DX center: Crossover of deep and shallow states in Si-doped $Al_xGa_{1-x}As$

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A new microscopic model for the origin of the DX center in Si-doped $Al_xGa_{1-x}As$ is proposed based on discrete variational $X\alpha$ cluster calculations. The calculated level structure shows that the antibonding A_1 state of Si, which lies in the conduction bands as a resonance state in the case of GaAs, shifts downwards into the energy gap upon distortion of the neighboring four As atoms in the case of $Al_xGa_{1-x}As$. The formation energy of this distorted configuration is estimated from the shift of the level of the antibonding A_1 state along with the Keating-model calculation for the lattice distortion energy. As a result, the distorted configuration is found to be stable in Si-doped $Al_xGa_{1-x}As$.

The semiconducting compound $Al_xGa_{1-x}As$ has been extensively studied in recent years because of its technological importance in high-speed and optoelectronic devices. These devices inevitably require n-type $Al_xGa_{1-x}As$ layers which can be accomplished by doping with Si,[1-3] Sn,[4,5] Te,[6-8] and Se.[5,9] In the case of rather small mole fraction of AlAs ($x<0.3$), each dopant induces a shallow level at a few meV below the bottom of the conduction band. With increasing AlAs mole fraction ($x>0.3$), however, the thermal activation energy determined from Hall-effect measurements[2-5,8-13] is found to increase drastically to more than 100 meV. Further, deep-level transient capacitance spectroscopy (DLTS) measurements show that this center (DX center) has activation energy of several tenths of eV to capture carriers which is different from the activation energy of carrier emission.[6,7,14-16] Moreover, in this range of mole fraction x, persistent photoconductivity effect is observed[6-8,10,17] after illumination of the sample, and the photoexcitation energy for this illumination has threshold of about 1 eV.

The observed increase in thermal activation energy has been discussed in terms of the effective-mass theory on the system of multivalleys.[4,10-12,18] Since the effective mass at the X valley, which is the conduction-band minimum in $Al_xGa_{1-x}As$ ($x>0.3$), is much heavier than the effective mass at the Γ point, which in turn is the conduction-band minimum in GaAs,[19] the observed increase in the thermal activation energy could be attributed to the crossover of the conduction-band minima with increasing AlAs mole fraction. The effective-mass model, however, cannot explain the persistent photoconductivity effect at all, unless another type of deep center is always assumed to exist. Persistent photoconductivity itself, along with the difference in excitation energies between carrier capture and carrier emission processes, strongly suggests the occurence of lattice distortion around the DX center. At an early stage of investigation on the DX center, Lang and his collaborators[6,7] proposed a large-lattice-relaxation model for persistent photoconductivity in compound semiconductors. They introduced the configuration-coordinate model for the DX center in Te-doped $Al_xGa_{1-x}As$, and explained both persistent photoconductivity effect and thermal activation energy. Further, they argued that microscopic origin of the configuration-coordinate model is the complex of the donor atom D and As vacancy V_{As}: the pair of a Te atom and an As vacancy at the second neighbor of the Te atom.[20] However, no reliable calculation until now shows that the pair of donor and As vacancy is formed upon increasing AlAs mole fraction, and the pair induces the deep level in the energy gap in $Al_xGa_{1-x}As$. Further, the existence of As vacancies is unlikely in recent n-type $Al_xGa_{1-x}As$ grown by molecular-beam epitaxy which operates with a rather high excess arsenic flux.

At this point, we propose a new microscopic origin of the DX center on the basis of discrete variational (DV) $X\alpha$ cluster calculations[21,22] performed for the first time in this paper. When Si is doped in GaAs, the Si atom is believed to substitute a Ga site. In this case, Si is in the field of tetrahedral symmetry. Thus, $3s$ and $3p$ orbitals of Si, along with the orbitals of neighboring atoms, construct the singlet A_1 and the triplet T_2 states, respectively. Further, the bonding A_1 and T_2 states lie in the valence bands of the host GaAs, while the antibonding A_1 and T_2 states lie in the conduction bands. The hydrogenlike shallow level is considered to be induced in this case due to net positive charge around Si. Next, when the AlAs mole fraction is increased, the band gap becomes wide and some of 12 second-neighbor Ga atoms around Si are replaced by Al atoms. The Al atom is slightly larger than the Ga atom so that the first-neighbor As atoms feel strain field. This strain field triggers the distortion of the first-neighbor As atoms around Si. Once the surrounding As atoms are dislodged from the lattice sites, the bonds between the Si atom and the As atoms are weakened. As a result of this weakening of the bond, the splitting between the bonding and antibonding A_1 or T_2 states becomes small. Therefore, the antibonding A_1 or T_2 state which is located in the conduction bands as a resonance state in GaAs could go down into the fundamental energy gap in $Al_xGa_{1-x}As$. We argue that this level is the deep

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level of the DX center.

