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Characterization of the *DX* center in the indirect $Al_xGa_{1-x}As$ alloy

M. Mizuta and K. Mori

Fundamental Research Laboratories, NEC Corporation, 4-1-1 Miyazaki, Miyamae-ku, Kawasaki, Kanagawa 213, Japan

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The behavior of the *DX* center in $Al_xGa_{1-x}As$ ($x \sim 0.6$) doped with Si and Se was investigated through photo-Hall measurements. The simultaneous existence of the shallow (metastable) and deep *DX* levels has been proven by the observation of persistent photoconductivity (PPC) whose existence was questioned previously in the indirect-gap region of this alloy. The observed PPC is much smaller in magnitude than that for $x \sim 0.3$, but this was found to be a simple consequence of the deepening of the shallow *DX* state, which is responsible for the PPC.

Appreciable interest has been paid in recent years to the origin and behavior of the *DX* center in $Al_xGa_{1-x}As$.[1-3] The structure of the *DX* center, first proposed as an As vacancy and donor complex,[2,4] is now considered to be a substitutional donor itself.[5-10] The origin of its deep nature with the associated persistent photoconductivity (PPC) phenomenon for a simple substitutional donor, however, is still open to question; an example is that the alloy dependence of the PPC magnitude reported recently[11] differs from that of the *DX*-center concentration, especially in the indirect-gap region.[2,12,13] Consequently, the existence of the PPC in the indirect-gap region has been questioned. In order to clarify the unique characteristics as well as the origin of the *DX* center, therefore, it is quite important to know the behavior of the *DX* center in the indirect region.

In this paper we will show that PPC does exist in the indirect region just as in the direct-gap region although the magnitude of the PPC is much smaller. This result can be easily explained by a deepening of the shallow (metastable) state of the *DX* center which is responsible for the PPC.

In this study Hall measurements were performed for Si- and Se-doped $Al_xGa_{1-x}As$ with an AlAs fraction (x) of ~ 0.6. Samples were 1-μm-thick epitaxial $Al_xGa_{1-x}As$ ($x = 0.59$) doped with Si (sample A) and $Al_xGa_{1-x}As$ ($x = 0.57$) doped with Se (sample B), both grown by metal-organic chemical-vapor deposition (MOCVD). Both samples have thick (~ 1 μm), undoped high-resistive $Al_xGa_{1-x}As$ layer with its Al mole fraction slightly larger ($x = 0.65-0.7$) than the doped layer in order to avoid any complex conduction behavior due to the $Al_xGa_{1-x}As$/GaAs interface. An AlAs fraction of the sample was determined by double crystal x-ray diffraction. Ohmic contact was formed by In-Sn alloying (380 °C 15 min) on the clover-leaf-patterned sample for a use in the Hall measurements. The PPC was induced by the light from a nonmonochromated tungsten-halogen lamp.

The results of the temperature dependence of electron density n are shown in Fig. 1 (sample A) and Fig. 2 (sample B). There are three *temperature ranges*, for which the behavior of the temperature dependence of n are distinctively different. The *range 1* corresponds to $1000/T = 3-9$ for the sample A (Fig. 1) and 3-10 for the sample B (Fig. 2). In this *range 1*, when the sample is cooled down in dark from room temperature (RT), n monotonically decreases (solid dots) and the change in n is reversible with increasing and/or decreasing temperature. From the slope of the Arrhenius plot, apparent activation energies are determined to be 136 meV for sample A and 71 meV for sample B. The true thermal depth of the deep *DX* (or so-called *DX*) levels has an ambiguity of a factor 2 depending on degree of acceptor compensation of the sample.[14] We believe that negligible compensation is applicable to our case since the undoped $Al_xGa_{1-x}As$ ($x = 0.6$) grown by our system exhibits quite a low acceptor density ($p = 2\times10^{15}$ cm^{-3} with mobility $\mu = 470$ $cm^2/V\,sec$). However, for clarity of presentation, we cite energy values

