the approximate $\epsilon(\omega)$ used for input to $I(E)$. Figure 3.7 gives sample plots of the real and imaginary parts of $\epsilon(\omega)$ corresponding to the spectrum model of figure 3.6 and evaluated using $\epsilon_c=1$ and $E_g=3.5\text{eV}$ (the smallest $q=0$ gap in Si). First of all, the only transitions explicitly included in $\epsilon(\omega)$ are those of the valence electrons to conduction band or continuum states. Higher energy transitions involving more deeply bound electrons such as *d*-shell or core electrons are simply lumped into the constant term ϵ_c . Thus $\epsilon(\omega)$ and $I(E)$ are both featureless beyond the plasma frequency (energy) and spectral structure such as that just beyond the plasmon peak in the GaAs spectrum shown at the beginning of this chapter is not included in the model. Beyond this, although the valence transitions are included, they are not modeled very realistically. The imaginary part of ϵ , which is directly related to the spectrum of optical transitions, comprises a single broadened transition at E_g rather than a more realistic collection of well-defined transitions reflecting the electronic band structure. This deficiency of the model is unimportant, however, since energy losses in the regime of the optical transitions do not make a significant contribution to the EELS spectrum. The more important events in measured EELS spectra at these energies involve surface plasmons and Čerenkov losses [53] whose contributions to the dielectric function have also been left out of the model.

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Figure 3.7 - Real (top) and imaginary (bottom) parts of complex dielectric function used in plasmon model of previous figure.

What the approximate $\epsilon(\omega)$ does include are the significant aspects of the behavior of ϵ_1 and ϵ_2 in the vicinity of the plasmon energy. The key points are: 1) Both vary smoothly within this range, 2) ϵ_1 crosses zero, with a small positive slope, and 3) ϵ_2 has a small but non-zero value at the zero of ϵ_1 . The zero of ϵ_1 determines the plasma frequency, ω_p , or equivalently, the energy of the plasmon peak, while the strength of optical transitions at that energy, reflected in the magnitude of $\epsilon_2(\omega_p)$, determines the degree of plasmon damping. Indeed, Sturm [25] has shown that the width of the plasmon peak is approximately given by

$$\text{FWHM} = 2\pi\epsilon_2(\omega_p) \left(\frac{\partial}{\partial\omega} \epsilon_1(\omega) \right)_{\omega=\omega_p}^{-1}$$

In physical terms, the plasmon resonance is determined by the frequency at which the magnitude of the dielectric constant achieves a minimum (ϵ_1 zero, ϵ_2 small) and the induced longitudinal fields are at a maximum, while plasmon damping is the result of interband transitions having energy and momentum matching that of the plasmon and providing a plasmon decay pathway. From the point of view of the plasmon line width, whether the transitions available at the plasmon energy are the result of well-defined energy level differences in the band structure or the result of broadened, finite-lifetime optical transitions with non-zero transition probabilities at ω_p (as is the case in the model $\epsilon(\omega)$) is immaterial. Either will contribute to plasmon decay. Thus, despite the crude $\epsilon(\omega)$ upon which it is based, the above plasmon line shape model, $I(E)$, can give a very good description of the plasmon peak of semiconductor EELS spectra.

3.2.2. Theory of Multiple Scattering

Starting from the physical picture given in section 3.1.3, the mathematical theory of multiple scattering is quite straightforward. What follows is a simplified development of

the basic results of Johnson and Spence. In order to facilitate implementation of the theory in a computer algorithm, the discrete and finite nature of measured EELS spectra is immediately taken into consideration. Since such a discrete formulation is not currently available in the literature, the mathematics is presented here in some detail.

The spectrum, $I(E)$, may be thought of as a set of N values, I_j , each value representing the spectral intensity in energy channel j according to

$$I(E) \rightarrow I(E_j) = I_j$$

where

$$E_j = E_0 + j\Delta E, \quad j=0, N-1$$

E_0 here is the energy loss corresponding to channel 0 and ΔE is the energy-loss increment per channel. If S_j^n represents the *normalized* energy-loss probability distribution of those beam electrons which have scattered n times in passing through the specimen, then the complete EELS spectrum may be written as the sum of all n -fold scattering contributions [47]

$$I_j = \sum_{n=0}^{\infty} c_n S_j^n$$

where the c_n determine the relative magnitude of each n -fold component. Assuming experimental conditions are such that the total probability of n -fold scattering over all energies does indeed follow the Poisson distribution, as discussed in section 3.1.3, then each of the c_n is given by

$$c_n = Ap(n) = A \frac{\tau^n}{n!} e^{-\tau}$$

where A is an appropriate scale factor and τ is the scattering parameter given by the ratio of specimen thickness to inelastic mean free path, t/λ_{inel} . The value of A can be found in terms of the total number of spectrum counts, I_{tot} , by substituting c_n above into

the expression for I_j and summing over all energy channels

$$\begin{aligned} I_{\text{tot}} &\equiv \sum_{j=0}^{N-1} I_j = \sum_{j=0}^{N-1} \sum_{n=0}^{\infty} A p(n) S_j^n \\ &= A e^{-\tau} \sum_{n=0}^{\infty} \frac{\tau^n}{n!} \sum_{j=0}^{N-1} S_j^n \\ &= A e^{-\tau} \sum_{n=0}^{\infty} \frac{\tau^n}{n!} = A e^{-\tau} e^{\tau} = A \end{aligned}$$

Thus the spectrum may be written

$$I_j = I_{\text{tot}} e^{-\tau} \sum_{n=0}^{\infty} \frac{\tau^n}{n!} S_j^n$$

In the ideal case of perfect energy resolution, S_j^0 is a delta function, δ_j , equal to 1 when j corresponds to the zero energy-loss channel and 0 otherwise. S_j^1 is the single-scattering probability distribution. Each S_j^n , as observed in section 3.1.3, is the convolution of S_j^1 with S_j^{n-1} . Thus I_j may be expressed as

$$I_j = I_{\text{tot}} e^{-\tau} \left\{ \delta_j + \tau S_j^1 + \frac{\tau^2}{2} [S^1 * S^1]_j + \frac{\tau^3}{6} [S^1 * S^1 * S^1]_j + \dots \right\}$$

This can be written more compactly through use of the discrete Fourier transform (FT) and its inverse (FT⁻¹) [54] defined by

$$\text{FT}\{G_j\} \equiv \frac{1}{N} \sum_{j=0}^{N-1} G_j e^{-\frac{2\pi u j}{N}} \equiv g_u, \quad u=0, N-1$$

and

$$\text{FT}^{-1}\{g_u\} \equiv \sum_{u=0}^{N-1} g_u e^{\frac{2\pi u j}{N}} = G_j, \quad j=0, N-1$$

It can be shown that the convolution of two discrete functions is related to the product of their FT's via

$$\text{FT}\{(F * G)_j\} = N \text{FT}\{F_j\} \text{FT}\{G_j\} = N f_u g_u$$

Thus I_j becomes

$$\begin{aligned}
I_j &= I_{\text{tot}} e^{-\tau} \text{FT}^{-1} \left\{ \frac{1}{N} + \tau s_u^1 + \frac{\tau^2}{2} N(s_u^1)^2 + \frac{\tau^3}{6} N^2(s_u^1)^3 + \dots \right\} \\
&= \frac{I_{\text{tot}}^0}{N} \text{FT}^{-1} \left\{ \sum_{n=0}^{\infty} \frac{(N\tau s_u^1)^n}{n!} \right\} \\
&= \frac{I_{\text{tot}}^0}{N} \text{FT}^{-1} \{ e^{N\tau s_u^1} \}
\end{aligned}$$

where s_u^1 is the FT of S_j^1 and $I_{\text{tot}} e^{-\tau}$ has been replaced by its equivalent, I_{tot}^0 , the total number of zero-scattering counts in the spectrum.

In practice, the energy resolution is not ideal and the measured spectrum is "smeared out" according to the zero-loss distribution. In other words, the measured spectrum, I_j^{meas} , is the result of convolving the (normalized) instrument resolution function R_j with I_j so that

$$I_j^{\text{meas}} = (I * R)_j = I_{\text{tot}}^0 \text{FT}^{-1} \{ r_u e^{N\tau s_u^1} \}$$

Since I_j^{meas} , R_j , I_{tot}^0 , and τ can all be measured, the above equation allows the SSD (S_j^1) to be extracted from the data.

3.3. Processing and Analysis of Low-Loss Spectra

The present section describes the specific procedures followed, based on the foregoing theoretical results, to analyze plasmon EELS spectra for the current study.

3.3.1. Correction for Multiple Scattering

Correcting for multiple scattering amounts to extracting the SSD from the measured spectrum. The equation for I_j^{meas} of the previous section dictates how this is to be done. Solving for S_j^1 yields

$$S_j^1 = \frac{1}{N\tau} \text{FT}^{-1} \left\{ \ln \left(\frac{i_u^{\text{meas}}}{I_{\text{tot}}^0 r_u} \right) \right\} = \frac{1}{N\tau} \text{FT}^{-1} \left\{ \ln \left(\frac{z_u^{\text{meas}}}{z_u^{\text{meas}}} \right) \right\}$$

where i_u^{meas} , r_u , and z_u^{meas} are the FT's of the measured spectrum, the instrument resolution function, and the measured spectrum's zero-loss peak, respectively, and N is the number of spectrum channels. Since the measured spectrum's zero-loss peak, Z_j^{meas} , is equal to $I_{\text{tot}}^0 R_j$, z_u^{meas} has been substituted for $I_{\text{tot}}^0 r_u$ above. In addition, since S_j^1 is normalized (by definition), the thickness of the probed area in units of the inelastic mean free path is determined via

$$\frac{1}{N} \sum_{j=0}^{N-1} \text{FT}^{-1} \left\{ \ln \left(\frac{i_u^{\text{meas}}}{z_u^{\text{meas}}} \right) \right\} = \frac{1}{N} \sum_{j=0}^{N-1} N\tau S_j^1 = \tau = t/\lambda_{\text{inel}}$$

Although the procedures suggested by the above formulae are in principle very simple, in practice a number of details must be attended to in order to achieve a correct extraction of the SSD. Foremost is the unavoidable problem of spectrum noise due to the inherent (counts)^{1/2} uncertainty in the event count of each energy channel and due to the effects of stray AC fields in steeply sloped regions of the spectrum (ie. near the zero-loss peak). As a result of the zero-loss deconvolution implicit in the above procedure, this

noise is inevitably amplified to the point where all useful information in S_j^1 is lost. This problem can be avoided by simply not attempting to remove the effects of the instrument resolution function, as first suggested by Leapman and Swyt [48]. Since the plasmon-regime features of semiconductor EELS spectra are inherently broad, the effect of the instrument energy resolution on the spectrum is not very pronounced anyway, as illustrated in figure 3.8. Hence, the main difference between the true, undegraded EELS spectrum and the measured one is in the zero-loss peak itself. By replacing the measured zero-loss peak with a δ -function having an equal count integral, this difference is removed. Mathematically, this amounts to writing

$$\begin{aligned} Z_j^{\text{meas}} &= I_{\text{tot}}^0 R_j \rightarrow I_{\text{tot}}^0 \delta_j \\ I_j^{\text{meas}} &= I_j^{\text{meas}} + Z_j^{\text{meas}} \rightarrow I_j^{\text{meas}} + I_{\text{tot}}^0 \delta_j \end{aligned}$$

where I_j^{meas} is the measured EELS spectrum minus its zero-loss peak. In terms of the FT's

$$\begin{aligned} z_u^{\text{meas}} &\rightarrow FT\{I_{\text{tot}}^0 \delta_j\} = I_{\text{tot}}^0 / N \\ i_u^{\text{meas}} &\rightarrow FT\{I_j^{\text{meas}} + I_{\text{tot}}^0 \delta_j\} = i_u^{\text{meas}} + I_{\text{tot}}^0 / N \end{aligned}$$

so finally,

$$\begin{aligned} S_j^1 &= \frac{1}{N\tau} FT^{-1} \left\{ \ln \left(\frac{i_u^{\text{meas}} + I_{\text{tot}}^0 / N}{I_{\text{tot}}^0 / N} \right) \right\} \\ &= \frac{1}{N\tau} FT^{-1} \left\{ \ln \left(1 + \frac{i_u^{\text{meas}}}{I_{\text{tot}}^0 / N} \right) \right\} \end{aligned}$$

In most cases, it is the actual single-scattering component, I_j^1 , of the EELS spectrum that is desired and not the normalized probability distribution S_j^1 . They are simply related via

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Figure 3.3 - Effect of convoluting measured EELS spectrum (dotted) with measured instrument resolution function (normalized zero-loss peak). Note that resulting spectrum (solid) is not significantly altered except near zero-loss peak.

$$I_j^1 = I_{\text{tot}} \tau e^{-\tau} S_j^1 = I_{\text{tot}}^0 \tau S_j^1$$

so that

$$I_j^1 = \frac{I_{\text{tot}}^0}{N} F T^{-1} \left\{ \ln \left[1 + \frac{i_u^{\text{meas}}}{I_{\text{tot}}^0/N} \right] \right\}$$

This very simple expression, requiring only the input of I_j^{meas} and I_{tot}^0/N , defines the algorithm actually used in the present work for extracting the single-scattering part of a measured spectrum without amplifying the noise. In order to remove the zero-loss peak from I_j^{meas} , a spectrum measured under identical microscope conditions but with the specimen removed from the beam path was scaled to fit the zero-loss peak of I_j^{meas} and subtracted. Residuals below $E=0$ due to noise differences in the two peaks were simply set to zero. The value of I_{tot}^0 was obtained by subtracting the count integral of the resulting I_j^{meas} from that of I_j^{meas} . Although this technique leaves the instrument resolution function in the spectrum and consequently yields a plasmon line width slightly larger than the true value, this small error was corrected using a method to be described in section 3.3.3.

One last detail involved in applying the above algorithm for S_j^1 to measured data should be mentioned. When taking a finite, discrete FT, it is well known that the actual implicit input to the transformation is the *periodic continuation* of the sampled points rather than simply the data points alone. Since I_j^{meas} begins with a value of 0 counts at $E=0$, the truncation of the spectrum at the maximum energy of its range can result in a strong discontinuity in its periodic continuation. Such a discontinuity can give rise to artifacts in the extracted SSD. The standard remedy for this problem is to artificially extend the spectral data range and subsequently taper the spectrum to zero counts. Since a fast Fourier transform (FFT) algorithm requiring 2^k points [54] was used to calculate

the discrete FT's, the number of spectrum channels was doubled from 1024 to 2048. Next, the discontinuity at the high end of the measured spectrum was extrapolated to 0 using a quadratic functional form matched in slope and value to the end of the measured data and meeting the horizontal axis with zero slope.

With I_j^{meas} in this form and the algorithm for S_j^1 derived above, a very accurate estimate of the SSD can be obtained. This is demonstrated in figure 3.9, which compares measured plasmon EELS spectra from Si and GaAs with their corresponding extracted SSD's. Note that the obvious multiple plasmon peaks in the original data are cleanly removed.

3.3.2. Fitting and Isolating the Plasmon Contribution

Once the SSD has been correctly extracted from the measured data, the next step is to identify and characterize the bulk plasmon component of the spectrum. This is accomplished by means of the plasmon line shape model developed in section 3.2.1. By varying the three parameters C , E'_p , and Γ , a χ^2 fit [55] of the model to the plasmon peak of the SSD data yields the desired information. The range of energies over which χ^2 is minimized in order to achieve a fit depends on the nature of the spectrum.

For the semiconductor plasmon spectra analyzed in the course of the present work, no attempt was made to include the 0-10eV range in the fit as significant surface plasmon and Čerenkov contributions not included in the $\epsilon(\omega)$ model occur in this range. For a specimen like Si, which has no core electrons with binding energies less than about 100eV, the entire SSD above about 10eV served as input to the fit. Most other semiconductors, particularly Ge and Ga- or In-containing III-V's, have d -shell electrons with binding energies of the same order as the plasmon energy and often give rise to structure on the high-energy side of the plasmon peak. As these transitions are also left out of the plasmon

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Figure 3.9a - Comparison between original data (top) and extracted SSD (bottom) of Si.

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Figure 3.9b - Comparison between original data (top) and extracted SSD (bottom) of GaAs.

spectrum model, the fits to the spectra of these samples were restricted to the immediate vicinity of the plasmon peak.

