ELECTRON PARAMAGNETIC RESONANCE OF MATERIAL PROPERTIES AND PROCESSES*

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ABSTRACT

The purpose of this paper is to demonstrate, primarily for the non-specialist and within the context of new and recent achievements, the diagnostic value of electron paramagnetic resonance (EPR) in the study of material properties and processes. I have selected three EPR studies which demonstrate the elegance and uniqueness of EPR in atomic defect studies and exemplify unusual achievements through the use of new techniques for material measurement and preparation. A brief introduction into the origin, interaction, and detection of unpaired electrons is included.

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I. INTRODUCTION

This series of papers focuses on EPR studies of materials such as semiconductors, glasses, catalysis, amorphous Si:H, anisotropic conductors, ... which are of relevance in today's technology. Our purpose and approach are intended to demonstrate, primarily for the benefit of the non-specialist and within the context of new and recent achievements, the diagnostic value of EPR in the study of material properties and processes. Following a brief introduction into some of the basic aspects of EPR in defect studies, I will highlight the results of EPR studies on 1) nitrogen in silicon by Brower and Peercy, 2) the boron interstitial in silicon by Troxell and Watkins--here the ideas of Anderson's negative U energy and the Bourgoin mechanism are exemplified, and 3) Si-SiO₂ interface states by Poindexter, Caplan, Deal, and Razouk.

II. EPR IN DEFECT STUDIES

A. Origin of Unpaired Electrons

It is convenient to characterize the electronic structure of a semiconductor or insulator in terms of a band structure in which, ideally, the valence band is filled with electrons and the conduction band, which is separated from the valence band by an energy gap, is empty. The chemical bonding of these $\sim 10^{23}$ valence electrons/cm³ is usually such that they are spin paired according to the Pauli principle. Under these conditions the solid is diamagnetic and yields a null EPR spectrum.

Imperfections such as vacancies, interstitials, impurities, ... in solids often have localized states with one or more localized energy levels within the band-gap. Whether an unpaired electron is trapped in one of these localized states depends in the case of semiconductors on the position of the Fermi level and in the case of insulators on the availability of electrons or holes. The effects of ionizing irradiation, n- or p-type doping, light illumination, temperature, etc., will sometimes induce paramagnetism in existing defects. Also, defects can be produced during crystal growth and material preparation, and by displacement or ionizing radiation, ion implantation, (photo-) chemical reactions, thermal or laser annealing, fracturing, catalytic surface reactions, shock waves, etc.

It is often convenient to represent a center in terms of a defect-molecule which is comprised of the defect plus a few neighboring host lattice atoms [1,2]. Two giant defects which have been identified in neutron-irradiated and ion-implanted silicon are illustrated in Fig. 1. Usually, the defects observed by EPR are somewhat smaller than those in Fig. 1. Macroscopic defects such as interstitial loops, vacancy loops, precipitates, dislocations, bubbles, etc. which have been inferred from other measurements (e.g., electron microscopy) usually arrange themselves so that they are diamagnetic. Even then, in the case of macroscopic imperfections, any dangling bond would still be localized on a very small portion of the total imperfection (e.g., see Sec. V). The link between microscopic and macroscopic imperfections, that is, how they evolve into each other, still remains to a great extent an unexplored frontier.

For simple defect models represented by defect-molecules, it is useful to represent the electronic structure in terms of one-electron molecular orbitals which are consistent with the symmetry of the defect (Fig. 2). Although this simple approach does not give the position of the localized levels in the

bandgap or even their relative splittings, it does give the experimentalist insights into many of the electronic properties of the defect as observed by EPR, such as Jahn-Teller effects, energy changes under uniaxial stress, effects of light, etc. First principle calculations of the electronic structure of even the simplest deep-level defects in silicon still present a profound challenge to the theorist [5]. Sometimes the position of the level in the bandgap (see Ref. 5 for a discussion of the concept "level") can be determined by probing with monochromatic light which affects the charge or spin state of the defect. In this connection, the position of electrically active levels in silicon have been measured by deep-level-transient-spectroscopy (DLTS) and correlated with specific defects observed with EPR [6]. Correlations between electrical conductivity and specific defects in silicon have also been made [7]. Thus, EPR is one of the important tools for correlating specific atomic defects with the physical properties of a material.

