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Defects in Semiconductors

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Defects in Semiconductors

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Preface

This book contains selected papers from the symposium on "Defects in Semiconductors" held in Boston, Massachusetts, November 16-20, 1980, sponsored by the Materials Research Society. The symposium represented an international forum in which scientists from over ten foreign countries participated. Although this conference had many similarities with previous international conferences on lattice defects in semiconductors, notably Freiburg (1974), Dubrovnik (1976), Nice (1978), Oiso (1980), one of the distinguishing features of this conference was the emphasis on the electronic properties of dislocations and the point defect-dislocation relationships. The scope of the present conference was to address the new advances in defect characterization techniques, and then focus attention on point defects, dislocations, and point defect-dislocation interrelationships in elemental as well as compound semiconductors. Properties of these defects were discussed in light of various physical processes and phenomena including nucleation and formation of macroscopic defects, thermal and laser annealing of ion implantation and neutron damage, thermal oxidation and oxygen precipitation, and crystal growth. It was heartening to see a significant progress being made in the understanding of the physical properties of point defects, in the correlations of atomic structures with the electronic properties of dislocations, in identifying the role of silicon self-interstitials in impurity diffusion, and in bridging the gap between the structures of point and extended defects. Substantial progress in the field of defects in compound semiconductors was noteworthy.

Manuscripts were submitted by symposium participants in camera-ready form. Each manuscript was reviewed by at least one referee and modified accordingly. We would like to thank the referees for their conscientious efforts and speedy return of their comments. Finally we wish to express our sincere gratitude to many of our colleagues for providing their advice, guidance and encouragement in organizing the meeting.

J. Narayan
T. Y. Tan

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A large part of the credit for the success of the symposium is due to conference participants, particularly the invited speakers who provided excellent summaries of specific areas and set the tone of the meeting. They are:

B. R. Appleton	B. C. Larson
J. Chikawa	S. Mahajan
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S. M. Hu	J. Washburn
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Plenum Press, New York 1979

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*Invited

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*Invited

CHAPTER VII. DEFECTS IN COMPOUND SEMICONDUCTORS

*Invited

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ELECTRON PARAMAGNETIC RESONANCE IN SEMICONDUCTORS

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ABSTRACT

The use of electron paramagnetic resonance (EPR) in the study of defects in semiconductors is briefly reviewed, including group IV (C-diamond, Si, Ge, SiC), III-V (AℓSb, GaAs, GaSb, GaP, InAs, InP, InSb), II-VI (BaO, BaS, BeO, CaO, CaS, CaSe, CdO, CdS, CdSe, CdTe, MgO, SrO, SrS, ZnO, ZnS, ZnSe, ZnTe) and miscellaneous systems. The identification of defects via EPR is described as is the exploitation of that identification as a tool in future studies. Particular attention is paid to Si, where is emerging an integrated panorama of identified defects ranging from point defects to aggregates through intermediate defect configurations (as discussed by Tan) to dislocations and stacking faults; EPR results in Si as a testing ground for the theory of shallow donors, in the understanding of diffusion at high temperatures and in the study of heat-treatment defects are discussed as examples of the use of EPR as a tool in defect studies.

INTRODUCTION

We have been asked to try to give a perspective view of the use of electron paramagnetic resonance (EPR) in semiconductors. Our space is too limited to give details or much depth, but we feel we can give a proper view of the past and future contributions of this field of research.

Spectroscopy in general makes contributions to defect studies by the identification of defects and by the use of that identification as a tool in further studies. Characteristically the sharper the spectroscopic lines the more incisive the technique can be. *Central to defect identification is the determination of the defect symmetry*, which may be manifest by a spectral variation with respect to crystal orientation and which may be probed by the use of polarized light in absorption and in luminescence, by the response to an external field, etc.

EPR is simply a form of spectroscopy, specifically Zeeman spectroscopy, except that the usual Zeeman effect involves the splitting of electronic transitions due to a magnetic field; EPR observes the direct transition between the Zeeman-split electronic levels. To observe EPR there must be an unpaired spin, i.e., a non-zero paramagnetism, such as may be due to electrons in the conduction band [and we will see that conduction electron spin resonance (CESR) has been done in many semiconductors] or a suitably charged point-, line-, or surface-defect state. For a free electron in space the energy difference between the two Zeeman-split levels of the spin 1/2 system is given by $g\beta H$ with H- the magnetic field, β- the Bohr magneton and g- a constant determined by the Dirac theory of the electron. If that electron is bound to a free atom in space, the Zeeman levels of the electron may be split and shifted due to various effects such as the hyperfine-interaction and the quadrupole interaction with the nucleus of that atom. If the electron is localized at a defect in a solid the possible interactions are even richer since the electron may not reside on just one atom, but on several or even many. Further the quantities describing those interactions are no longer scalars but are tensors reflecting the crystal environment. These additional interactions can be a severe disadvantage since the resultant lines may be so broadened as to be effectively unobservable. The overall situation may be seen in Table I where we list the isotopes making up the several semiconductors that we consider, the isotopic abundances, their spins, magnetic moments and quadrupole moments.

