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[7]If $N=1$, the energy of an electron added to the lattice is $\epsilon_k - \Delta$ with $\Delta > 0$, because of the attractive interaction between two electrons involved, but the energy of an electron removed from the lattice with $N=1$ is ϵ_k since only a single electron is present. This illustrates that the difference Δ is the activation energy needed to break up the bound pair. This two-electron N-site problem was originally solved exactly by J. C. Slater, H. Statz, and G. F. Koster, Phys. Rev. 91, 1323 (1953). The present result suggests that the same attractive interaction appears between the lattice with $N \to \infty$ and an electron added.

Observation of Recombination-Enhanced Defect Reactions in Semiconductors

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Recombination-enhanced annealing of defects in semiconductors has been observed directly for the first time. The defects were produced in GaAs by 1-MeV electron irradiation and observed by transient-junction-capacitance techniques. The data clearly relate the enhanced defect annealing rate to electron-hole recombination processes at the defect.

We have observed a new mechanism for the enhancement of defect reactions in semiconductors, namely enhancement by electron-hole recombination at the defect. A direct correlation of defect reactions with electron-hole recombination processes at the defect has not previously been observed. The details of such recombination-enhanced processes are crucial to the basic understanding of both defect motion and nonradiative recombination phenomena in semiconductors.

The recombination-enhanced mechanism was observed to produce a significant increase in the annealing rate of 1-MeV-electron irradiation defects in n-GaAs under conditions of minority-carrier injection. The specific identity of these defects is at this time unknown, but it is reasonable to expect that they are isolated vacancies, interstitials, and/or simple complexes. These radiation-induced defects are observed by a new junction-capacitance technique, deep level transient spectroscopy (DLTS).[1] With this technique it is possible to measure for each defect the activation energy for thermal emission of a carrier to the nearest band edge, the concentration, and the capture rates for electrons and holes. These properties are highly specific to a particular defect and allow us to resolve five levels whose activation energies for electron emission to the conduction band are 0.08, 0.19, 0.45, 0.76, and 0.96 eV and three levels with activation energies for hole emission to the valence band of 0.32, 0.44, and 0.76 eV. A typical DLTS spectrum is shown in Fig. 1. The full details of the properties of these defects will be published elsewhere.[2] For the purpose of demonstrating recombination enhancement we will focus on the 0.45-eV electron trap shown in Fig. 1.

Junction-capacitance techniques such as DLTS are ideal for these studies since it is possible to independently vary both the average charge state and the electron-hole (e-h) recombination rate at a particular defect. The charge state can be var-

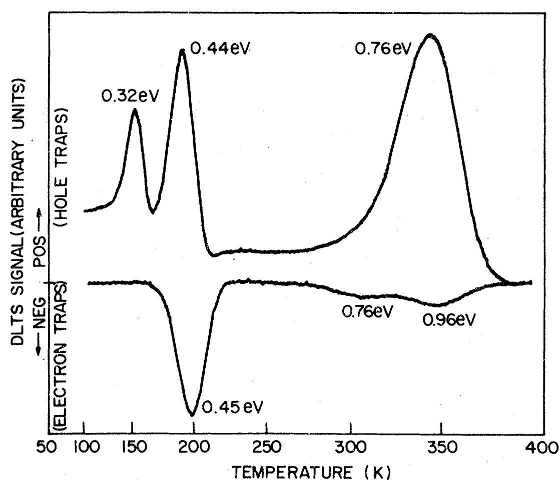

FIG. 1. A typical DLTS spectrum of 1-MeV electron irradiated n-GaAs. The energies shown are the measured activation energies for emission of a carrier to the nearest band edge. The positive signals are due to hole traps (injection pulse scan) while the negative signals are due to electron traps (majority-carrier pulse scan).

ied by placing the observed traps either in the depletion region (reverse bias) or in neutral material (zero bias). The effects of e-h recombination as well as charge-state changes are present in the annealing behavior under forward bias. It is known that a change in the charge state of a defect can have a significant influence on its annealing rate. This has been observed for the vacancy in silicon by EPR,[3,4] for the F center in alkali halides by optical spectroscopy,[5] and for the phosphorus-vacancy pair in silicon by Hall effect[6,7] and by junction-capacitance techniques.[8] Thus it is important to determine whether the enhanced annealing observed in our experiments is due to the dynamics of e-h recombination or to a change in the defect charge state.

The GaAs samples used in this study were asymmetric p^+n junctions grown by liquid-phase epitaxy. The p side of the junction in all cases was doped to 2×10^{18} cm^{-3} with Ge. In various samples the n-GaAs net donor concentration was between 4×10^{15} and 8×10^{16} cm^{-3} with the lower values in undoped samples and higher values in Sn-doped samples. Under these conditions the DLTS spectrum is sensitive to defects in only the n-type material. Our measurements showed that a radiation fluence of 1×10^{15} 1-MeV electrons/cm^2 at room temperature produced a uniform density of 7×10^{14} cm^{-3} of the 0.45-eV electron traps in undoped samples.