B. Interactions of Unpaired Electrons

The relative splittings of the localized defect level containing an unpaired electron can be described by a spin Hamiltonian of the rather general form [8]

$$\begin{aligned}
 H_{\text{spin}} = & \mu_B \vec{S} \cdot \vec{g} \cdot \vec{B} + \vec{S} \cdot \vec{D} \cdot \vec{S} + \sum_j \vec{S} \cdot \vec{A}_j \cdot \vec{I}_j \\
 & \text{(electronic Zeeman)} \quad \text{(spin-spin)} \quad \text{(hyperfine)} \\
 & - \sum_j \left(\frac{g_{n,j} \mu_N}{I_j} \right) \vec{I}_j \cdot \vec{B} + \sum_j \vec{I}_j \cdot \vec{Q}_j \cdot \vec{I}_j \\
 & \text{(nuclear Zeeman)} \quad \text{(quadrupole)}
 \end{aligned}$$

It is possible to account for many of the details (e.g., line position, relative intensity, etc.) in an observed spectrum to a very high degree of accuracy with a suitable spin Hamiltonian. The various magnetic interactions are represented by explicit terms in the spin Hamiltonian; whereas, the spatial parts of the wave functions reflecting Coulomb interactions, exchange, symmetry, etc. are buried in the $\vec{g}$, $\vec{D}$, $\vec{A}$, $\vec{Q}$, etc. coupling tensors. Much of the information used in modeling defects comes from interpreting these coupling tensors in quantum mechanical terms while the defect dynamics (migration, reorientation, electrical levels, etc.) can be probed through annealing, stress, light, electric field, ionizing irradiation, etc. Although these are intriguing but difficult tasks, there have been considerable insights gained by these approaches, and they have been extremely fruitful. Clearly, the more interactions a spectrum exhibits, the more information that becomes available. In this respect, it is possible to "load" a defect, for example, by isotopic doping, so it will reveal more.

1. $\vec{g}$ Tensor. The $\vec{g}$ tensor gives the overall symmetry of a defect. In the case of silicon, general characteristics in the anisotropy of $\vec{g}$ have been systematized by Lee and Corbett in terms of bonding characteristics of the paramagnetic electron [4]. It is yet very difficult to calculate anisotropies in $\vec{g}$ for many defects because this calculation requires information about excited states which is usually unknown; however, in some cases ratios in the anisotropy have been qualitatively predicted [9]. The numerical values for g_{kl} are usually unique to each defect--very minor perturbations (charge state, neighboring impurities, etc.) tend to affect it to a measureable extent.

2. $\vec{A}$ Tensor. The hyperfine (hf) interaction, which is the magnetic dipole-dipole interaction between the unpaired electron(s) and nuclei with nuclear spin I , is essential for purposes of positive defect identification

and modeling. The number of hf lines corresponds to $2I + 1$, and the relative intensity indicates directly the relative abundance of each isotope. This information usually allows a positive identification of the impurities in a defect. In addition, isotopic doping by equilibrium (e.g., thermal-chemical doping [10]) or non-equilibrium (e.g., ion implantation [11]) techniques can also be used to expand ones insights.

This interaction also gives a semiquantitative description of the paramagnetic one-electron molecular orbital in terms of s and p character and localization. It is usually possible to fit this together with a more general molecular orbital description of the bonding for a specific defect model based on the symmetry considerations mentioned in Sec. II A.

The spatial region over which the unpaired electron is mostly localized varies with the solid and defect. In silicon, the paramagnetic electron usually spreads out over the defect as seen through the ^{29}Si and impurity hf spectra, but for insulators, such as SiO_2 which have wider bandgaps and more ionic bonding, the resolved hf spectra barely span the defect so that ones view is more myopic. A deeper view into the surrounding lattice, which is under the tail of the wave function, can sometimes be extended by electron-nuclear-double-resonance (ENDOR). For example, in silicon ≈ 30 shells of neighboring silicon atoms can sometimes be resolved [12]; but in MgO , only the 1st, 3rd, and 5th shell of Mg atoms around the oxygen vacancy have been observed with ENDOR [13]. The 2nd and 4th shells containing oxygen were not observable.

3. $\mathbf{D}$ Tensor. The spin-spin interaction occurs for defects and impurities with $S \geq 1$. For cases in which this interaction is dominated by the magnetic dipole-dipole interaction between two spins ($S = 1$) in a defect, it is possible to deduce the spacing between the unpaired electrons. This information has been very useful in identifying the length of multiple vacancy (oxygen) centers in silicon [3] and diamond [14]. There are also defects in which $\mathbf{D}$ is dominated by other interactions (e.g., spin-orbit, exchange) which are not easily interpreted in terms of structural features in the defect.

