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Defects in Electronic Materials

Editors: Michael Stavola, S. J. Pearton and G. Davies

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MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS VOLUME 104

Defects in Electronic Materials

Symposium held November 30-December 3, 1987, Boston,
Massachusetts, U.S.A.

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Preface

This Proceedings volume results from a Materials Research Society symposium designed specifically to present the spectrum of defect studies in electronic materials. These range from the basic physics of point and line defects in silicon and compound semiconductors, to the effects of such entities on device performance. Invited papers on topics that span much of the range of interest in this field are given in the first section, followed by invited and contributed papers on impurities and defects in Si, GaAs and other compound materials.

Of continuing interest at the present time are studies of oxygen and transition metals in Si. Several metastable defects in Si have been discovered and are receiving attention. The dominant defects in GaAs (EL2) and in AlGaAs (the DX center) have crucial technological impact - EL2 because of its role in producing semi-insulating GaAs for device applications, and the DX centers because of their deleterious effect on GaAs-AlGaAs heterostructure transistors. This volume contains the most up-to-date results and models for these defects. Perhaps the greatest upswing in activity was focused on the properties of hydrogen in Si and III-V materials and indeed this impurity represents an excellent example of the intimate connection between basic defect studies, and technological applications of such knowledge. New insights into the variety of effects that involve hydrogen in semiconductors and the number of ways hydrogen is introduced were forthcoming at this meeting and these are detailed in a number of review and contributed papers.

Finally, the role of lattice defects in controlling the electronic and structural properties of multilayer semiconductors was also a major topic of the symposium. The ability to control the intermixing of III-V heterostructures and superlattices leads to the exciting vistas of selective area bandgap engineering on a sub-micron scale. Together with the growth of large lattice mismatched systems (e.g. GaAs on Si) this use of defects to control the properties of novel semiconductor structures is bringing us the next generation of optoelectronic devices, as well as an array of new quantum-confinement effects accessible only in these artificially layered structures.

The symposium was extremely well attended, with over two hundred participants at each session. Invariably there was standing room only in the meeting room. Over 110 papers were included in the oral and poster sessions, representing contributions from 21 different countries. The poster session was especially successful, and provided a lively ending to the symposium.

Symposium Co-Chairs

Michael Stavola

S. J. Pearton

G. Davies

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These proceedings are the permanent record of Symposium E entitled Defects in Electronic Materials, which was part of the Materials Research Society Meeting held in Boston, MA, Nov. 30 - Dec. 3, 1987.

The outstanding success of the symposium was due in no small part to the efforts of the following people: the authors and speakers who presented their technical work at the meeting and composed the papers in these proceedings; the symposium organizers, who put together the program and saw that it ran smoothly; the session chairpersons, who ran the individual sessions and reviewed the manuscripts (T. A. Kennedy, E. Lightowers, H. G. Grimmeiss, J. Chevallier, L. C. Kimerling, M. Levinson, J. Weber, B. Monemar, R. C. Newman and E. Weber); the staff of the Materials Research Society, who provided the backdrop for each symposium; and perhaps most importantly of all the government and corporate sponsors listed below, whose financial contributions enabled the organizers to provide the highest quality speakers and cover the meeting expenses. The editors of these Proceedings extend our sincere appreciation to all of those who contributed to the success of the symposium.

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DEFECTS IN SEMICONDUCTORS 1987

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ABSTRACT

A brief discussion of recent developments in the study of defects in semiconductors is given, as they are evidenced in these proceedings.

INTRODUCTION

The research concerned with defect studies in semiconductors has undergone a rapid transition in the last decade: from a quite limited area concerned with the basic understanding of simple, mostly radiation-induced defects, which had only limited practical significance, to a field whose research results are in the center of interest for many technological applications. This change is caused by two developments. On one side, the increasing complexity of devices, the decrease in device dimensions, and the increased interest in compound semiconductor material require improved understanding of lattice defects, whose concentrations might not have been relevant 10 to 20 years ago, but whose presence is now limiting further development. On the other side, the pioneering work in the last twenty years has yielded significant progress in basic defect identification and understanding of defect properties and has thus provided the tools to help semiconductor technology. This fourth in a series of MRS symposia on the general topic of defects in semiconductors (after Boston in 1980 and 1982 and San Francisco in 1985) clearly demonstrates this development.