Figure 3.10 gives examples of plasmon peak fits for both Si and GaAs over the intervals indicated above. The fits visually match the SSD data quite well in the immediate neighborhood of the bulk plasmon peak. The associated value of the reduced chi-squared, $\chi^2_{\nu} \equiv \chi^2/N$, is shown with each plot. Since counting statistics account for most of the channel-to-channel noise of the original spectrum and since the noise is unaffected by the SSD extraction, the uncertainty in each data point input to the fit was taken to be the square root of the number of counts in the corresponding channel of the original spectrum. For a good fit, χ^2_{ν} will typically be of order one or less. The values obtained here, although somewhat larger than one, indicate the fit is reasonable. Detailed analysis of the differences between fit and data indicate that the excess χ^2_{ν} is not due to incorrect estimates of the data uncertainties but is rather a result of systematic deviations, indicating that the functional form of the model is not quite correct. As expected, the fits have fewer counts than the data in the $<10\text{eV}$ range, showing that there are indeed additional energy-loss mechanisms in effect at these energies which are not included in the simple model of the dielectric function. For Si the fit is excellent throughout the remainder of the spectral range while the additional transitions expected in GaAs again show up clearly as an excess of counts in the data over the fit. This suggests the possibility of using this procedure to remove the bulk plasmon part of such semiconductor EELS spectra to study the *d*-electron transitions separately or to use them for quantitative analysis of the specimen [52]. This is taken up further in chapter 6. The excellent fit over the entire Si plasmon spectrum opens the possibility of precise studies of plasmon line shape changes as a function of specimen properties. These are taken up in chapter 4.

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Figure 3.10 - Results of χ^2 fits of theoretically-based spectrum model (dotted) to measured SSD's (solid) of Si (top) and GaAs (bottom).

3.3.3. Extraction of Accurate Line Shape Parameters

Fitting a plasmon line shape model to the plasmon peak of a measured EELS spectrum makes it possible to isolate the plasmon contribution to the spectrum. In addition, the values of the fit parameters, E'_p and Γ , provide means by which to precisely characterize the plasmon line. As indicated previously, E'_p and Γ give the plasmon peak position and FWHM. However, a truly accurate measurement of the plasmon line shape requires that the finite energy resolution of the measured spectrum be taken into consideration. Since the instrument resolution function is generally symmetric about $E=0$, it does not affect the plasmon peak position. It does, however, increase the plasmon line width. This increase can be corrected for via the following technique. First, a spectrum model with the same E'_p as the fit to the SSD but a somewhat smaller Γ is calculated. This model is then resolution-degraded in the same way as the measured spectrum by convoluting it with a zero-loss peak measured in conjunction with the spectrum. A new χ^2 fit is carried out on the degraded model and the new values of the fit parameters are compared to the values obtained with the data. The width parameter, Γ , of the initial undegraded spectrum model is adjusted until the fit to its zero-loss convoluted version exactly matches that found for the data. The input model parameters are then taken to be the correct values for the plasmon line shape parameters. For the two examples of the previous section, the uncorrected fits yield

$$\text{Peak}^{\text{Si}} = 16.67\text{eV} \quad \text{FWHM}^{\text{Si}} = 3.51\text{eV}$$

$$\text{Peak}^{\text{GaAs}} = 15.83\text{eV} \quad \text{FWHM}^{\text{GaAs}} = 4.13\text{eV}$$

After correction the FWHM's become

$$\text{FWHM}^{\text{Si}} = 3.36\text{eV}$$

$$\text{FWHM}^{\text{GaAs}} = 3.77\text{eV}$$

CHAPTER 4

Plasmon Line Shape Variations in Silicon

The analytical method developed in chapter 3 points the way to precise characterization of semiconductor plasmon line shapes. The procedures described in chapter 2 illustrate the use of TEM EELS to collect energy-loss data characteristic of isolated regions of a specimen. In the present chapter, the above are applied to experimental studies of the plasmon line shape variation in several inhomogeneous silicon samples. Specifically, alterations of the plasmon line shape near free surfaces, regions of amorphous structure, and grain boundaries are examined. In the current understanding [25], the main sources of plasmon damping and energy shift in semiconductors are interband transitions made possible by the Bloch nature of the semiconductor band states. As this is a direct result of the crystal potential, deviations from the bulk crystal potential within the above sorts of specimen regions can lead to a locally modified plasmon line shape. The studies described in this chapter attempt to measure and account for such line shape variations.

Silicon was chosen for these studies since the line shape model and analytical method developed in the preceding chapter were found to work particularly well for this material, thus providing a sensitive way to measure line shape changes. As there is already an established literature on the bulk plasmon of silicon, this provides a context for interpreting the results of the present studies. Finally, silicon is the simplest semiconductor to display clearly defined plasmon excitations, being elemental, purely covalently bonded, and having no electronic transitions or other excitations with energies near that of the bulk plasmon to complicate its energy-loss spectrum. This will facilitate interpretation of any observed line shape changes.

4.1. Plasmons Near Free Surfaces

The geometry of a typical specimen prepared for TEM is ideal for studying plasmon excitations in the vicinity of the specimen-vacuum interface (here, "vacuum" means the microscope column vacuum of about 5×10^{-8} Torr). Since the wedge-like thickness profile of the specimen tapers gradually to zero at the perforation, one can probe either bulk or near-surface material by collecting data from either thick specimen regions far from the perforation or thin regions very near the perforation, respectively. By comparing plasmon spectra obtained in these two regions, the effects on the plasmon line shape can be assessed directly.

4.1.1. Experiment

Sets of EELS spectra were collected from a Si single-crystal specimen in two separate runs. The specimen was ultrasonically cut from a commercial-grade (111) wafer, mechanically ground to $75\mu\text{m}$ thickness, and thinned to electron transparency via ion milling. Each experimental run sampled various thicknesses by collecting spectra from regions 10-20nm in lateral dimension at a range of distances with respect to the perforation, as illustrated in figure 4.1. Taking the thickness profile of the specimen to have a wedge angle of about 10° , the lateral size of each probed region ensures uniformity of its thickness to $\pm 1.5\text{nm}$. The experimental setup and data acquisition followed the optimized procedures described in detail in chapter 2. For the particular case of silicon spectra, the $\pm 0.5\%$ uncertainty in the energy scale calibration can be reduced by using the silicon $L_{2,3}$ edge for internal calibration. According to compiled data [56], the energy of this edge (representing the threshold for $2p$ to conduction band transitions) is 99.8eV. Using this as a standard, the absolute accuracy of the calibration is $\pm 0.2\%$. Reproducibility checks indicate the stability of the calibration within a given run to be of the same order.

Top View

Cross-section

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Figure 4.1 - Schematic view of the experiment, indicating positions and dimensions of probed specimen regions.

4.1.2. Data

In the first run, EELS spectra were collected in thicker regions of the specimen only, primarily to establish a base set of data for comparison. The specimen was mounted without any tilting of the stage. Analysis of a diffraction pattern taken with this set-up showed the actual orientation of the specimen to be 5.5° from the initial $[111]$ wafer plane, tilted along $(2\bar{1}1)$. Although this orientation avoids the strong dynamical elastic scattering of a completely symmetric orientation, significant systematic Bragg reflections were active during the experiment. Nevertheless, specimen orientation is not expected to have significant effects on the plasmon spectra presented here as previously reported measurements [22] of the silicon plasmon anisotropy with respect to momentum transfer show it to be insignificant over the range of scattering angles relevant to the present study (0-6mrad).

A sampling of the measured spectra is shown in the left column of figure 4.2. The effects of multiple scattering are quite evident in the raw data in the form of increasing loss intensity at multiples of the plasmon energy with increasing thickness. The specimen thickness, in units of the mean free path for inelastic scattering, λ_{inel} , is given with each spectrum and is determined from the data in the manner described in chapter 3. There is currently no consensus on the precise value of λ_{inel} in silicon and its effective value in a given experiment depends on the collection angle. In the present case, however, a value of 100nm is likely to be correct to within $\pm 10\%$ [57].

Using the deconvolution procedure discussed in chapter 3, multiple scattering is removed from the raw data. The resulting single-scattering distributions (SSD's) are displayed in the right column of figure 4.2. The only apparent difference among the extracted SSD's is the relative strength of the small feature immediately below the main

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Figure 4.2 - Left: Measured plasmon EELS spectra from crystalline Si for various specimen thicknesses, given in units of the inelastic mean free path. Right: Corresponding SSD's (solid) and plasmon model fits (dotted).

plasmon peak. This feature has been observed previously by Chen and co-workers [58] and has been attributed to loss events involving surface plasmon modes. Notably, its relative contribution to the spectra of figure 4.2 diminishes virtually to zero with increasing specimen thickness, confirming its association with the surface. Beyond this small surface plasmon feature, the SSD's show that the low-loss EELS spectrum of silicon consists exclusively of bulk plasmon-loss events. The excellent fit of the plasmon line shape models shown superimposed on the SSD's further supports this conclusion.

Although there are no gross changes in the plasmon line shape as the proportion of near-surface material probed increases, detailed comparison of the fitted line shape model parameters indicate a small increase in the plasmon linewidth. In an effort to verify this trend, a second set of data including thinner specimen regions was collected. The specimen and experimental conditions substantially the same as before. The one difference worthy of note is that the specimen was tilted well away from [111] to ensure that no systematic Bragg reflections were excited. The measured spectra and extracted SSD's are shown in figure 4.3. As before, bulk plasmon excitations dominate over surface plasmon events in each of the SSD's, indicating the plasmon resonance is still well-defined even in the thinnest specimen regions probed. In addition, the plasmon line shape model fits are again quite good. In this series of spectra, however, the slight broadening of the plasmon line with decreasing specimen thickness is visibly apparent.

Since the plasmon line shape fits to the above spectra are virtually indistinguishable from the data, the values of the fit parameters provide a quantitative measure of line shape changes which is much more sensitive than mere visual inspection. The fitted values of the peak position and peak FWHM are tabulated versus thickness in table 4.1.

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Figure 4.3 - Left: Measured plasmon EELS spectra from crystalline Si for various specimen thicknesses, given in units of the inelastic mean free path. Right: Corresponding SSD's (solid) and plasmon model fits (dotted).

Si plasmon vs. probed thickness		
$t/\lambda_{\text{inel}} (\pm 5\%)$	Peak ($\pm .04\text{eV}$)	FWHM ($\pm .05\text{eV}$)
.17	16.64	4.61
.22	16.66	3.87
.32	16.70	3.48
.32	16.64	3.58
.34	16.64	3.38
.39	16.64	3.34
.43	16.63	3.43
.52	16.59	3.26
.90	16.63	3.14

Table 4.1 - Plasmon peak position and FWHM in crystalline silicon versus sample thickness. Values obtained from line shape fits to measured SSD's.

Details of the extraction of these values from the fits have been given in chapter 3. The uncertainties in the peak position and FWHM given in the table represent those of the statistical fitting procedure.

A clear picture of the line shape variation is provided by the plots of the tabulated results in figure 4.4. Within uncertainties, the energy of the bulk plasmon resonance does not change over the thickness range probed. In contrast, its linewidth displays a clear increase with decreasing specimen thickness, indicating enhanced plasmon damping near the specimen surface.

4.1.3. Interpretation of Results

A number of possible effects could conceivably account for the above findings. Two obvious possibilities can be eliminated at the outset. First, there is the well-known ~ 2 -

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Figure 4.4 - Plots of plasmon peak position and FWHM versus probed sample thickness in crystalline silicon.

5nm native oxide layer which forms on any silicon surface not held under strictly ultra-high vacuum (UHV) conditions. As this oxide has a broad plasmon-like feature [59,60], losses within this layer might be viewed as a possible source of the observed broadening. As the specimen thickness decreases and oxide-layer events comprise a larger fraction of the collected data, their contribution to the EELS spectrum would become increasingly important. However, the oxide plasmon resonance occurs at 22-23eV. Simple addition of such a feature cannot explain the observed broadening without an accompanying upward peak shift closer to the oxide plasmon energy. As this is not observed, oxide plasmon losses cannot be an important effect here.

A second obvious potential source of the broadening effect is the amorphized layer near the specimen surfaces resulting from ion-milling damage during sample preparation. Compiled data [61] on the plasmon peak in amorphous silicon indicate that although its width may be greater than in the crystalline case, it is also slightly lower in energy. Such an energy shift is not observed in the present results. Furthermore, the linewidth reported for amorphous silicon (4.0eV) is significantly smaller than that found in the thinnest regions above (4.6eV). Thus, the amorphous layer also appears to be ruled out as an explanation for the results. This point cannot be considered completely settled, however, due to questions which arise upon careful examination of the literature results. These questions and the role of the amorphous layer are given further consideration in section 4.2.

With compositional or structural inhomogeneities near the surface excluded as the source of the observed line shape change, it becomes evident that the effect is directly related to the free surfaces themselves. An issue that should be addressed is whether the observed broadening is an artifact of enhanced surface plasmon contributions to the

EELS spectra of thin specimens. Although the dominant surface plasmon contribution appears to be the distinct feature observed just below the bulk plasmon, it has been suggested [62] that an additional feature associated with radiative surface plasmons should appear on the high side of the bulk plasmon peak. The combined effect of surface plasmon events above as well as below the bulk peak could account for the observed line shape broadening without a concomitant shift. But although radiative surface plasmons have been observed in aluminum [63], there is no reported experimental evidence for them in silicon [58]. In addition, the bulk plasmon model used here fits the high side of the bulk peak extremely well at all thicknesses, while its mismatch on the low side clearly points up the non-radiative surface plasmon contribution. If surface plasmons loss events were a significant background to the bulk peak, mismatch of the model would be expected on both sides. Indications are, therefore, that the line shape broadening truly reflects a change in the bulk plasmon excitation and is not simply a surface plasmon artifact.

What sorts of mechanisms, then, might account for enhanced bulk plasmon decay near free surfaces? One possibility is an increase in the density of interband transitions with energies and momentum transfers appropriate for plasmon decay due to changes in the electronic structure of the sample near the surface. Put into other words, surface-related changes in the electronic structure are likely to modify the dielectric response of the specimen, showing up as a change in the absorptive part of the complex dielectric function, $\epsilon_2(\omega)$. As discussed in chapter 3, an increase in ϵ_2 at $\omega=\omega_p$ leads to a larger plasmon width (given that the slope of ϵ_1 at ω_p remains fixed). Following the procedure of Egerton [0], calculation of ϵ_1 and ϵ_2 in the vicinity of ω_p from the spectra obtained in the thickest and thinnest regions show that $\epsilon_2(\omega_p)$ is indeed larger in the thinner specimen, as shown in figure 4.5. It is noteworthy, however, that this enhancement appears to be a residual effect of the structure in ϵ_2 contributed by the surface plasmon excitations.

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Figure 4.5 - Complex dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, in vicinity of plasmon energy calculated from silicon EELS spectra taken from .90 λ_{inel} (solid) and .17 λ_{inel} (dashed) sample thicknesses.

This suggests that the actual mechanism of the bulk plasmon decay in near-surface regions may involve damping through excitation of surface plasmons.

Another possibility is a damping effect brought about by boundary conditions imposed upon the plasmon wave function. Such an effect has been observed and correlated with grain size in polycrystalline aluminum [64] and has been accounted for theoretically in terms of plasmon scattering from grain boundaries [65]. Essentially, it is found that enhanced plasmon decay occurs when the plasmon wavelength becomes greater than the grain size of the polycrystalline sample. Using the momentum transferred to the plasmon at zero scattering angle, the maximum plasmon wavelength set up by an incident beam of energy E_0 is given by

$$\lambda_{\max} = \lambda_0 \frac{2E_0}{E_p}$$

where λ_0 is the incident electron wavelength and E_p is the plasmon energy. For $E_0=100\text{keV}$, $\lambda_{\max}$ is 44.5nm. Referring back to the plot of FWHM versus sample thickness, it is noteworthy that the curve only indicates a significant thickness dependence for thicknesses smaller than about $\lambda_{\max}$. This suggests that a damping mechanism similar to that due to grain boundary scattering may also be operative at free surfaces and thereby account for the broadening observed here.

4.1.4. Summary

To summarize, it has been found that the bulk plasmon line shape of single-crystal silicon broadens near the surface whereas its energy position remains fixed. Explanations of the observations as artifacts due to oxide or amorphous layers at the surface appear to be excluded. Possible mechanisms for the broadening include enhanced plasmon decay mediated by surface-related interband transitions or surface plasmon excitations, and

poorer definition of the plasmon resonance due to scattering of the plasmon wave function from the bounding surfaces. The present results alone, however, are not sufficient to draw more specific conclusions about the broadening mechanism.

4.2. Plasmons in Amorphous Silicon

In the preceding section, it became of interest to know the characteristics of the plasmon peak of amorphous silicon in order to assess the amorphous layer's role in the line shape broadening observed with decreasing specimen thickness. It was of particular importance to know how the amorphous and crystalline plasmon line shapes compare. Relevant information is provided by three papers in the earlier EELS literature [66-68]. Although these reports give consistent results at a cursory level, careful reading shows that they do not really lead to a consensus on the precise amorphous plasmon line shape or on whether it differs significantly from that of crystalline silicon. In an effort to clarify the situation, an attempt has been made to obtain an unambiguous result with the present instrumentation and precise line shape measurement technique. The present section describes the results of this effort.

