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MASTER

DEFECT STUDIES WITH ISOTOPICALLY DESIGNED SEMICONDUCTORS

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Abstract. Most semiconductors consist of elements which are made up of a number of stable isotopes. Access to highly enriched isotopes in macroscopic quantities opens up new and unique possibilities for semiconductor defect research. The use of isotope mass sensitive effects including the frequencies of local vibrational modes, nuclear spin, as well as nuclear cross sections for thermal neutron capture for the study of native and impurity defects will be reviewed and illustrated with relevant examples.

Introduction

Most elements which form semiconductors either by themselves (Si, Ge) or in the form of compounds (GaAs, InP, etc.) consist of more than just one stable isotope [1]. Because the separation of the isotopes of a particular element can not be achieved with standard chemical processes but requires sophisticated technologies (e.g. centrifuges [2]) which typically consume vast quantities of energy, it has been impractical (expensive!) to grow semiconductors with highly enriched or specifically designed mixtures of isotopes. However, because of the very limited quantities which are required, isotopically controlled impurities (e.g. hydrogen, deuterium) have been used in a wide variety of semiconductor defect studies. Hydrogen containing complexes are especially noteworthy because they have enjoyed great interest by the semiconductor community for many years [3]. These complexes are prototypical examples for the usefulness of stable isotopes in the study of defect centers. Isotope related shifts in vibrational mode frequencies belong to the most solid proofs for the presence of a particular element in a defect complex.

Through collaborations with scientists from countries of the former Soviet Union it has become possible recently to grow bulk and thin film semiconductors with deliberately designed isotopic composition. This has opened up new and unique possibilities for the study of defects and processes dominated by defects (e.g. self and impurity diffusion in a variety of semiconductors). Phonon and local vibrational mode frequencies, phonon propagation (thermal conductivity), hyper fine interaction between nuclear spins and electrons are all affected by the isotopic composition of a semiconductor. Secondary ion mass spectroscopy (SIMS), Raman and local vibrational mode spectroscopy (LVM), nuclear magnetic and electron paramagnetic resonance spectroscopies (NMR, EPR) are but a few spectroscopic techniques which can be used in advantageously isotope specific measurements. The range of possibilities is too large to be adequately addressed in this short paper and we will restrict our discussion to a few illustrative samples.

First, the extreme simplification of the LVM spectrum of oxygen in Ge obtained through isotopic control of the Ge host lattice will be reviewed with emphasis on the spectral features which became accessible through this simplification. Then a number of possible LVM studies in other semiconductors will be pointed out.

Second, self and impurity diffusion studies with isotopically designed multilayer structures will be discussed. Excellent self diffusion results have been obtained with $^{70}\text{Ge}/^{74}\text{Ge}$ bilayers on natural Ge substrates [4] and studies of Ga self diffusion in $^{69}\text{GaAs}/^{71}\text{GaAs}$ structures are in progress. These diffusion studies will yield information on some of the most basic but still elusive native defects (e.g. vacancies, interstitials) which dominate many semiconductor properties. Here we would like to recall the fact that the self interstitial in perhaps the best studied solid, crystalline Si, is still not well understood despite its importance in dopant diffusion and a vast number of sophisticated studies conducted over the past 25 years. It appears that isotopically engineered Si multilayer structures may yield new information on the formation and migration enthalpies and the charge states of this important native defect.

Third, we will discuss defect and dopant investigations based on the neutron transmutation doping (NTD) technique. The extreme homogeneity and the relatively low annealing temperatures are the attractive features of this doping technique. The use of isotopically controlled semi-

conductor structures allows for selective doping. For the case of Ge both acceptors and donors can be created with NTD and the net-doping concentration as well as the compensation can be adjusted precisely and independently through isotope mixture control and the neutron fluence. Radiation defects caused by residual fast neutrons, defect-dopant interactions and the effects of the random electrical fields created by ionized dopants and defects on the hydrogenic excited state spectrum of acceptors and donors are but a few possible topics which can be addressed by NTD and isotopically controlled semiconductors.

