PROGRESS REPORT

(REQUEST FOR CONTINUATION GRANT SUPPORT)

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Submitted by:

Y.H. Kao

Department of Physics
State University of New York at Buffalo
Amherst, NY 14260

Telephone Number: (716) 645-2576
FAX Number: (716) 645-2507

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A. Brief Statement of Accomplishments From the Past Year (since last report filed in 1993)

We have performed experiments to pursue studies in the following areas:

1. **Interfacial Microstructures of Si$_{1-x}$Ge$_x$ and Ultrathin Ge Layers on Si**

   This is a continuation of our on-going comprehensive x-ray studies of semiconductor Si/Ge layered structures using the grazing-incidence x-ray scattering (GIXS) and fluorescence techniques. Normal and inverted Si$_{1-x}$Ge$_x$/Si heterostructures and ultrathin (4-17 Å) Ge layers were grown on bulk Si by our collaborators at UCLA and IBM using MBE. Angular dependence of grazing-incidence x-ray scattering and Ge Kα fluorescence were measured. The data are compared with theoretical models to obtain information on the rms roughness and correlation-lengths of height fluctuations at the interfaces, and also on the Ge density profile. The interfacial roughness at neighboring interfaces is found to be highly correlated. Significant changes of microstructures in the Ge epilayers were observed for films with thickness approaching the critical thickness. For details up to this date, please see the attached reprint [Phys. Rev. B47, 16373 (1993)] and a preprint. More work is in progress.

2. **Thickness Modulation in InGaAs/GaAs Superlattices**

   Superlattices of 100-period InGaAs(15 Å)/GaAs(100 Å) grown on GaAs (100) substrates by MBE were studied by means of large angle x-ray scattering. In contrast to the usual superlattice satellites corresponding to structural periodicity in the direction normal to the sample surface, satellite peaks in the lateral direction were also observed in a sample grown at 480°C, indicating an in-plane periodic structure. This result is found in agreement with high resolution TEM observations that thickness modulation in the layers gives rise to long-range regular arrangements of cluster-like microstructures with a lateral periodicity of a few hundred Ångstroms. For comparison, no lateral satellites were observed in similar superlattices grown at 510°C with a relatively uniform layer thickness. This technique can be conveniently employed for nondestructive characterization of semiconductor thin films containing disordered arrays of quantum dots or quantum wires prepared by epitaxial growth. For discussions up to this date, please see the attached preprint.

3. **Local Structures Around Mn in Mn-Doped Nanocrystals of ZnS**

   X-ray absorption fine structure (XAFS) measurements were made near the Mn K-absorption edge for two samples of Mn-doped ZnS nanocrystals with different size distributions of 50-55 Å and 30-35 Å, respectively. By comparison with bulk ZnS:Mn powders, our EXAFS results show that Mn dopants occupy the Zn sites of ZnS in the nanocrystals
but with substantial local lattice distortion depending on the nanocrystal size distribution. The possibility of forming small Mn clusters in these nanocrystals was investigated. Our NEXAFS results indicate that the effective valence of Mn in both samples is close to +2. For details up to this date, please see the attached preprint. More work is in progress.

4. Local Environment Surrounding Mn Atoms in In\(_{1-x}\)Mn\(_x\)As Diluted Magnetic Semiconductors

We continued to investigate the local environment surrounding Mn atoms in In\(_{1-x}\)Mn\(_x\)As III-V diluted magnetic semiconductors grown by MBE using the XAFS techniques. Near neighbor distances, coordination number, and local disorder around the x-ray absorbing Mn central atoms were investigated in samples prepared with different Mn concentrations, substrate temperatures, and annealing conditions. Before annealing, samples prepared at various substrate temperatures around 280°C and 210°C were found to exhibit different local structures and physical properties. However, annealing at 480°C for 74 minutes in the MBE chamber was shown to result in phase separation and the formation of MnAs clusters. For details up to this date, please see the attached reprint [Phys. Rev. B47, 7187 (1993)] and a preprint. More work is in progress.