4.2.1. Experiment

For the present study, an amorphous silicon film was grown via evaporation onto a rock salt substrate at room temperature, floated off in distilled water, and picked up on a copper mesh grid. Experimental conditions were as before except that a lower on-screen magnification of 26,000 $\times$ was used to probe a larger specimen area ($\sim 30\text{nm}$) and thereby achieve a higher count rate at the spectrometer. Since the sample was an evaporated film, it was not necessary to work with high spatial resolution to ensure the probed area was of uniform thickness. To further enhance the loss signal, the specimen was tilted 30° to increase its apparent thickness. Selected area diffraction confirmed the amorphous structure of the film, showing only diffuse rings. A quick check with characteristic X-ray analysis confirmed its composition, showing no evidence for any elements other than silicon within the X-ray detector's sensitivity range.

4.2.2. Data

A few EELS spectra from different areas of the film were collected and analyzed to check for variation of the film thickness. None was detected, as all spectra gave a thickness of $.38\lambda_{\text{inel}}$. Consequently, all the data were summed into the single spectrum shown in figure 4.6. The extracted single-scattering distribution and the optimum line shape fit are shown in figure 4.7. Although the fit appears to be acceptable, the value of the reduced χ^2 ("goodness of fit" parameter) associated with it is about 10 times poorer than that obtained for the fits in the crystalline case above. This indicates that the line shape model used up until now is not correct for the amorphous silicon plasmon line shape. Since the model gives a poor match to the data, the plasmon peak energy and FWHM in this case were instead measured by hand from the SSD with the following results:

$$\text{Peak}^{\text{am-Si}} = 16.7 \pm 1.1 \text{ eV} \quad \text{FWHM}^{\text{am-Si}} = 4.9 \pm 1.1 \text{ eV}$$

As before, the FWHM quoted here has been corrected for the 1.0 eV spectral energy resolution using the convolution procedure described in chapter 3.

4.2.3. Interpretation of Results

Comparing the above measurement with the results found in section 4.1 for a similar thickness of crystalline silicon (assuming the λ_{inel} 's are comparable) shows that amorphous silicon displays considerably greater plasmon damping than its crystalline counterpart whereas the two have identical plasmon resonance energies. Direct comparison of corresponding SSD's, as given in figure 4.8, points up the difference very clearly. The difference found here is significantly more pronounced than that observed in either of the previously reported comparisons of amorphous and crystalline silicon plasmons. Table 4.2 summarizes the literature results.

Figure 4.6 - Measured EELS spectrum from an amorphous Si film.

Figure 4.7 - SSD extracted from the above spectrum (solid) and optimum fit of plasmon model used for crystalline case (dotted).

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Figure 4.8 - Comparison between plasmon line shapes measured from equal thicknesses of amorphous (solid) and crystalline (dotted) silicon.

Data on plasmons in Si					
Authors	crystal		amorph		δE
	Peak	FWHM	Peak	FWHM	
Zeppenfeld Raether [67]	16.45 ± 1	$3.6 \pm ?$	16.1 ± 1	$4.0 \pm ?$	.3-.5
Aiyama Yada [68]	16.5 ± 1	3.8 ± 2	16.4 ± 1	4.0 ± 2	.6-.8

Table 4.2 - Values of plasmon line shape parameters in crystalline and amorphous silicon quoted in the literature and EELS energy resolution, δE , with which they were measured. All values are in eV.

Since the authors differ as to their treatment of the effect of the finite energy resolution on the plasmon FWHM, only its raw uncorrected value in each case is quoted here. The energy resolutions claimed are not very different, so the raw results should be directly comparable. Taken as a whole, the literature values are consistent with each other, but taken separately, they point to different conclusions. Zeppenfeld and Raether conclude the amorphous plasmon has a lower resonance energy and a greater linewidth than that of the crystalline form, although they give no estimate of the uncertainties in their FWHM determinations. Within uncertainties, Aiyama and Yada's results, on the other hand, indicate the plasmon line shapes of these two forms are the same. In any case, neither observes a line shape broadening as large as the one found here. In an early measurement of the amorphous silicon plasmon line, Sueoka found a value of 4.6 ± 5 eV for the FWHM with 0.8 eV energy resolution, consistent with the result of the present work. Unfortunately, the possibility of a systematic deviation of Sueoka's result due to instru-

mental factors cannot be excluded since it is not accompanied by a measurement on crystalline silicon for comparison.

Careful reading of the above papers points up a number of distinctions between the conditions of those experiments and the present one, distinctions which may account for their widely differing results for the plasmon linewidth. One potentially important difference is that the "crystalline" samples of the earlier experiments were actually polycrystalline films obtained by heat treatment of amorphous samples. Although the authors claim grain sizes considerably larger than the maximum plasmon wavelength, as discussed in section 4.1.3, it is conceivable that the structural distortions associated with the grain boundaries may alter the sample's dielectric response and plasmon damping characteristics even in the absence of direct plasmon-boundary scattering. This possibility is investigated in section 4.3. Another distinction between the experiments is the collection angle over which loss events are integrated in the spectrum. In all of the earlier studies the collection angle was much smaller than that applicable to the spectra presented here, .3mrad as opposed to 6.0mrad. Thus the disparity in observed linewidth may be a manifestation of plasmon width dispersion. Finally, the variability of the results may be an indication that the specimens were not all the same despite apparently similar preparation conditions. As is known to occur with carbon films [69,70], nominally "amorphous" films may display a range of physical properties due to unknown or undetected details of their structure and composition.

In light of the above, the only conclusion that can be drawn about the plasmon line shape of amorphous silicon is that it has yet to be properly characterized. Although indications are that plasmons are more strongly damped in amorphous silicon (as physical intuition would lead one to guess), firm conclusions as to the true linewidth will require

further study.

The finding that the plasmon line shape broadening in amorphous silicon may be considerably larger than previously thought necessitates reconsideration of the role of the amorphous layer in the broadening observed in very thin crystalline samples. The magnitude of the plasmon FWHM measured here (4.9eV) is clearly sufficient to account for the width (4.6eV) observed in the thinnest regions of the ion-milled silicon monocrystal above. Indeed, the plasmon line shape observed in the thinnest sample above can be reproduced quite well by suitable linear combination of the amorphous silicon SSD with that obtained from the thickest crystalline region (likely to be closest to the true bulk plasmon line shape). This is illustrated in figure 4.9. Hence, enhanced plasmon damping in the amorphous layer must still be considered a possible source of the line shape broadening observed above in very thin regions of silicon single crystals.

Figure 4.9 - Comparison between plasmon-regime SSD measured from $.17\lambda_{\text{inel}}$ thickness of ion-milled single-crystal silicon (solid) and that obtained by mixing measured line shapes of amorphous silicon and thicker $(.90\lambda_{\text{inel}})$ single-crystal in 3:1 ratio (dotted).

4.3. Plasmons Near an Internal Grain Boundary

As mentioned in the first section of this chapter, it is known that very finely grained polycrystalline materials display increased plasmon damping as compared to single crystals of the same materials. This effect has been attributed [64,65] to plasmon scattering from the structural discontinuity at the boundaries between grains (see figure 4.10a). However, the distortions and concomitant electronic band structure changes associated with grain boundaries may themselves lead to changes in the plasmon line shape and give an additional contribution to the apparent plasmon damping which is active even in the absence of plasmon-boundary scattering (see figure 4.10b). In the previous section, such a mechanism was considered as a potential explanation for the contrast between the weak plasmon line shape differences reported in the literature between amorphous and polycrystalline silicon and the much stronger differences observed in the present study between amorphous and monocrystalline silicon. As yet, there appear to have been no attempts to test for such an additional contribution to plasmon decay in polycrystalline material. Due to the ready availability of an artificially grown silicon bicrystal with a single, virtually perfect, planar grain boundary, it was possible to carry out a more controlled study of grain boundary effects. The present section reports the results of this study and demonstrates the usefulness of the spatially resolved capabilities of TEM EELS.

4.3.1. Experiment

For this experiment a silicon grain boundary specimen previously studied and characterized by Rose [71] was available for use. The geometry of the boundary, as indicated by high-resolution TEM, is illustrated in figure 4.11. This particular boundary comprises two neighboring grains with parallel [110] axes. The grains are tilted symmetrically about these axes through a relative angle of 38.94° , causing the $(\bar{2}21)$ planes of one

Figure 4.10a - Schematic illustration of plasmon scattering from grain boundary leading to modification of plasmon resonance and damping.

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Figure 4.10b - Even without direct plasmon-boundary scattering, plasmon resonance may also be modified by change in dielectric response of sample in vicinity of grain boundary due to associated structural distortion.

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Figure 4.11 - Schematic view of grain boundary specimen used to test boundary-related effects on plasmon line shape in silicon.

to correspond with the $(\bar{2}\bar{2}1)$ planes of the other. The grain boundary is parallel to these planes. The specimen was oriented to excite symmetrical reflections from the $(\bar{2}\bar{2}1)$ and $(2\bar{2}1)$ planes so that the boundary was edge-on with respect to the beam. This orientation, combined with the collection of predominantly forward scattered events, should minimize direct plasmon scattering from the boundary and allow any additional plasmon damping effect to be isolated. Specimen regions at various lateral distances, D , from the grain boundary were sampled, as shown in figure 4.12, to assess the effect of grain-boundary related distortions on the plasmon line shape. Presumably such effects, if any, will be most pronounced nearest the boundary. An attempt was made to keep the distance from the edge of the specimen constant in an effort to sample a constant thickness and avoid complications due to thickness effects. Image magnification and spectrometer aperture were selected to sample regions about 8nm in lateral dimension.

4.3.2. Data

A sampling of the SSD's obtained at various positions, D , are shown in figure 4.13. No obvious line shape change occurs in the vicinity of the boundary. As in the thickness variation study, line shape model fits were found to fit the data very well and were used to precisely measure the plasmon energy and FWHM. A complete tabulation of the extracted plasmon peak parameters as well as the calculated thicknesses of the probed regions is given in table 4.3.

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Figure 4.12 - Composite bright-field micrograph of specimen grain-boundary region from which EELS spectra were collected; specific sample points are indicated by pointers.

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Figure 4.13 - Measured plasmon line shape in silicon bicrystal as a function of lateral position, D , with respect to an edge-on grain boundary.

Si plasmons near a grain boundary			
D ($\pm 5\text{nm}$)	t/λ_{inel} ($\pm 5\%$)	Peak ($\pm 0.04\text{eV}$)	FWHM ($\pm 0.05\text{eV}$)
320	.40	16.62	3.41
220	.38	16.71	3.46
105	.35	16.58	3.49
50	.35	16.58	3.49
10	.40	16.61	3.45
0	.39	16.62	3.48
0	.38	16.63	3.50
-35	.36	16.56	3.50
-70	.38	16.62	3.53
-150	.39	16.56	3.46

Table 4.3 - Plasmon peak position and FWHM as a function of lateral position, D, with respect to an edge-on grain boundary.

Note that, within the measurement uncertainty, the thicknesses sampled were all about $.38\lambda_{\text{inel}}$ ($\sim 40\text{nm}$). Even with the refinements provided by the numerical analysis, however, there is no detectable line shape change in the vicinity of the boundary. The measured values of the line shape parameters at all distances from the grain boundary are consistent with those found earlier in single-crystal silicon of the same thickness.

4.3.3. Interpretation of Results

Since the line shapes of plasmons generated in the vicinity of the grain boundary (but not interacting with it) are not significantly different from that observed in defect-free material, it can be concluded that the grain boundary used as a test case here does not change the electronic structure of the surrounding material sufficiently to affect its dielectric response to incident electrons. Although this one example does not allow a

general conclusion, it provides some evidence that direct plasmon-boundary interaction is the sole source of plasmon damping observed in finely grained polycrystalline material. It should be noted that no changes in the plasmon line shape are observed even when the probed region contains the grain boundary itself. This would seem to indicate that even the strong distortions in the immediate vicinity of the grain boundary do not significantly affect the band structure and, consequently, the polarization response measured by the EELS spectrum. One aspect of the above experiment, however, precludes any definitive statement on this matter. The sampled volumes, roughly of dimensions $8\text{nm} \times 8\text{nm} \times 40\text{nm}$, are quite large relative to the range of the strongest grain-boundary related distortions suggested by figure 4.11. Hence, their effects may not be strong enough or sufficiently isolated under the above sampling conditions to show up in the plasmon EELS spectrum.

4.4. Integration of Findings

It is now appropriate to try to consolidate the findings of the present chapter. Conclusions can be drawn about the factors leading to modifications of the plasmon line shape in non-ideal silicon samples as well as about the precise characteristics of the line shape in bulk single-crystal silicon.

4.4.1. *Factors Affecting the Silicon Plasmon Line Shape*

Before remarking on the plasmon line shape changes that *were* observed in silicon, it is worth noting what was *not* observed, namely, shifts of the plasmon peak position. In all of the cases examined here, the plasmon peak did not deviate (within uncertainties) from a value of 16.6eV. This is probably one reason for the loss of interest in early efforts at applying plasmon spectroscopy to materials characterization via measurement of plasmon peak shifts [72]. The plasmon peak position is simply not a very sensitive measure of the physical properties of a sample. The plasmon linewidth, on the other hand, seems to be a different story.

The strongest effects on the silicon plasmon line shape observed in the preceding studies were the changes in linewidth. The most pronounced of these changes was that resulting from amorphization of the structure. Not only does amorphous silicon show the largest plasmon damping, as reflected in its 4.9eV linewidth, but its overall line shape is also altered so that it is no longer adequately described by the semiconductor plasmon model developed in chapter 3. Amorphization apparently introduces fundamental changes in the dielectric response of silicon, changes that are very likely a reflection of intrinsic changes in the electronic band structure. Undoubtedly, the approximation of concentrating all interband transitions into a single transition at an energy of the order of the gap energy used to arrive at the functional form of the line shape model, and which

works very well for crystalline silicon, is no longer valid in the amorphous case.

A significant alteration of the line shape was also observed in thin ($<30\text{nm}$) regions of crystalline samples, a marked linewidth broadening again being the main effect. Considering the ion mill preparation of the samples studied in this connection and the width of the amorphous silicon plasmon observed here, it is conceivable that this broadening might ultimately be traced to the contribution of loss events occurring within the ion-mill-induced amorphous layer at the surface. Further experiments could check this in a number of ways. For example, the thickness dependence measurement could be repeated with crystal samples thinned by suitable chemical polishing techniques to minimize the amorphous layer. If broadening at small thicknesses is no longer observed, the role of the amorphous layer in the enhanced plasmon damping would be confirmed. Alternatively, measurements on various thicknesses of amorphous films could be carried out to see whether a thickness effect is still observed. One piece of evidence relevant to this question can be gleaned from the data here. It is significant that the broadened plasmon lines of even the thinnest crystal regions are still well described by the line shape model of the fitting routine, whereas that of amorphous silicon is not. If amorphous material were truly the cause of the broadening in the former case, one would expect the fit to become gradually poorer as the linewidth increased, but this is not observed. This suggests that the amorphous layer is not the main source of the enhanced plasmon damping in thin crystal samples.

A candidate alternative damping mechanism is plasmon-boundary scattering analogous to that believed to occur in polycrystalline samples. That this is indeed an independent mechanism from disorder-induced damping was verified to some degree by the absence of any observed broadening in the grain-boundary study of the last section. If

grain-boundary plasmon damping were due to the associated structural disorder, it should have shown up in the EELS spectra collected from regions closest to the boundary. Apparently, then, alterations of the plasmon wave function due to direct interaction with grain boundaries is the dominant cause of plasmon damping in polycrystalline material. It is reasonable to expect a similar scattering mechanism to occur at crystal-vacuum boundaries since they presumably present a much stronger potential barrier from which plasmons might scatter. Again, additional experiments would help decide this possibility. The simplest would be to check the thickness dependence of the plasmon linewidth as a function of the maximum plasmon wavelength. The latter can be indirectly varied by selecting different incident beam energies (see section 4.1.3). Since the plasmon wavelength to crystal grain size ratio is the significant parameter in "anomalous" plasmon damping in polycrystalline material, a similar role would be played by the plasmon wavelength to specimen thickness ratio if plasmon-surface scattering is indeed the relevant damping mechanism.

