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Breathing-mode lattice relaxation associated with the vacancy and phosphorus-vacancy-pair (E-center) defect in silicon

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Comparison of published theoretical results on the lattice volume (breathing-mode) relaxation associated with the formation of the vacancy in silicon with the experimentally determined relaxation associated with the closely related phosphorus-vacancy-pair (or E-center) defect is used to provide a badly needed calibration on both the theoretical and experimental methods and leads to definitive conclusions about the sign (*outward*) and magnitude ($\sim 5\%$ of the Si-Si bond length) of this relaxation for the neutral charge states of both defects. The charge-state dependence of this relaxation is also discussed.

I. INTRODUCTION

The vacancy in silicon (Si) is one of the most important and fundamental defects in covalent semiconductors. Knowledge of its properties is basic to the understanding of many electronic phenomena, defect interactions, diffusion, annealing, and substitutional impurities.[1,2] A long-standing question about this vacancy has been the nature of the lattice volume relaxation (i.e., breathing-mode relaxation or distortion) associated with it in its various charge states. Do the nearest-neighbor Si atoms relax inward or outward on vacancy formation and by how much? The answer to this question is crucial to the understanding of the above-mentioned properties and phenomena as well as many others (see below).

There are apparently no experimental results dealing with this question, but there are some theoretical results. However, these results have left considerable uncertainty about both the sign and magnitude of the effect. Early calculations[3] suggested an *inward* relaxation on forming the neutral vacancy, but a more recent estimate[2] and calculations based on self-consistent Green's function methods[4,5] yield an *outward* relaxation.

While there are no experimental data on the breathing-mode relaxation associated with the Si vacancy, we have some recent results[6] deduced from high-pressure experiments on a closely related defect, namely, the phosphorus (P)-vacancy pair (or E center) in Si. This defect consists of a Si vacancy trapped next to a substitutional P impurity atom.[7] Since P and Si are neighbors in the Periodic Table and have nearly the same size, size considerations alone suggest that the introduction of P at a substitutional site in Si should not lead to any significant lattice relaxation around the P. However, the extra nuclear charge on the P probably leads to some relaxation, but we expect it to be quite small. This is confirmed by recent total-energy gradient calculations by Scheffler[8] which show negligible relaxation of the host Si neighbors for substitutional P. Thus, to a first approximation, the lattice configuration of the E center is not too unlike that of the Si vacancy. There are, however, significant differences in the electronic structure of the two defects[1,7] caused by differences in local symmetries, Jahn-Teller distortions, and the extra charge on the phosphorus, which must be kept in mind (see Sec. V below). Nevertheless, the above-mentioned similarity in the overall lattice configurations suggests that it is useful to compare the experimentally deduced breathing-mode relaxation associated with the E center and the theoretical results obtained for the vacancy. In view of the fact that there appears to be (1) no experimental results for the Si vacancy and (2) no theoretical results for the E center, and the experimental results[6] on it are indirect (but based on well-founded kinetic and thermodynamic arguments), this comparison is important because it could serve as a badly needed calibration which could provide confidence in the accuracy of both the theoretical and experimental results.

The purpose of this paper then is to perform such a comparison and to discuss the results. In Sec. II we give a brief description of the nature of lattice relaxations. The theoretical results on the Si vacancy are summarized in Sec. III, and the experimental E-center results in both the neutral and negatively charged states are summarized in Sec. IV. Some comparisons and concluding remarks are given in Sec. V.

II. LATTICE RELAXATIONS

The presence of defect centers caused by impurities, vacancies, or interstitials in covalent semiconductors can generally be expected to produce significant lattice relaxation (or distortion) whereby the host atoms surrounding the defect center assume new equilibrium positions. Additional lattice relaxation results from the change in local charge density brought about by the emission or capture of electronic charge carriers by deep electronic levels produced by such defect centers. These relaxations, of course, determine the local atomic geometry around the defect, and knowledge of their magnitude and symmetry is crucial to the understanding of many of the properties of defects and deep levels.[2,3,9] These properties include, in addition to those mentioned above, the defect's formation and migration energies, the positions and order in the gap of the electronic energy levels associated with the different charge states of the defect, and such deep-level phenomena as the Jahn-Teller effect, the persistent photoconduc-

tivity (PPC) effect, the negative-U phenomenon, and recombination-enhanced defect reactions.