4. $\mathbf{Q}$ Tensor. The quadrupole interaction may only occur for nuclei with $I > 1/2$ and is due to the interaction between the electric quadrupole moment of a nucleus and the electric field gradient of the crystal at the nucleus. This interaction is usually not perceptible in EPR measurements, but may need to be considered in ENDOR experiments [15].

C. Detection of Unpaired Elections

Typical energy level splittings for a simple $S = 1/2$, $I = 1/2$ spin system are illustrated in Fig. 3. The solid vertical lines indicate the levels between which magnetic dipole transitions observable by EPR are allowed. Experimentally, one places the sample in a microwave cavity where the $\vec{B}_1 \cos \omega t$ of the microwave field is the strongest and perpendicular to the applied quasi-static magnetic field $\vec{B}$. Usually, $E_1 \cos \omega t$ is the weakest in this region. It is desirable to pick sample configurations and locations as well as a cavity (cylindrical vs. rectangular) and mode which minimize ohmic losses since the sensitivity of a spectrometer is proportional to the cavity Q. Since the microwave frequency is tuned to the cavity, resonances are found by sweeping the applied magnetic field, $\vec{B}$. Resonance may occur when the microwave quantum, $\hbar \omega$, equals the energy difference between levels. Macroscopically, the spins as a whole exhibit a complex magnetic susceptibility, $\chi = \chi' - i\chi''$, at resonance which causes a detectable change in the Q of the cavity due to changes in χ'' corresponding to absorption of microwave energy and a related

change in resonant frequency of the cavity due to changes in χ' (dispersion effect). The two main spectrometer designs used for detecting resonances are the superheterodyne spectrometer, which is very sensitive at low microwave powers ($\lesssim 1 \mu\text{W}$), and the 100 kHz homodyne spectrometer, which operates with higher microwave powers ($\sim 1 \text{ mW}$). Sensitivities of EPR spectrometers are $\gtrsim 10^{10}$ spins/G [16].

ENDOR involves inducing nuclear magnetic dipole transitions (dotted lines in Fig. 3, $\Delta M = 0$, $\Delta m = 1$) by an applied rf field, $\vec{B}_{\text{rf}} \cos \omega_{\text{rf}} t$, with $\vec{B}_{\text{rf}}$ perpendicular to B . This resonance is detected indirectly with EPR by detecting (transient) changes in a partially saturated EPR resonance due to unbalances in the spin population of the energy level common to the electronic and nuclear magnetic dipole transitions [17]. The main advantage of this technique is that the resolution in hf structure is about 10^3 times greater than with EPR.

III. EPR OF NITROGEN IN SILICON

Although the group V elements P, As, Sb, and Bi are shallow, substitutional donors in silicon, N, which is also a group V, has been a curious exception. Crystal growers found it impossible to make silicon n-type by doping with N using conventional thermal-chemical procedures; instead, silicon nitride precipitates tended to form [18]. Later, experimentalists approached this difficulty using non-equilibrium techniques such as ion implantation and thermal annealing. Although they did succeed in producing an n-type layer [19], other studies showed a complexity of electrical and insulating behavior depending on N fluence and annealing history [20]--properties vastly different from those of the other group V dopants. In fact, nuclear reaction and channeling experiments were unable to detect any substitutional N; instead, the N appeared to be trapped on random sites like nitride precipitates or damage clusters [21].

Recently, we discovered a paramagnetic N center in silicon while doing EPR studies on laser-annealed, ion-implanted silicon [22]. In particular, we were looking with EPR and Rutherford backscattering (RBS) at the effects of laser annealing on the recrystallization of amorphous silicon. The silicon had been made amorphous by implantation with typically 4×10^{15} 160 keV $^{28}\text{Si}^+/\text{cm}^2$. After a pulsed ruby laser anneal ($\lambda = .6954 \mu\text{m}$) of $\approx 2 \text{ J/cm}^2$ in 20 nsec, the amorphous layer was restored to crystallinity as measured by EPR and RBS, but invariably a residual paramagnetic spectrum was observed (Fig. 4). We identified this spectrum as being due to ^{14}N , which has a nuclear spin of 1 and is 99.6% naturally abundant. Our EPR studies indicate that N is introduced during ion implantation as a result of contamination of the $^{28}\text{Si}^+$ beam with $\approx 1/2\%$ $^{14}\text{N}_2^+$ (same mass and charge). In particular, the depth distribution of the N was measured by EPR and matches the calculated depth distribution for $^{14}\text{N}_2^+$ implanted with the same energy as $^{28}\text{Si}^+$.

