Negative-U property of the DX center in $Al_xGa_{1-x}As$:Si

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We present two major points in this paper: (1) Statistics derived from the negative-U property of the DX center are not consistent with existing Hall experiments of Si-doped $Al_xGa_{1-x}As$. (2) The discrepancy between the negative-U model and Hall experiments can be improved if there exist two different donors SD and DX with comparable concentrations N_{SD} and N_{DX}. N_{SD}/N_{DX} increases with increasing N_{Si}. DX is a negative-U center binding two electrons and SD is a shallow donor. SD centers provide electrons and the electrons are captured by DX centers, and therefore the Fermi energy is no longer pinned to the DX energy level. Many experiments are reinterpreted in this view.

(I) Statistics derived from the negative-U property of the DX center are not consistent with existing Hall experiments.

The DX center has been one of the primary interests in the last decade for the electronic properties of III-V ternary semiconductors.[1,2] Recently, there has been significant progress since the negative-U argument of the DX center was proposed independently by Chadi and Chang,[3] and by Khachaturyan, Weber, and Kaminska.[4] The two-electron negative-U state, which is associated with a large lattice relaxation, explains a series of experiments including the absence of an ESR signal from DX centers.[4] Chadi and Chang's *ab initio* self-consistent calculations for substitutional donors in GaAs give a more quantitative description of the DX center. For a negatively charged center denoted by DX^-, a metastable resonant state with large lattice relaxation was found which is consistent with Theis, Mooney, and Wright's experiment.[5] A pressure of 18 kbar caused the DX^- center to be stable in the energy gap with large optical- and small thermal-ionization energies, a result that is consistent with recent pressure experiments.[6-8]

Although the negative-U model is very attractive in many aspects, conclusions derived from the current negative-U model are not consistent with existing Hall experiments, at least for Si in $Al_xGa_{1-x}As$. In the following, we focus our attention on the case of Si in $Al_xGa_{1-x}As$. According to the negative-U model,[3,4] Si occupying a Ga site has two possible bound electronic states: a shallow state E_d with no lattice relaxation or a very localized state E_{DX} which binds two electrons with large lattice

relaxation and negative U. Following Baraff, Kane, and Schluter,[9] the energy difference between the positively charged Si center denoted by d^+ and the negatively charged Si center occupied by two electrons and denoted by DX^- is $2E_{DX}$. We have derived from grand-canonical-ensemble theory[10] the result that the probability of Si to be the DX^- center binding two electrons is

$$f_{DX^-} = \frac{1}{1+\exp[-2(E_F - E'_{DX})/kT]} , \qquad (1)$$

when

$$E_d - E'_{DX} \gg kT . \qquad (1a)$$

Here E_F is the Fermi energy of electrons. E'_{DX} is the free energy related to E_{DX} by

$$E'_{DX} = E_{DX} - S_{DX}T , \qquad (2)$$

$$S_{DX} = (k \ln g_{DX})/2 . \qquad (2a)$$

g_{DX} is the degeneracy factor of the DX^- state. According to Chadi and Chang's model, $g_{DX} = 4$. S_{DX} is the increase of entropy averaged to one electron. In deriving Eq. (1), we have neglected the probability f_{d^0} of Si being the d^0 state (the d^0 state is one electron with energy E_d with no lattice relaxation)

$$f_{d^0} = (\exp\{-[(E'_d - E'_{DX}) + (E_F - E'_{DX})]/kT\})f_{DX^-} ,$$

which is much smaller than f_{DX^-} when Eq. (1a) holds.