We distinguish between two types of lattice relaxation: symmetry-conserving (or breathing mode) and symmetry-breaking relaxations. In the first type, the defect's near-neighbor host atoms move either inward or outward in a "breathing-mode" fashion, and it is necessary to know both the sign and magnitude of the relaxation. This type of relaxation is expected to accompany both defect formation and capture (or emission) processes. Superimposed on this breathing-mode relaxation there can be a symmetry-breaking relaxation such as the well-known Jahn-Teller effect in which a partially filled, orbitally degenerate system lowers its energy and lifts its degeneracy by distorting to lower symmetry. Information on the symmetry of these latter relaxations can be obtained from optical and resonance (especially EPR) techniques, but knowledge about breathing-mode relaxations and their magnitude (i.e., changes in bond lengths) is essentially nonexistent. Consequently, a very important aspect of the defect and deep-level relaxation problem remains unknown.

Fortunately, however, recent advances in both theoretical and experimental methods have begun to address this problem. Reported theoretical results have employed self-consistent Green's-function total-energy techniques[4,5] and cluster methods.[10,11] On the experimental side, we have recently proposed and demonstrated techniques, based on deep-level transient capacitance and deep-level transient spectroscopy (DLTS) measurements under hydrostatic pressure, for quantitatively determining breathing-mode relaxations accompanying defect annealing[6] and emission and capture processes.[12,13] These transient techniques have extremely high sensitivity and are able to detect deep-level defect concentrations as low as $\sim 10^{12}$ cm^{-3}. Hydrostatic pressure couples directly to the totally symmetric breathing-mode distortion of the lattice. Unfortunately, these techniques have not been applied to the study of the Si vacancy because of the experimental difficulties involved. This vacancy, which is produced by irradiation, is highly mobile and cannot be isolated except at low cryogenic temperatures.[1] To do the pressure experiments, it would be necessary to transfer the irradiated sample at very low temperatures into a suitable high-pressure apparatus, a task which is extremely difficult.

Extended x-ray-absorption fine-structure (EXAFS) measurements are also beginning to be applied to the problem; however, such measurements require high defect concentrations (generally $> 10^{19}$ cm^{-3}), and the results could be strongly influenced by defect-defect interactions. In two recent studies the local relaxations around the arsenic impurity in Si (Ref. 14) and sulfur impurities in GaAs (Ref. 15) were determined.

III. THE Si VACANCY

The Si vacancy exists in several charge states most of which are accompanied by Jahn-Teller distortions.[1] As a strongly coupled defect-lattice system,[1,2] the formation of the vacancy as well as electronic transitions among its various charge states undoubtedly involve significant breathing-mode relaxations. There have been several calculations and estimates of this relaxation for the neutral vacancy (V^0) and in some cases for its singly- and doubly-positive charged states (V^+ and V^{2+}). These calculations are difficult and involve considerable uncertainties. The results are summarized in Table I where the relaxations are expressed alternatively (1) in terms of the change Δr in the distance from the center of the vacancy to nearest-neighbor (NN) Si atoms and the ratio of Δr to the normal Si-Si bond length r_0(=2.35 Å), or (2) in terms of the change ΔV in the volume of a spherical shell centered at the vacancy and extending to the NN Si atoms and the ratio of ΔV to the volume V_0 of a normal Si cage of radius r_0 (V_0=54.33 Å^3). It should be emphasized that here we are dealing only with breathing-mode relaxation which is assumed to be symmetric. A positive (negative) sign for Δr or ΔV implies *outward* (*inward*) relaxation [i.e., expansion (contraction)] on vacancy formation. The opposite effect would obtain on vacancy annealing.

In an early calculation, Larkins and Stoneham[3] used the defect-molecule (cluster) method and an empirical valence-force potential. Their results suggest a softening of the lattice around the neutral vacancy and an *inward* relaxation of $\Delta V/V_0 \approx -22\%$.

By analogy with the unreconstructed Si(111) surface, where each surface atom is left with a single dangling bond pointing into the vacuum and where the surface atoms undergo a relaxation, one of whose components is motion of the surface plane towards the bulk of the crystal, Baraff, Kane, and Schluter[2] concluded that the breathing-mode relaxation around the vacancy must be *outward*. By moving outward, the NN Si atoms shorten

TABLE I. Comparison of theoretical values of the breathing-mode lattice relaxation associated with the various charge states of the Si vacancy (V) with experimental values for two charge states of the phosphorus-vacancy (P-V) pair (or E center). Δr is the relaxation in the NN Si bond length compared to the normal Si-Si bond length r_0. The relaxations are also expressed in terms of the volume change ΔV and the ratio ΔV to the volume (V_0) of a sphere through the four Si nearest neighbors around a Si atom. Positive (negative) changes indicate outward (inward) relaxation.