The multitude of excellent contributions in this volume does not allow one to attempt a comprehensive review of all topics covered. The following brief survey is rather a subjective discussion of some recent developments in this field, given as a conference conclusion.

VACANCIES

Vacancies in silicon are considered to be present together with Si self-interstitials at high temperatures in thermal equilibrium. Their electronic properties are quite well understood ¹. One of the most important current questions is the determination of their thermodynamic properties, such as entropy and enthalpy of formation determining the vacancy concentration in thermal equilibrium. Total energy calculations presented at this conference ² yielded values near $3k_B$ and 4.2 eV, respectively, which is in quite good agreement with other recent theoretical work ³. This high enthalpy of formation combined with a quite small formation entropy results in only 10^{11} vacancies/cm³ at the melting point in thermal equilibrium and 10^7 cm⁻³ at 1000°C. It is difficult to see how such small vacancy concentrations would allow for any role of vacancies in substitutional diffusion or self-diffusion, which has been established quite convincingly by experiment ⁴.

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Our present knowledge of the properties of vacancies in GaAs and other III-V compounds is still inferior to our knowledge of the situation in silicon. Recent positron annihilation experiments indicate the presence of large concentrations of vacancy-related defects in as-grown GaAs ⁵, which will be an important subject of future investigations.

The magnetic resonance experiments with Frenkel pairs in ZnSe ⁶ reported here include a detailed study of vacancy properties in this II-VI compound. The optical investigations of this material are consistent with V_{Zn} being a double acceptor.

INTERSTITIALS

The thermodynamic parameters calculated for Si self-interstitials include a very high formation entropy ², which results in equilibrium concentrations near the melting point in the 10^{16} cm^{-3} range. Whereas experimental results of the electronic properties of Si self-interstitials are still lacking, recent work on the isoelectronic C_i -related defects in Si allows one to gain some insight into the behavior of self-interstitial-type defects in Si. Most noteworthy is the observed metastability of C_i -related complexes ⁷.

Ga self-interstitials have recently been identified by optically detected magnetic resonance (ODMR) in ternary III-V compounds and GaP ⁸. This finding is surprising, as it implies that these interstitials are thermally quite stable, in contrast to the expected instability in silicon. Arsenic is present in most bulk GaAs crystals in supersaturation because of the normally As-rich growth conditions. Arsenic precipitates in GaAs have been identified by transmission electron microscopy ⁹. These precipitates might be a source for mobile, interstitial As and might explain some of the effects of changes of electrical properties of GaAs upon thermal annealing.¹⁰⁻¹² Interstitial As might be part of the EL2 defect discussed in the next section.

Interstitial Zn in the II-VI compound ZnSe has been identified by magnetic resonance ⁶, and a double donor energy level scheme has been proposed. As expected, this defect is unstable at room temperature.

ANTISITE DEFECTS

Antisite defects are the only native point defects in semiconductors that show thermal stability up to temperatures close to the melting point ¹². Arsenic antisite defects in GaAs are of great practical relevance, as they are a constituent of the EL2 midgap donor dominating the compensation mechanism in LEC GaAs ¹³. The original identification by photo-EPR of the double donor nature of As_{Ga} ¹⁴ with a midgap single donor level and a double donor level near $E_v + 0.5 \text{ eV}$ has been confirmed for EL2 as well ¹⁵. However, EPR measurements alone do not allow one to distinguish isolated As_{Ga} defects from complexes of As_{Ga} with, e.g., V_{Ga} or As_i in the second neighbor shell, and the detailed atomistic structure of EL2 is still not yet satisfactorily determined. The most widely accepted model of EL2 as an As_{Ga} - As_i complex was based on indirect EPR evidence ¹⁶, optically detected electron nuclear double resonance measurements (OD-ENDOR) ¹⁷, and self-consistent Greens-function calculations ¹⁸. Yet this conference revealed clearly a major problem of this model: an As_{Ga} - As_i complex is expected to

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be a triple donor, with a quite shallow single donor level (0/+) and a midgap level of double donor (+/++) character. Pinning of the Fermi level at a midgap double donor level is only possible if compensating acceptors are present in precisely one to two times the EL2 concentration in the material. This problem renews the discussion of the correct model of EL2, which still includes vacancy-related complexes¹² as well as simple As_{Ga} antisite defects¹⁹. The metastable behavior of EL2 alone is no longer an argument against identification with a simple As_{Ga} defect, as shown by most recent self-consistent calculations²⁰. Additional experimental evidence from measurements of ballistic phonon scattering is presented in these proceedings²¹. These measurements show a decrease in phonon scattering with the transformation of EL2 to its excited state, consistent with the removal of trigonally distorted defects. However, they fail to provide a direct measurement of the symmetry of EL2 in the ground state.