As mentioned above, the defect under study was observed by monitoring the electron trap level with a 0.45-eV activation energy shown in Fig. 1. This state was observed to disappear in a single thermal-annealing stage at approximately 200°C. No new states or increases in other states were observed. Measurements between 175 and 225°C give an activation energy $\Delta E_{\mathrm{th}} = 1.4 \pm 0.15$ eV for a first-order annealing process with an exponential prefactor of 10^{11} sec^{-1}.

All observations of recombination-enhanced processes were below 100°C where the thermal annealing rate was negligible both at zero bias and under reverse bias. Thus the charge state of the defect had no effect on the annealing below 100°C. This conclusion follows from the fact that at zero bias the 0.45-eV electron traps which are observed by DLTS are in neutral material below the Fermi level and thus filled with electrons, whereas under reverse bias these same traps are in the depletion region of the junction where they are empty of electrons due to the fact that their charge state here is determined by the respective carrier thermal emission rates (electron emission rate ≫ hole emission rate). The physical basis of the DLTS measurement scheme[1] is, in fact, this same phenomenon: the alternate capture of electrons by the trap at zero bias followed by thermal emission of electrons at reverse bias. Thus the traps observed by DLTS are *by definition* those which undergo charge-state changes as a result of bias changes. A significant amount of annealing was observed, however, when the diode was in forward bias at these temperatures. The dependence of the defect annealing rate on injected current density at 100°C is shown for a sample with net donor concentration of 4×10^{15} cm^{-3} in Fig. 2.[9] This type of saturation versus current behavior is also characteristic of the e-h recombination rate at the defect. The rate is initially linear with current where capture of injected minority carriers is the limiting process and constant at large values of current where majority capture is the limiting process. DLTS measurements between 216 and 272 K show that the steady-state minority carrier (hole) occupation of this level, and hence the recombination rate, saturates at roughly the same forward current density as the annealing rate in Fig. 2. Measurements of the saturated annealing rate as a function of temperature between room temperature and 100°C yield an activation energy of 0.34 ± 0.03 eV. The saturated annealing rate at a fixed temperature in different samples is proportional to the net donor concentration as shown in Fig. 3. The saturated e-h recombination rate is also proportional to the net donor concentration.

We conclude from the above that the rate of the

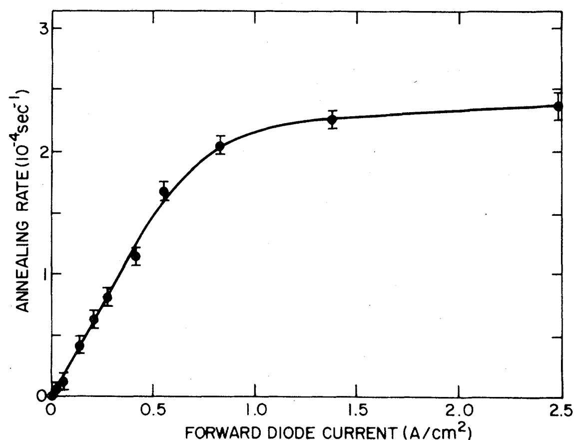

FIG. 2. Annealing rate of the 0.45-eV electron trap versus forward diode current at 100°C in a sample with a net donor concentration of 4×10^{15} cm^{-3}.

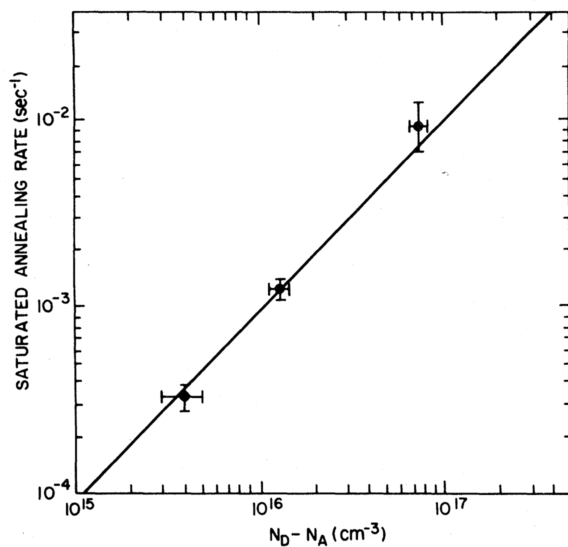

FIG. 3. Saturated annealing rate of the 0.45-eV electron trap versus net donor concentration in three sets of samples at 100°C. The solid line is a linear fit to the data.

enhanced defect annealing process is directly related to the rate of recombination at the defect. In addition, it has been determined that the enhancement under forward bias results from a recombination event at the defect and *not the accompanying change in the average defect charge state which is also described by the saturation versus current in Fig. 2.* This is because, as mentioned above, we saw no change in the signal due to heat treating at 100°C in either charge state.[10] Thus we rule out the possibility that the enhancement is due to a low-energy path characteristic of an alternate charge state.

