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**X-RAY STUDIES OF SEMICONDUCTOR
SUPERLATTICES AND HETEROSTRUCTURES**

(FINAL TECHNICAL REPORT)

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FINAL TECHNICAL REPORT

Title: X-ray Studies of Semiconductor Superlattices and Heterostructures

Abstract

A variety of microstructure-probing techniques using high intensity x-rays from synchrotron radiation were employed for a comprehensive study of the short-range-order structures and interfaces in layered semiconductors grown by epitaxy. These layered materials are important for novel electronic and opto-electronic device applications. The experimental approaches were based on our extensive experience in using the measurements of x-ray fluorescence, absorption, reflectivity, and electron yield to probe the local structures about selected atomic species and interfaces in compound and multilayer semiconductors. Emphasis was placed on determining the local environment surrounding the impurity atoms, as well as the local structures around the interface, for various compound semiconductors and multilayers prepared by our collaborators at IBM. The results obtained may be viewed as a good example of successful university-industry collaboration sponsored by ONR. Efforts were also devoted to converting observations made in the laboratory to become service tools in the field for further investigations of multilayer semiconductor electronic materials.

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I. INTRODUCTION

In the development of semiconductor electronic materials, short-range-order microscopic structures are known to play some important and unique roles in controlling the physical properties of the solids. For fundamental interest as well as for technological applications, it is essential to have a quantitative understanding of the microstructures such as atomic interdiffusion and roughness near the interface between different materials, lattice distortion and local environment surrounding the impurity sites, and depth profile of constituent atoms in multi-element compounds. Due to the lack of long range structural order, these microstructures cannot be effectively determined by the conventional diffraction methods. Electron microscopy has been useful, but it suffers from the main difficulty of not maintaining the integrity of delicate specimens. Development of *nondestructive* experimental techniques which are sensitive to short range atomic arrangements for probing these microstructures would seem necessary.

The advent of synchrotron radiation has made it possible to determine the microscopic structures in condensed matter with unprecedented high intensity of x-rays. By the measurements of x-ray absorption, fluorescence, scattering, and electron yield as a function of photon energy and incidence angle, much detailed useful information about the microstructures can be obtained without deteriorating the quality of the materials under study. In the past several years, we have been using these x-ray techniques for a comprehensive study of various compound semiconductor heterostructures and superlattices prepared by our collaborators at IBM, UCLA, and Philips Laboratories. The results are very promising. Through this extensive study, some new methods for probing the

microstructures around the interfaces have been successfully developed.

By virtue of these useful x-ray techniques, unique information pertaining to the *local* structure around impurity atoms and interfacial roughness in a variety of electronic materials has been obtained. Our efforts were also devoted to converting some innovative approaches from quantitative understanding in the laboratory to "service tools" in the field. Special emphasis is placed on the development of a convenient *nondestructive* tool for determining the roughness and correlations of *buried interfaces* in layered semiconductors. In addition, by measuring the x-ray fluorescence of selected atomic species as a function of photon energy and incidence angle, the local environment and microstructures around specific constituent atoms in the layer materials have been determined.

II. EXPERIMENTAL STUDIES

Several state-of-the-art techniques making use of both soft and hard x-rays from synchrotron radiation were employed to obtain specific structure parameters required to understand and characterize the microstructures in layered semiconductors. These microscopic structural parameters are closely related to various physical properties.

II(A). X-ray Absorption Fine Structure (XAFS) Spectroscopy

XAFS generally refers to extended x-ray absorption fine structure (EXAFS) above an absorption edge and near edge x-ray absorption fine structure (NEXAFS or XANES). These spectra contain information on the local environment surrounding a specific atom in multi-element systems such as the interatomic distance, coordination number, and local

disorder, thus are especially useful for the present study. Detailed description of these techniques can be found in several review articles [1].

We have obtained useful information in applying the XAFS technique to the study of local structures in various semiconductor systems, including As-doped Si [2], As-doped Bi [3], as well as the heterostructures of InAs/AlSb [4], InAs/GaAs [5], and InGaAs/InP [6].