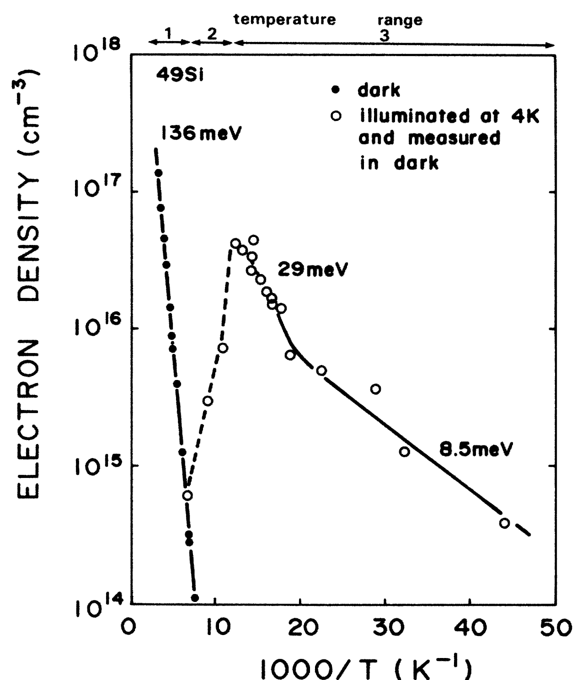

FIG. 1. The temperature dependence of the electron density n for $Al_{0.59}Ga_{0.41}As$:Si as determined by Hall measurement. Measurements were done in the dark by reducing the temperature from 300 K for filled circles and by raising the temperature after irradiating the sample at 4.2 K for open circles. Note that n depends on holding time at the measuring temperature only in *range 2*.

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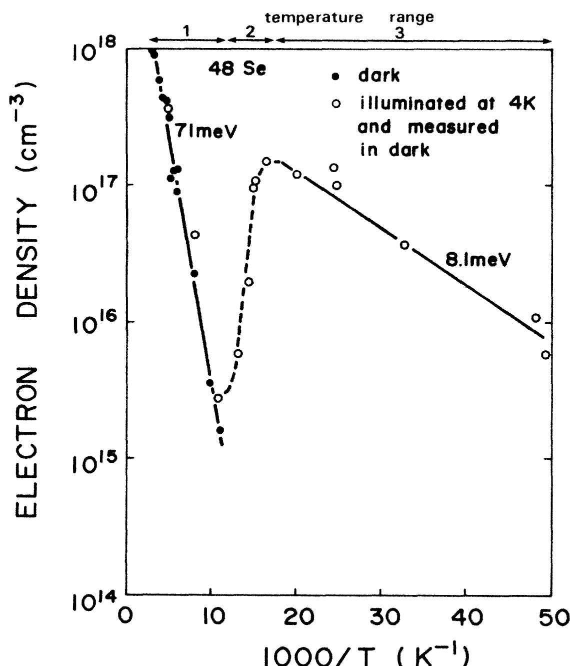

FIG. 2. The temperature dependence of the electron density n for $Al_{0.57}Ga_{0.43}As$:Se as determined by Hall measurement. The measurement conditions are the same for Fig. 1.

determined directly from the Arrhenius plot in this paper.[14]

Now the temperature dependence of n after light exposure is described in the *temperature range 2* ($1000/T = 9-13$ for sample A and 10–18 for sample B) and the *range 3* ($1000/T = 13-50$ for sample A and 18–50 for sample B). When the sample is cooled down to liquid-helium temperature (LHT), the dark conductivity of the sample is too low to measure. Even after light exposure at LHT the conductivity remains low. However, the sample is once exposed to the light at LHT, and then a measurable dark conductivity appears at elevated temperatures *ranges 2 and 3*, as seen in Figs. 1 and 2. In the *temperature range 3* the change in n is reversible on temperature up and down and also it does not decrease on time at a fixed temperature. This is a clear indication of PPC. If the sample is not illuminated by the light, however, there is no PPC effect; dark conductivity remains too low to measure in *ranges 2* and *3*. Therefore light illumination at LHT causes the transition of an electron from the donor ground state (deep *DX* state) to a certain excited state (metastable or shallow *DX* stable),[15,16] resulting in the PPC. The depth of this shallow *DX* state can be determined from the activation energies in *range 3*: 29 meV and 8.5 meV for the sample A and 8.1 meV for sample B in *range 3*. For the case of sample B we could not find an activation energy corresponding to 29 meV of sample A but the PPC phenomenon observed for the sample B is quite similar to that for sample A.