Oscillatory changes in the charge state were also found to produce no measureable enhancement of the annealing process. By pulsing the reverse bias on and off at a high rate (1.7 MHz) in a 4×10^{15} cm^{-3} doped sample at 100°C we can produce the same total number of charge-state oscillations in 3 h as occur during 11 min of saturated e-h recombination (2×10^{10} oscillations). The bias oscillations produced essentially no change in the defect concentration (i.e., less than the noise level of 0.5%) while the recombination produced a 14% change. Thus the dynamics of e-h recombination and not simply charge-state oscillations are the important factor in enhancing the annealing rate of the defect.

Since we observe no increase in the concentrations of other defects and no new defects during the course of the annealing experiments we conclude that the decrease in the concentration of the 0.45-eV electron trap most probably corresponds to the annihilation of the corresponding lattice defect. Such an annihilation process could be the result of only a few reorientational jumps as in the case of a near-neighbor vacancy-interstitial pair (Frenkel defect) or an antistructure pair (Ga atom on As site and vice versa). It also could result from long-range diffusion of the defect to a suitable sink, e.g., vacancy or interstitial diffusion to a dislocation or a surface. In either case atomic jumps on the scale of a lattice constant are involved. The fact that e-h recombination at a defect can significantly enhance such jumps, which would otherwise require 1.4 eV of thermal energy, indicates strong electron-lattice coupling at the defect.

We believe that these data firmly establish the phenomenon of recombination-enhanced defect reactions in semiconductors. We have ruled out charge-state effects of the type observed for the vacancy in silicon[3,4] and proposed to explain injection annealing experiments in silicon.[11] In addition, a charge-state dependent saddle-point mechanism[12,13] has been eliminated by the null result of the oscillating bias experiments. Thus the enhancement is believed to be a unique result of a recombination event at the defect and related in no simple way to the defect charge state.

The effect may be of importance in a wide variety of systems. In particular it explains the observation that γ irradiated GaAs laser diodes regain their initial efficiency after operating at forward bias.[14] Recombination-enhanced processes of this type may also be active in the observed degradation only under forward bias of a wide variety of injection-mode devices such as GaAs tunnel diodes,[15] GaP light-emitting diodes,[16] and GaAs injection laser diodes.[15,17]

Clearly, a detailed understanding of recombination-enhanced lattice processes is very important for it will greatly increase our understanding not only of defect motion but also of possible mechanisms of nonradiative recombination as well.

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Brillouin-Scattering Evidence for a New Phase Transition in Perovskite Crystals: $PrAlO_3$

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Brillouin scattering experiments have revealed a new structural phase transition in $PrAlO_3$ at 118 K, in which strain is the sole order parameter. This fact, together with the second-order nature of the transition, suggests that it belongs to a class of structural transitions first delineated nearly ten years ago by Anderson and Blount.

The cubic perovskite family of solids is well known to be potentially unstable toward structural phase transitions driven by soft phonon modes.[1] Several such purely lattice-dynamical phase transitions have been observed, driven by both Brillouin-zone-center[1] and -zone-boundary soft modes. $PrAlO_3$, for example, undergoes a cubic-rhombohedral transition at 1320 K driven by a soft R-point phonon.[2] In this respect it is similar to $LaAlO_3$ and several other members of the perovskite family.[3] However, because of the interaction between the Pr^{3+} $4f$ electronic levels and the $PrAlO_3$ lattice phonons, two additional structural phase transitions are known to occur as the temperature is lowered: a first-order rhombohedral-orthorhombic transition at 205 K, and a second-order orthorhombic-monoclinic transition at 151 K.[2,4]

We report here a new structural phase transition, of second order, at 118.5 K, which is driven by a soft transverse acoustic phonon. Despite several previous careful studies by a wide variety of techniques (optical absorption[2,5] and fluorescence,[2] neutron[4,6] and Raman scattering,[2] x-ray,[7] ESR,[8] specific heat,[9] and refractive index[10] measurements) this transition has remained heretofore undetected. This fact, together with the extremely large (~99%) acoustic anomaly observed in our Brillouin scattering experiments, strongly suggests that strain is the sole order parameter for this transition. Since the transition is apparently second order and involves a change of crystal symmetry, we suggest that this transition belongs to a class of structural transitions first delineated nearly a decade ago by Anderson and Blount.[11] Furthermore, it lies entirely outside the framework of present theories[2,6] of $PrAlO_3$, its properties, and its phase transitions, which have otherwise proven so successful in imposing order on the multitude of magnetic, structural, and spectroscopic observations in this material.

The sequence of the previously known phase transitions in $PrAlO_3$ can conveniently be viewed in terms of changes in the direction of the axis about which the AlO_6 octahedra rotate in adjacent cubic unit cells.[2,6] Between 1320 and 210 K this axis is along $\langle 111 \rangle$. Between 210 and 151 K, it is $\langle 101 \rangle$. Below 151 K it begins to rotate, and continuously approaches $\langle 001 \rangle$ as the temperature