We temporarily suppose that there are no acceptors, no other shallow donors, and no other source to supply elec-

trons. From the electrical neutrality condition, we have

$$f_{DX^-} = \frac{1}{2}\left(1 - \frac{n_0}{N_{Si}}\right). \qquad (3)$$

Here n_0 is the free-carrier concentration in the conduction band and N_{Si} is the doping concentration of Si. By substituting Eq. (3) into Eq. (1), we obtain

$$E_F = E'_{DX} - \frac{kT}{2}\ln\frac{1+(n_0/N_{Si})}{1-(n_0/N_{Si})}. \qquad (3a)$$

Therefore, the following inequality is always valid:

$$f_{DX^-} \leq \tfrac{1}{2} \qquad (4)$$

or

$$E_F \leq E'_{DX}. \qquad (4a)$$

When increasing doping concentration N_{Si}, n_0 increases, E_F rises and is finally pinned to E'_{DX}. From Eq. (3), E_F is pinned to E'_{DX} when $n_0 \ll N_{Si}$ and the corresponding carrier concentration n_{0p} is determined by

$$n_{0p} = \left(\frac{1}{g_{DX}}\right)^{1/2} N_c \exp[-(E_c - E_{DX})/kT]. \qquad (5)$$

Here N_c is the effective density of states at the bottom of the conduction band E_c. For the case of a direct band gap with Γ valley predominant, the preexponential factor $(1/g_{DX})^{1/2}N_c$ in Eq. (5) can be evaluated by taking $g_{DX} = 4$ and $m_\Gamma = (0.067+0.083x)m_0$.[11] Here m_0 is the free-electron mass and m_Γ is the effective mass of electrons at the Γ conduction valley. For instance, for $x \sim 0.3$, $(1/g_{DX})^{1/2}N_c \sim 3.6 \times 10^{17}$ cm^{-3} at room temperature. The large amount of temperature-dependent Hall experimental data reported by various laboratories does not satisfy Eq. (5) in the following three aspects:[12-15]

(1) For moderate doping concentration, $E_c - E_{DX}$ is independent of N_{Si} when x is fixed. Equation (5) predicts a saturated n_{0p} value independent of N_{Si}. The Hall electron concentration n_H determined by Hall experiments is always higher than n_{0p} evaluated by Eq. (5) and increases with increased N_{Si} with no saturation.

(2) For high-doping concentration, $E_c - E_{DX}$ increases with increased N_{Si}. The value of $E_c - E_{DX}$ can be determined from the temperature-dependent Hall data and n_0 can be estimated by Eq. (5). The carrier concentration determined by Hall measurement n_H is systematically higher than n_{0p}. For samples of $x \sim 0.3$, room-temperature n_H can reach as high as[13,14] 10^{18} cm^{-3}, the corresponding E_F is above the bottom of the conduction band E_c, and Eq. (4a) is no longer valid.

(3) The ratio n_H/n_{0p} varies from sample to sample, indicating a general trend to increase with increasing doping concentration but with some random exceptions.

For illustration, we show in Fig. 1 some typical experimental data of n_H vs T (Ref. 12) and compare with n_{0p} evaluated by Eq. (5). The aforementioned discrepancy between theory and experiment is evident.

The following effects have been considered to improve the theory. When the combination of the Γ, X, and L valleys' contributions to N_c is considered,[12] N_c is increased and temperature dependent. In high-doping concentration, the effective mass of electrons in the conduction band
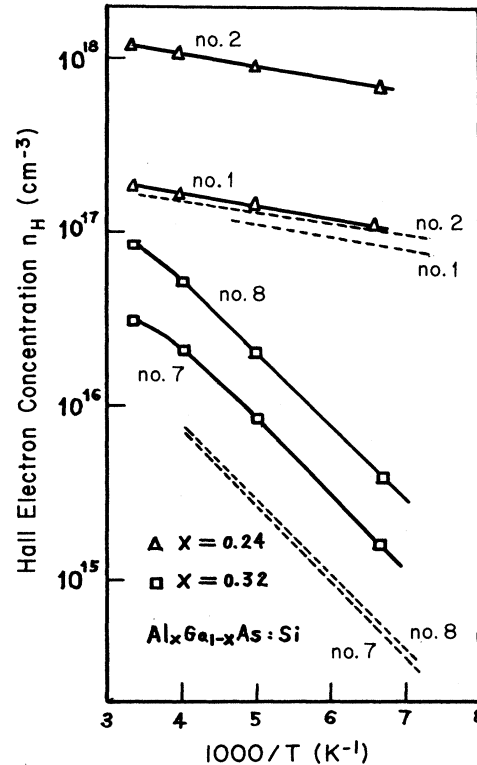