A different behavior of n was found by further increasing the temperature to *range 2*; n monotonically decreases on time. Therefore, the change in n is no more reversible upon temperature up and down (dotted lines in Figs. 1 and 2, showing only one way temperature change with an arbitrary time sequence). It is noted that this breakdown of the reversible nature begins at somewhat lower temperature for sample B than for sample A. Further increasing the temperature to the *range 1*, the measured n coincides with that measured in dark as seen in Fig. 2 (open circles in *range 1*).

Now we interpret the above results based on the capture and emission barrier configuration as depicted in Fig. 3. For the Si-doped sample A, the deep and shallow *DX* states (136 meV in *range 1* and 29 meV in *range 3*, respectively) were observed. Apparently, the value of 136 meV is the thermal depth of the deep *DX* state. On the other hand, the value of 29 meV is believed to be the thermal depth of the shallow *DX* center. As seen in Fig. 1, maximum n observed in *range 3* is only 4×10^{16} cm^{-3}, which is two-tenths of n at RT. Here, one may think that n measured in *range 3* would increase up to a value of the Si donor density in the layer: the situation often observable for the $x\sim0.3$ case. However, consider the energy-level scheme as depicted in Fig. 3(b) where the shallow *DX* state is deeper and the capture barrier for electron from the conduction-band (CB) to the deep *DX* state is smaller than the $x\sim0.3$ case, and then the thermal equilibrium between the deep *DX* and CB will be realized *before* electrons at the shallow *DX* state fully ionize into CB. This thermal equilibrium between three states (deep *DX*, shallow *DX*, and CB), results in an electron population mainly at the deep *DX* center, which corresponds to a decrease in measured n in *range 2*. The donor binding ener-

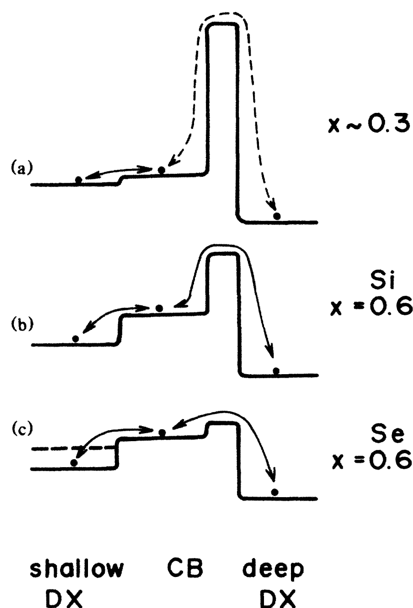

FIG. 3. Schematic diagrams showing the electron transition between the shallow *DX*, conduction band (CB) and the deep *DX* states. (a) for AlAs composition, $x\sim0.3$; (b) for Si donor at $x\sim0.6$; and (c) for Se donor at $x\sim0.6$. Note for changes in the depth between CB and the *DX* states as well as capture barrier between CB and the deep *DX* state on alloy composition (not to scale). The dotted line in (c) represents the two-electron state of the shallow *DX* state.

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gy for an effective-mass state at $x=0.6$ is estimated to be 86 meV ($m^*=0.808$, $\varepsilon=11.3$). This value should be compared to the experimental value of 58 meV ($=2\times29$ meV for negligible compensation). The difference may be due to an ambiguity of effective mass for X band. In any case, our experimental value of 58 meV is a representative of an effective-mass-like donor state. For the case of a Se-doped sample B, the lack of manifestation of an 29-meV activation energy (or corresponding value for Se) can be understood by considering a much smaller capture barrier between CB and the deep *DX* state than the Si case [Fig. 3(c)]. In this case three-states thermal equilibrium at lower temperatures than for the Si case results in an electron population at the deep *DX* center before an appreciable ionization of electrons from the shallow *DX* state to CB is taking place (see the discussion below for an 8.5-meV activation energy). For the onset of electron capture to the deep *DX* state (low-temperature side of *range 2*) the fact that the temperature is lower for Se than for Si, as noted before, supports the different capture barrier height for two cases.