Defect	Δr (Å)	$\Delta r/r_0$ (%)	ΔV (Å^3/defect)	$\Delta V/V_0$ (%)	Reference
	(a) Vacancy: Theoretical results				
V^0	~ -0.17	~ -7.3	~ -12	~ -22	3
	~ 0.1	4.3	7	13	2
	0.32	13.5	22	40	4
	0.11	4.7	7.6	14.1	5
V^+	0.17	7.2	11.7	21.6	2
V^{2+}	0.23	9.8	16.0	29.4	2
	0.15	6.4	10.4	19.2	5
	(b) Phosphorus-vacancy pair: Experimental results				
(P-V)^0	0.14	6.1	10.0	18.4	6
(P-V)$^{-1}$	0.07	3.2	5.2	9.6	6

and strengthen their bonds with the next nearest neighbors. Baraff *et al.*[2] estimated a relaxation $\Delta r \simeq 0.1$ Å for the neutral vacancy, and, using this value, they deduced values of $\Delta r = 0.17$ and 0.23 Å for V^+ and V^{2+}, respectively.

Lindefelt[4] appears to be the first to have carried out a detailed self-consistent Green's function calculation to determine the sign of the relaxation around the Si vacancy. He obtained an *outward* relaxation, and, with the use of an empirical valence-force potential, he also calculated the amplitude of this relaxation. He found that the four NN Si atoms relax outward by 0.32 Å or 13.5% of the undistored bond length, with much smaller relaxation for the more distant Si shells. Lindefelt suggested that a reduction in the anisotropic charge density around the vacancy is the mechanism for this outward relaxation. Specifically, since a highly anisotropic charge density is the fingerprint of covalent bonding, the deficiency in the number of valence electrons caused by the vacancy weakens the bonds and drives the outward relaxation.

Scheffler, Vigneron, and Bachelet[5] have employed a parameter-free, self-consistent Green's function total-energy and force method to calculate the lattice relaxation around the Si vacancy. Their results yield an *outward* relaxation of NN Si atoms of $\Delta r = 0.11$ and 0.15 Å for V^0 and V^{2+}, respectively. Here the outward relaxation is again related to the deficiency in electronic charge and the breaking of the strong sp^3 bonds caused by the vacancy. Each of the four Si NN atoms then strengthens its covalent bonds with, and moves closer to, its three NN Si atoms in the second shell.

In summary, the calculated (or estimated) results in Table I allow us to reasonably conclude that the NN Si atoms relax *outward* on vacancy formation, and that this relaxation increases in magnitude as the vacancy becomes more electron deficient, i.e., on going from V^0 to V^{2+}. Qualitatively, these results can be understood in terms of weakening of the covalent bonds caused by the deficiency in the number of valence electrons. Scheffler *et al.*'s results[5] are based on the most detailed and parameter-free calculations, and may thus be the most accurate. One would then conclude that the relaxation associated with V^0 is most likely ≈ 0.1 Å, as was also deduced by Baraff *et al.*[2]

IV. THE PHOSPHORUS-VACANCY PAIR (*E* CENTER)

The phosphorus (P)-vacancy (V) pair defect is the dominant observable defect produced by high-energy electron or photon irradiation of P-doped float-zone silicon. It produces an acceptor deep level at $E_c - 0.44$ eV. Early EPR studies by Watkins and Corbett[7] showed that this defect is formed by the trapping of a mobile lattice vacancy next to a substitutional P-impurity atom. Although recent DLTS studies[16,17] have suggested that there may be more than one configuration of this defect, we shall restrict our comments to the originally established configuration, or the E center.

Barnes and Samara[6] have reported the activation volumes associated with the annealing of the E center in boths its neutral $(\text{P-}V)^0$ and negatively charged $(\text{P-}V)^-$ states. The results were deduced from isothermal measurements of the hydrostatic pressure dependence of the annealing kinetics. Briefly, the annealing rate a can be written as[6]

$$a = a_0 \exp(-\Delta G/kT) , \tag{1}$$

where ΔG is the total change in Gibbs free energy accompanying annealing and a_0 is an attempt frequency factor. Recalling the well-known thermodynamic identity $dG = VdP - SdT$, where V, P, T, and S are the volume, pressure, temperature, and entropy, we note that $(\partial \Delta G/\partial P)_T = \Delta V$, i.e., the isothermal pressure dependence of ΔG is a volume change, which is interpreted to be the total volume change accompanying annealing. With these considerations and the negligible pressure dependence of a_0, it is readily seen that to a good approximation[6]

$$\Delta V = -kT(\partial \ln a/\partial P)_T , \tag{2}$$

where $(\partial \ln a/\partial P)_T$ is the directly measured quantity. The negative sign indicates that an increase in a with pressure, as is observed for the E center,[6] corresponds to an inward relaxation.