FIG. 1. Selected data of temperature-dependent Hall electron concentration n_H in Al$_x$Ga$_{1-x}$As, as quoted from Ref. 12. Samples No. 1: $x = 0.24$, $N_{Si} = 2.5 \times 10^{17}$ cm^{-3}. Sample No. 2: $x = 0.24$, $N_{Si} = 4.0 \times 10^{18}$ cm^{-3}. Sample No. 7: $x = 0.32$, $N_{Si} = 4.5 \times 10^{16}$ cm^{-3}. Sample No. 8: $x = 0.32$, $N_{Si} = 2.5 \times 10^{17}$ cm^{-3}. The dashed lines are evaluated from Eq. (5) with $g_{DX} = 4$ and $m_\Gamma = (0.067 + 0.083x)m_0$ (Ref. 11).

is slightly increased,[16] and thus N_c is increased. All these effects have been estimated to be too small to explain the experiments. The ratio of true electron concentration and Hall concentration n_T/n_H is in the range of 1-3,[12] which enlarges the discrepancy between theory and experiment. Another possible cause is the temperature dependence of $E_c - E'_{DX}$.[14] If $E_c - E_{DX}$ has a negative linear temperature coefficient, or a negative-entropy term in Eq. (2a), this will increase the preexponential factor in Eq. (5). The negative entropy means that when the defect is occupied by two electrons, the number of different microscopic states decreases. Such a picture is out of Chadi and Chang's model but is not impossible. However, this effect is independent of the doping concentration. In summary, all these considerations can at most to some extent improve the systematic discrepancy between theory and experiment but they are not able to explain all three aspects satisfactorily.

(II) The possible existence of shallow donors.

We suppose that there exist two different kinds of donors. The first kind of donor, denoted by DX with concentration N_{DX}, is the negative-U center which binds two electrons with energy level E_{DX} as suggested in Refs. 3 and 4. Here, we follow Lang, Logan, and Jaros to reserve the name of DX to the center itself[1] rather than use it ex-

clusively to refer to the broken-bond configuration as did Chadi and Chang.[3] The second kind of donor, denoted by SD with concentration N_{SD}, is a shallow donor. The following equation is satisfied:

$$N_{SD} + N_{DX} + N_A = N_{Si}. \qquad (6)$$

Here N_A is the concentration of compensating acceptors due to the amphoteric nature of Si in $Al_x Ga_{1-x} As$. The previous deep-level transient spectroscopy (DLTS) and Hall experiments have led to extensive belief in early days that

$$N_{SD} \ll N_{DX}, \qquad (7)$$

when Eq. (1a) holds. However, if DX binds two electrons, inequality (7) is not necessary and can be replaced by

$$N_{SD} - N_A < N_{DX}. \qquad (8)$$

We like to emphasize that there is no existing experiment to our knowledge which excludes the possible existence of the SD center with concentration N_{SD} comparable to N_{DX} if DX binds two electrons. Many experiments should be reexplained. For instance, the electrons supplied by SD are first activated to conduction band, then captured by DX centers. Therefore, the carrier density n_0 is much lower than the electron density trapped in DX centers, as measured by DLTS or Hall experiments. The lack of an ESR signal[4] and the increase of mobility of conduction electrons after persistent photoconductivity effect[4,12] do not exclude the existence of SD centers. As long as Eq. (8) holds, the electrons supplied by SD are trapped by DX centers and, therefore, no ESR signal can be detected from either SD or DX centers. The far-infrared experiments of Theis $et\,al.$[17] should be carefully reinterpreted. They reported that the $1s$-$2p$ transition of shallow Si donors in $Al_x Ga_{1-x} As$ was observed only after material is exposed to visible or near-visible light. The absorption showed strong correlation with $N_{Si} - N_A$, thus they concluded that the photoionized DX centers act as shallow donors. However, their conclusion was based on the assumption of Eq. (7). If Eq. (7) is not valid and N_{SD} is comparable to N_{DX}, their experiment should be carefully reexplained.

