Defect Symmetry from Stress Transient Spectroscopy

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Uniaxial stress has been used with transient spectroscopy to study the level at $E_c - 0.17$ eV in neutron-irradiated silicon. The defect symmetry, observed stress-induced electronic redistribution, and preferential stress-induced defect orientation have been determined and the reorientation activation energy has been measured. All of these effects are consistent with the A center.

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Deep-level transient spectroscopy (DLTS)[1] has become extremely useful in determining the thermal emission properties of deep levels in semiconductors. This technique offers excellent defect sensitivity,[2] can detect all charge states of a defect, and is applicable to most semiconductors, conditions which do not always apply to electron-paramagnetic resonance (EPR). Unfortunately, these advantages are offset by a lack of microscopic information concerning the origins of the deep levels observed with DLTS. We have been able to overcome this limitation by the application of uniaxial stress to the diodes during a standard DLTS measurement. We have chosen, as a test of this new technique, to study an energy level in neutron-irradiated silicon located at $E_c - 0.17$ eV. This level anneals between 350 and 400 °C. Good correlative experimental evidence exists suggesting that this level is associated with the vacancy-oxygen A center (Si-B1).[3,4] Furthermore, this center is extremely difficult to observe with EPR in neutron-irradiated silicon because of interference from other centers.[5]

Samples were x ray oriented so that a uniaxial stress could be applied along the long dimension (6.0 mm) which was parallel to either the [001], [110], or [111] directions. Sample dimensions perpendicular to the stress axis were 1.5×1.5 mm^2. Gold or aluminum dots 0.8 mm in diameter were evaporated on one of the faces to form Schottky barriers. Samples were cut from two pulled silicon boules of 12 and 30 Ω cm resistivity. Both boules were n-type phosphorus doped. Samples were neutron irradiated to a fluence of 1.4 or 3.1×10^{12} neutrons/cm^2 ($E > 0.1$ MeV) in a cadmium ratio on a gold flux wire of ~10. The production of the 0.17-eV level was about 1.0 cm^{-1}. Uniaxial stresses of up to 1.1 GPa (10^9 N/m^2) were obtained with a compound level apparatus attached to a closed-cycle refrigerator. The details of this system will be described elsewhere.

The resolution in a DLTS experiment can be substantially improved by setting the measurement gates close to each other. In all the experiments to be described, we used $\beta = t_2/t_1 = 2$, where t_1 and t_2 are the two measurement gate times. This yields a narrower DLTS peak at the expense of signal-to-noise ratio. The line shape is distorted by this procedure as shown for the unstressed case in Fig. 1(a); however, this is of little consequence since the line shapes are easily analyzed for any combination of gate settings.

Figure 1 shows the $E_c - 0.17$ eV level for the unstressed case (a), and for uniaxial stresses

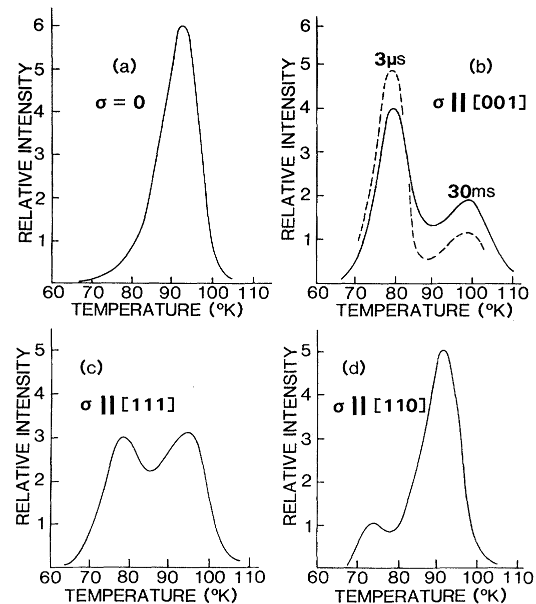

FIG. 1. DLTS spectra of the $E_c - 0.17$ eV level in neutron-irradiated Si under uniaxial stress. For all spectra, $t_1 = 4$ ms and $\beta = t_2/t_1 = 2$. Stresses for these spectra were (a) zero stress, (b) 0.48 GPa along [001], (c) 1.05 GPa along [111], and (d) 0.62 GPa along [110]. In (b) the solid line was obtained with use of a filling pulse width of 30 ms while the dotted line was for a pulse width of 3 μs.