In fact, we have calculated the electron states for the distorted configuration shown in Fig. 1 as a candidate for the origin of DX center in Si-doped $Al_xGa_{1-x}As$. Namely, each two of the four nearest-neighbor As atoms are paired due to the strain field caused from the mixture of neighboring Al and Ga atoms. The calculation is performed with the basis set of numerical atomic orbitals: from $1s$ to $4p$ orbitals for Ga and As, and from $1s$ to $3p$ orbitals for Si and Al. The Slater's exchange-correlation parameter α is fixed to be 0.7, which is well recognized as the most optimum value for variety of materials from atoms to crystal.[21,22] The matrix elements are estimated by 400 sampling points per atom, which is found to be enough to discuss the relative eigenvalues within an accuracy of 0.05 eV.[21–23] The finite-size effects of the cluster have been carefully examined, and the cluster consisting of 59 atoms is found to be suitable. Further, we include the contribution to the electrostatic potential in the cluster from 159 surrounding atoms. The 59-atom cluster calculation is performed for three cases for both GaAs and $Al_xGa_{1-x}As$: the host cluster without Si, the cluster with substitutional Si in the host, and the cluster with pairing configuration of As atoms around Si. The calculation, however, is not fully self-consistent in the sense that the self-consistent atomic charges in each cluster are obtained from the DV-$X\alpha$ calculations for another smaller cluster consisting of 29 atoms because of the capacity of the computer. Figure 2 shows the calculated level structure for the $Al_xGa_{1-x}As$ host cluster, the cluster with substitutional Si, and the cluster with distorted As atoms. Al atoms are situated at specific sites, and the ratio of the number of Al atoms to the number of Ga atoms is about 1 (effective x equals 0.5). In case of the $Al_xGa_{1-x}As$ perfect cluster [Fig. 2(a)], the energy gap is 2.3 eV in our calculation. The top of the valence band which corresponds to the highest occupied molecular orbital in the cluster calculation has E character in its symmetry. When the central Ga atom is replaced by an Si atom [Fig. 2(b)], the antibonding A_1 state related to the $3s$ orbital of Si occurs at 2.4 eV above the top of the valence band. The wave function of this A_1 state consists of the $3s$ orbital of Si and the $4p$ orbitals of first-neighbor As atoms. (60% of the amplitude of the wave function lies at the Si site and at the neighboring As sites, and there is no virtual contribution to the wave function from the orbitals at outer atoms in the cluster.) Namely, this A_1 state in the conduction band is a somewhat localized resonance state which could be affected considerably by the local perturbation. In fact, this antibonding A_1 state is found to shift downwards into the middle of the gap [Fig. 2(c)], when the neighboring four As atoms are dislodged from the lattice sites by amount of $\frac{1}{6}$ of the bond length so that each two of the four atoms are paired. In the case of GaAs, the calculated energy gap is 1.4 eV, and the antibonding A_1 state of Si near the conduction-band edge is fairly extended. (25% of the amplitude of the wave function lies at outer atoms, while 40% lies at the Si site and at the neighboring As sites.) Thus, in this case, the A_1 level does not shift significantly by the local perturbation.[24] The wave function of a resonance state is generally extended. However, in case that the system has the character of randomness as in $Al_xGa_{1-x}As$, the resonance state can be localized to some degree.