Our model for this N center [23] is shown in Fig. 5. The N is essentially substituting for a silicon, and the extra electron of the N gives rise to its paramagnetism. Unlike the EPR spectra of the other group V donors, which are isotropic (T_d symmetry) and show no resolved ^{29}Si hf structure, this N spectrum at low temperatures corresponds to a defect having $\langle 111 \rangle$ axial (C_{3v}) symmetry. Also, there is a strong ^{29}Si hf interaction [23] which indicates that $\approx 73\%$ of the paramagnetic orbital is localized on the Si $\langle 111 \rangle$ in Fig. 5 and only $\approx 9\%$ is localized on the N atom. These features are characteristic of deep donors. This peculiarity may arise if the donor electron is associated

with an orbitally degenerate level rather than a singlet A_1 level as observed for P, As, Sb, and Bi. Consequently, the symmetry of the N center is lowered by virtue of a Jahn-Teller distortion which is indicated in Fig. 5 by the arrows. Nitrogen in diamond exhibits similar effects [24,25]. Paramagnetic N centers have also been observed in the various polytypes of silicon carbide [26].

Under uniaxial stress it is possible to induce a preferential alignment in the N center observed in silicon. Stress-relaxation measurements indicate that the electronic reorientation of this N center follows the Arrhenius relationship $\tau = \tau_0 \exp(E/kT)$ with activation energy $E = .084 \pm .005$ eV and $\tau_0 \approx 4 \times 10^{-9}$ sec. This implies that the paramagnetic orbital and distortion are thermally activated from one $\langle 111 \rangle$ to another with a half-life of ≈ 1 sec at 50 K. If the sample is cooled under $[110]$ uniaxial stress from 50 to 7 K and then the stress removed, our EPR spectrum shows a preferential alignment of the paramagnetic orbital perpendicular to the direction of applied stress. This preference in alignment means that the paramagnetic or donor electron is in an antibonding orbital which would tend to displace the N and Si $[111]$ in Fig. 5 away from each other. We observe that $\geq 70\%$ of these N centers reorient under stress, which suggests that they are reasonably isolated in the lattice. The other $\leq 30\%$, depending upon the sample, do not realign under stress, which suggests that perhaps they are pinned by the strain field of nearby imperfections.

One of the points of practical interest is the location of this donor level in the bandgap. By exciting the sample with monochromatic light with wavelength which can vary from 0.4 to 0.9 eV, we observe that stress induced polarizations are quickly randomized at 7 K for $h\nu \geq .58$ eV. This energy is interpreted as an ionization energy and suggests that the electrical level is near the middle of the bandgap. The deepness of this donor level is in contrast to that of the other group V donors which have ionization energies of $\approx .050$ eV.

Although isolated N atoms are quenched into substitutional sites by pulsed laser annealing, thermal annealing near 430°C results in the disappearance of isolated N centers and the brief appearance of another distinct ^{14}N hf spectrum with a smaller hf interaction. It appears that these isolated N centers are involved in the formation of other N impurity related complexes for $T \geq 430^\circ\text{C}$. These centers might be the precursors to those centers or complexes which give rise to shallow donor levels observed by others in electrical measurements [20].

IV. EPR OF THE INTERSTITIAL BORON IN SILICON

The EPR and DLTS studies of Troxell and Watkins on interstitial boron are of special interest because they exemplify for the first time Anderson's negative U concept and Bourgoin's ionization enhanced migration mechanism for a specific defect [15,27]. Watkins found from his EPR studies that substitutional boron is displaced into interstitial sites by 1.5 MeV electron irradiation at ≤ 20 K. Boron interstitials, like other group III impurities, are believed to be created by the replacement mechanism.

According to this model [2], Si interstitials, which are produced in the primary radiation damage event, undergo long range migration even at 4 K. Upon encountering a substitutional group III impurity, the Si interstitial replaces the impurity in the lattice ejecting the impurity into an interstitial site.

The mechanism by which the self-interstitial migrates at low temperature has not yet been determined, which is why studies on the enhanced migration of impurity interstitials in silicon under ionizing irradiation and minority carrier injection are of particular relevance to this intriguing phenomenon [28].