5. Correlations Between Interfacial Roughness and Epilayer Thickness

Grazing incidence x-ray scattering (GIXS) and diffraction techniques have been used to investigate an important problem in epitaxial growth concerning the correlations between interfacial roughness and layer thickness, especially near the region of critical thickness. By choosing an appropriate content of Ge in the Si\(_{1-x}\)Ge\(_x\) system, it is possible to have a value of critical thickness about 100Å and reasonable lattice mismatch on Si, a condition suitable for experimental investigations using the x-ray techniques. Our preliminary data are very encouraging. These results also suggest an interesting scaling behavior near the critical thickness (please see Figs. 1-3). More experiments are in progress.

B. Brief Statement of Plans for the Next Budget Year (11/1/94-10/31/95)

As described in the 1993 renewal proposal, our main goals of future experiments can be classified in two categories: (a) Interfacial microstructures in layered materials, and (b) Effects of chemical doping and local structures in compound materials. In each case, a series of experiments will be carried out to address some fundamental issues which are important for the development of advanced electronic and optoelectronic materials. These issues are also interrelated.
Fig. 1 -- Typical data of grazing-incidence specular reflectivity taken with a Si$_{0.4}$Ge$_{0.6}$ epi-layer grown on Si(100). The data points (circles) are in excellent agreement with theoretical calculations (line) based on a model described in our previous paper [Phys. Rev. B47, 16373 (1993)]. From the close fit, the interfacial roughness parameters and layer thickness can be accurately determined. Deviation at low incidence angle ($Q_z$) is due to a shadow effect below the critical angle.
Roughness vs Thickness SiGe $x=0.6$

- solid circle: surface
- box: interface

Fig. 2 -- Surface and interfacial roughness determined from the GIXS experiments for a series of Si$_{0.4}$Ge$_{0.6}$ epilayers with different thickness ($h$) grown on Si(100). Abrupt change in the interfacial roughness is observed around the critical thickness (about 120 Å). Similar behavior is also found in surface roughness but the change takes place at probably a slightly larger thickness. The variation of both the surface and interfacial roughness immediately below the critical thickness can be described by a power law with a critical exponent in the form of $\sigma = \text{Constant} \times h^{3/4}$. 
Fig. 3 -- Large angle diffraction data for the epilayers shown in Fig. 2. Variations of the broad peak indicate the change in crystalline structure above the critical thickness, in agreement with the observations of interfacial roughness in Fig. 2. The sharp peak at $23.4^\circ$ is due to the substrate.
We will continue our present active research programs on the studies of semiconductor heterostructures and superlattices using various x-ray techniques. In addition, an effort will be devoted to exploring a technique called REFLEXAFS, which will make use of grazing-incidence reflectivity to obtain EXAFS data. The advantage of this technique is its high sensitivity to the interfacial microstructures, e.g., the interfacial roughness. Thus, by a combination of the conventional fluorescence EXAFS, grazing-incidence x-ray scattering, and REFLEXAFS, more useful information can be obtained for a better understanding of the interfaces in layered materials.

Our immediate plans for the next year (11/1/94-10/31/95) are outlined in the following:

1. **Studies of Si$_{1-x}$Ge$_x$ Layered Semiconductor Systems**

   This is a continuation of our successful on-going experiments on a comprehensive study of the Si/Ge epilayers. This two-component system is a prototype material most suitable for fundamental structural studies. Its lattice mismatch on Si and critical thickness values can be well-controlled so that epilayers can be prepared with manageable thickness and morphology variations for comparison with theoretical models. Several sets of high-quality MBE-grown Si$_{1-x}$Ge$_x$ and ultrathin Ge layers have been prepared by our collaborators. We are aiming at a clear physical understanding of some basic problems concerning the critical thickness of compound semiconductor epilayers which are of current interest for potential device applications. Grazing-incidence x-ray scattering and diffraction experiments with various layer thickness values will be carried out and the results will be compared with recent theoretical calculations based on models of dynamical scaling.

2. **Correlations Between Interfacial Roughness and Epilayer Thickness**

   We will address one of the most fundamental issues in epitaxial growth of layered semiconductors from below to above the critical thickness. A physical understanding of this basic problem is very much needed in the field in order to control the morphology and various properties important for the development of high-quality electronic and optoelectronic materials. Our preliminary data on GIXS and large angle diffraction have already shown promise for probing the variations of interfacial roughness in the region of critical thickness. These measurements will be one of the main goals of our research in the next year.