When both N_{SD} and N_A are comparable to N_{DX}, from electrical neutrality condition we have

$$f_{DX^-} = \frac{N_{DX^-}}{N_{DX}} = \frac{1}{2} \left[1 + \frac{N_{SD}}{N_{DX}} - \frac{n_0}{N_{DX}} - \frac{N_A}{N_{DX}} \right], \qquad (9)$$

$$N_{d^+} = N_{DX} - N_{DX^-}. \qquad (9a)$$

Here N_{DX^-} is the concentration of negatively charged DX centers. N_{d^+} is the concentration of the positively charged DX center. When we substitute Eq. (9) into Eq. (1), we have

$$E_F = E'_{DX} + \frac{kT}{2} \ln \frac{1 + (N_{SD}/N_{DX} - N_A/N_{DX} - n_0/N_{DX})}{1 - (N_{SD}/N_{DX} - N_A/N_{DX} - n_0/N_{DX})}. \qquad (10)$$

E_F may exceed E'_{DX} if N_{SD} is comparable to N_{DX}. The corresponding carrier concentration n_0 is

$$n_0 = \left[\frac{N_{DX} + N_{SD} - N_A - n_0}{N_{DX} - N_{SD} + N_A + n_0} \right]^{1/2} N_c \left[\frac{1}{g_{DX}} \right]^{1/2}$$
$$\times \exp[-(E_c - E_{DX})/kT]. \qquad (11)$$

When $n_0 \gg N_{DX} - N_{SD}$, Eq. (11) reduces to

$$n_0 = \left[\frac{N_{DX} + N_{SD} - N_A}{N_{DX} - N_{SD} + N_A} \right]^{1/2} N_c \left[\frac{1}{g_{DX}} \right]^{1/2}$$
$$\times \exp[-(E_c - E_{DX})/kT]. \qquad (11a)$$

Comparing Eq. (11a) with Eq. (5) clearly shows that the role of N_A is to decrease the preexponential factor of n_0. Therefore, consideration of N_A enlarges the discrepancy between theory and Hall experiments. On the contrary, if N_{SD}/N_{DX} increases with increasing N_{Si}, the existence of N_{SD} improves the consistency overall between theory and Hall experiments because the extra preexponential factor in Eqs. (11) or (11a) may be much larger than unity and increases with increasing N_{Si}.

The origin of SD is not yet clear. A possible candidate may be a complex Si_{sub}-Si_{int} pair or something else. Si_{sub}-Si_{int} is a reasonable candidate to explain the tendency of increasing N_{SD}/N_{DX} when N_{Si} is increased. Formation of silicon complexes have been reported by Maguire, Murray, and Newman for infrared measurement in GaAs.[18] An alternate possible explanation is that SD and DX are bistable states of one center and there is a very large barrier between the SD state and the DX state. The defect never overcomes the barrier at room temperature so there is no transfer from SD to DX or vice versa. Finally, it is interesting to note that Henning and Ansems[19] have recently argued from their optical experiments that the Si donor in $Al_x Ga_{1-x} As$ has double faces. One face has large lattice relaxation and the other face has small lattice relaxation. Although the starting points and the methods are very different between our work and that of Henning and Asems, the two conclusions might be related. More detailed investigations and experiments are in progress in our laboratory.

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