4.4.2. Plasmon Line Shape of Bulk Single-Crystal Silicon

Before leaving these results it is worth commenting on what they imply about the plasmon characteristics in the bulk of a single crystal of silicon. First of all, it has been found that the angle-integrated plasmon line shape model found in chapter 3, given by

$$I(E) = \frac{CE \ln(2E_0/E)}{(E_p'^2 - E^2)^2 + \Gamma^2 E^2}$$

provides an excellent fit to the measured line shape even for a collection semi-angle of only 6mrad (at 100keV). Fitting this model to measured spectra corrected for multiple scattering (SSD's) makes it possible to determine E_p' and Γ , and consequently, the plasmon peak position and full width at half maximum fairly precisely. The internal cali-

bration provided by the silicon $L_{2,3}$ edge ensures the accuracy of the results. Since the peak position was not found to change in the series of spectra collected from single-crystal specimens in sections 4.1 and 4.3, all these measurements can be averaged to yield a value of the plasmon peak energy with a precision limited only by the residual $\pm 0.2\%$ uncertainty in the energy scale calibration. The plasmon width, on the other hand, was found to have a significant dependence on the sample thickness, precluding any averaging of measurements to yield a precise value of the FWHM. However, by extrapolating the FWHM versus t plot of figure 4.4 to its apparent asymptotic value at large thickness, the value of the plasmon FWHM in the bulk of single-crystal silicon can be estimated from the present data. The results are

$$\text{Peak}^{\text{cr-Si}} = 16.63 \pm 0.03 \text{ eV} \quad \text{FWHM}^{\text{cr-Si}} = 3.1 \pm 1 \text{ eV}$$

Based on these values, the best model of the bulk silicon plasmon contribution to the EELS spectrum (assuming perfect energy resolution) is given by the above equation with $E_p = 16.70 \text{ eV}$ and $\Gamma = 3.1 \text{ eV}$.

CHAPTER 5

Study of Plasmon Line Shapes of Various Semiconductors

The preceding chapter demonstrated the applicability of the plasmon line shape model developed in chapter 3 to the characterization of the plasmon excitation of Si. Chi-squared fits of the model to measured EELS data provided a means of making sensitive and precise measurements of the Si plasmon energy and linewidth and their dependence on sample properties. In the present chapter, the applicability of this technique to other diamond and zinc-blende semiconductors is explored. Specifically, the results of TEM EELS measurements of InP, AlAs, GaAs, InAs, and Ge plasmon excitation spectra are described and analyzed following the same procedures applied previously to Si.

The goals of this chapter are threefold. Firstly, by comparing the plasmon model to the low-loss EELS spectra of the above semiconductors it will be determined whether the functional form of the line shape model is sufficiently general to describe the plasmon lines of semiconductors other than Si. If so, this model would provide a handy tool for the dissection of semiconductor low-loss EELS spectra and would enhance the usefulness of electron energy-loss spectroscopy as a materials characterization technique. Secondly, to the extent that the model does indeed describe other semiconductor plasmon lines, χ^2 fits of the model to measured data will yield the best values for the plasmon energies and linewidths yet reported for the above materials. Thirdly, while the preceding chapter addressed the effects of structural distortions on bulk plasmon properties, the results of the present chapter provide a base set of data for studying what correlation, if any, exists between the composition and electron energy level structure of these diamond and zinc-blende semiconductors and the details of their bulk plasmon line shapes. Elucidation

of any such correlation will further understanding of the factors influencing plasmon properties and advance materials characterization applications of plasmon-regime EELS.

5.1. Plasmon Line Shape Measurements

Below are presented TEM EELS results obtained for the plasmon line shapes of InP, AlAs, GaAs, InAs, and Ge. The results reported here for InP and AlAs represent the first attempts to characterize the bulk plasmons of these materials via transmission EELS as there are no reports of such measurements in the literature. In the case of InAs, previous data exist, but only in early papers [64] in which no attempt was made to accurately determine the plasmon line width. In general, earlier measurements of the plasmon widths of the Ga- and In-containing semiconductors are not very precise due to uncertainties introduced by "background" subtraction procedures to correct for the effects of the d -band transition structures very near the plasmon peaks in the EELS spectra of these materials. Such uncertainties are avoided in the present method since the analysis focuses on matching the data in regions where background, if any, is only a small component. On the other hand, the plasmons of GaAs and Ge have been the subjects of more recent studies. Consequently, quite accurate plasmon line shape data are already available for these materials [23,24]. The results of measurements on these semiconductors are included here for completeness and, more importantly, so that the entire body of data can be contrasted and compared without concern for systematic differences between measuring apparatus or data analysis procedures.

Since a general discussion of the experimental procedure has been given in chapter 2, only the unique aspects of each of the present experiments are provided in the following subsections. A number of points apply generally to what follows. First, due to the thickness effect observed in the case of silicon, an attempt was made to collect spectra from a number of different specimen thicknesses to check for such an effect in each of the cases presented here. As in the silicon studies, all the spectra shown below were collected with

100keV beam energy in microscope image mode. As usual, efforts were made to use the largest possible image magnification and smallest possible spectrometer aperture, while maintaining practical count rates, to minimize the lateral extent of the probed areas and consequently their thickness nonuniformity. The main focus here is on the data itself and the comparison between the measured line shapes and the generic plasmon model. The implications of the results are discussed in section 5.2.

5.1.1. Indium Phosphide

TEM EELS spectra were measured from an InP specimen thinned from a bulk, single-crystal sample [73]. Final thinning was achieved with a chemical solution of chlorine dissolved in methanol. The specimen was oriented within 1° of a $\langle 100 \rangle$ pole and spectra were collected and processed by the same procedures followed previously for Si. Measured spectra and the extracted single-scattering distributions (SSD's) are shown in figure 5.1. The thicknesses of the probed sample regions, derived from the data in terms of the InP inelastic mean free path, are given with the spectra. The data for the thinnest region is actually the sum of three independently measured, but virtually indistinguishable, spectra, hence its lower statistical noise and smoother appearance.

The EELS spectral structure in this case is clearly more complicated than that of Si. Unlike Si, InP has occupied electron levels in the 15 to 100eV region. Specifically, the In $4d$ and $4p$ electrons occupy levels bound by $\sim 19\text{eV}$ [74] and 77eV [75], respectively. Thus the distinct structure just above the bulk plasmon peak in the SSD can be attributed to excitations of the In $4d$ electrons.

Despite this additional fine structure, however, the bulk plasmon peak still dominates the InP spectrum and allows good χ^2 line shape fits to be carried out in the 12-17eV range as illustrated in figure 5.2. The corresponding values of χ_p^2 are given with the

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Figure 5.1 - Measured plasmon-regime EELS spectra (left) and extracted single-scattering distributions (right) from crystalline InP. Relative thicknesses, t/λ_{inel} , of specimen regions indicated.

Figure 5.2 - χ^2 fits of plasmon line shape model (dotted) to InP single-scattering spectra (solid) over 12-17eV range.

plots. Although visually the fits appear to be equally good, the χ^2_ν values indicate that the plasmon spectrum derived from the thicker specimen region follows the plasmon model much more closely. In actuality, the χ^2_ν of the fit to the data from the thinner region is probably larger due to slight systematic differences between the true plasmon line shape and the model which show up more strongly in the smoother, more noise-free spectrum. For the present purpose of line shape characterization, however, both fits are quite satisfactory. The values of the fitted line shape parameters for each of the extracted SSD's are tabulated in table 5.1.

InP plasmon parameters		
$t/\lambda_{\text{inel}} (\pm 5\%)$	Peak ($\pm 0.04\text{eV}$)	FWHM ($\pm 0.05\text{eV}$)
.53	14.50	4.08
.58	14.48	4.07
.89	14.37	3.66

Table 5.1 - Plasmon peak position and FWHM in crystalline InP. Values obtained from line shape fits to single-scattering distributions measured from several different sample regions.

5.1.2. Aluminum Arsenide

The sample for these measurements was a 100nm thick, nominally pure AlAs test layer which was part of an MBE-grown $\text{Al}_x\text{Ga}_{(1-x)}\text{As}$ quantum-well structure on a crystalline GaAs substrate. TEM specimens had been originally prepared from this sample for an unrelated high-resolution electron microscopy imaging study [73]. The specimens

were prepared in cross-section using standard semiconductor cross-section techniques [73] in which several pieces of wafer material are glued into a stack, sliced transversely with a wafering saw, and thinned to electron transparency by ion milling. Once placed in the microscope column, the AlAs layer became a specimen region 100nm in lateral dimension and of varying thickness along the beam direction. Diffraction patterns from the substrate region give the orientation of the specimen as 5° from a $\langle 110 \rangle$ pole. The use of spatially-resolved TEM EELS techniques, as described in chapter 2, ensured that only events from the AlAs layer contributed to the collected spectra and that any given spectrum was obtained from as narrow a thickness range as possible.

Representative spectra and the extracted SSD's for several different specimen thicknesses are shown in figure 5.3. At first glance, the plasmon line shape observed here appears to be typical of the semiconductor plasmon peaks observed so far. However, careful comparison with the plasmon line shape model used to fit the other semiconductor plasmon line shapes shows the results for AlAs to deviate significantly from the model. As indicated in figure 5.4, even the best possible χ^2 fit to the main body of the peak fails to match the data on the high-energy side of the peak. It appears that either the simple plasmon model used so far fails in the case of AlAs or some additional contribution to the EELS spectrum other than that of AlAs plasmon excitation has been neglected.

With regard to the latter possibility, it should be noted that AlAs does not have d -shell (or other) electrons with binding energy near that of the plasmon excitation, contrary to the case of InP and the In $4d$ electrons. The AlAs data itself demonstrates this point as the events unaccounted for by the plasmon model do not comprise a clear ionization-edge type of spectral structure such as is generally observed in the EELS spectra of InP, InAs, and GaAs (see following sections). Another possible source of extraneous

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Figure 5.3 - Measured EELS data (left) and extracted SSD's (right) from nominally pure crystalline AIAs. Relative thicknesses of probed regions as indicated.

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Figure 5.4 - Measured SSD (solid) and optimum line shape fit (dotted) over the 13-18eV range for plasmon spectra obtained from two different thicknesses of AlAs. As illustrated, reduced chi-squared values indicate a poor fit.

events would be oxide or other impurity layers on the AlAs surface. Given the well-known instability of AlAs under normal atmospheric conditions the presence of a considerable oxidized or otherwise altered layer on the specimen is very likely [77]. Although exposure to atmospheric conditions was minimized by either transferring the specimen as quickly as possible from ion mill to microscope column or by storing it under bell-jar vacuum, the experience of other investigators indicates that these precautions would not be sufficient to prevent damage to the AlAs material [78].

With this likelihood in mind, a reasonable explanation for the excess events above the main plasmon peak would be that they are due to a plasmon-like excitation in the proposed altered layer. In order to test this possibility, an attempt was made to fit the AlAs data with the following model consisting of two overlapping plasmon peaks, each having the functional form successfully applied so far:

$$I_{2-plasmon}(E) = \frac{C_1 E \ln(2E_0/E)}{(E_{p,1}^2 - E^2)^2 + \Gamma_1^2 E^2} + \frac{C_2 E \ln(2E_0/E)}{(E_{p,2}^2 - E^2)^2 + \Gamma_2^2 E^2}$$

The results of such fits on two of the SSD's of figure 5.3 are shown in figures 5.5a and 5.5b. The correspondence between the data and the two-plasmon model is excellent. The bottom halves of these figures show the two individual plasmon components of each of the fits. Note that the data can indeed be accounted for in terms of a main semiconductor-like plasmon near 16eV and a secondary peak in the vicinity of 20eV, an energy closer to that of plasmon excitation in aluminum oxide [33]. With this approach, the values of the characteristic energy and linewidth of each plasmon contribution, as derived from the χ^2 fit parameters, were measured for several different AlAs thicknesses. These values along with the measured ratio of secondary to primary plasmon counts obtained by integrating the model peaks are compiled in table 5.2.

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Figure 5.5a - Comparison of 2-plasmon model of AlAs low-loss EELS (dotted) and measured SSD, $t = 0.49\lambda_{\text{inel}}$ (solid). Top, data and model virtually indistinguishable. Bottom, two plasmon components of model displayed separately.

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Figure 5.5b - Similar comparison between 2-plasmon model and measured SSD for $t = 1.74\lambda_{\text{inel}}$.

AlAs plasmon parameters					
t/λ_{inel} ($\pm 5\%$)	Main plasmon		"Damage" plasmon		Intensity ratio
	peak ($\pm 0.04\text{eV}$)	FWHM ($\pm 0.05\text{eV}$)	peak ($\pm 0.2\text{eV}$)	FWHM ($\pm 0.3\text{eV}$)	
.49	15.83	3.84	19.4	8.6	0.27
.56	15.70	3.56	18.8	8.2	0.36
.59	15.70	3.65	18.8	8.0	0.32
.71	15.67	3.49	18.9	7.5	0.31
1.01	15.70	3.64	19.3	7.8	0.22
1.74	15.73	3.56	19.1	7.9	0.26

Table 5.2 - Summary of results of spectral decomposition of AlAs EELS data into two plasmon components. Entries give characteristic line shape parameters of main peak, associated with undamaged crystalline AlAs, and of secondary peak, associated with damaged or oxidized material. Final column gives intensity ratio (damaged/undamaged) of the two components.

Despite the large number (6) of parameters involved in the two-plasmon model, the results it gives for each of the measured spectra are remarkably consistent. That the plasmon energy and linewidth associated with true crystalline AlAs are reproducibly determined to be $15.70 \pm 0.03\text{eV}$ and $3.60 \pm 0.05\text{eV}$ is not overly surprising since this feature dominates the spectrum. However, even the secondary plasmon peak, associated with altered material and contributing what appears to be only a small asymmetry to the measured spectrum, is consistently found to have an energy of $19.0 \pm 0.2\text{eV}$ and a FWHM of $7.9 \pm 0.3\text{eV}$. The consistency of the results, despite significant variations in the sample thickness and in the ratio of secondary to primary plasmon peak intensity, confirms that the measured asymmetry is real and not simply an artifact of the data collection or

analysis.

Despite the success of the two-plasmon spectrum model, without further study its application in this case must be considered a largely empirical measure taken to model the data as closely as possible and thereby achieve the best possible determination of the AlAs plasmon line shape. However, the choice of this model is not completely arbitrary and evidence in support of its applicability can be found in the literature. As mentioned earlier, previous studies [77] suggest that a certain amount of oxidation of the AlAs sample is to be expected. It is quite reasonable to assume that any oxidized material within the probed volume will contribute its own unique plasmon-like structure. Although the plasmon energy of Al_2O_3 is known to have a value close to 23eV, either incomplete oxidation of the AlAs or a more complex chemical reaction in the damaged material could account for the observed 19.0eV secondary plasmon energy. For example, recent work [60] on the energy of plasmon excitations in oxygenated silicon has demonstrated a continuous shift in the plasmon energy as silicon is gradually oxidized from pure semiconductor ($E_p=16.7\text{eV}$) to pure SiO_2 ($E_p=23.2\text{eV}$).

5.1.3. Gallium Arsenide

As the preceding specimen was grown on a crystalline GaAs substrate, preparation of the AlAs layer for TEM EELS immediately provided electron-transparent regions of crystalline GaAs as well. TEM EELS data for this material were acquired concurrently with the AlAs data, consequently the experimental conditions (including specimen orientation, due to the epitaxial growth) were identical for these two sets of measurements. Although the thickness profiles of the AlAs and GaAs regions were similar, the stronger elastic scattering in GaAs forced attention to be focussed on thinner areas than in AlAs in order to maintain reasonable count rates without increasing the collection angle. The

data presented in this section are therefore taken from a more restricted range of thicknesses. A sampling of the spectra and corresponding SSD's measured from crystalline GaAs are shown in figure 5.6.

As in the case of InP, the GaAs single-scattering distributions show the clear presence of additional fine structure beyond the bulk plasmon peak. In this instance it is the Ga 3d electrons, bound by $\sim 21\text{eV}$ [74], which contribute the extra feature. Once again, the plasmon peak dominates the spectrum and excellent plasmon model fits can be obtained in the 13-18eV range, as demonstrated in figure 5.7. The values of the plasmon peak parameters extracted from the χ^2 fits as a function of specimen thickness are compiled in table 5.3.

GaAs plasmon parameters		
$t/\lambda_{\text{inel}} (\pm 5\%)$	Peak ($\pm 0.04\text{eV}$)	FWHM ($\pm 0.05\text{eV}$)
.18	16.10	5.27
.28	15.95	4.26
.42	15.97	4.08
.54	15.92	3.94
.74	15.92	3.91

Table 5.3 - Plasmon peak position and FWHM in crystalline GaAs for a range of sample thicknesses. Values obtained from χ^2 fits of plasmon line shape model to measured SSD's.

Figure 5.6 - Measured EELS data (left) and extracted SSD's (right) from crystalline GaAs. Relative thicknesses of probed regions as indicated.

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Figure 5.7 - χ^2 fits of plasmon line shape model (dotted) to GaAs single-scattering spectra (solid) over 13-18eV range.

5.1.4. Indium Arsenide

Samples of crystalline indium arsenide [73] were prepared from bulk, single-crystal material following the same procedures as for InP. Again, final thinning to electron transparency was carried out with a chlorine-methanol polishing solution. Due to problems with beam-induced contamination, the sample was briefly ion-milled before insertion into the microscope column in order to clean its surfaces. Although the ion-milling led to the formation of what appeared to be isolated In precipitates, large enough regions of the specimen were precipitate-free to permit collection of EELS spectra characteristic of the bulk semiconductor material alone. Specimen orientation in this case was not near any high-symmetry pole. Measured spectra and extracted SSD's for three sample thicknesses are shown in figure 5.8.