TABLE I
Relevant Properties of Elements [1]

Isotope	Natural Abundance (%)	Spin	Magnetic Moment (μ_N)	Electric Quadrupole Moment ($10^{-24}cm^2$)
Al^{27}	100	5/2	+3.6414	+0.15
As^{75}	100	3/2	+1.439	+0.29
B^{10}	19.78	3	+1.8007	±0.08
B^{11}	80.22	3/2	+2.6885	+0.04
Ba^{132}	0.097	—	—	—
Ba^{134}	2.42	0	0	0
Ba^{135}	6.59	3/2	+0.8365	+0.18
Ba^{136}	7.81	—	—	—
Ba^{137}	11.32	3/2	+0.9357	+0.28
Ba^{138}	71.66	0	0	0
Be^{9}	100	3/2	-1.1776	+0.05
C^{12}	98.89	0	0	0
C^{13}	1.11	1/2	+0.7024	—
Ca^{40}	96.97	0	0	0
Ca^{42}	0.64	—	—	—
Ca^{43}	0.145	7/2	-1.317	—
Ca^{44}	2.06	—	—	—
Ca^{46}	0.0033	—	—	—
Ca^{48}	0.18	—	—	—
Cd^{106}	1.22	—	—	—
Cd^{108}	0.88	0	0	0
Cd^{110}	12.39	0	0	0
Cd^{111}	12.75	1/2	-0.5943	—
Cd^{112}	24.07	0	0	0
Cd^{113}	12.26	1/2	-0.6217	—
Cd^{114}	28.86	0	0	0
Cd^{116}	7.58	0	0	0
Ga^{69}	60.4	3/2	+2.016	+0.19
Ga^{71}	39.6	3/2	+2.562	+0.12
Ge^{70}	20.53	0	0	0
Ge^{72}	27.43	0	0	0
Ge^{73}	7.76	9/2	-0.8792	-0.22
Ge^{74}	36.54	0	0	0
Ge^{76}	7.76	0	0	0
In^{113}	4.28	9/2	+5.523	+0.82
In^{115}	95.72	9/2	+5.534	+0.83
Mg^{24}	78.70	0	0	0
Mg^{25}	10.13	5/2	-0.8553	+0.22
Mg^{26}	11.17	0	0	0
O^{16}	99.759	0	0	0
O^{17}	0.037	5/2	-1.8937	-0.026
O^{18}	0.204	0	0	0
P^{31}	100	1/2	+1.1317	—
S^{32}	95.0	0	0	0

Isotope (continued)	Natural Abundance (%)	Spin	Magnetic Moment (μ_N)	Electric Quadrupole Moment ($10^{-24}cm^2$)
S^{33}	0.76	3/2	+0.6433	-0.055
S^{34}	4.22	0	0	0
S^{36}	0.014	0	0	0
Sb^{121}	57.25	5/2	+3.359	-0.29
Sb^{123}	42.75	7/2	+2.547	-0.37
Se^{74}	0.87	0	0	0
Se^{76}	9.02	0	0	0
Se^{77}	7.58	1/2	+0.534	—
Se^{78}	23.52	0	0	0
Se^{80}	49.82	0	0	0
Sr^{84}	0.56	—	—	—
Sr^{86}	9.86	0	0	0
Sr^{87}	7.02	9/2	-1.093	+0.36
Sr^{88}	82.56	0	0	0
Te^{120}	0.089	—	—	—
Te^{122}	2.46	—	—	—
Te^{123}	0.87	1/2	-0.7359	—
Te^{124}	4.61	—	—	—
Te^{125}	6.99	1/2	-0.8871	—
Te^{126}	18.71	0	0	0
Te^{128}	31.79	0	0	0
Te^{130}	34.48	0	0	0
Zn^{64}	48.89	0	0	0
Zn^{66}	27.81	0	0	0
Zn^{67}	4.11	5/2	+0.8755	+0.17
Zn^{68}	18.57	0	0	0
Zn^{70}	0.62	—	—	—

For silicon we see that the predominant isotope (Si^{28} = 95.3% abundant) has spin zero and so contributes nothing in the way of spectral splittings; the remaining isotope (Si^{29}) has spin 1/2 so that it creates the simplest of splittings and its abundance (4.7%) is just about ideal to provide a dilute label on lattice sites. In the III-V compounds on the other hand we find the lattice constituents often have several magnetically active isotopes with large spins which split the lines into many sub-lines with strong (and overlapping) anisotropies; little wonder that the lines (when observed) in III-V compounds tend to be very broad.