The main objectives of our XAFS experiments are three-fold:

- (a) To find the location of the impurity atoms and the interatomic distances between the impurity atom and its near neighbors.
- (b) To investigate the coordination and *local disorder* around the impurity atoms.
- (c) To investigate the local structure around the interfaces in multilayer semiconductors.

Since the K and L absorption edges of most elements are well separated in energy, the structural information obtained from the XAFS measurements is *element-specific*. Most of the XAFS experiments were carried out by measuring the x-ray fluorescence yield (FY). The specimens used in the FY measurements need not be in the form of powders or free-standing thin films (as for x-ray transmission measurements), hence the integrity of some delicate materials prepared by epitaxial growth can be safely preserved.

II(B). Grazing Incidence X-ray Fluorescence and Scattering

The angular dependence of x-ray fluorescence and reflectivity at grazing incidence have been demonstrated as important tools for investigating the atomic profile, morphology and interfaces of layered materials [7-18]. We have applied these techniques to the study of interfacial roughness in several heterostructure systems, including InAs/GaAs [19,20],

InGaAs/InP, InGaAs/GaAs [21], and SiO₂/Si [22]. Our data were analyzed using a modified Fresnel equation in conjunction with a vector scattering theory which takes into account the effects of interface scattering [17]. These results thus form the basis for *nondestructive evaluation of buried interfaces in layered structures*.

The fluorescence measurements give structural information which is element-specific. By a control of the probing depth of x-rays through variations of the grazing incidence angle, the depth profile of a selected atomic species inside the material and near the interfaces can be probed. This allows the possibility of investigating the effects of impurity accumulation and interdiffusion of atoms in the interfacial region. When used in conjunction with the XAFS measurements, these experiments will provide us with specific information on the interfacial structure which is not obtainable from other measurements. This grazing incidence fluorescence yield (GIFY) technique is therefore especially valuable for the study of semiconductor thin films. Theoretical analysis for the propagation of x-rays in layered structures and the methods used to obtain the interfacial roughness have been discussed in our previous publication [17] and also more recently by de Boer [18].

Similar to FY, x-ray scattering at grazing incidence can be used to obtain information on roughness of the sample surface and buried interfaces, layer thickness, and atomic density profile [9-13]. The specular reflection technique has been used in many of our previous studies to measure the interfacial roughness and for accurate determination of the epilayer thickness [23-25].

II(C). Total Electron Yield as a Tool for Probing Surface and Interfaces

This is a variation of the fluorescence method discussed above, from which the interfacial roughness pertaining to buried interfaces in multilayer systems can be probed. Through an analysis of the electric field and Poynting vector at varying depths, the total electron yield (TEY) method can provide information on the interfacial structure with an information depth larger than the electron mean free path [26,27]. In a single layer, TEY offers a probing depth comparable to the escape length of low energy electrons. Hence, when TEY is used in conjunction with the fluorescence measurements, much detailed information pertaining to the changes in the surface layer can be derived. This is useful for distinguishing the effects arising from the bulk in comparison with that from the surface.

II(D). Experimental Facilities

All of our x-ray experiments are conducted at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. We have been using both the X3B1 and U15 beamlines for hard and soft x-ray studies. Ample beamtimes are regularly scheduled for use by our group. The X3B1 beamline is a dedicated XAFS facility for which our group is formally responsible for managing its operation. The U15 beamline is mainly run by our group together with Dr. D. Hanson of Chemistry Department, SUNY at Stony Brook.

III. COLLABORATION WITH IBM

We have been collaborating with an IBM group (Leroy Chang and H. Munekata) since 1984 on a variety of research projects related to semiconductors using synchrotron radiation.

Our results have already revealed some unique information important for understanding the short-range-ordered structures in various compound semiconductors.

IV. CONCLUSIONS AND GENERAL COMMENTS

No significant progress in new materials can be made without knowing where the atoms are. This research addressed several microstructure-related issues which must be *quantitatively* understood before the novel layered semiconductor materials can be developed for practical applications. Synchrotron radiation provides great opportunities for solving these materials problems.