Only the neutral charge state of the B interstitial (B_i^0) has been observed with EPR. In order to see this spectrum, it is necessary to illuminate the sample with near-bandgap light. This result indicated that the neutral, paramagnetic state of the B interstitial is metastable. Furthermore, the failure to observe the B_i^0 spectrum ($S = 1/2$) in the absence of light in either n- or p-type silicon (in thermal equilibrium) suggested that the B interstitial ordinarily is in the diamagnetic negative or positive charge state. In fact, the loss of the B_i^0 spectrum upon warming to 50 K in high resistivity, p-type silicon was attributed to the thermal excitation of the trapped electron from the donor state at $\sim E_c - .15$ eV to the conduction band.

More recently, DLTS measurements have indicated a level at $E_c - .45$ eV which is identified as the B interstitial acceptor level [27]. Also, the donor level for the B interstitial has now been detected at $\approx E_c - 0.12$ eV by DLTS measurements [29]. In order to account for the metastable state of B_i^0 and the existence of the stable, diamagnetic B_i^+ and B_i^- for all positions of the Fermi level, the electrical levels for the B interstitial were arranged as shown in Fig. 6. Such an arrangement of electrical levels is possible if the configuration of the defect changes significantly for different charge states.

In other words, a different defect exist for each charge state, but each defect configuration involves the same B atom. Consequently, it is energetically more favorable for two-electron transitions to occur such as $B_i^- \leftrightarrow B_i^+ + 2e^-$ than for one-electron transitions such as $B_i^+ + e^- \rightarrow B_i^0$ or $B_i^- \rightarrow B_i^0 + e^-$. Such two electron transitions are the essence of Anderson's "effective negative U" concept [30] which says, in effect, that an "energy-lowering structural distortion may be sufficiently enhanced by the presence of a second electron so that the energy gain more than compensates for the electron-electron repulsive energy" [5]. This concept was originally proposed by Anderson to explain the properties of defects in chalcogenide glasses. In the case of the B interstitial, further evidence that two electrons are involved in a charge transition has been inferred directly from DLTS measurements [27].

One model which Troxell and Watkins suggested that could account for the migrational behavior of the B interstitial is illustrated in Fig. 7. They have also indicated an alternative model which is also consistent with the known experimental data (Fig. 8). In particular, their EPR results indicate that the B_i^0 is puckered off from a $\langle 111 \rangle$ into one of six equivalent distortions, and the B_i^+ has $\langle 111 \rangle$ axial symmetry. EPR stress-relaxation measurements indicate that the activation energy for jumps from one $\langle 111 \rangle$ axis to another $\langle 111 \rangle$ axis is 0.6 eV; this also corresponds to the activation energy for long range migration of the B interstitial as measured by EPR and DLTS. Troxell and Watkins propose that the B_i^- corresponds to a $\langle 001 \rangle$ B-Si interstitialcy as illustrated in Figs. 7 and 8. The important feature of these models is that migrational jumps may occur as B_i^0 decays to either B_i^- or B_i^+ . In fact, DLTS measurements indicate that the annealing rate of the boron interstitial is considerably enhanced under minority carrier injection in either n- or p-type silicon [27]. Furthermore, the quadratic dependence on injected current suggests a two step process: the capture of two electrons (holes) in p-type (n-type) material. Consequently, the enhanced

migration of the B interstitial involves the alternation between charge states which differ by two electronic charges [27].

Prior to these findings, Bourgoin and Corbett [31] had proposed that the equilibrium position in the lattice for some interstitials might depend upon their charge state and that successive changes in charge state might lead to motion of the interstitial through the lattice. The B interstitial is the first example of a specific defect which migrates by the Bourgoin mechanism.

V. EPR OF Si-SiO₂ INTERFACE STATES

Si-SiO₂ structures, which are an essential element in today's MOS technology, are produced by the thermal oxidation of silicon in either water vapor or oxygen at 800 to 1200°C. Imperfections in stoichiometry and chemical bonding at the Si-SiO₂ interface give rise to localized states [32]. The positions of these localized levels with respect to the band structure, in terms of bonding configurations, bond-angle distortions, and defects at the interface, have been the subject of various theoretical studies. Unfortunately, some of these defects can trap charge and affect the electrical performance of an MOS device. Therefore, the identification of specific defect structures and their relationship to particular processing techniques and electrical properties is of interest, but it is an exceedingly difficult task because the density of specific interface states is very small--typically $\lesssim 10^{12}/\text{cm}^2$ - eV.