LVM Studies with Isotopically Controlled Semiconductors

An impurity atom with a mass which is smaller than the masses of the neighboring host lattice atoms vibrates at a frequency which is higher than the fundamental modes of the lattice vibrations. Because the high frequency mode can not propagate through the lattice it is localized to nearest and next nearest neighbors of the impurity. In its simplest form this vibrational system can be described by a spring and ball model. The stretch vibration frequency is given by

$$\nu_{\text{loc}}^2 = C(A^{-1} + M_{\text{lattice}}^{-1}) \quad (1)$$

with C = effective spring constant, A = impurity mass and M_{lattice} = interaction mass of the lattice (of the order of the sum of the neighbor masses).

Eq.(1) readily shows the direct dependence of ν_{loc} on the impurity and lattice atom masses. One part of this dependence is routinely used in the study of hydrogen containing complexes by the substitution of hydrogen with deuterium [3]. The resulting shift in ν_{loc} is a rather direct proof for the presence of hydrogen in any impurity complex. For multihydrogen complexes, one detects a splitting of the vibrational mode lines in case some interaction occurs between the various hydrogen atoms [5]. The ratio of $\nu_{\text{loc}}(\text{H})$ and $\nu_{\text{loc}}(\text{D})$ is a little smaller than $\sqrt{2}$ both because of the finite M_{lattice} and anharmonicity effects.

Fig. 1 a) High resolution spectra of the ν_3 local mode vibrations of ^{16}O in natural Ge. Each of the 11 lines is split due to $\nu_2 + \nu_3$ coupling; b), c) temperature dependence of the $\nu_2 + \nu_3$ coupling excitations of ^{16}O in ^{70}Ge . (Ref. [8])

Semiconductor crystals consisting of elements with several isotopes can lead to very complicated LVM spectra. Take for example C or B on the As sublattice of GaAs. Natural Ga consists of 39.9% ^{69}Ga and 60.1% ^{71}Ga . The four Ga neighbors, each with two possible mass values, leads to nine distinct values of ν_{loc} . Several of these values are almost degenerate resulting in five closely spaced lines which have been studied experimentally [6] and theoretically [7].

The case of oxygen in natural and isotopically controlled Ge is particularly interesting. In its bond center position oxygen is bound to two Ge atoms. The "quasi-molecule" Ge-O-Ge, with oxygen slightly removed from the Ge-Ge axis, has its fundamental vibrational modes labeled, ν_1 , ν_2 and ν_3 . The wag-mode ν_3 exhibits the highest frequency. There are five stable isotopes in natural Ge: ^{70}Ge (20.5%), ^{72}Ge (27.4%), ^{73}Ge (7.8%), ^{74}Ge (36.5%) and ^{76}Ge (7.8%). Because only the average mass of the two Ge neighbors of the O determines the oxygen vibrational frequencies, we obtain 11 distinct mass combinations leading to 11 closely spaced vibrational absorption lines (Fig. 1a). The splitting of each line is due to the coupling between the ν_3 and the ν_2 modes. Not until recently has this splitting been studied in detail because of the strong interference by all the different isotope combinations. We have grown a series of oxygen doped, isotopically pure Ge single crystals [8]. Fig 1b and c show the LVM spectra of ^{16}O in ^{70}Ge at two different temperatures. Through the significant reduction in spectral complexity and interference it is now possible to analyze the $\nu_2 + \nu_3$ coupling excitations. The small double peak at 863.4 cm^{-1} is due to the ~4% ^{72}Ge isotope contamination leading to an oxygen LVM frequency corresponding to an average Ge mass of 71 amu.

Self Diffusion and Native Defects

Diffusion of host lattice atoms as well as impurities represent some of the most fundamental processes in a solid. The importance in semiconductor device processing can hardly be over emphasized. Despite these aspects, diffusion processes are still not well understood at the atomic level. Native defects are believed to play a key role in all diffusion processes except in the cases where interstitial impurities travel through the interstitial spaces of the lattice (e.g. Li in Si and Ge). The main reason why it has been so difficult to make progress is the fact that the native defects which assist diffusion, i.e., vacancies and interstitials, are present at only very small concentrations even at the elevated diffusion temperatures. We know very little about the structure and electronic states of these native defects at high temperatures because no direct observations have been made. From radiation damage studies at low temperatures we have excellent information on the vacancy in silicon [9] but direct observations in other semiconductors are very limited.