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along [001], [111], and [110] in (b)–(d), respectively. The unstressed spectrum has been normalized to a peak intensity of 6 units. The intensities of the stressed spectra are given in the same units. This level splits into components of intensity ratios (±4%) of 4:2, 3:3, and 1:5 for stresses along [001], [111], and [110]. The first number in these ratios corresponds to the lower-temperature peak representing those components which rise in energy (move closer to the conduction band). All energy-level splittings are linear with the applied stress. It should be noted that the observed intensity ratios are incompatible with the splittings of the conduction-band minima which split into ratios of 4:2 [001], 2:4 [110], and no splitting for [111].[6] We conclude, therefore, that the splitting is an intrinsic property of the defect and that we are observing energy differences between the lower component of the conduction band and the split defect levels.

The observed intensity ratios can easily be understood in terms of the model of the A center presented by Watkins and Corbett.[3] The electron trap at $E_c - 0.17$ eV is an antibonding orbital between two nearest-neighbor silicon atoms of the vacancy site, while the other two nearest neighbors form a Si-O-Si bond (see Fig. 5 of Ref. 3). This defect has C_{2v} symmetry.

The A center is negative when this antibonding level is occupied and neutral when ionized. Therefore, the cross section should be characteristic of capture at a neutral center. We observe a capture cross section of 7×10^{-15} cm^2 which agrees with this model.[7]

The A center has six orientations in the lattice corresponding to the six possible orientations of the ⟨110⟩ axes defined by the two silicon atoms involved in the electron trap.[3] A stress in an arbitrary direction lifts this orientational degeneracy and would, in general, split the line into six components. According to the model of Watkins and Corbett, strain along the ⟨110⟩ Si-Si direction raises the energy of the trapped electron.[3] For a [001] stress, two ⟨110⟩ defect axes are perpendicular to the applied stress (lower energy, higher peak temperature) while four other ⟨110⟩ axes are at an angle of 45° (higher energy, lower peak temperature) explaining the 4:2 intensity ratio for this orientation. For a [111] stress, three axes are perpendicular while the other three make an angle of 35.3°. For a [110] stress, one axis is parallel, one perpendicular, and four at an angle of 60°. Thus, the intensity ratios versus directions of the energy-level splittings observed are consistent with Watkins and Corbett provided the peak of 5 units for the [110] stress is an unresolved doublet.

Watkins and Corbett have measured the splitting of this doublet with EPR and find an energy difference, kT_β^*, of 2.59×10^{-4} eV for a stress of 8.62×10^7 Pa.[3] The stress in Fig. 1(d) was 7.2 times larger than in their experiment. We therefore expect a splitting of 1.86 meV. This corresponds to about a 1 K difference in the peak positions which clearly would not be resolved in our experiment. Furthermore, of all the possible defect symmetries in a cubic lattice, only rhombic-I centers are consistent with the intensity ratios observed for stresses applied along [111] and [001].[8-9] For a rhombic-I center, the [110] stress is expected to produce a splitting of 1:4:1. We therefore interpret the 5-unit peak as an unresolved pair of levels with an intensity ratio of 4:1. Of all rhombic-I centers, only those of C_{2v} symmetry are possible for a defect about a T_d site. We conclude that the splittings are consistent with the symmetry of the A center.

Two other effects have been induced by stress which strongly confirm this identification. We observed that the intensity ratio increases for the [001] stress for short filling pulses (~3 μs) as shown in Fig. 1(b) by the dotted curve. Under these conditions, not all the defects are populated during the bias pulse. There is a preferential filling of those defects tending to be parallel to the stress (45°) at the expense of those which are perpendicular to the stress. This electronic redistribution is similar to the EPR experiments where the lower split energy level was preferentially populated under conditions of thermal equilibrium.[3] However, in the nonequilibrium conditions of the diode junction, we observe that the higher-energy level tends to be populated. We observed this population inversion for strains in both the [001] and [110] directions. If the traps are completely filled, no electronic redistribution can be observed. By using long filling pulses (>30 ms), we were able to eliminate this electronic effect and observe atomic preferential orientation of the defect under a [001] stress.

We applied a [001] stress of 0.417 GPa at 150 K for 5 min and then rapidly cooled the sample to below 90 K while maintaining the stress. This oriented nearly all the defects (99.5%) into those orientations at 45° with respect to the stress direction, i.e., the intensity of the smaller peak in Fig. 1(b) decreased to nearly zero. To observe this stress-induced orientation, the gate times

were increased so that $\tau_{max} = 144$ ms. This shifted the spectrum approximately 20 K lower in temperature so that the entire spectrum could be obtained below 90 K. However, at these temperatures the reorientation time for the A center is greater than 10^8 sec.[3] Therefore, the stress-oriented spectrum could be obtained at these lower temperatures without the measurement stress disturbing the orientation effects induced at higher temperatures.