Recently, Poindexter, Caplan, Deal, and Razouk (PCDR) [33,34] have applied EPR to the study of interface states in Si-SiO₂, and it appears that they have identified one of the dominant, electrically-active interface states--namely $\cdot\text{Si} \equiv \text{Si}_3$. In order to help clarify the relationship between electrical properties and defects, both EPR and capacitance-voltage (CV) measurements were made on (001) and (111) silicon wafers oxidized and annealed by a variety of device-relevant procedures.

Although PCDR observed several different spectra, the spectrum of principal interest and study has been the P_b spectrum, which was first reported by Nishi [35]. In the case of (111) Si-SiO₂ interfaces, this spectrum is characterized by a $\vec{g}$ tensor having axial symmetry about the $\langle 111 \rangle$. Ordinarily, if this center were embedded in bulk silicon, it would be randomly oriented among the four equivalent $\langle 111 \rangle$ directions, and a unique resonance would be associated with each defect orientation for various orientations of the applied magnetic field. The EPR measurements of PCDR were particularly interesting because the P_b spectrum they observed from a (111) Si-SiO₂ interface consisted of only one of the four resonances. This resonance corresponded to P_b centers with only one orientation--namely with their axis of axial symmetry perpendicular to the Si-SiO₂ interface. These measurements indicated that the P_b center was on the silicon side of the Si-SiO₂ interface and reflected crystalline order. It may be surprising to some that this interface can be as planar on an atomic scale as these measurements indicate; however, this quality is also consistent with the results of high resolution electron microscopy [36].

In the case of (001) Si-SiO₂ interfaces, PCDR observed a slightly different P_b spectrum which they labeled P_{b0} . In this case, all four resonances were observed. In addition they also observed another distinct spectrum which they labeled P_{b1} . The $\vec{g}$ tensors for these spectra are specified in Table I.

Because of extensive and detailed EPR studies on a variety of defects in silicon as well as SiO_2 , it is possible to infer overall features in the structure of the P_b center. For the P_b center, PCDR [33] indicate that the anisotropy in the g tensor is consistent with the model of a paramagnetic electron localized on a silicon atom which is bonded to only three other silicon atoms ($\cdot\text{Si} \equiv \text{Si}_3$). In the case of the (111) Si-SiO₂, the features in the P_b spectrum tell us that this $\cdot\text{Si} \equiv \text{Si}_3$ defect is on the silicon side of the Si-SiO₂ interface with the paramagnetic electron perpendicular to the (111) interfacial plane [33]. This model is illustrated in Fig. 9a.

Although a ^{29}Si hf interaction has not been detected, it should be part of the P_b spectrum; however, it may not be easily detected due to excessive broadening. This broadening is expected to arise because of the sensitivity of the contact part of the hf interaction to lattice disorder [37,38] which in this case exists at the interface.

In the case of the (001) Si-SiO₂ interface, the P_{b0} corresponds to essentially the same model--namely a $\cdot\text{Si} \equiv \text{Si}_3$, but now the paramagnetic dangling bond is canted with respect to the (001) interfacial plane. This breaks the $\langle 111 \rangle$ axial symmetry of the defect, and this may account for the slight perturbations in the g tensor of the P_{b0} center (see Table I). Furthermore, all four $\langle 111 \rangle$ broken bonds at the (001) interface are equivalent, which accounts for the observation of four resonances in the P_{b0} spectrum. In the case of the (001) Si-SiO₂ interface, PCDR also observe the P_{b1} spectrum which they speculate corresponds to a $\cdot\text{Si} \equiv \text{Si}_2\text{O}$ defect [34]. This defect appears to be a natural consequence of the structure of the advancing (001) Si-SiO₂ interface; however, it does not appear to be needed for the growth of the (111) Si-SiO₂ interface where it is not observed. These models are illustrated in Fig. 9.

Calculations of the local density of states versus energy indicate that broken bond defects, such as these, lead to distinct interface states within the silicon bandgap [39]. PCDR have, in fact, measured the density of P_b centers with EPR and the density of electrically active interface states with CV techniques for a variety of processing and cooling procedures. For the case of (001) and (111) Si-SiO₂ interfaces oxidized in dry O₂ at various temperatures and quickly cooled in O₂ (O₂FP) on either n- or p-type silicon, the density of P_b centers is approximately equal to the midgap interface density, D_{it} , as shown in Fig. 10 [34]. Additional EPR and CV measurements have indicated the sensitivity in the density of D_{it} and P_b centers to annealing and cooling in various gases (H₂, N₂, Ar), impurities, and oxide thicknesses. Also the effects of electric fields in "pulling" charge on and off the P_b center is under investigation by this group.