When the lines are resolved, all these interactions can prove very incisive. For example in ordinary spectroscopy it is not unusual to determine the overall defect symmetry and perhaps, via an isotope effect, the identity of the dominant elements involved. In EPR the overall symmetry is encompassed in the anisotropy of the g-tensor; for the silicon defects it is not uncommon to find this g-tensor anisotropy varying and thereby revealing changes in the defect environment, e.g., the hopping of electrons from one bonding configuration to another, or the changing influence of lattice strains at the defect. In addition in silicon it is not uncommon for the defect spectra to exhibit resolved hyperfine lines, which reveal the extent to which the wave-function extends over the neighboring atoms of the lattice, and may reveal the presence of impurity atoms, which ordinary spectroscopy would miss. Further there are double resonance techniques which have already had considerable impact and have promise of much, much more, e.g., electron-nuclear double resonance (ENDOR), electron-electron double resonance (ELDOR), optical detection of magnetic resonance (ODMR). For example, the extensive ENDOR studies [2-8] of the shallow donors in silicon, which have mapped the electron wave-function over thirty shells of atoms in the lattice surrounding the donor atom, has proven to be a challenging testing ground for the theory of shallow donors [9-18], a challenge which theory has largely, but not completely met. Although EPR of the shallow acceptors has been observed [19-22], ENDOR measurements to test the more difficult theory [12,23-26] have not been carried out. Other ENDOR measurements have been carried out on deep-level systems and stand as a formidable testing-ground for the more difficult theory of deep-levels. Specifically Ludwig [27] has mapped out the wave-function on eight shells of neighboring atoms to the sulfur deep-donor, and Ammerlaan and co-workers have mapped out the wave-function for nineteen shells of atoms for the positive divacancy spectrum [28] and thirty-three shells of atoms for the negative divacancy spectrum [29]. Although substantial work on the theory of the divacancy has been done [30-32], there remain substantial discrepancies to be reconciled.

SURVEY OF DEFECTS IN SEMICONDUCTORS

In this section we present lists of defects for which an at least tentative identification exists in the EPR literature. Certainly there are defects which have been well identified without the help of EPR, many of which are inaccessible to EPR because they do not involve an unpaired spin. For example, the oxygen interstitial in silicon has a well-established configuration, arrived at by studies of the vibrational absorbtion lines [33-36]. As a further example, one should realize that the defects which we list represent a specific charge state of the defect; many of the defects have several charge states in the forbidden gap and typically a charge state change converts a paramagnetic state to a non-paramagnetic state (or vice-versa) and the latter is inaccessible to EPR. Like other forms of spectroscopy, EPR provides a limited "window" with which to view defects; if the defects are not visible through that window the spectroscopy is no help, but if it is visible, EPR may provide extensive information about the atomic and electronic configuration of the defect.

In Tables II, III and IV we list the defects for the group II-V, III-V and IV semiconductors [37].

TABLE II

Defects with Identified EPR Spectra in II-VI Compounds in the Literature [37]. In each system there may be spectra due to unidentified defects. V_X denotes a vacancy at an X site; X_{INT} - the element X in an interstitial site; X - the element (X) in a substitutional site; (X·Y) - an association of X and Y; CESR - conduction electron spin resonance; a-X, Surface - a resonance attributed to the amorphous X and to the surface, resp.; etc.

BaO
V_O
Gd, Mn
BaS
V_S

TABLE II (CONTINUED)

BeO

V_{Be}, V_{O}

Aℓ, B, Cu, F, Li

B_{INT}

CaO

V_{Ca}, V_{O}; $(V_{O} \cdot V_{O})$; $(V_{O} \cdot V_{Ca} \cdot V_{O})$

O_{INT}

Ag, Ce, Co, Cr, Cu, Eu, F, Fe, Gd, Ir, K, Li, Mg, Mn, Mo
Na, Nd, Ni, Pb, Ti, Tm, V, Yb

(Li·H), (Li·Li), (OH), $(V_{O} \cdot Mo)$, (Mn·Mn)

Surface

CaS

Eu, Mn, Sn, Yb

Surface

CaSe

Pb, Sn

CdO

Cu, Ni

$(V_{Ca} \cdot V_{O} + OH)$

CESR

CdS

V_{Cd}, V_{S}

Ag, Br, Cℓ, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, I
Mn, Ni, Nd, Pb, Sn, Ti, Tm, V, Yb

(Fe·Ag), (Fe·Ag), (Fe·Cu), (Fe·Li), (Gd·?), (N·N)

CESR, Surface

CdSe

V_{Cd}

Co, Eu, Fe, Gd, Mn, Nd, Sn, Ti, V

CESR, Surface