The results are $\Delta V = -10.0$ Å^3/defect for $(\text{P-}V)^0$ and -5.2 Å^3 for $(\text{P-}V)^-$. The ΔV's represent the total volume changes associated with the annealing process which may involve activation over a barrier and some motion of the defect in addition to its annihilation. The high-pressure annealing data show that the pressure dependence of the activation energy, or ΔH (where $\Delta G = \Delta H - T\Delta S$) is very small so that the pressure dependence of the barrier height (if present) should also be small. Additionally, the motional contribution to ΔV should be small for an open lattice such as Si.[18] Thus, the above ΔV's should reflect to a large extent the intrinsic ΔV's associated with the annihilation of the defect. We note that the ΔV's are negative, i.e., there is *inward* relaxation on annealing, for both $(\text{P-}V)^0$ and $(\text{P-}V)^-$, but the magnitude is larger for $(\text{P-}V)^0$. We expect *positive* ΔV's of the same magnitude on formation of the E center, and, to avoid any possible confusion in the comparison with the theoretical results on the Si vacancy, we list the *positive formation values* in Table I.

The smaller ΔV for the negatively charged state $(\text{P-}V)^-$ is qualitatively consistent with the arguments discussed in Sec. III, namely the addition (or capture) of an electron into bonding-type orbitals strengthens the bonds around the vacancy and lessens the relaxation. The difference in the ΔV's between $(\text{P-}V)^0$ and $(\text{P-}V)^-$ is 4.8 Å^3. This difference corresponds largely to the volume relaxation associated with electron capture by the E center. The sign of the effect implies an *inward* relaxation of ~ 4.8 Å^3 on electron capture and an *outward* relaxation of the same amount on subsequent emission. We have recently confirmed both the sign and magnitude of this charge-state effect by an independent technique[12] involving measurements of the pressure dependences of the electron emission rate and capture cross section for the E center.[19]

The above ΔV's deduced from the pressure results represent the *total* breathing-mode relaxation around the de-

fect. In order to compare these ΔV's with the theoretical results on the Si vacancy in Table I, we need to know the volume relaxation associated with the NN shell of Si atoms. Fortunately, the theoretical results on the Si vacancy[4,5] show that most of the relaxation is taken up by the NN shell. Similarly, EXAFS results on the relaxation associated with substitutional As in Si show that the relaxation of the NN shell is an order of magnitude greater than that of the next shell of Si atoms.[14] Thus, the above experimentally derived ΔV's for the E center, reflect, to a first approximation, the relaxation of the NN shell of Si atoms. The Δr's in Table I are based on this approximation.

V. COMPARISON AND CONCLUDING REMARKS

The comparison of results in Table I is very gratifying in that the experimentally deduced relaxation for the E center is very close in magnitude to the recent theoretical results on the Si vacancy. Given the overall structural similarities of the two defects, this finding provides confidence in both the experimental and theoretical results. The *outward* breathing relaxation associated with the formation of both defects is definitively established as is the sign of the relaxation associated with the indicated charge states. Specifically, for the latter effect, the magnitude of the relaxation increases (decreases) as electrons are removed (added) to bonding-type orbitals. This effect can be qualitatively understood in terms of the influence of these electrons on the bonding of the NN atoms to their three Si neighbors in the second shell of Si atoms.

A note of caution should be made here. The sign of the relaxation associated with a given charge state of a defect depends on the nature of the bonding character of the orbital into which the electron goes. Thus, e.g., it would be wrong to assume that the breathing-mode relaxation in going from V^0 to V^- is about the same as that observed in going from $(\text{P-}V)^0$ to $(\text{P-}V)^-$. In the latter case the extra electron goes into a bonding-type orbital of a symmetry[7] and produces an inward relaxation. On the other hand, in forming V^- the extra electron goes into an antibonding orbital of b_1 symmetry,[1] and an outward relaxation can be expected on electron capture. Such an outward relaxation has been observed experimentally on electron capture by the oxygen-vacancy pair deep level[12] which has the same symmetry and antibonding character as the V^- level.

As for the experimental results on the E center, we estimate the absolute accuracy of the ΔV's calculated from Eq. (2) to be better than $\pm 10\%$. Taking into consideration the additional factors already discussed in Sec. III, namely, that the experimental ΔV's probably contain small contribution from a barrier, the motion of the vacancy before annihilation and the relaxation of shells outside the NN shell, we estimate that the true Δr's may be up to (30–40)% smaller than the values listed in Table I. Thus, we conclude that the magnitude of the experimentally determined relaxation for the $(\text{P-}V)^0$ E center is very nearly the same as the theoretical value of Scheffler *et al.*[5] and the estimate of Baraff *et al.*[2] for the V^0 state of the Si vacancy. The closeness of the two results speaks highly of both the advanced level of current theoretical techniques and the viability of the experimental methods used. This is especially impressive in view of the complicated nature of the calculations.[2,5]

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