VI. CONCLUSIONS

The studies reviewed in this paper demonstrate the utility of EPR in probing complex problems in solid state physics. The nitrogen work is novel and illustrates how materials prepared by new and innovative methods can be investigated with EPR. In the case of the boron studies, the complex properties of the boron interstitial are now better understood in terms of Anderson's negative U concept and the Bourgoin diffusion mechanism through the combined use of EPR and DLTS. EPR is perhaps presently the only tool which can look at specific atomic defects at the Si-SiO₂ interface. The potential for other discoveries through the combined use of EPR and other experimental techniques on interfacial structures and materials appears promising.

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REFERENCES

1. C. A. Coulson and M. J. Kearsley, Proc. Roy. Soc. A241, 433 (1957).
2. G. D. Watkins, in Radiation Damage in Semiconductors, (Dunod, Paris, 1965) p. 97.
3. K. L. Brower, Radiat. Eff. 8, 213 (1971).
4. Y. H. Lee and J. W. Corbett, Phys. Rev. B 8, 2810 (1973).
5. G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 21, 5662 (1980).
6. L. C. Kimerling, in Radiation Effects in Semiconductors, 1976, edited by N. B. Urli and J. W. Corbett (Institute of Physics, London, 1977), p. 221.
7. H. J. Stein, Radiat. Eff. 9, 195 (1971).
8. B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. 18, 108 (1953).
9. G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).
10. K. L. Brower, Phys. Rev. B 9, 2607 (1974); Phys. Rev. B 17, 4130 (1978).
11. K. L. Brower, Phys. Rev. B 5, 4274 (1972).
12. E. G. Sieverts, S. H. Muller, and C. A. J. Ammerlaan, Phys. Rev. B 18, 6834 (1978).
13. L. E. Halliburton, D. L. Cowan, and L. V. Holroyd, Phys. Rev. B 12, 3408 (1975).
14. J. N. Lomer and A. M. A. Wild, Radiat. Eff. 17, 37 (1973).
15. G. D. Watkins, Phys. Rev. B 12, 5824 (1975).
16. C. P. Poole, Jr., Electron Spin Resonance (Interscience Publishers, New York, 1967).
17. L. Kevan and L. D. Kispert, Electron Spin Double Resonance Spectroscopy (John Wiley, New York, 1976).
18. W. Kaiser and C. D. Thurmond, J. Appl. Phys. 30, 427 (1959).
19. P. V. Pavlov, E. I. Zorin, D. I. Tetel'baum, and Yu S. Popov, Dokl. Akad. Nauk. SSSR 163, 1128 (1965) [Sov. Phys. Dokl. 10, 786 (1966)].

20. J. B. Mitchell, J. Shewchun, D. A. Thompson, and J. A. Davies, J. Appl. Phys. 46, 335 (1975).
21. J. B. Mitchell, P. P. Pronko, J. Shewchun, D. A. Thompson, and J. A. Davies, J. Appl. Phys. 46, 332 (1975).
22. K. L. Brower and P. S. Peercy, in Laser and Electron Beam Processing of Materials, edited by C. W. White and P. S. Peercy (Academic, New York, 1980), p. 441.
23. K. L. Brower, Phys. Rev. Lett. 44, 1627 (1980).
24. W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. 115, 1546 (1959).
25. R. P. Messmer and G. D. Watkins, Phys. Rev. Lett. 25, 656 (1970), and Phys. Rev. B 7, 2568 (1973).
26. M. F. Deigen, I. M. Zaritskii, and L. A. Shul'man, Fiz Tverd. Tela 12, 2902 (1970); [Sov. Phys. - Solid State 12, 2343 (1971)].
27. J. R. Troxell and G. D. Watkins, Phys. Rev. B, to be published.
28. J. R. Troxell, A. P. Chatterjee, G. D. Watkins, L. C. Kimerling, Phys. Rev. B 19, 5336 (1979).
29. G. D. Watkins, Lehigh University, PA; private communication.
30. P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).
31. J. C. Bourgoin and J. W. Corbett, Phys. Lett. 38A, 135 (1972).
32. B. E. Deal, J. Electrochem. Soc. 121, 198C (1974).
33. P. J. Caplan, E. H. Poindexter, B. E. Deal, R. R. Razouk, J. Appl. Phys. 50, 5847 (1979).
34. E. H. Poindexter, P. J. Caplan, B. E. Deal, and R. R. Razouk, J. Appl. Phys., to be published.
35. Y. Nishi, Jap. J. Appl. Phys. 10, 52 (1971).
36. O. L. Krivanek, D. C. Tsui, T. T. Sheng, and A. Kamgar, in The Physics of SiO₂ and Its Interfaces, edited by S. T. Pantelides (Pergamon, New York, 1978), p. 356.
37. J. G. de Wit and C. A. J. Ammerlaan, in Ion Implantation in Semiconductors, edited by I. Ruge and J. Graul (Springer, Berlin, 1971), p. 39.
38. K. L. Brower and W. Beezhold, J. Appl. Phys. 43, 3499 (1972).
39. R. B. Laughlin, J. D. Joannopoulos, and D. J. Chadi, Phys. Rev. B 21, 5733 (1980).