Overall, the InAs low-loss EELS spectrum is very similar to that of InP, as one might expect. As usual, bulk plasmon excitation of the semiconductor's valence electrons dominates the spectrum while the additional structure associated with excitations of individual In $4d$ electrons once again appears at about 19eV, just beyond the plasmon peak. One slight difference in the structure of the InAs spectrum is the appearance of a weak feature at around 40eV which can be associated with excitations of the $3d$ electrons of As [75].

Despite these superficial similarities, refined analysis easily distinguishes the plasmon EELS spectrum of InAs from that of InP. Since these two materials have different lattice parameters ($a_{\text{InAs}} = .606\text{nm}$ and $a_{\text{InP}} = .587\text{nm}$) and (consequently) different valence electron densities, some difference in plasmon energy is expected. Proceeding as before, the characteristic parameters of the InAs plasmon peak are obtained via line shape model fits to the dominant peak as shown in figure 5.9. The numerical results obtained from the

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Figure 5.8 - Measured EELS data (left) and extracted SSD's (right) from crystalline InAs. Relative thicknesses of probed regions as indicated.

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Figure 5.9 - χ^2 fits of plasmon line shape model (dotted) to InAs single-scattering spectra (solid) over 12-16eV range.

line shape fits are given in table 5.4. Comparison with the InP data of section 5.1.1 confirms that the plasmon energy of InAs is indeed lower, in qualitative agreement with the relationship between plasma frequency and valence electron density quoted in chapter 1.

InAs plasmon parameters		
$t/\lambda_{\text{inel}} (\pm 5\%)$	Peak ($\pm 0.04\text{eV}$)	FWHM ($\pm 0.05\text{eV}$)
.40	13.86	4.24
.49	13.95	4.11
.72	13.86	3.99

Table 5.4 - Plasmon peak position and FWHM in crystalline InAs at various sample thicknesses. Values obtained from line shape fits to measured SSD's.

5.1.5. Germanium

The bulk starting material for the Ge TEM EELS specimen consisted of 99.99% pure Ge chips from a commercial supplier. Specimens were prepared by grinding appropriately sized chips down to 100 μm -thick discs suitable for mounting in the microscope specimen stage. Final thinning to electron transparency was achieved via room temperature ion-milling. Bright-field microscopy and diffraction data from the samples showed them to be single-crystalline, at least within the context of the present study (grain size no smaller than $\sim 10\mu\text{m}$). The specimen was oriented well away from any high-symmetry pole. Although the bulk of the specimen appeared to be crystalline, noticeable diffuse rings were superimposed over the crystalline spot patterns of the

diffraction micrographs. This indicates the presence of a significant amorphous layer on the specimen and is undoubtedly a consequence of the rather crude specimen preparation procedure. Unfortunately, practical constraints on this project precluded the refinement of the Ge specimen preparation technique to obtain higher quality specimens. Nevertheless, reasonable-looking plasmon spectra were collected from this sample and the results are reported here for completeness. A sample measured spectrum is shown in figure 5.10 along with its corresponding SSD.

A couple of points about the Ge spectrum are noteworthy. First, it appears as though the multiple-scattering correction procedure has failed to extract the true SSD since the double-plasmon peak, although reduced, does not seem to have been completely removed. Quick reference to compiled atomic energy-level data [75], however, shows that the Ge 3d electrons are bound by $\sim 29\text{eV}$ and that a corresponding feature in the SSD is to be expected. Hence the appearance of precisely such a feature in the extracted SSD, despite being initially superimposed upon the double plasmon loss peak, serves as testimony to the accuracy of Fourier-log deconvolution method. Secondly, as in the case of AlAs, it was again found that the usual plasmon line shape model does not give a satisfactory fit to the data, there being an excess of counts in its high-energy-side tail. Considering the specimen damage observed in diffraction, it is not unreasonable to expect the damaged component to again contribute its own distinct plasmon-like feature analogous to that found for damaged/oxidized AlAs. Hence, a two-plasmon model fit to the measured plasmon peak was also applied to the Ge data and found to be very successful, as illustrated in figure 5.11. The extracted plasmon peak parameters of the primary plasmon peak, i.e. that presumably associated with plasmon excitations in the undamaged crystalline bulk of the Ge specimen, are given in table 5.5.

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Figure 5.10 - Top, sample plasmon-regime EELS spectrum from crystalline Ge sample with some sputtering-induced damage of near-surface layers, specimen thickness as shown. Bottom, extracted SSD.

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Figure 5.11 - Top, 2-plasmon χ^2 fit compared with measured SSD of damaged Ge. Bottom, two plasmon components of model shown separately.

Ge plasmon parameters		
$t/\lambda_{\text{inel}} (\pm 5\%)$	Peak ($\pm 0.04\text{eV}$)	FWHM ($\pm 0.05\text{eV}$)
.36	16.05	3.63

Table 5.5 - Plasmon peak position and FWHM in crystalline Ge. Values obtained from line shape fit to measured SSD.

5.2. Discussion of Results

It is now appropriate to examine the semiconductor plasmon results in their entirety to see what conclusions, if any, may be drawn from them.

5.2.1. Applicability of the Plasmon Line Shape Model

In all of the cases studied, the plasmon peak model given by

$$I_p(E) = \frac{CE \ln(2E_0/E)}{(E_p^2 - E^2)^2 + \Gamma^2 E^2}$$

was found to give a complete account of the measured plasmon peak shape. In two cases, namely for AlAs and Ge, it was necessary to augment the model with an additional peak of the same functional form in order to obtain a good match to the data. This two-plasmon model allows for the possibility that two different plasmon contributions may be superimposed in a single spectrum due to specimen inhomogeneity. Indeed, in both the AlAs and Ge cases, uncertainties about specimen quality and purity warranted the use of such a model. The fact that even the minor, presumably non-semiconductor, plasmon contributions to the EELS spectra of these samples appear to obey the above functional form gives an indication of the potential generality of the model. Nevertheless, to firmly conclude that the plasmon EELS spectrum of AlAs and Ge are truly described by the above equation will require repetition of the measurements on specially handled samples for which the possibility of structural or chemical alteration can be excluded. Regretfully, due to practical constraints, such measurements could not be carried out within the present study. For the case of Ge, previous related work by Raether and Hinz [24] has shown that a similar plasmon line shape model for *angle-resolved* EELS spectra completely accounts for the Ge plasmon line shape, suggesting that the the excess "tail" observed here is not an inherent feature of the pure, crystalline Ge plasmon line.

Unfortunately, their report does not include a graphic comparison of measured and calculated Ge plasmon spectra by which the correspondence between model and data might be assessed.

In any event, even if the model is not quite correct from a fundamental standpoint, it nevertheless provides an excellent empirical method for isolating the plasmon background to low-energy edges. In this respect, the functional form above might serve as the low-loss regime analog of the power-law background model applied to the higher-energy core-loss regime. This point is pursued further in the next chapter.

5.2.2. Values for the Plasmon Peak Energy and FWHM

Due to the excellent match between the plasmon peak models and the measured plasmon lines above, the peak energies and linewidths derived from the fits represent the most precise measurements of these quantities available to date. For the purpose of a comparative analysis of the measured line shape results, the preceding data are compiled into a single table below. In surveying the data above, one again finds, as in the case of Si, a clear trend of plasmon line broadening with decreasing specimen thickness. Thus a meaningful comparison of plasmon linewidths can only be made with line shape data collected at equivalent sample thicknesses. Since most of the experimental runs reported above included sample regions with t/λ_{inel} close to 0.5, this was chosen as the reference thickness. The final, best estimates for the plasmon peak energy and $\text{FWHM}(t/\lambda_{\text{inel}}=0.5)$ for each of the samples studied are compiled in table 5.6.

Semiconductor plasmon peak characteristics		
Sample	Position ($\pm 0.05\text{eV}$)	FWHM($t/\lambda_{\text{inel}}=0.5$) ($\pm 1.0\text{eV}$)
Si	16.63	3.25
AlAs	15.72	3.7
Ge	16.10	3.65*
GaAs	15.97	4.0
InAs	13.89	4.1
InP	14.45	4.1

* value for thickness $.36\lambda_{\text{inel}}$

Table 5.6 - Plasmon peak position and FWHM for various diamond and zinc-blende semiconductors. FWHM estimated for sample thickness of $0.5\lambda_{\text{inel}}$.

5.2.3. Correlation with Electronic Structure

Table 5.6 shows that there are unambiguous distinctions between the plasmon peaks of the semiconductors examined. It would be of interest to know how these distinctions are related to the differences between the physical properties of the samples. Since the line shape model applied here is based on fundamental parameters, a more detailed analysis of the fit parameters provides one possible approach to this question. Referring back to the derivation of the model functional form given in chapter 3, one finds that the peak-position parameter, E_p' , can be expressed in terms of three basic physical quantities: E_g , roughly the average energy of $\mathbf{q}=0$ band transitions (mean direct band gap), ϵ_c , the dielectric constant of the core electrons at frequencies on the order of ω_p , and n , the valence (and conduction) electron density. Specifically,

$$E_p'^2 = E_g^2 + E_p^2/\epsilon_c = E_g^2 + 4\pi n e^2 \hbar^2 / m \epsilon_c$$

where e and m are the free-electron charge and mass. This expansion of the fit parameter E_p' shows explicitly that its dominant dependence is on the the valence electron density via the free-electron equivalent plasma frequency, $\omega_p = 4\pi n e^2 / m$. The average band gap pushes the value of E_p' , and thus the plasmon peak position, up in energy, while the core dielectric constant causes it to decrease relative to the free-electron value. The phenomenological basis of these shifts has been discussed by Wilson [79].

With this approach, it is apparent that comparison of measured E_p' values with calculated free-electron E_p values provides information about the relative importance of the E_g and ϵ_c terms and will thereby clarify the effect of electronic energy-level structure on semiconductor plasmon peak characteristics. Such a comparison is made in table 5.7. Note that E_p' is an actual adjustable parameter of the line shape model and that a correction for the finite plasmon linewidth must be applied to it in order to obtain the plasmon peak position (see section 3.2.1). Thus the difference between the E_p' values and the corresponding plasmon peak energies given in the previous table.

Semiconductor plasmon model parameter E'_p			
Sample	E'_p (± 0.05 eV)	$a_0^*(300^\circ\text{K})$ (nm)	E_p^{calc} (eV)
Si	16.71	.5431	16.60
AlAs	15.84	.5660	15.60
Ge	16.22	.5658	15.61
GaAs	16.14	.5653	15.63
InAs	14.08	.6058	14.09
InP	14.60	.5869	14.77

* see reference [56]

Table 5.7 - Measured value of the plasmon peak model parameter, E'_p , for each of the semiconductor samples. The corresponding free-electron plasmon energy, E_p , has been calculated from the valence electron density (32 electrons/ a_0^3) of each sample and is included for comparison.

This comparison shows that, except for the In-containing samples, the measured E'_p is consistently higher than E_p . This indicates that the upward shift in plasmon energy due to the presence of the band-gap transitions outweighs the effects of the core polarization in these materials. For Si, AlAs, and Ge this is not surprising as the most weakly bound core electrons in these semiconductors have binding energies significantly greater than E_p . Thus their core dielectric constants at the valence plasma frequency are very nearly equal to 1. The situation is different for GaAs due to the presence of the Ga 3d electrons at ~ 21 eV binding energy. Similarly for InP and InAs, in which the In 4d electrons are bound by ~ 19 eV. Thus for the latter three samples, one might expect the measured E'_p to be closer to and perhaps even below E_p . This is indeed the case for the In semiconductors, although GaAs does not follow this expectation.

More quantitatively, the magnitude of the upward plasmon energy shift due to band transitions can be estimated from the average direct band gap of each sample. An approximate value of the latter may be extracted by examining $\hbar\omega\text{Im}\{\epsilon(\omega)\} \equiv \hbar\omega\epsilon_2(\omega)$ obtained from optical experiments. This quantity is proportional to the oscillator strength of optical band transitions [80] and the mean of its distribution should give a reasonable estimate of E_g . Figure 5.12 shows the $\hbar\omega\epsilon_2$ distributions of several semiconductors, as derived from optical data of Philipp and Ehrenreich [81]. Values of E_g estimated from this data and the implied values of ϵ_c for Si, Ge, GaAs, and InAs are listed in Table 5.8. Here the enhanced core polarizability of InAs is indicated explicitly by its ϵ_c significantly greater than 1.

Parameters E_g and ϵ_c		
Sample	E_g ($\pm 0.5\text{eV}$)	ϵ_c
Si	5.0	$1.08 \pm .02$
Ge	5.0	$1.03 \pm .02$
GaAs	5.5	$1.07 \pm .02$
InAs	5.5	$1.18 \pm .04$

Table 5.8 - Estimated values of parameters E_g and ϵ_c for Si, Ge, GaAs, and InAs. E_g values are based on $\hbar\omega\epsilon_2$ distributions shown in figure 5.12. ϵ_c values are derived from relationship between measured E'_p , calculated E_p , and above E_g values.

Besides the plasmon energy, the plasmon linewidth also appears to reflect the increasing influence of low-energy d -shells on semiconductor plasmon decay. In the case of Si, which has no d -levels at all, the plasmon peak is the narrowest, indicating the least

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Figure 5.12 - Distributions of $\hbar\omega\epsilon_2$ versus transition energy for various diamond and zinc-blende semiconductors. Curves derived from optical data of Philipp and Ehrenreich [81].

amount of damping due to decays via single-electron transitions. For AlAs and Ge, in which there are d -levels bound by about $2.6E_p$ and $2.0E_p$, respectively, the rate of decay is somewhat higher, resulting in increased plasmon linewidth. The linewidth is largest for those samples with d -level binding energies most closely matched to the plasmon energy, namely in GaAs, InAs, and InP with the Ga $3d$ -electrons and the In $4d$ -electrons bound by about $1.3E_p$ in each case (20.9eV and 18.6eV, respectively). This suggests that transitions on the part of d -shell electrons make a significant (although not dominant) contribution to semiconductor plasmon properties.

In conclusion, the plasmon line shape modeling technique leads to a sensitive, quantitative characterization of plasmon line shapes, permitting a clear differentiation of the rather similar plasmon lines of several diamond and zinc-blende semiconductors. The fitted parameters of the modeling technique can to some degree be interpreted in terms of certain properties of the electronic structure, such as valence electron density, inter-band transition energies, and core-level polarization. Specific results for Si, AlAs, Ge, GaAs, InAs, and InP generally show that the low-energy d -levels of the latter three semiconductors lower the plasmon energy (frequency) and increase the plasmon damping as a result of their polarizabilities and transition energies near that of the plasmon resonance.

CHAPTER 6

Plasmon Background Fitting for Low-Loss EELS Analysis

In the preceding two chapters it was found that the simple plasmon line shape model introduced in chapter 3 gives a good description of the plasmon peak of each of the semiconductors Si, Ge, AlAs, GaAs, InAs, and InP. That model, matched to measured EELS spectra via least-squares fitting, yielded optimized values of the plasmon line shape parameters, E_p' , and Γ , for each of these materials. Besides aiding plasmon measurements in this way, the plasmon line shape modeling approach also has potential applications to quantitative analysis with low-loss EELS ionization edges. Edges in this energy-loss regime often have relatively large cross-sections and are thus well-suited for detection of minor constituents in a sample. These edge signals are often inaccessible, however, because the complex plasmon background cannot be removed by the standard power-law extrapolation method. The parameterized plasmon model applied here, provides an alternate approach to the background subtraction problem.

In this chapter, the potential role of plasmon models in low-loss core-edge background removal is considered. What follows is a report of preliminary findings, based on data already presented in this thesis, rather than an extensive study. However, as this approach to background modeling in EELS does not appear to have been attempted before, it has been deemed worthwhile to mention even these preliminary results. The chapter begins with a closer look at the level of agreement between plasmon line shape fits and measured plasmon data from Si. Rather than focusing on the plasmon peak region alone, the comparison is carried out to 80eV beyond the peak in order to evaluate the accuracy of background models extrapolated from plasmon line shape fits.

Thereafter, the results of straightforward subtraction of plasmon fits from the EELS spectra of Ge, AlAs, GaAs, InAs, and InP are presented and discussed.

6.1. Evaluation of Model Accuracy

The important aspect of a useful background model in EELS is that it must be possible to correctly extrapolate the background counts under an edge based only on information about the background preceding the edge. The success of the power-law background model at energy-losses above 100eV, for example, is a result of the fact that it describes the drop in energy-loss intensity leading up to an edge almost perfectly and thereby gives a very reasonable extrapolation of the background beyond it. It remains to be established whether the plasmon line shape model gives an equally accurate description in the low-loss (below 100eV) region.