When a deep level in the gap appears, transferring an electron from a shallow level to the deep level results in gain in the electronic energy. If this gain in energy overcomes the cost of energy to distort surrounding atoms, the distorted atomic configuration becomes stable. In Fig. 2 we see that the antibonding resonance state shifts downwards with increasing magnitude of distortion Q, crosses the edge of the conduction band at Q_0, and then goes deep into the gap. Thus, when we assume linear dependence of

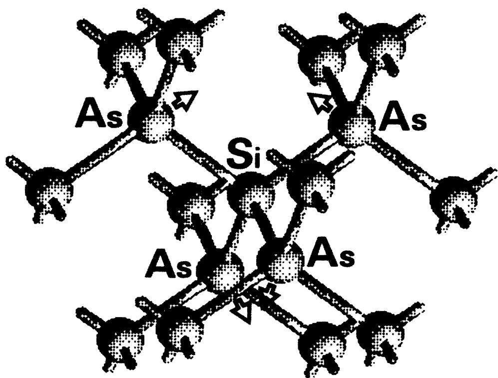

FIG. 1. Possible atomic configuration for the origin of the DX center in $Al_xGa_{1-x}As$. The second neighbor of Si is the mixture of Ga and Al atoms. Four As atoms are dislodged from the lattice sites in the direction shown by the arrows.

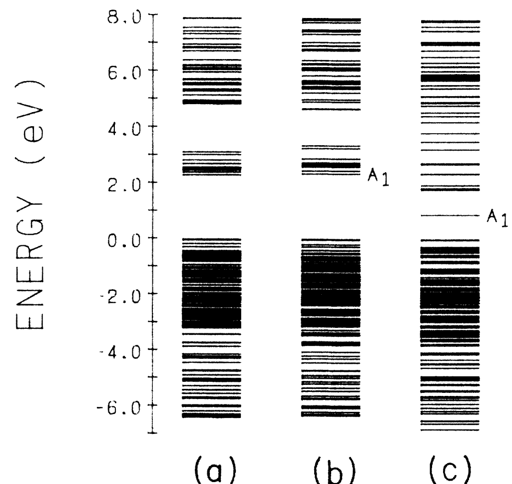

FIG. 2. Calculated level structure for three kinds of clusters: (a) $Al_xGa_{1-x}As$ perfect cluster, (b) the cluster with substitutional Si in $Al_xGa_{1-x}As$, and (c) the cluster with distorted As atoms around Si in $Al_xGa_{1-x}As$. The energies are measured from the top of the valence band (E state), and the antibonding A_1 state is denoted by A_1. The surface states whose wave functions consist exclusively of the orbitals at the boundary atoms in the clusters are eliminated in these figures.

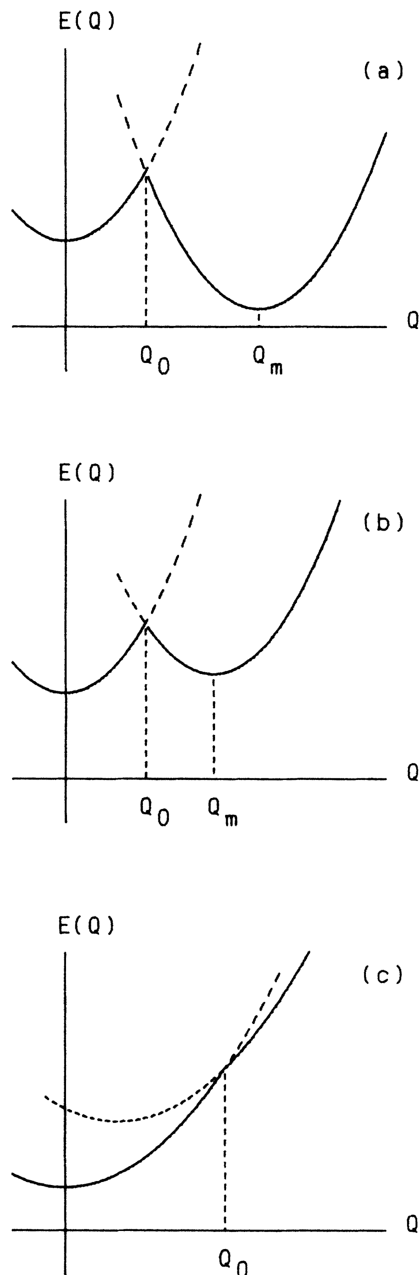

FIG. 3. Total energy $E(Q)$ for the distorted atomic configuration.