FIGURE CAPTIONS

Figure 1. (a) Model of the four-vacancy for the Si-P3 center (Ref. 3). The distance between end silicon atoms from which broken bonds a and b dangle is $\approx 9.6 \text{ \AA}$. (b) Model of the five-vacancy for the Si-P1 center according to Lee and Corbett (Ref. 4). The V's symbolize vacancies and a, b, ..., ℓ represent dangling bonds.

Figure 2. Electronic structure of the four- and five-vacancy defects (Ref. 3 and 4). The lower four levels, which are filled with electrons, correspond to bonding orbitals (valence band-like), and the upper four levels which are empty correspond to antibonding states (conduction band-like). The middle two levels, which may contain paramagnetic electron(s), are in the bandgap.

Figure 3. Splitting of a $S = 1/2$, $I = 1/2$ paramagnetic level in an applied magnetic field.

Figure 4. (a) EPR spectrum of amorphous silicon, (b) EPR spectrum of the N center in laser-annealed, ion-implanted silicon (Ref. 22).

Figure 5. Model of substitutional N in silicon with directions of possible displacements due to a Jahn-Teller $\langle 111 \rangle$ axial distortion indicated by arrows (Ref. 23).

Figure 6. Proposed electrical level structure for interstitial boron based on DTLs measurements. The inverted order implies a "negative U" system (Ref. 27).

Figure 7. Possible model for Bourgoin migration of interstitial boron in silicon: a) B_i^+ is bond-centered interstitialcy, b) B_i^0 is metastable, distorted bond-centered interstitialcy, and c) is a B-Si $\langle 001 \rangle$ split interstitialcy (Ref. 27).

Figure 8. Alternate model for Bourgoin migration with B_i^+ in a hexagonal interstitial site and B_i^- in a B-Si $\langle 001 \rangle$ split interstitialcy (dashed lines). The metastable B_i^0 is in an intermediate position (dotted circle). "T" and "H" represent tetrahedral and hexagonal interstitial sites in a $\{110\}$ plane (Ref. 27).

Figure 9. a) Schematic of (111) Si-SiO interface with P_b centers (Ref. 33). b) Schematic of (001) Si-SiO₂ interface with P_{b0} and P_{b1} defects (Ref. 34).

Figure 10. Midgap interface-state density, D_{it} , versus number of spins in (111) and (001) Si-SiO₂ interfaces with n- and p-type silicon substrate after oxide growth and quench in O₂ (O₂FP) (Ref. 34).

TABLE I. Summary of paramagnetic defects and respective $\vec{g}$ tensors; θ is the angle between g_1 and the [001] direction, and g_3 is parallel to $[\bar{1}10]$.

Center	Model	Interface	g_1	g_2	g_3	θ
P_b	$\cdot Si \equiv Si_3$	(111) Si-SiO ₂	2.0013	2.0086	2.0086	54.7°
P_{b0}	$\cdot Si \equiv Si_3$	(001) Si-SiO ₂	2.0014	2.0080	2.0087	62°
P_{b1}	$\cdot Si \equiv Si_2O$	(001) Si-SiO ₂	2.0012	2.0076	2.0052	32°

Fig. 3

Fig 5

Fig. 6.

Fig. 7

Fig. 8

○ oxygen
● silicon

(a) $\{111\}$ Si-SiO₂ interface

(b) $\{001\}$ Si-SiO₂ interface

732.

Fig. 9