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# The Theory of Deep Donor State in Al<sub>x</sub>Ga<sub>1-x</sub>As

## Si-Chen Lee and J-S Jan\*

Department of Electrical Engineering National Taiwan University, Taipei, Taiwan . China \*National Tsing Hwa University, Hsinchu, Taiwan, China

A new "zero relaxation" model is proposed to explain the origin of deep donor in  $Al_sGa_{1-s}As$ . The central idea of this model comes from the fact that  $Al_sGa_{1-s}As$  is a polar crystal, the alternating positive and negative potential superimposed with the hydrogen and the central cell potential give rise to an extremely localized ground state which is associated with L band.

### INTRODUCTION

The deep donor states Si,Sn,Te and Se in Al<sub>s</sub>Ga<sub>1-s</sub>As (x>0.2) all exhibit similar characteristics  $^{1-7)}$ ;(1)low temperature persistent photoconductivity(PPC),(2)higher thermal emission barrier than activation energy,(3)large threshold  $(\sim 1eV)$  for optical transition,etc.

Two major schools of microscopic theory are currently applied to explain the origion of these deep donor states. The earlier one is the "donor-unknown center" (DX) model<sup>2)</sup> consisting of the donor and an arsenic vacancy  $(V_{As})$  with a large lattice relaxation . This model explained experiments very well, and had been widely accepted. However, there have been several recent results which are opposed to this model <sup>8-10</sup>). First, it was found that the behavior of DX centers is independent of the preparation methods, i.e., liquid phase epitaxy(LPE), metal organic chemical vapor deposition (MOCVD) or molecular beam epitaxy(MBE), it is quite unlikely that such a high concentration of  $V_{As}$  (> 10<sup>18</sup> cm<sup>-3</sup>) can be introduced in high excess of As environment during the MOCVD or MBE growth. Furthermore, the hydrostatic pressure experiment on Sn or Si doped GaAs<sup>11,12</sup>) revealed that the shallow donor which is related to the substitutional donor speces can converts to DX center after a critical pressure is applied that rules out the role of VAR.Indeed, the Mössbauer effects<sup>13,14</sup>) clearly showed that the dominant shallow impurity in Sn or Te doped GaAs is in tetrahedral symmetry which completely eliminates the possibility of a nearby vacancy. Therefore, a new microscopic model, the "single donor" (D) model is proposed<sup>9,15,16</sup>) which incorporates small lattice relaxation around the donor, and the donor level is assumed to follow L band. The newest data measured by the extended Xray absorption fine structure (EXAFS) technique<sup>17</sup>) showed that the lattice relaxation is extremely small (less than 0.04  $\lambda$ )and support the "small" relaxation model.

In this paper, we propose a new theory, i.e., "zero relaxation" model to explain (1) the origin of D center, i.e., the origin of deep and shallow levels, (2) the physical meaning of "following L band" for  $Al_sGa_{1-s}As$  with 0.2<X<0.5 and "following X band" when x > 0.5 and (3) the large threshold for optical transition.

#### ZERO RELAXATION MODEL

The central idea of this model comes from the fact that AlGaAs is a polar crystal, therefore, the Coulomb potentials generated by the net charge on Ga and As sites play very important role in determiing the energy of the localized state. For example, the (110) charge neutral plane of AlGaAs is a natural cleavage plane although the number of bonds in this plane is larger than that on(111) polar plane. Therefore, the alternating positive and negative potential superimposed with the hydrogen potential with a central cell correction may give rise to an extremely localized ground state for donor, the so-called D center.

LetH<sub>0</sub> be the Hamiltonian of the perfect host crystal

$$H_0\chi_{k,n} = E_n(k)\chi_{k,n} \tag{1}$$

$$\chi_{k,n}(\vec{r}) = u_{k,n}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \tag{2}$$

where  $E_n(k)$  is the *n*th energy band at wavevector  $\vec{k}$  and  $\chi_{k,n}$  is the corresponding Bloch eigenfunction. The electron wave function  $\Psi_{im}$  of the donor can be written in the form<sup>18</sup>).