Detailed diffusion studies in numerous doped and undoped semiconductors have been performed and have been used to arrive at conclusions regarding the formation and migration enthalpies of the native defects which assist diffusion. It lies in the physical nature of the random diffusion process that the diffusivity D_x and the atomic concentration C_x of a particular defect X typically appear as a product in all diffusion transport equations. Under the usual assumption that both terms depend exponentially on the inverse of the absolute temperature, there is no simple way to separate the enthalpies for defect formation H_f and defect migration H_m :

$$D_x(T)C_x(T) = D_x^0 C_x^0 \exp[(H_m + H_f)/kT] \quad (2)$$

This is also one reason why it has been impossible to clearly and accurately distinguish between vacancy and interstitial assisted diffusion in Si. Elegant short time [10] and transient diffusion experiments [11] have improved this situation recently.

The use of stable isotope superlattices for diffusion and native defect studies may bring a completely new angle to the present picture. If performed carefully, many external effects which are inherent to all radioactive tracer and dopant in-diffusion experiments can be minimized or eliminated. Using $^{70}\text{Ge}/^{74}\text{Ge}$ bilayers on natural Ge substrates we have studied Ge self diffusion. Fig. 2a) and b) show the SIMS concentration profiles before and after self diffusion for 55.55 hrs at 586°C . The SIMS technique is sensitive enough to reveal all the residual stable isotopes in the two isotopically enriched layers. The profiles rising in concentration moving away from the surface to the interior are much sharper than the falling profiles because of ion knock-on. We used only the steeper profiles for our fits. Data from diffusion runs at five temperatures were recorded and the

resulting dependence of the self diffusion coefficient agrees very well with the best published data. The redundancy in the data obtained simultaneously from the various stable isotopes further reduces the errors of the diffusivity values.

Fig. 2. SIMS concentration profiles of the Ge isotopes in a bilayer of ^{70}Ge and ^{74}Ge grown on a natural Ge substrate: a) as-grown sample, b) after diffusion at 586°C for 55.55 hr. (Ref. [4])

Neutron Transmutation Doping

In addition to differences in nuclear mass and spin, the thermal neutron cross sections of nuclei vary over many orders of magnitude. Typically cross sections are a few barns ($1\text{ barn} = 10^{-24}\text{ cm}^2$) but in some extreme cases, such as ^{113}Cd , the cross section may exceed 20'000 barn. Depending on the nuclear decay channels a nucleus may simply change into a heavier nucleus of the same element. In many cases, however, the nucleus is no longer stable after neutron capture and decays into a different element. Several hundred tons of P doped Si are produced in this way per year:

The atomic fraction of ^{28}Si is only 3.1%, limiting NTD of Si to medium P concentrations with the neutron fluences available in modern nuclear reactors.

The case of Ge is particularly interesting for NTD because Ga acceptors As donors and Se double donors can be formed [12]:

In natural Ge the compensation ratio ($[\text{As}] + 2[\text{Se}] / [\text{Ga}]$) is close to 0.4 and is given by the relative atomic abundances and the neutron capture cross sections. Controlling the isotopic composition and neutron fluence allows the selection of both the net-dopant concentration and the compensation. This opportunity has been used for neutral impurity scattering studies [13]. At this

conference we also learned about investigations of the widths of acceptor ground state to bound excited state transitions in isotopically controlled NTD Ge [14]. The unique advantage of this approach lies in the perfectly random homogeneous distribution of the dopant atom locations throughout the lattice.

Conclusions

We have pointed out a few examples of dopant and defect studies which have made use of isotopically designed semiconductor structures. Due to space limitations none of the possibilities offered by electron paramagnetic and nuclear magnetic resonance have been discussed. We recall the fact that in Ge donor EPR lines become significantly narrower in crystals with reduced content of ^{73}Ge (nuclear spin 9/2). Isotopically designed semiconductors allow a re-evaluation of such possibilities.

The special appeal of studies with isotopically designed semiconductor structures lies in the fact that isotopes of a particular element are *chemically identical*. Their different nuclear masses and spins do not change, to first order, the semiconductor crystal structure and its major electronic properties. Inter-diffusion in an isotope superlattice is caused exclusively by the random walk of host crystal atoms in the absence of any disturbances. We expect that such studies will yield basic information on the elusive nature of interstitials, vacancies and other more complicated defects.

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