the shift of the level on the magnitude Q, the electronic energy $E_e(Q)$ gained by transferring an electron from the shallow level to this deep level is $E_e(Q)=-a(Q-Q_0)$. On the other hand, the energy cost $E_1(Q)$ to distort the lattice is $E_1(Q)=bQ^2$. Thus, the total energy $E(Q)=E_e(Q)+E_1(Q)$ to form the distorted atomic configuration around the dopant exhibits three types of curvatures shown in Fig. 3. First, when $Q_0<a/(4b)$, $E(Q)$ has the minimum at finite value of $Q=Q_m$, and there is a barrier for the transition from metastable state at $Q=0$ to the stable state at $Q=Q_m$ [Fig. 3(a)]. At the stable state, the deep level originated from the antibonding A_1 state is present in the gap. Second, when $a/(4b)<Q_0<a/(2b)$, $E(Q_m)$ becomes larger than $E(0)$ [Fig. 3(b)]. Thus, in this case the stable configuration is an undistorted one, and there is no deep level in the gap. However, the configuration of $Q=Q_m$ exists as a metastable state which may be detected experimentally. Third, when $Q_0>a/(2b)$, Q_0 becomes larger than Q_m [Fig. 3(c)]. This corresponds to the ordinary case of little lattice distortion around the dopant. In the case of Si-doped $Al_xGa_{1-x}As$, the present DV-$X\alpha$ calculation gives the values of $a=1.4$ eV/a.u. and $Q_0=0.03$ a.u. As for the lattice-distortion energy, we use the Keating model[25,26] for the cluster consisting of 169 atoms which are permitted to be relaxed to minimize the distortion energy. This gives the value of $b=7$ eV/(a.u.)^2. Therefore, the total energy $E(Q)$ has the type of curvature shown in Fig. 3(a). The thermal activation energy for an electron trapped in this center is $E(Q_m)-E(0)$ in this scheme, and is calculated to be 30 meV. From the experiments, the thermal activation energy is about 150 meV and the barrier for the capture of carriers is about 0.4 eV. Then the calculated values in the present work is rather smaller than the experimental values. However, the overall feature of the obtained curvature of $E(Q)$, i.e., minimum at $Q=Q_m$ and barrier for the transition from $Q=0$ to $Q=Q_m$, could provide qualitative explanation for both thermal activation energy and persistent photoconductivity.

The essential feature of the above microscopic model for the origin of the *DX* center is the downward shift of the level of the antibonding state due to the weakening of the bond upon lattice distortion. Thus, it is possible that another type of distortion makes the antibonding state go deep into the gap. Recently, Mizuta *et al.*[27] performed DLTS measurements on Si-doped and Sn-doped GaAs under hydrostatic pressure, and have found that the *DX* center appears when the pressure is more than 24 kbar. This can be understood by noting that the widening of the band gap due to increasing pressure causes crossover of the conduction-band minimum and the level of the antibonding state. The position of the deep level in the gap, however, is different from that of the *DX* center in $Al_xGa_{1-x}As$. This data, along with the recent Hall effect measurements on n-GaAs/n-AlAs and n-GaAs/AlAs superlattice structures,[13] suggests that the variety of observed *DX* centers is not a unique atomic configuration but a class of distorted atomic configurations.[28]

In conclusion, we propose a new microscopic model for the origin of the *DX* center in Si-doped $Al_xGa_{1-x}As$: the Si atoms surrounded by the distorted neighboring As atoms. The DV-$X\alpha$ calculation for the 59-atom clusters performed in this paper support the above model. The obtained total-energy curve has the characteristics to explain both thermal activation energy and the persistent photoconductivity effect. In order to make a definite identification for the *DX* center, however, a first-principles formation-energy calculation is required.

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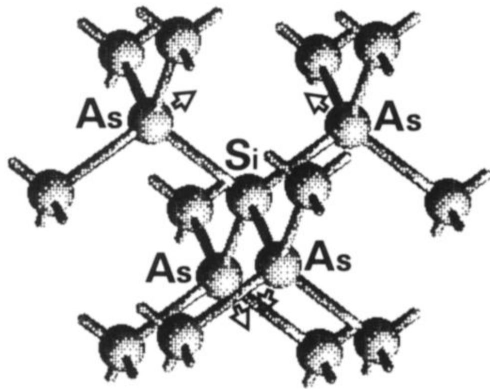

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