The Si data presented in chapter 4 provides at least a partial answer to this question. Since Si has no electron energy levels in the range between the plasmon peak energy (16.6eV) and the deeply bound 2p electrons at roughly 100eV binding energy, its low-loss EELS spectrum beyond about 12eV consists entirely of plasmon-loss events. There are no single-particle transitions to complicate its structure, thus making this a perfect test case. By examining, in detail, the differences between the measured Si single-scattering distributions and plasmon model fits, the accuracy of the plasmon model can be evaluated directly.

Figure 6.1 provides a detailed view of these differences for Si data from three different specimen thicknesses. The plasmon spectrum models shown were obtained from a least-squares fit over the entire 14-90eV interval. Overall, the agreement between model and SSD data is good in all cases. In the SSD's from the two thicker samples the noise in the data beyond the main peak is rather high due to the statistical noise of the original data. Since the thicker regions yield higher absolute counts in this energy range due to multiple scattering, the $N^{1/2}$ counting noise, which remains after the Fourier-log

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Figure 6.1 - Detailed comparison between measured SSD's of Si (solid) and fitted plasmon line shape (dotted) for three different specimen thicknesses (in λ_e). Fits carried out over 14-90eV interval.

deconvolution, is larger. The plasmon model is, however, generally within the noise. A systematic discrepancy as large as 50% occurs within a very narrow energy range near the double-plasmon energy, but this is due to what appears to be a small residual artifact of the single-scattering extraction and is therefore a defect of the processed data and not of the model. For the thinnest sample region, a systematic discrepancy occurs between about 35eV and 60eV. This one is not localized in energy and may indicate a true deficiency of the model. The magnitude of the difference is, however, less than 1% of the peak plasmon count intensity. Thus if counts were to appear here from an ionization edge of another component, the error in the background model would not be important as long as the edge intensity is significant compared to the plasmon peak.

The above establishes that the plasmon line shape model

$$I_p(E) = \frac{CE \ln(2E_0/E)}{(E_p^2 - E^2)^2 + \Gamma^2 E^2}$$

does indeed give the correct functional form of the plasmon contribution to the entire low-loss EELS spectrum of Si. A more pertinent question is how well data and model agree if the fit is carried out over a restricted region near the peak. In a practical situation, only a small region near the plasmon peak may be free of ionization edge signals. For example, in the case of the Ga- and In- containing samples, energy-loss structure due to excitations of *d*-shell electrons appears immediately following the plasmon peak. It is from the peak region alone, then, that the background must be modeled and extrapolated. With the same Si data as above, plasmon line shape models were fitted to the 14-20eV region alone and extrapolated in order to answer this question. Figure 6.2 shows the results. The model changes very little as a result of the restricted fitting region and overall agreement with the SSD data is still within the statistical noise for the thicker sample regions.

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Figure 3.2 - Detailed comparison between measured SSD's of Si (solid) and fitted plasmon line shape (dotted) for three different specimen thicknesses (in λ_e). Fits carried out over 14-20eV interval.

6.2. Application to Background Subtraction

Insofar as valence plasmon and low-energy ionization edge contributions to EELS spectra are independent, the foregoing detailed examination of the entire Si plasmon spectrum verifies that the plasmon line shape model is a significant improvement over the power-law approach to background subtraction in the low-loss regime. In particular, it should be applicable to the semiconductors examined in chapter 5. All of these, in contrast to Si, have *d*-shell edges immediately following the plasmon peak, namely the $M_{4,5}$ (*3d* ionization) edges of Ga, Ge, and As and the $N_{4,5}$ (*4d* ionization) edge of In.

Starting with the results presented in chapter 5, removal of the plasmon contributions to the single-scattering distributions is straightforward. The fitted line shape model used to extract the plasmon energy and linewidth parameters from each spectrum is simply subtracted in each case. Unfortunately, with the data obtained in the present work, the total ionization edge counts in any individual spectrum were quite low, thus all the data for a given sample were summed (*after* single-loss deconvolution) in order to achieve the best possible statistics in the background-subtracted edge profiles. The results are shown in figure 6.3.

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a

Figure 6.3a - $M_{4,5}$ edges of Ga and As and $N_{4,5}$ edge of In obtained from AlAs, GaAs, and InAs EELS spectra after subtraction of modeled plasmon component. For clarity, AlAs spectrum has been smoothed via 5-point averaging.

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b

Figure 6.3b - $M_{4,5}$ edge of Ge and $N_{4,5}$ edge of In obtained from Ge and InP EELS spectra after subtraction of modeled plasmon component. For clarity, Ge spectrum has been smoothed via 5-point averaging.

6.3. Assessment of Results

The extracted edge profiles have a number of noteworthy features. First of all, each of the spectra shows significant counts in excess of the plasmon model in the pre-plasmon energy regime. This is not unexpected as the plasmon line shape model does not include surface plasmon contributions which are likely to occur below the bulk plasmon energy. In general, the bulk plasmon peak itself appears to be cleanly removed, leaving the surface plasmon and core-edge features as the dominant components of the residual spectra. The only exception to this appears to be the AlAs data, which shows significant oscillatory deviations from zero intensity in the vicinity of the plasmon peak energy, indicating that there is systematic error in the plasmon model subtracted from this spectrum. Considering the difficulty encountered in attempting to find a good plasmon fit in this case (see section 5.1.2), such an error is not surprising. Nevertheless, the model is quite well behaved beyond the plasmon region and the extracted As and Al edge profiles appear to be reasonable (*cf.* Al $L_{2,3}$ edge in *EELS Atlas*, reference [33]).

As there appear to have been no previous attempts to isolate and measure these low-energy edges, there are no precedents against which to compare the results here. However, the validity of the extracted edge profiles is verified to some degree by their self-consistency. Despite the many stages of processing involved in isolating the edge data, the As $M_{4,5}$ edge, for example, is reproduced fairly well in each spectrum from the As-containing samples. Further self-consistency is demonstrated by the In $N_{4,5}$ edges of InAs and InP. The detailed structure and threshold energies of these edges are in substantial agreement, as shown by direct comparison in figure 6.4.

Although these extracted edge results appear on the surface to be reasonable and internally consistent, examination of the edge count integrals calls into question whether

Figure 6.4 - Direct comparison of In $N_{4,5}$ edges extracted from InAs (solid) and InP (dotted) by plasmon background subtraction method. Edge profiles normalized to their respective peak intensities.

the intensities of the extracted edges are truly representative of the concentrations of their associated atomic species. In particular, the apparent strong correlation between edge threshold intensity and proximity to the valence plasmon peak (eg. compare Ga and As $M_{4,5}$) is somewhat suspicious, potentially indicating some systematic error in the plasmon background model. Table 6.1 gives a quantitative summary of the observed edge intensities.

Low-loss semiconductor core edges		
Edge (range)	Σ edge/SSD intensity	Sample
As $M_{4,5}$ (35-60eV)	.0131	AlAs
	.0170	GaAs
	.0272	InAs
Ge $M_{4,5}$ (25-50eV)	.0365	Ge
Ga $M_{4,5}$ (15-40eV)	.101	GaAs
In $N_{4,5}$ (15-40eV)	.139	InAs
	.208	InP

Table 6.1 - Intensities of various low-energy edges relative to total intensity of corresponding single-scattering distribution (SSD). Extracted via plasmon background subtraction technique.

In order to be able to compare the edge intensities in a meaningful way, the relative intensities given in table 6.1 were derived by summing all counts within 20eV of an edge threshold and normalizing the result to the total counts in the original single-scattering distribution. Since the As $M_{4,5}$ edge rides on the tails of the Ga and In edges in GaAs and InAs, empirical procedures were employed to isolate the As counts in these cases. For GaAs, a power-law of the form $A(E-E_0)^{-r}$ with $E_0 = 20\text{eV}$ was found to give a

reasonable description of the Ga $M_{4,5}$ tail. For InAs, the measured In $N_{4,5}$ edge of InP was simply scaled to match that of InAs and subtracted to yield the As edge (eg. see figure 6.4). Immediately apparent from the tabulated data is the lack of agreement between the various measurements of the As $M_{4,5}$ intensity. This would seem to imply that the ionization cross-section of the As $3d$ electrons is different in each of these samples. However, given their common binding energy at a moderately tight 40eV, such a difference, particularly as large as observed here, is not very likely. Also very striking is the roughly 5-fold larger intensity observed for the Ga $M_{4,5}$ edge over that of the As $M_{4,5}$ in GaAs. This is unexpected given the equal atomic concentrations of these species, the presumably equal occupancy of their $3d$ levels, and only a 2-fold difference in their binding energies. For comparison, note that the Ge $M_{4,5}$ intensity matches that of As in GaAs fairly well (after correcting for Ge's 2-fold higher atomic concentration). A similar large discrepancy is observed between In $N_{4,5}$ and As $M_{4,5}$ in InAs, although here different electron levels (In $4d$) are involved, making such a simple comparison less meaningful.

Further problems with the plasmon background subtraction approach are found when one examines edge profiles taken from single-scattering distributions extracted from different thicknesses of the same sample. Figure 6.5, for example, displays the Ga and As edge profiles obtained from various thicknesses of GaAs. Note the systematic change in shape of the Ga $M_{4,5}$ edge with increasing thickness. Not only the shape, but the intensity of the edge changes as well. Table 6.2 summarizes the edge intensities (within 20eV beyond threshold) measured as a function of thickness for these data.

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Figure 6.5 - Ga and As $M_{4,5}$ edge profiles extracted from various thicknesses of GaAs via the plasmon background subtraction approach.

GaAs $M_{4,5}$ edge vs. thickness			
Thickness (λ_{inel})	Ga/SSD	As/SSD	Ga/As
.18	.156	.015	10.6
.28	.098	.017	5.9
.42	.091	.019	4.8
.54	.091	.017	5.2
.74	.081	.026	3.1

Table 6.2 - Relative intensities of Ga and As $M_{4,5}$ edges (within 20eV of edge threshold) measured from various thicknesses of GaAs by subtracting modeled plasmon peak from extracted single-scattering distribution (SSD).

From the tabulated results it appears that the general trend is for the measured Ga $M_{4,5}$ intensity to decrease with increasing thickness, whereas the As $M_{4,5}$ intensity remains fairly constant (apart from the somewhat spurious results obtained at $.74\lambda_{\text{inel}}$ thickness). This suggests that either the plasmon model does not hold for all the thicknesses probed or some additional contribution to the original spectrum which appears only at small thickness may be masking the true Ga $M_{4,5}$ profile. Obvious potential candidates for such a contribution would be surface plasmon excitation or a plasmon associated with a surface contaminant of the sort postulated in the analysis of the AlAs and Ge plasmon spectra in chapter 5.

In summary, although plasmon line shape modeling based on the techniques described in this dissertation appears to give good fits to the plasmon peaks of semiconductor samples, attempting to use these fits as background models in order to extract the intensities of the low-energy edges such as Ga, Ge, and As $M_{4,5}$ or In $N_{4,5}$ leads to ques-

tionable results. The weak features associated with these edges in the original measured spectra can indeed be isolated for analysis with this approach, but the quantitative results achieved display a number of inconsistencies. In light of the preliminary nature of these results and the limited quality of the data, firm conclusions as to the utility of plasmon background modeling and low-energy core-edge signals in quantitative analysis of samples must await more in-depth study. Nevertheless, the approach proposed here provides a starting point for analyzing the information conveyed by low-loss EELS and might serve as the basis for continued study of this relatively unexplored energy-loss regime.

CHAPTER 7

Summary and Conclusions

It is time to review and summarize the conclusions of this dissertation and bring it to a close, but first, a brief recapitulation of its aims and content.

The main focus of this work has been the development, application, and testing of a model of the plasmon-scattering component of electron energy-loss spectroscopy (EELS) data. The goal of this effort has been to develop the materials characterization potential of plasmon spectroscopy and to achieve a more detailed understanding of the information available in the 0-100eV energy-loss range of EELS spectra, and how that information might be exploited. Specifically, this dissertation has concentrated primarily on the plasmon line shapes of crystalline semiconductors with diamond and zinc-blende structures.

Following a brief historical introduction, the dissertation began by discussing the experimental considerations involved in acquiring plasmon-regime EELS data amenable to detailed analysis. The need for multiple scattering correction in order to extract the true plasmon line shape was a particular concern and guided the choice of many of the experimental parameters. Next followed a description of the basic theory of the plasmon-regime EELS spectrum and the derivation of a relatively simple plasmon line shape model. The model could be directly compared with single-scattering energy-loss probability distributions extracted from measured EELS spectra. Using the model as the basis for least-squares line shape analysis, subtle variations in the plasmon of Si with specimen thickness and structure were measured. The results were compared with previous studies of the silicon plasmon line shape and possible explanations for the observed

variations were considered in detail. The line shape model was subsequently applied to detailed measurements and comparison of plasmon lines from a range of diamond and zinc-blende semiconductors. As the parameters of the model derive from physical parameters of the specimens, an attempt was made to correlate the observed plasmon line shape differences with other specimen properties. Finally, the applicability of the plasmon line shape model to background subtraction in low-loss quantitative EELS was explored.

7.1. Summary of Findings

The findings of this work are as follows:

- The following plasmon line shape model has been verified experimentally to give an accurate description of the plasmon features of angle-integrated EELS spectra of semiconductors:

$$I(E) = \frac{2e^2\Gamma E_p^2}{\pi\hbar v_0 \epsilon_c^2} \frac{E \ln(2E_0/E)}{(E_p^2 + E_p^2/\epsilon_c - E^2)^2 + \Gamma^2 E^2} = \frac{CE \ln(2E_0/E)}{(E_p'^2 - E^2)^2 + \Gamma^2 E^2}$$

where E is the energy loss, E_0 and v_0 are the incident electron energy and velocity, E_p reflects the average band gap of the sample (alternatively, the mean of the interband transition spectrum), ϵ_c is the dielectric constant of its ion cores, Γ is a phenomenological plasmon damping parameter, and E_p is the free-electron plasmon energy associated with the valence electron density, n , via $E_p = 4\pi n e^2/m$. This result arises from the dielectric theory of electron energy losses in solids, as first developed by Fröhlich [49], via the following expression for the energy-loss probability distribution:

$$P(E) = \frac{2e^2}{\pi\hbar v_0} \text{Im} \left\{ \frac{-1}{\epsilon(E)} \right\} \ln \left\{ \frac{2E_0}{E} \right\}$$

A connection with the electronic properties of the material is provided by the complex dielectric function which, for the semiconductor case of interest here, has been approximated by $\epsilon(E) = \epsilon_c + E_p^2/[(E_p^2 - E^2) - i\Gamma E]$. The parameters of the model, E_p' and Γ , are related to the plasmon peak position and full-width at half-maximum (FWHM) via

$$\text{Peak Position} \approx E_p'(1 - \Gamma^2/8E_p'^2)$$

$$\text{FWHM} \approx \Gamma(1 - \Gamma^2/16E_p'^2)$$

- Using the above model as the basis for a least-squares analysis of measured plasmon lines, variations in the silicon plasmon line shape were detected and quantified. Specifically, it was found that the plasmon linewidth measured from a (nominally) crystalline silicon sample increased as the thickness of the probed area decreased. As demonstrated by the plot in figure 4.4, the increase is most rapid at thicknesses smaller than about 30nm. No corresponding change in the plasmon energy or in the functional form of the plasmon peak was observed. A similar broadening without energy shift was observed in amorphous versus crystalline silicon, although in this case the functional form of the model above no longer gave as good a fit to the overall line shape. A consistent explanation of these observations is that a change in the spectrum of interband transitions associated with deviations from perfect crystallinity near surfaces or in the amorphous sample leads to enhanced plasmon damping and thus a broadening of the plasmon line. The precise nature of such a change, however, cannot be determined from the data obtained here. As an added point, no line-shape change was detected in the vicinity of an isolated planar grain boundary in a silicon bicrystal.

- Continuing with the least-squares line shape analysis approach, plasmon lines measured from crystalline InP, AlAs, GaAs, InAs, and Ge were also found to follow the above functional form. The values of the model parameters, E'_p and Γ , measured for each of these materials (plus Si) are summarized in table 7.1 below. Note that the Γ values quoted here are for a reference specimen thickness of one-half inelastic mean free path.

Semiconductor plasmon line shape parameters			
Sample	$E'_p (\pm 0.05\text{eV})$	$\Gamma (t/\lambda_{\text{inel}}=0.5) (\pm 10\text{eV})$	$E_p^{\text{calc}} (\text{eV})$
Si	16.71	3.25	16.60
AlAs	15.84	3.7	15.60
Ge	16.22	3.65*	15.61
GaAs	16.14	4.0	15.63
InAs	14.08	4.1	14.09
InP	14.60	4.1	14.77

* value for thickness $.36\lambda_{\text{inel}}$

Table 7.1 - Plasmon energy and linewidth parameters measured for various diamond and zinc-blende semiconductors. Free-electron plasmon energy calculated from valence electron density included for comparison. Linewidth parameter, Γ , is estimated for sample thickness of $0.5\lambda_{\text{inel}}$.