Closely related to the question of the identification of EL2 is the search for compensating acceptors in low-impurity LEC GaAs, which might as well be of the antisite defect type, such as B_{As} or Ga_{As}.

DEEP DONORS IN COMPOUND SEMICONDUCTORS

The metastability of deep donors in AlGaAs and other III-V alloys has been interpreted for many years as evidence for a complex defect structure ("DX-centers"), consisting of a donor atom and an unknown -- possibly vacancy-type -- partner "X," which upon change of charge state can undergo a large lattice relaxation²². This complex model for the DX center has been questioned already based on simple defect formation arguments, as all donors in AlGaAs turn out to be DX-centers²³. The observation of such metastable deep donors in GaAs subjected to hydrostatic pressure provided strong further evidence for DX centers being deep donor levels of isolated atoms in a specific band structure²⁴. The metastability of such isolated atoms can be explained by polaron-type extrinsic self-trapping of carriers²⁵ or Jahn-Teller type distortions²⁶. A major part of the current discussion in this field deals with the question, whether the observed metastability is due to a large or a small lattice relaxation²⁷, neither of which contradicts an isolated donor model. It is obvious that state-of-the-art calculations of symmetry-breaking distortions of isolated donor atoms, as they have been done for As_{Ga} in GaAs²⁰, are badly needed to help clarify the situation.

OTHER METASTABLE DEFECTS

These proceedings contain several well-documented examples of metastable defect complexes, such as metal-acceptor pairs²⁸ and other interstitial-substitutional complexes in silicon⁷. These defects should be very interesting to test self-consistent calculations of defect complexes, as the experimental evidence is well established.

OXYGEN IN SILICON

A comprehensive understanding of the complexing and precipitation of oxygen in Si is the subject of many investigations. Still there exists no generally accepted model for the smallest

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oxygen complexes in silicon, the thermal donors. A detailed kinetic study presented here ²⁹ gives evidence that thermal donors are "Neanderthals" in the process of oxygen precipitation, as they might represent species disappearing upon further heat treatment, rather than the nuclei for final oxygen precipitation.

HYDROGEN IN SEMICONDUCTORS

These proceedings show strongly increasing interest in hydrogen-related phenomena in semiconductors. For acceptor hydrogenation, the model in which hydrogen takes a bond-centered site between an acceptor and one of its neighbors appears to be gaining acceptance ³⁰. Donor passivation is generally only partial and might include hydrogen in an antibonding configuration. No evidence has been found for passivation by simple electric compensation with new defects of opposite electrical character. Microscopic models for deep level hydrogenation or for the very interesting bulk passivation of thick Si samples during room temperature polishing ³¹ are still inconclusive. Hydrogen-related defects produced during dry etching of semiconductors in a hydrogen-containing plasma have a direct technological impact. It has been suggested that such defects are responsible for the small penetration depth of hydrogen in plasma-treated semiconductors ³¹.

DEFECTS IN HETEROSTRUCTURES

The basic understanding gained by the study of defects in bulk semiconductors is very useful in explaining defect-related phenomena in thin film heterostructures, as demonstrated in a number of contributions to this volume. The defect phenomena include the enhanced interdiffusion of superlattices during implantation annealing or dopant diffusion ³² and the formation and propagation of dislocations in lattice mismatched heteroepitaxy ³³. The growing interest in applications of heterostructures will without doubt result in a further expansion of this field.

CONCLUSION

The few examples discussed in this summary demonstrate the advancing microscopic understanding of defect-related phenomena in semiconductors, which will be of increasing relevance to the use of technologically more and more demanding device structures, such as submicron devices, high-electron mobility transistors with a two-dimensional electron gas, or hybrid Si-GaAs devices making use of GaAs-on-Si heteroepitaxy.

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