$$\Psi_{im} = C_k(\vec{r})\chi_k(\vec{r}) \tag{3}$$

where  $C_k(\vec{r})$  is an envelope function satisfying the following Schrödinger equation<sup>18</sup>)

$$[E(K_0) - \frac{\hbar^2}{2m_t} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}) - \frac{\hbar^2}{2m_l} \frac{\partial^2}{\partial z^2} + H_c - \frac{e^2}{\epsilon r}]C_k(\vec{r}) = EC_k(\vec{r})$$
(4)

where  $K_0$  is any wave vector and  $E(K_0)$  is the band energy at  $K_0$ ,  $m_t$  and  $m_l$  are, respectively, the transverse and longitudinal effective masses associated with band at  $K_0$ .  $H_e$ is the center cell correction term, which is due to the energy difference between the impurity atom and host atom,  $e^2/\epsilon_r$ is the hydrogen potential screened by the host crystal with dielectric constant  $\epsilon$ . The use of  $\epsilon$  is valid only when the envolope function extends many lattice sites. Clearly, we have a band of energies by varying  $K_0$  in Eq. (4), i.e., the impurity band. In a lattice,  $K_0$  will run over the entire Brillouin zone, but we only consider three levels associated with the three energy band minimum ( $\Gamma$ , L and X).

## Case 1 : $K_0 = \Gamma$ point.

At  $\Gamma$  point,  $m_t = m_l$  is small which results in a large electron orbit. The overlap between the electron orbit and the localized central cell potential  $H_c$  becomes small and can be treated as a perturbation solving Eq.(4). Then Eq.(4) is reduced to a hydrogen problem which gives rise to a selfconsistent shallow impurity level (6 meV for GaAs) associated with  $\Gamma$  band.

### Case 2 : $K_0 = L$ point.

Since the magnitude of the longitudinal effective mass is large at L point, the electron orbit tends to be relatively confined. In addition, since  $Al_x Ga_{1-x}As$  is a polar crystal with Ga and Al positively and As negatively charged, the much localized electron will experience the large alternating potential and the central cell potential  $H_c$  and may form an extremely localized ground state much more than that predicated by the effective mass theory.

Case 3 :  $K_0 = X$  point.

This impurity level will follow X band, and the level will be also deep, the reason is the same as case 2.

The lowest of the above three states would be the stable state that determines the material properties. The other two will exist in the form of the metastable states. In  $Al_x Ga_{1-x}As$ when x < 0.2, the stable level is the shallow  $\Gamma$  level. But when the donor concentration is increased, the Fermi level is pushed up to approach and populate the metastable L state. This phenomenon has been observed by Theis et. al.<sup>19</sup>) using the deep-level transient spectroscopy (DLTS) technique. They found that when the donor concentration n<sub>0</sub> is larger than  $6.0 \times 10^{18}$  cm<sup>-3</sup>, the DLTS peak corresponding to the capture of electrons by metastable L state increases monotonically with n<sub>0</sub>.

When 0.2 < x < 0.5, the stable level switches to the deep L state and shallow  $\Gamma$  level becomes a metastable state as revealed by the far-infrared transmission measurement<sup>20,2)</sup> that it exists only at low temperature such that persistent photoconductivity effect appears. This strongly suggests that at low temperature, once the electrons are excited from the deep L state to the conduction band ( $\Gamma$  band) and frozen there, they form the shallow metastable state with the ionized donor. Therefore, the important consequence of this model is that the shallow and deep levels of a donor are mutually exclusive<sup>15,20,21</sup>). When x > 0.5, the stable level becomes the deep X state as being confirmed by hydrostatic pressure experiment <sup>11</sup>).

#### THERMAL TRANSITION

The most well-studied region of  $Al_{z}Ga_{1-z}As$  is at 0.2 < x < 0.5. The impurity wave function in this region has been given in Eq.(3) It is well-known that the thermal transition from deep donor state is first to L band and then thermalized to  $\Gamma$  band. The reason is discussed below:

1. To  $\Gamma$  band. The matrix element of the thermal transition rate is

$$M = \int \chi_{\Gamma}^* H_T \Psi_{im} d^3 r \tag{5}$$

where  $H_T$  is the electron-phonon interaction Hamiltonian and has the form  $H_T = De^{i\vec{q}\cdot\vec{r}}$ , where D is a deformation potential due to lattice vibration, and can be regardarded as a constant,  $\vec{q}$  is the phonon momentum. Substituting Eqs. (2), (3) and expression for  $H_T$  into Eq. (5), we obtain

$$M = \int u_{\Gamma}^*(\vec{r}) e^{-i\vec{k}_{\Gamma}\cdot\vec{r}} D e^{i\vec{q}\cdot\vec{r}} C_L(\vec{r}) u_L(\vec{r}) e^{i\vec{k}_L\cdot\vec{r}} d^3r \quad (6)$$

The localized envolope function  $C_L(\vec{r})$  can be expanded in Fourier series as

$$C_L(\vec{r}) = \sum_k C(\vec{k}) e^{i\vec{k}\cdot\vec{r}}$$
(7)