In the derivation of the plasmon line shape model, the following theoretical connection is established between E'_p and E_p , the free-electron plasmon energy of the valence electrons,

$$E'^2_p = E_p^2 + E_p^2/\epsilon_c$$

From the comparison between the measured E'_p and calculated E_p values given in table 7.1, the above relationship leads to the conclusion that in all but the In-containing semiconductors, the upward shift in plasmon energy due to interband transitions (reflected by the E_p^2 term) outweighs the downward shift due to the core polarizability ($\epsilon_c > 1$). In the case of InAs or InP, the core dielectric constant becomes significant, canceling the upward shift due to interband transitions. This result is consistent with the fact that the In 4d electrons are relatively weakly bound at an energy of about 19eV and could thereby make a significant contribution to the core dielectric constant at 14.8eV (the plasmon energy).

• Beyond analysis of plasmon line shapes themselves, the line shape model was also found to give a good description of the background to low-energy ionization edges. This permitted very low-lying edges, such as the Ga $M_{4,5}$ and In $N_{4,5}$, to be extracted (from the plasmon tails in which they are buried) for the first time. This gave a first glimpse of the true shapes of these edges, as shown in figure 6.3.

7.2. Suggestions for Further Study

The present findings are to a large degree preliminary results as this represents a first attempt at detailed modeling of the plasmon component of EELS spectra for purposes of plasmon analysis and other low-loss EELS applications. Many questions remain to be answered.

With regard to the plasmon model itself, the excellent match between it and the plasmon line shapes measured here is actually somewhat unexpected since the well-known phenomenon of plasmon dispersion has not been considered in the derivation of the model. Why doesn't the dispersion of the plasmon energy with increasing scattering angle give rise to a significant tail on the high-energy side of the angle-integrated plasmon peaks studied here? The most obvious explanation is that the approximations made in deriving the model are actually quite good. Specifically, it may simply be true that the plasmon dispersion is negligible over the range of scattering angles significantly represented in the angle-integrated EELS spectra measured here. Considering that the characteristic scattering angle for plasmon excitations induced by 100keV electrons is only $\sim 0.08\text{mrad}$ ($q=0.14\text{nm}^{-1}$), this would not be surprising. On the other hand, the excellent fit of the model might be fortuitous, the tail contributed by dispersed plasmon events simply not distorting the overall shape of the plasmon peak enough to deviate from the model's functional form, but nevertheless giving erroneous results for the plasmon energy and linewidth. A complete measurement of the *angle-resolved* EELS spectrum over the range of angles in question would help put this question to rest. Such a measurement will involve some difficulties, however. One obstacle is the inherently low count rate achieved when the additional constraint of a specific scattering angle is imposed upon collected EELS events, particularly when nonzero angles are sampled. The vastly improved collec-

tion efficiency of a parallel-recording EELS system will be essential for such work. Another problem will be the need for a different approach to multiple scattering correction as the technique employed here depends critically on having *angle-integrated* spectra. The very thorough measurement of the loss function of aluminum carried out by Batson and Silcox [82] provides an excellent guide on how such a measurement might be carried out.

Another question relevant to the plasmon line shape model itself is whether it might be generalized to describe the EELS plasmon features of materials other than semiconductors. The basic theory of the energy-loss probability distribution applies equally well to all condensed matter. The complex dielectric function provides the only input to the model which is specific to a given material. Thus the question of generalizing the plasmon line shape model to other cases boils down to how well the complex dielectric function in each case can be modeled with a simple parameterized functional form. Simple metals, those without complicating *d* or *f* levels, should be ideal candidates for an extension of this approach as the Drude model yields a reasonably accurate $\epsilon(\omega)$ which is even simpler than that for semiconductors. However, a quick check on the classic "plasmon metal", aluminum, has already shown that the model fails in this case. The reason for this is that, due to the much smaller linewidth of the aluminum plasmon as compared to that of semiconductors, dispersion effects are no longer negligible in angle-integrated spectra. Indeed, the asymmetric plasmon tail brought about by these effects is clearly visible in the aluminum EELS spectrum shown in figure 2.9. Perhaps a more detailed model which explicitly includes a dispersion term in the plasmon energy parameter might be devised for the simple-metal case. Clearly, however, its complexity will be much greater and it will be far more cumbersome to apply than the simple semiconductor plasmon model. The situation is even worse for transition metals and insulators as the

complex dielectric functions of these materials are not likely to be described by simple functional forms at all.

With regard to plasmon line shape measurements, questions still remain as to what firm conclusions may be drawn from observed changes in the shape of the plasmon peak. For example, although a clear trend of plasmon line broadening with decreasing specimen thickness was found in virtually all the samples studied, the physical mechanism which gives rise to this broadening could not be unambiguously established. To a large extent, this was the result of uncertain conditions at the specimen surfaces due to possible contaminant or damage layers introduced during specimen preparation and handling. Repetition of some of these measurements on specimens prepared via techniques which avoid these uncertainties would help pin down the exact broadening mechanism. As another example, it was observed that the plasmon linewidth is greater in amorphous silicon than in monocrystalline silicon. This can be attributed to enhanced damping of plasmon excitations in amorphous silicon due to differences in its spectrum of interband transitions, but it doesn't lead to any detailed information as to how the electronic structure actually differs. This is a more fundamental point as it indicates that the usefulness of plasmon spectroscopy as a practical characterization tool may be very limited.

Finally, one potentially very useful outgrowth of this work is in the area of background modeling for low-loss quantitative EELS. Although it was found here that the plasmon line shape model could be employed to isolate ionization edges associated with various weakly bound inner shell electrons, the results obtained were not completely consistent or reproducible. For example, the intensities of the edges extracted from single-scattering distributions were found to depend on the thickness of the sample from which they were taken. The cause of this effect and of the other inconsistencies observed with

regard to extracted edge intensities must be better understood before this background modeling technique can be routinely applied.

References

- [1] E. Rudberg, "Characteristic energy losses of electrons scattered from incandescent solids," *Proceedings of the Royal Society (London) A*, **127**, (1930) p.111.
- [2] G. Ruthemann, "Diskrete Energieverluste schneller Elektronen in Festkörpern," *Naturwissenschaften*, **29**, (1941) p.648.
- [3] R. Kronig and J. Korringa, "Zur Theorie der Bremsung schneller geladener Teilchen in metallischen Leitern," *Physica*, **10**, (1943) p.406.
- [4] D. Pines, "Collective energy losses in solids," *Reviews of Modern Physics*, **28**, (1956) p.184.
- [5] D. Pines and D. Bohm, "A collective description of electron interactions: II. Collective vs individual particle aspects of the interactions," *Physical Review*, **85**, (1952) p.338.
- [6] L. Marton, L.B. Leder, and H. Mendlowitz, "Characteristic energy losses of electrons in solids," in *Advances in Electronics and Electron Physics*, **7**, L. Marton, ed., New York: Academic Press, (1955) p.183.
- [7] P.A. Wolff, "Theory of plasma waves in metals," *Physical Review*, **92**, (1953) p.18.
- [8] P. Nozieres and D. Pines, "Electron interaction in solids. General formulation," *Physical Review*, **109**, (1958) p.741.
- [9] H. Fröhlich and H. Pelzer, "Plasma oscillations and energy loss of charged particles in solids," *Proceedings of the Physical Society A*, **68**, (1955) p.525.
- [10] P. Nozieres and D. Pines, "Electron interaction in solids. Collective approach to the dielectric constant," *Physical Review*, **109**, (1958) p.762.
- [11] P. Nozieres and D. Pines, "Electron interaction in solids. Characteristic energy loss spectrum," *Physical Review*, **113**, (1959) p.1254.
- [12] H. Raether, "Solid state excitations by electrons," *Springer Tracts in Modern Physics*, **38**, Berlin: Springer-Verlag, (1965) p.84.

- [13] C. von Festenberg, "Energieverlustmessungen an III-V-Verbindungen," *Zeitschrift für Physik*, **227**, (1969) p.453.
- [14] J. Daniels, C. von Festenberg, H. Raether, and K. Zeppenfeld, "Optical constants of solids by electron spectroscopy," *Springer Tracts in Modern Physics*, **54**, Berlin: Springer-Verlag, (1970) p.77.
- [15] D.B. Wittry, R.P. Ferrier, and V.E. Cosslett, "Selected-area electron spectrometry in the transmission electron microscope," *Journal of Physics D*, **2**, (1969) p.1767.
- [16] R.F. Egerton and M.J. Whelan, "High-resolution microanalysis of light elements by electron energy loss spectrometry," in *Electron Microscopy - 1974*, **1**, 8th International Congress, J.V. Sanders and D.J. Goodchild, eds., Canberra: Australian Academy of Science, (1974) p.384.
- [17] D. Maher, P. Mochel, and D. Joy, "A data collection and reduction system for electron energy-loss spectroscopy," in *Proceedings 19th Annual Conference of the Microbeam Analysis Society*, Washington D.C.: NBS Analytical Chemistry Division, (1978) p.53A.
- [18] P.E. Batson, "Digital data acquisition of electron energy-loss intensities," *Ultramicroscopy*, **3**, (1979) p.367.
- [19] R.F. Egerton and D. Kenway, "An acquisition, storage, display, and processing system for electron energy-loss spectra," *Ultramicroscopy*, **4**, (1979) p.221.
- [20] S.G. Louie, J.R. Chelikowsky, M.L. Cohen, "Local-field effects in the optical spectrum of silicon," *Physical Review Letters*, **34**, (1975) p.155.
- [21] K. Sturm, "Local-field effects in the plasmon line shape of semiconductors of the diamond and zinc-blende structures," *Physical Review Letters*, **40**, (1978) p.1599.
- [22] J. Stiebling and H. Raether, "Dispersion of the volume plasmon of silicon at large wave vectors," *Physical Review Letters*, **40**, (1978) p.1293.
- [23] R. Manzke, "Wavevector dependence of the volume plasmon of GaAs and InSb," *Journal of Physics C*, **13**, (1980) p.911.
- [24] H.-J. Hinz and H. Raether, "Line shape of the volume plasmons of silicon and germanium," *Thin Solid Films*, **58**, (1979) p.281.

- [25] K. Sturm, "Electron energy loss in simple metals and semiconductors," *Advances in Physics*, **31**, (1982) p.1.
- [26] I. Egri, "Excitons and plasmons in metals, semiconductors, and insulators: a unified approach," *Physics Reports*, **119**, (1985) p.364.
- [27] M. Scheinfein and M. Isaacson, "Electronic and chemical analysis of fluoride interface structures at subnanometer spatial resolution," *Journal of Vacuum Science and Technology B*, **4**, (1986) p.326.
- [28] C. Colliex, "An illustrated review of various factors governing the high spatial resolution capabilities in EELS microanalysis," *Ultramicroscopy*, **18**, (1985) p.131.
- [29] H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons*, Springer Tracts in Modern Physics, **88**, Berlin: Springer-Verlag, (1980).
- [30] D.B. Williams, *Practical Analytical Electron Microscopy in Materials Science*, Mahwah, New Jersey: Philips Electronic Instruments, Electron Optics Publishing Group, (1984) Ch. 5, p.91.
- [31] D.C. Joy, "The Basic Principles of Electron Energy-Loss Spectroscopy," in *Principles of Analytical Electron Microscopy*, D.C. Joy, A.D. Romig, and J.I. Goldstein, eds., New York: Plenum Press, (1986) Ch. 7, p.249.
- [32] R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, New York: Plenum Press, (1986).
- [33] C.C. Ahn, O.L. Krivanek, and P. Burgner, *EELS Atlas*, Warrendale, Pennsylvania: Gatan, Inc., (1983) p.xvii.
- [34] R.A. Ferrell, "Angular dependence of the characteristic energy loss of electrons passing through metal foils," *Physical Review*, **101**, (1956) p.554.
- [35] J.M. Howe, "Atomic mechanisms of γ prime precipitate plate growth in the Al-Ag system," PhD thesis, University of California, Berkeley, (1985). [LBL Report 19286]
- [36] H.R. Philipp and E.A. Taft, "Optical Constants of Silicon in the Region 1 to 10eV," *Physical Review*, **120**, (1960) p.37.
- [37] P. Nozieres and D. Pines, "Electron interaction in solids. Characteristic energy loss spectrum," *Physical Review*, **113**, (1959) p.1254.

- [38] J. Sticbling, "Optische Eigenschaften des einkristallinen Siliziums aus Elektronenenergieverlustmessungen," *Zeitschrift für Physik B*, **31**, (1978) p.355.
- [39] See reference 32 pp.180-183.
- [40] H. Fröhlich, *Theory of Dielectrics*, Oxford: Oxford University Press, (1949).
- [41] H. Fröhlich and R.L. Platzman, "Energy loss of moving electrons to dipolar relaxation," *Physical Review*, **92**, (1953) p.1152.
- [42] D. Bohm and D. Pines, "A collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas," *Physical Review*, **92**, (1953) p.609.
- [43] D. Pines, "A collective description of electron interactions: IV. Electron interaction in metals," *Physical Review*, **92**, (1953) p.626.
- [44] P. M. Platzman and P. A. Wolff, "Waves and interactions in solid state plasmas," in *Solid State Physics*, suppl. **13**, H. Ehrenreich, F. Seitz, and D. Turnbull, eds., New York: Academic Press, (1973).
- [45] S. E. Schnatterly, "Inelastic electron scattering spectroscopy," in *Solid State Physics*, **34**, H. Ehrenreich, F. Seitz, and D. Turnbull, eds., New York: Academic Press, (1979).
- [46] D.L. Misell and A.F. Jones, "The determination of the single-scattering line profile from the observed spectrum," *Journal of Physics A*, **2**, (1969) p.540.
- [47] D.W. Johnson and J.C.H. Spence, "Determination of the single-scattering probability distribution from plural-scattering data," *Journal of Physics D*, **7**, (1974) p.771.
- [48] R.D. Leapman and C.R. Swyt, "Electron energy loss spectroscopy under conditions of plural scattering," in *Analytical Electron Microscopy - 1981*, R.H. Geiss, ed., San Francisco: San Francisco Press, (1981) p.164.
- [49] H. Fröhlich, "Phenomenological theory of the energy loss of fast particles in solids," *Max Planck Festschrift*, W. Frank, ed., Berlin: Deutscher Verlag, (1958) p.277.
- [51] D. Pines, *Elementary Excitations in Solids*, New York: W. A. Benjamin, (1963) p.126.

- [52] M.K. Kundmann, "Analysis of semiconductor EELS in the low-loss regime," in *Microbeam Analysis - 1986*, A.D. Romig, Jr. and W.F. Chambers, eds., San Francisco: San Francisco Press, (1987) p.417.
- [53] See reference 14 pp.81-86.
- [54] R.C. Gonzalez and P. Wintz, *Digital Image Processing*, Reading, Massachusetts: Addison-Wesley, (1977) p.41.
- [55] P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, New York: McGraw-Hill, (1969).
- [56] O. Madelung, ed., "Physics of group IV elements and III-V compounds," in *Numerical Data and Functional Relationships in Science and Technology, III-17a*, K.-H. Hellwege, ed., Berlin: Springer-Verlag, (1982) p.74.
- [57] See reference 29 pp.40-42 or reference 32 p.154.
- [58] C.H. Chen, J. Silcox, and R. Vincent, "Electron energy losses in silicon: Bulk and surface plasmons and Čerenkov radiation," *Physical Review*, **B12**, (1975) p.64.
- [59] U. Buechner, "The dielectric function of mica and quartz determined by electron energy losses," *Journal of Physics*, **C8**, (1975) p.2718.
- [60] J. Wong, D.A. Jefferson, T.G. Sparrow, J.M. Thomas, R.H. Milne, A. Howie, and E.F. Koch, "High resolution electron microscopic and spectroscopic characterization of semi-insulating polycrystalline silicon and its interface with single-crystal silicon," *Applied Physics Letters*, **48**, (1986) p.65.
- [61] See reference 29 p.51.
- [62] C.H. Chen, J. Silcox, and R. Vincent, "Dispersion of Solid-State Excitations," in *Physical Aspects of Electron Microscopy and Microbeam Analysis*, B.M. Siegel and D.R. Beaman, eds., New York: John Wiley and Sons, (1975) Ch.19, p.303.
- [63] R. Vincent and J. Silcox, "Dispersion of radiative surface plasmons in aluminum films by electron scattering," *Physical Review Letters*, **31**, (1973) p.1487.
- [64] C. von Festenberg, "Zur Dämpfung des Al-15eV-Plasmaverlustes in Abhängigkeit vom Streuwinkel und der Kristallitgröße," *Zeitschrift für Physik*, **207**, (1967) p.47.