The main results of our research supported by ONR are summarized in the list of publications in Section V. The following general remarks seem useful:

(a) The XAFS techniques are well suited for probing the microstructures in semiconductor epilayers. We have made effective use of these techniques to obtain useful information in a variety of semiconductor heterostructures and superlattices.

(b) The grazing incidence fluorescence, reflectivity, and total-electron-yield measurements provide element-specific information on the microstructures around the interfaces and impurity atomic profile. This information, when used in conjunction with the XAFS results, are extremely useful for understanding the electronic and opto-electronic properties of the layered materials.

(c) As the important physical properties of the novel layered semiconductors depend critically on the epilayer growth conditions, the microscopic structural information obtained in our experiments can be used as a feedback to epilayer growers to characterize the materials and to select more appropriate conditions for further processing. These results will also be useful for the development of other new semiconductors. Successful examples can be found in the recent studies (unfortunately, not supported by ONR) of new III-V diluted magnetic semiconductors as well as $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructures and superlattices.

V. SUMMARY OF RESEARCH RESULTS

PUBLICATIONS BY Y.H.KAO -- SUPPORTED BY ONR (1985-1991):

All the main results obtained during the period of research supported by ONR are included in the following publications by the principal investigator. These reprints have already been filed with ONR. Additional copies are available when requested.

1. "Interatomic Distance and Local Order in InAs-AlSb Semiconductor Superlattices" (with E. Canova, A.I. Goldman, S. Woronick and L.L. Chang) Phys. Rev. B31 (1985) 8308.
2. "Probing the Structure of Semiconductor Superlattices and Heterostructures by EXAFS" (with S.C. Woronick, E. Canova, G.W. Su and L.L. Chang) Proc. Second Int'l. Conf. on Modulated Semiconductor Structures (Kyoto, 1985), p. 375.
3. "EXAFS Studies of Ion Implanted Bismuth" (with E.M. Kunoff and M.S. Dresselhaus) Mat. Res. Soc. Symp. Proc. 41 (1985) 281.
4. "Transmission Measurements of Soft X-ray Absorption Fine Structure in Solids by a New Scintillation Technique" (with B.X. Yang, J. Kirz, C.X. Gu, R.N. Bhargava, D.A. Cammack and R.J. Dalby) Phys. Lett. 113A (1985) 283.
5. "Soft X-ray Spectroscopy With a Scintillation Detector" (with B.X. Yang, J. Kirz and T.K. Sham) Proc. Int'l. Conf. on X-ray and VUV Synchrotron Radiation Instrumentation (Stanford, 1985); Nucl. Instr. and Meth. A246 (1986) 523.
6. "Probing the Structure of Semiconductor Superlattices and Heterostructures by EXAFS" (with S.C. Woronick, E. Canova, G.W. Su and L.L. Chang) Surface Science 174 (1986) 567.
7. "Effect of Ion Implantation on the Electronic Structure of Bismuth" (with E.M. Kunoff and M.S. Dresselhaus) Phys. Rev. B34 (1986) 8460.
8. "Lattice Relaxation of InAs Heteroepitaxy on GaAs" (with H. Munekata, L.L. Chang and S.C. Woronick) Proc. 4th Int'l. Conf. on MBE (York, 1986); J. Crystal Growth 81 (1987) 237.