Once all the defects were oriented by this procedure, the sample was annealed for 15 min without stress at successively higher temperatures in order to determine the activation energy for reorienting into the random ratio of 4:2. The sample was returned to 150 K and a stress applied to orient all the defects again after each anneal. The annealing time constant, τ, was determined for each anneal temperature from the ratio of the intensity of the smaller peak after each anneal to its random intensity of 2 units under the assumption of first-order kinetics. These time constants are plotted versus $1/T$ as the solid circles in Fig. 2. The open circles are EPR data for the A-center reorientation energy obtained by Corbett and Watkins for a [110] stress.[3] We find from our data a reorientation energy of 0.37 ± 0.05 eV

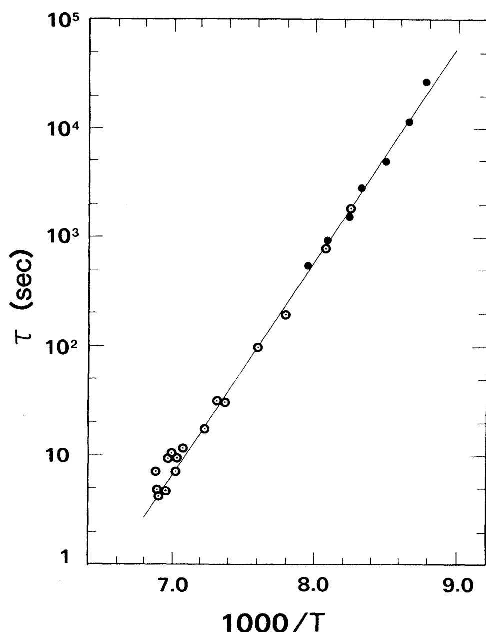

FIG. 2. The rate of A-center reorientation vs temperature. Solid circles are for [001]-stress–oriented defects (DLTS measurements) while the open circles are from Ref. 3 for [110]-stress–oriented defects (EPR measurements).

and a frequency factor of 1.6×10^{12} s^{-1} which agree within experimental error with the EPR results. It is interesting to note that this energy is the same for defects oriented under different stress directions, i.e., [001] stress in our experiments versus [110] stress in the EPR experiments.

We have made estimates of the magnitude of the splittings in Fig. 1, also in terms of the model by Corbett and Watkins.[3] They assume that these splittings can be described in terms of only the strain along the Si-Si bond axis. They find that their data are consistent with ~8.0 eV per unit strain along this axis for all three orientations of the stress. This model assumes that the energy shifts for strains at right angles to this defect axis are negligible.[8,9] We have made preliminary estimates of this energy based on the same assumptions. We observe 7 to 9 eV per unit strain in our experiments for stresses along [111] and [110] in agreement with their data; however, we measure an apparent 14 eV per unit strain for the [001] orientation. We believe this energy to be distorted in a DLTS measurement by the splitting of the conduction band which is largest for the [001] stress direction. This effect is currently under investigation.

To summarize, we have applied the uniaxial stress technique to a DLTS experiment. Although A centers are not easily seen with EPR in neutron-irradiated silicon, we can conclude from our DLTS stress measurements that this level is associated with the A center. This conclusion is based on the depth of the energy level, the annealing temperature, the capture cross section, the symmetry obtained from the uniaxial stress splitting, the magnitude of the splittings, the observed electronic redistribution effects, the stress orienting effects, and reorientation energy. To our knowledge, no previous DLTS experiments have yielded such conclusive evidence concerning the origins of a deep level.

We believe this technique to be generally applicable to a wide class of defect problems. We have observed stress splitting of most of the levels in n-type neutron-irradiated silicon. Many of these are currently under investigation. The symmetry information obtained from these experiments is essentially the same as that obtained from the EPR g tensor. Correlation with EPR is still extremely useful since we can obtain no hyperfine information and since the resolution of EPR is clearly superior. The energy levels for many EPR defects have not been discussed in detail; however, the DLTS stress technique can

clarify this situation. Furthermore, considerable microscopic information can be obtained from this technique in those materials where EPR measurements are difficult, i.e., Ge and GaAs.

Recently, Stavola and Kimerling have applied stress at 433 K to induce divacancy alignment which they subsequently observed at low temperatures with polarized excitation photocapacitance.[10] Their experiment would not work without modification on the A center since the alignment of this defect anneals below room temperature. Furthermore, the energy-level splitting and stress-induced population effects have not been observed with polarized excitation photocapacitance. It is possible, however, that a combination of their technique with ours could provide additional information in those cases where the energy-level splittings are not well resolved.

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