- [65] V. Krishan and R.H. Ritchie, "Anomalous damping of volume plasmons in polycrystalline metals," *Physical Review Letters*, **24**, (1970) p.1117.
- [66] O. Sueoka, "Plasma oscillation of electrons in Be, Mg, Al, Si, Ge, Sn, Sb, and Bi," *Journal of the Physical Society of Japan*, **20**, (1965) p.2203.
- [67] H. Zeppenfeld and H. Raether, "Energieverluste von 50keV-Elektronen an Ge und Si," *Zeitschrift für Physik*, **193**, (1966) p.471.
- [68] T. Aiyama and K. Yada, "Plasmon damping in Be, Mg, Al, Si, Ge, and Sn," *Journal of the Physical Society of Japan*, **30**, (1974) p.1554.
- [69] J.J. Hauser, "Electrical, structural, and optical properties of amorphous carbon," *Journal of Non-Crystalline Solids*, **23**, (1977) p.21.
- [70] H. Tsai, D.B. Bogy, M.K. Kundmann, D.K. Veirs, M.R. Hilton, and S.T. Mayer, "Structure and properties of sputtered carbon overcoats on rigid magnetic media disks," *Journal of Vacuum Science and Technology A*, **6**, (1988) p.2307.
- [71] J.H. Rose, "Imaging structure and impurities in the core of silicon dislocations and grain boundaries: A high-resolution transmission electron microscopy and computer image simulation study," PhD thesis, University of California, Berkeley, (1985). [LBL Report 20381]
- [72] D.B. Williams and J.W. Edington, "High resolution microanalysis in materials science using electron energy loss measurements," *Journal of Microscopy*, **108**, (1976) p.113.
- [73] All InP, InAs, and AlAs samples were provided through the courtesy of Dr. T. Sands, Bell Communication Research, Red Bank, NJ.
- [74] W. Gudat, E.E. Koch, P.Y. Yu, M. Cardona, and C.M. Penchina, "Core levels of III-IV semiconductors," *physica status solidi b*, **52**, (1972) p.505.
- [75] *CRC Handbook of Chemistry and Physics*, R.C. Weast, ed., Boca Raton, Florida: CRC Press, (1987) p.E-183.
- [76] J.C. Bravman and R. Sinclair, "The preparation of cross-section specimens for transmission electron microscopy," *Journal of Electron Microscopy Techniq.* **1**, (1984) p.53.

- [77] R. Ludeke and L. Esaki, "Electron spectroscopy of GaAs and AlAs surfaces," *Surface Science*, **47**, (1975) p.132.
- [78] Dr. Matsuo Ogura, private communication.
- [79] C.B. Wilson, "A phenomenological theory of the characteristic energy losses of fast electrons in metals," *Proceedings of the Physical Society (London)*, **76**, (1960) p.481.
- [80] See reference 51 pp.215-216.
- [81] H.R. Philipp and H. Ehrenreich, "Optical properties of semiconductors," *Physical Review*, **129**, (1963) p.1550.
- [82] P.E. Batson and J. Silcox, "Experimental energy-loss function, $\text{Im}[-1/\epsilon(q,\omega)]$, for aluminum," *Physical Review*, **B27**, (1983) p.5224.

APPENDIX A

Program ACQELS

The following is a listing of the multi-sweep monitored data acquisition program used to acquire EELS spectra. This version, written in FORTRAN, was designed to run on the Kevex 8000 MCA. Many of the subroutine calls are to system subroutines supplied by Kevex.

The program initializes the Kevex 8000 for acquisition and sets up data group 1 as the single-sweep buffer and data group 2 as the sum spectrum display. User is prompted for a dwell time; 16.7msec is recommended to average out 60Hz-harmonic noise. After acquiring an initial sweep and prompting for the total number of sweeps desired, successive scans of the energy-loss range are collected in data group 1, compared to the sum spectrum via cross-correlation, and either added after appropriate energy-scale shift correction or optionally discarded if the correlation coefficient is too small ($<.99$). If any change is detected in either the correlation between spectra or the zero-loss intensity, acquisition is temporarily halted until the user checks for changes in the setup and gives the OK to resume acquisition. When acquisition is complete, the data are stored in a floppy disk file.

PROGRAM ACQELS

```

C
C
C
LOGICAL*1 INITSQ(94),CLRSQ(5),FNLDSP(5),FILNAM(14)
LOGICAL*1 TXTBUF(144)
INTEGER*2 I,J,K,IBEG,IEND,ISWP,LSWP,JSWP,KSWP,NSWPS
INTEGER*2 ISHIFT,JSHIFT,IBUF
REAL*4 SWPBUF(1024),SUMSPC(2048),RPARM(10),CTMTR1,CTMTR2
REAL*4 DWELL,DSPGAN,DGNBUF,COCOEFC,COCFMN,COCFMX,RBUF
REAL*8 EELBUF(1048)
EQUIVALENCE (EELBUF,TXTBUF),(EELBUF(19),RPARM)
EQUIVALENCE (EELBUF(24),BFLAG),(EELBUF(25),SUMSPC)
DATA EELBUF/1048*0.0D00/
DATA INITSQ/-31,54,13,49,13,50,13,55,13,49,13,52,13,13,13,
*          -31,-23,50,-23,-6,-27,-6,-23,13,
*          49,13,51,13,50,13,49,13,52,13,49,13,56,13,49,13,
*          49,50,13,32,101,86,32,13,13,49,13,49,13,51,13,50,
*          13,50,13,51,13,52,13,52,13,49,13,53,13,50,13,54,
*          13,49,13,56,13,49,13,49,50,13,32,101,86,32,13,13,-23,
*          -28,49,32,50,13/
DATA CLRSQ/-27,-40,-6,-27,-6/
DATA FNLDSP/-28,50,32,50,13/
DATA FILNAM/'D','Y',' ','6*0',' ','E','E','L',0/

C
C      Initialization of KEVEX 8000 for program execution
C
      CALL ADRBLD
      CALL OPENCH
      CALL FMWRSQ(INITSQ,94)

C
C      Prepare data group 1 for acquisition
C
10 CALL FMWRSQ(CLRSQ(3),3)
   CALL SETCUR(5,1)
   CALL RTTR4('ENTER eV/channel (set on EELS CONTROL UNIT): ',
*           45,RPARM(2))
   IF (RPARM(2).LT.0.05.OR.RPARM(2).GT.10.) GO TO 10
20 CALL FMWRSQ(CLRSQ(3),3)
   CALL SETCUR(5,1)
   CALL RTTR4('ENTER dwell time per channel (msec): ',37,DWELL)
   IF (DWELL.LT.0.01.OR.DWELL.GT.9999.) GO TO 20
   CALL SETOFF(0,1)
   CALL SETINC(RPARM(2),1)
   CALL SETDWL(DWELL,1,1)
   CALL FMWRSQ(CLRSQ,5)
   ENCODE(9,30,TXTBUF) 1
30 FORMAT('SWEEP #',12)
   CALL CHRWR(2,21,TXTBUF,9,2,0)

C
C      Acquire first sweep and use it to determine NSWPS and offset
C
      CALL ACQON(1)
      CALL SLIP(IINT(10.*DWELL))
40 CALL FRDLT('2000'0,IBUF)
   IF (IBUF.EQ.1) GO TO 40
   CALL FMWRSQ(CLRSQ(3),3)
   CALL SETCUR(5,1)
   CALL RTT12('ENTER total number of sweeps to be acquired: ',
*           45,NSWPS)

```



```

IF (NSWPS.LE.0) STOP 'ACQELS ABORTED'
CALL FMWRSQ(-8,1)
CALL FMWRSQ(CLRSQ(3),3)
CALL SETCUR(5,1)
TYPE 50
50 FORMAT(' Place cursor on a channel of known energy')
PAUSE '-- Hit RETURN when ready'
CALL RDCURS(1BUF)
CALL FMWRSQ(CLRSQ(3),3)
CALL SETCUR(5,1)
CALL RTTR4('ENTER energy of this channel: ',30,RPARM(1))
RPARM(1)=RPARM(1)-1BUF*RPARM(2)
CALL SETOFF(RPARM(1),1)

C
C Set up correlation window and paint it PURPLE
C
55 TYPE 60, 'first'
60 FORMAT(' Place cursor on ',A,' channel of correlation window')
PAUSE '-- Hit RETURN when ready'
CALL RDCURS(1BEG)
CALL FMWRSQ(CLRSQ(3),3)
CALL SETCUR(5,1)
TYPE 60, 'last'
PAUSE '-- Hit RETURN when ready'
CALL RDCURS(1END)
IF (1BEG.LT.1END) GO TO 80
CALL FMWRSQ(CLRSQ(3),3)
CALL SETCUR(5,1)
TYPE 70
70 FORMAT(' BAD WINDOW, try again')
GO TO 55
80 IF (1BEG.GE.15.AND.1END.LE.1008) GO TO 100
CALL FMWRSQ(CLRSQ(3),3)
CALL SETCUR(5,1)
TYPE 90
90 FORMAT(' Window too near an endpoint of horizontal axis,
* try again')
GO TO 55
100 CALL FMWRSQ(-8,1)
CALL PAINT(1BEG,1END-1BEG+1,5,0)
1BEG=1BEG+1
1END=1END+1

C
C Set up data group 2 and display sum array using result of sweep #1
C
CALL SETOFF(RPARM(1),2)
CALL SETINC(RPARM(2),2)
CALL RDSPEC(0,1024,SWPBUF,0)
CTMTR1=0.
DO 110 I=1,1024
SUMSPC(1)=SWPBUF(1)
IF (1.GE.1BEG.AND.1.LE.1END) CTMTR1=CTMTR1+SWPBUF(1)
110 CONTINUE
DSPGAN=1.
115 DO 120 I=1,1024
RBUF=SUMSPC(1)*DSPGAN
CALL WRSPEC(I-1,1,RBUF,1)
120 CONTINUE
CALL FMWRSQ(CLRSQ(3),3)
CALL SETCUR(5,1)

```

```

      CALL RTTR4(' Display gain for sum spectrum: ',31,DGNBUF)
      IF (DGNBUF.EQ.0.) GO TO 130
      DSPGAN=DGNBUF
      GO TO 115
C
C   Acquire and accumulate requested number of sweeps
C
130 DGNBUF=DSPGAN
      ISWP=2
      LSWP=NSWPS
      ISHIFT=0
      COCFMN=0.99
155 DO 220 I=ISWP,LSWP
157 CALL FMWRSQ(CLRSQ,5)
      ENCODE(9,30,XTXBUF) I
      CALL CHRWR(2,21,XTXBUF,9,2,0)
      CALL ACQON(1)
      CALL SLIP(IINT(10.*DWELL))
160 CALL FRDLT('2000'O,IBUF)
      IF (IBUF.EQ.1) GO TO 160
      CALL RDSPEC(0,1024,SWPBUF,0)
      SUMNRM=0.
      DO 170 J=IBEG,IEND
      SUMNRM=SUMNRM+SUMSPC(J)**2
170 CONTINUE
      COCFMX=0.
      IBUF=0
      DO 190 J=ISHIFT-10,ISHIFT+10
      SWPNRM=0.
      COCOEF=0.
      DO 180 K=IBEG,IEND
      KSWP=K-J
      SWPNRM=SWPNRM+SWPBUF(KSWP)**2
      COCOEF=COCOE+SUMSPC(K)*SWPBUF(KSWP)
180 CONTINUE
      IF (SWPNRM.NE.0.) GO TO 185
      IBUF=1
      GO TO 190
185 COCOEF=COCOE/(SWPNRM*SUMNRM)**.5
      IF (COCOE.LE.COCFMX) GO TO 190
      COCFMX=COCOE
      JSHIFT=J
190 CONTINUE
      IF (IBUF.EQ.0) GO TO 191
      CALL FMWRSQ(CLRSQ(3),3)
      CALL SETCUR(5,1)
      PAUSE ' - - LOST BEAM: check set-up'
      ISHIFT=0
      GO TO 157
191 IF (IABS(ISHIFT-JSHIFT).LT.10) GO TO 192
      CALL FMWRSQ(CLRSQ(3),3)
      CALL SETCUR(5,1)
      PAUSE ' - - MAVERICK SHIFT: rezero'
      ISHIFT=0
      GO TO 157
192 ISHIFT=JSHIFT
      IF (COCFMX.GE.COCFMN) GO TO 195
      CALL FMWRSQ(CLRSQ(3),3)
      CALL SETCUR(5,1)
      TYPE 193,I,ISHIFT,COCFMX

```

```

193 FORMAT(' SWEEP #',I2,' Shift=',I3/12X,'Correlation='F7.4)
    CALL RTTS('Keep sweep? ',12,TEXTBUF,1)
    IF (TEXTBUF(1).EQ.89) GO TO 194
    PAUSE '-- check set-up'
    ISHIFT=0
    GO TO 157
194 COCFMN=COCFMX
195 CTMTR2=0.
    DO 200 J=1BEG-ISHIFT,IEND-ISHIFT
    CTMTR2=CTMTR2+SWPBUF(J)
200 CONTINUE
    IF (ABS(CTMTR2-CTMTR1).LE.0.05*CTMTR1) GO TO 205
    IF (ABS(CTMTR2-CTMTR1).LE.2.*CTMTR1*.5) GO TO 205
    CALL FMWRSQ(CLRSQ(3),3)
    CALL SETCUR(5,1)
    TYPE 203,CTMTR2,CTMTR1
203 FORMAT(' SWP window counts=',G14.7/' REF window counts=',G14.7)
    CALL RTTS('Keep sweep? ',12,TEXTBUF,1)
    IF (TEXTBUF(1).EQ.89) GO TO 204
    PAUSE '-- check set-up'
    ISHIFT=0
    GO TO 157
204 CTMTR1=CTMTR2
205 DO 210 J=1,1024
    JSWP=J-ISHIFT
    IF (JSWP.LT.1.OR.JSWP.GT.1024) GO TO 210
    SUMSPC(J)=SUMSPC(J)+SWPBUF(JSWP)
210 CONTINUE
    DSPGAN=DGNBUF/FLOAT(1)
    DO 215 J=1,1024
    RBUF=SUMSPC(J)*DSPGAN
    CALL WRSPEC(J-1,1,RBUF,1)
215 CONTINUE
    IF (1ABS(ISHIFT).LE.15) GO TO 220
    CALL FMWRSQ(CLRSQ(3),3)
    CALL SETCUR(5,1)
    PAUSE '-- SHIFT HAS BECOME TOO LARGE: rezero'
    ISHIFT=0
220 CONTINUE
C
C   Query for additional sweeps
C
    CALL FMWRSQ(CLRSQ(3),3)
    CALL SETCUR(5,1)
    CALL RTT12('ENTER number of additional sweeps: ',35,NSWPS)
    IF (NSWPS.EQ.0) GO TO 230
    ISWP=LSWP+1
    LSWP=LSWP+NSWPS
    GO TO 155
C
C   Add details to accumulated spectrum and display
C
230 CALL FMWRSQ(FNLDSP,5)
    CALL FMWRSQ(CLRSQ(3),3)
    CALL SETCUR(5,1)
    TYPE 240
240 FORMAT(' Type up to two lines for spectrum label and
* description: ')
    ACCEPT 250,TEXTBUF
250 FORMAT(72A1/72A1)

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      CALL WRTLBL(TXTBJF,40)
      DO 260 I=1,1024
      SUMSPC(I+1024)=SUMSPC(I)**.5
260  CONTINUE
270  CALL FMWRSQ(CLRSQ(3),3)
      CALL SETCUR(5,1)
      CALL RTTR4('ENTER gain for final display: ',30,DGNBUF)
      IF (DGNBUF.EQ.0.) GO TO 300
      DSPGAN=DGNBUF
      DO 280 I=1,1024
      RBUF=SUMSPC(I)*DSPGAN
      CALL WRSPEC(I-1,1,RBUF,1)
280  CONTINUE
      GO TO 270

C
C   Store spectrum and associated uncertainties on disk
C
300  CALL FMWRSQ(CLRSQ(3),3)
      CALL SETCUR(5,1)
      CALL RTTS('ENTER six-character output filename: ',37,
*          FILNAM(4),6)
      IBUF=10
      DO 310 I=9,4,-1
      IF (FILNAM(I).EQ.' ') IBUF=I
310  CONTINUE
      DO 320 I=IBUF,IBUF+4
      FILNAM(I)=FILNAM(I-IBUF+10)
320  CONTINUE
      OPEN(UNIT=3,FILE=FILNAM,STATUS='NEW',FORM='UNFORMATTED')
      WRITE(3) (EELBUF(I),I=1,24)
      WRITE(3) (EELBUF(I),I=25,1048)
      CLOSE(UNIT=3)
      STOP 'DATA COLLECTION COMPLETE'
      END

```

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