3. **Local Structures in In$_{1-x}$Mn$_x$As Diluted Magnetic Semiconductors**

   We plan to continue our present work on the new III-V diluted magnetic semiconductors. After our first XAFS experiments on this material system, *substitutional
doping of magnetic impurities in III-V compounds has now been demonstrated to be indeed possible. This capability of impurity control may provide unprecedented opportunities for making new III-V magnetic semiconductors. The local environment surrounding the magnetic impurity (Mn) atoms usually contains some disorder and lattice distortion, and Mn can become amphoteric depending on the local arrangement of neighboring atoms. These issues must be addressed for practical application reasons. The XAFS technique is uniquely suited for this task. We are in a strong position to take a leading role in this approach.

4. Development of the REFLEXAFS Technique

Our recent model calculations have shown that the REFLEXAFS technique can provide us with more detailed information on the local structures about interfaces in multilayer materials. We would like to explore the possible realistic applicability of this method as a convenient tool for probing the interfacial microstructures. We believe this technique can be developed in a way similar to Diffraction Anomalous Fine Structure (DAFS). In light of the recent progress being made in the understanding of DAFS, plus our extensive experience in the studies of interfacial structures using x-ray scattering techniques, it appears very promising that the REFLEXAFS method can be developed to become a service tool for probing the interfaces. Several prototype heterojunctions, including Si/Ge and (Si,Ge)/Si, are being prepared for this study.

5. Investigation of Doped Semiconductor Nanocrystals

A new class of semiconductors has been discovered by doping magnetic impurities (e.g. Mn) into small clusters of ZnS. These nanocrystals show some very peculiar optical properties mainly because of confinement effects on the transition probabilities [see e.g. R.N. Bhargava et al. Phys. Rev. Lett. 72, 416 (1994), and our preprint]. Because of the small dimensions of the nanocrystals (around 30Å), the diffraction techniques are not useful for investigating the structure. This is an area in which we believe our EXAFS studies can make important contributions.

Our XAFS results on Mn-doped ZnS have demonstrated that this approach is uniquely suited to the study of short-range-order structures in fine particles of doped semiconductors with sizes about 30Å or smaller. These nanocrystals have already shown some unusual physical properties which could potentially be useful for the development of new solid state lasers. We would like to continue our collaboration with Dr. R.N. Bhargava of Nanocrystal Technology where these special nanocrystals will be made in the future.
C. Recent Publications of Y.H. Kao (since last report in 1993)


10. "Local Environment Surrounding Mn Atoms in $\text{In}_{1-x}\text{Mn}_x\text{As}$ Diluted Magnetic Semiconductors" (with Y.L. Soo, S. Huang, Z.H. Ming, A. Krol, H. Munekata, and L.L.
Chang), (preprint).

11. "Thickness Modulation of InGaAs/GaAs Superlattices Studied by Large Angle X-ray Scattering" (with Z.H. Ming, Y.L. Soo, S. Huang, K. Stair, G. Devane, and C. Choi-Feng), (preprint).

D. Students and Postdoctoral Fellows

Dr. Z.H. Ming -- Post-doctoral fellow, appointed in January, 1994. Currently stationed at NSLS, Brookhaven National Laboratory, Upton, NY. Mainly responsible for GIXS experiments and data analysis.

Mr. Jack Soo -- Graduate student, expected to finish his thesis work by Dec. 1994. Currently stationed at NSLS, Brookhaven National Laboratory, Upton, NY.

Mr. S.W. Huang -- Graduate student, expected to finish his thesis work by Dec. 1995. Currently stationed at NSLS, Brookhaven National Laboratory, Upton, NY.

E. Current Financial Support

"X-ray Studies of Microstructures in Semiconductor and Superconducting Materials"

DOE 11/1/93-10/31/96 $297,000 (P.I. 30% effort)

"Studies of Ceramic Superconductors: Flux Flow and Chemical Doping"

NSF 4/15/93-3/30/96 $312,630 (P.I. 20% effort)

F. DOE Support Requested for the Next Budget Year (11/1/94-10/31/95)

$100,000