Since  $C_L(\vec{r})$  is a localized function, k spreads from the center of Brillouin zone to maybe 1/3 to 1/2 of zone boundary depending on the actual size of  $C_L(\vec{r})$ . Substituting Eq.(7) back to Eq.(6), we obtain

$$M = D \sum_{k} C(\vec{k}) \sum_{j} exp[i(-\vec{k}_{\Gamma} + \vec{q} + \vec{k} + \vec{k}_{L}) \cdot \vec{R}_{j}] \cdot$$

$$\int_{u_{\Gamma}} u_{\Gamma}^{*}(\vec{r}) u_{L}(\vec{r}) e^{i(-\vec{k}_{\Gamma} + \vec{q} + \vec{k} + \vec{k}_{L}) \cdot \vec{r}} d^{3}r \qquad (8)$$

where  $\vec{R}_j$  is the lattice translation vector, M is not zero only when  $-\vec{k}_{\Gamma} + \vec{q} + \vec{k} + \vec{k}_L = 0$ . Since  $\vec{k}_L - \vec{k}_{\Gamma} + \vec{k} = \vec{k}_L - \vec{k} + \neq 0$ , the phonon with large wave vector  $\vec{q} = -\vec{k}_L - \vec{k}$  must be involved to give nonzero transition. Then the magnitude of the transition is determined by  $\int_{\Gamma} u_{\Gamma}^*(\vec{r}) u_L(\vec{r}) d^3r$ .

Now, check the Eq.(5) to see if the transition is allowed or forbidden. An important fact must be bear in mind that at certain temperature, the conduction band electron will be described by a wave packet due to its thermal energy. The uncertainty in energy  $\Delta E$  translates to uncertainty in  $\Delta K$ and the confinement of wavefunction in real space. The  $\Delta K$ of the L and X band are large as compared to that of  $\Gamma$  band due to their larger effective mass, therefore, the wave packet of the L and X electrons will be more confined. The integral of Eq.(5) will be small because of the overlap of the two functions  $\Psi_{im}$  (local) and  $\chi_{\Gamma}$  (broaden) is small. In addition, the integral  $\int u_{\Gamma}^*(\vec{r})u_L(\vec{r})d^3r$  is extremely small as can wait cell be told from the band state wavefunction shown in Fig. 1 which are calculated using linear combination of atomic orbital (LCAO) methods<sup>22)</sup>. So the transition rate from deep donor to  $\Gamma$  band is extremely small.

2. To X band.

Using the same reasoning, this process absorbs or emits phonon. But now because the wave packet associated with X band is also confined to a small volume in the real space, so the integaral of  $\Psi_{im}$  and  $\chi_X$  is not small. But this metastable state associated with X band has the highest energy, therefore, it is unlikely that the electron is ever going to jump to this state.

## 3. To L band.

Since the lowest energy impurity state is associated with L band, the wave function overlap between them is large. So the transition is allowed. The thermal activation energy of deep donor state measured from the slope of carrier concentration versus reciprocal temperature 1000/T plotis about  $0.16\pm0.04$  eV, whereas the emission barrier of the same state exceeds 0.3 eV. This suggests that electrons transit from deep donor state directly to L band and then thermalized to  $\Gamma$  band.

## OPTICAL TRANSITION

The threshold energy for optical transition of D center ranging from 0.6 eV for Se and Te to 0.95 eV for Si<sup>2,23,24,25</sup>, seems much larger than its thermal activation energy. This is because the optical transition is a dipole transition which couples two states with opposite polarities, whereas thermal transition couples two states with the same polarity. Therefore, higher energy band states, such as X<sub>7</sub>, L<sub>6</sub> and L<sub>4,5</sub> must be involed. However, since the energy difference between the higher energy band L<sub>6</sub>, L<sub>4,5</sub> and the L band minimum is too large (about 3 eV), we propose that the higher energy band at X point (X<sub>7</sub>) is the good candidate for optical transition from deep L state. Phonons must be involved and this transition is an indirect transition like in the case of crystal Si.

### CONCLUSION

A new "zero relaxation" model is proposed to explain the origin of deep donor as well as shallow donor in  $Al_{z}Ga_{1-z}As$ . This deep donor is substitional one rather than a DX center Its existence is the fundamental physical property of the III-V compound material, and cannot be eliminated by improving material preparation techniques. The thermal transition from deep L donor state to the  $\Gamma$  band is forbbiden.



Fig. 1 Band state wavefunctions at (a)  $\Gamma$ , (b) L,

and (c) X points of AlGaAs.

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