9. "Determination of Interface Roughness in Heterostructures by X-ray Reflectivity" Chinese J. of Physics 25 (1987) 260.
10. "Short-Range-Order Structure of an InGaAs Compound Semiconductor Grown by Liquid-Phase Epitaxy" (with S.C. Woronick, M.E. Hills, T.W. Nee and V. Rehn) J. Appl. Phys. (1987) 2836.
11. "X-ray Reflectivity of InAs/GaAs Heterostructures with Surface and Interfacial Roughness" (with S.C. Woronick, B.X. Yang, A. Krol, H. Munekata, L.L. Chang and J.C. Phillips) Proc. Third Int'l. Conf. on Modulated Semiconductor Structures (1987); J. de Physique C5 (1987) 51.
12. "X-ray Studies of Interfacial Roughness in ZnSe/GaAs Heterostructures" (with A. Krol, C.J. Sher, S.C. Woronick, R.J. Dalby, D.A. Cammack and R.N. Bhargava) Superlattices and Microstructures 4 (1988) 435.
13. "Characterization of Interfacial Roughness in Semiconductor Heterostructures by X-ray Reflectivity" (with A. Krol, C.J. Sher, H. Resat, S.C. Woronick and W. Ng) Mat. Res. Soc. Symp. Proc. 103 (1988) 355.
14. "Studies of Lattice Distortion and Crystal Curvature in Arsenic-Implanted Silicon" (with C.L. Kuo, E. Arnold and J.C. Bilello) J. Appl. Phys. 64 (1988) 1791.
15. "X-ray Fluorescence of Layered Synthetic Materials with Interfacial Roughness" (with A. Krol and C. Sher) Phys. Rev. B38 (1988) 8579.
16. "Probing the Short-Range-Order Structure in Solids Using Synchrotron Radiation" Proc. Third Asia Pacific Physics Conf. (Hong Kong, 1988), p. 408.
17. "Probing the Microstructure in Semiconductor Heterojunctions by X-ray Techniques" (with A. Krol, S.C. Woronick, C. Sher, and H. Resat) Proc. Int'l. Conf. on Electronic Materials (Tokyo, 1988), p. 229.
18. "Studies of an InAs/GaAs Heterojunction by Total Electron Yield" (with A. Krol, C.J. Sher, D.R. Storch, S.C. Woronick, L. Krebs, and L.L. Chang) Mat. Res. Soc. Symp. Proc. 143 (1989) 25.
19. "Local Environment of Arsenic Impurities in Semi-Insulating Polycrystalline Silicon" (with E. Canova, E. Arnold, and T.M. Marshall) Phys. Rev. B39 (1989) 3131.

20. "Interfacial Roughness in InAs/GaAs Heterostructures Determined by Soft X-ray Reflectivity" (with S.C. Woronick, B.X. Yang, A. Krol, H. Munekata, and L.L. Chang) J. Appl. Phys. 66 (1989) 3566.
21. "A Low Pressure, Parallel Plate Avalanche Chamber for Detection of Soft X-ray Fluorescence" (with G.C. Smith and A. Krol) Nucl. Instr. and Meth. A291 (1990) 135.
22. "Total-Electron-Yield of Synthetic Layered Structures with Interfacial Roughness" (with A. Krol and C.J. Sher) Phys. Rev. B42 (1990) 3829.
23. "Soft X-Ray Investigation of the Effect of Growth Conditions on InAs/GaAs Heterostructures" (with A. Krol, C.J. Sher, D. Storch, S.C. Woronick, L.L. Chang and H. Munekata) Proc. 4th Int'l. Conf. on Modulated Semiconductor Structures, Ann Arbor, MI, 1989; Surface Science 228 (1990) 108.
24. "Local Structure Around Mn Impurities in InMnAs/InAs Diluted Magnetic Semiconductors" (with A. Krol, Z.H. Ming, C.S. Lin, Y.L. Soo, C.X. Gu, H. Munekata, and L.L. Chang) Mat. Res. Soc. Symp. Proc. (Symp. B, 1990), p.189.
25. "Characterization of SiO₂/Si Heterostructures by Soft X-ray Reflection" (with S.C. Woronick, W. Ng, A. Krol, and E. Arnold, J. Appl. Phys. 69 (1991) 1631.
26. "Investigation of Interfacial Roughness of InGaAs Epitaxial Layers on GaAs and InP Substrates by Soft X-ray Reflectivity" (with A. Krol, H. Resat, C.J. Sher, S.C. Woronick, W. Ng, T.L. Cole, A.K. Green, C.K. Lowe-Ma, T.W. Nee, and V. Rehn) J. Appl. Phys. 69 (1991) 949.

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