Figure 4 shows quite a similar temperature dependence of the n measured for Se heavily doped $Al_xGa_{1-x}As$ $x=0.38$). The details of the sample preparation and measurement conditions will be reported elsewhere.[17] There are three *temperature ranges* quite similar to those in Figs. 1 and 2. It is noted here that the activation energy of the shallow *DX* state for this sample is only 16 meV, resulting in the maximum n measured in *range 3* being comparable to n at RT.

The magnitude of the PPC, which is typically measured at 77 K,[11,13] thus strongly depends on the depth of the shallow *DX* center and also on the capture barrier for the deep *DX* state. Therefore, the strange alloy dependence of the PPC magnitude as reported by Chand *et al.*[11] can easily be understood in this context: the depth of the shallow *DX* state being quite shallow in the direct-gap region, however, becomes deep in the indirect-gap material (see the later discussion). One thing is noted here that, for $x<0.3$ alloys, the large value of PPC (typically larger than RT electron density) and large value of n at low temperatures in the dark (an example can be found in Fig. 1 of Ref. 11) clearly indicate that the capture barrier for electrons from CB to the deep *DX* center is quite large as depicted in Fig. 3(a). This alloy dependence of the capture barrier has been determined by the deep-level transient spectroscopy (DLTS) measurements of Mooney, Calleja, Wright, and Heiblum[18] and its tendency agrees quite well with the present results.

We have to explain, here, the cause of the ~8-meV activation energy (8.5 and 8.1 meV for samples A and B, respectively) observed in *range 3.* The activation energies of n in *range 3* smoothly changes from ~8 to 29 meV for sample A. It is natural, therefore, to think that the origin of the states responsible for these two activation energies is the same, that is, ~8 meV level corresponding to an excited state of the shallow *DX* center (29 meV); one possibility is the two-electron state or D^- state of the shallow *DX* state. If this is the case, the population of electrons to

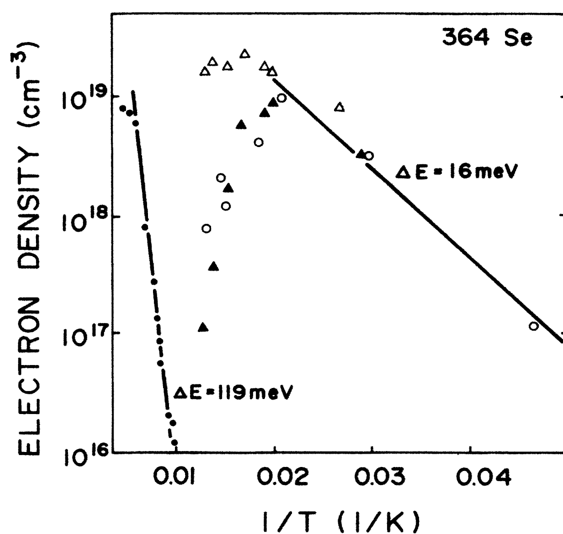

FIG. 4. The temperature dependence of electron density, n, as determined by *C-V* measurement for Au/undoped GaAs (200 A)/$Al_{0.38}Ga_{0.62}As$:Se structure (Ref. 17). Measurements were done in the dark by reducing the temperature from 300 K for filled circles and by raising the temperature after irradiating the sample by a nonmonochromated 100-W halogen lamp at 10 K for open circles. n was measured in the light at each temperature for open triangles and 10 min after the light was shut off at the same temperature for closed triangles. Note that all data in the range $0.05>1/T>0.02$ are on the same activation-energy line, clearly indicating the PPC condition.

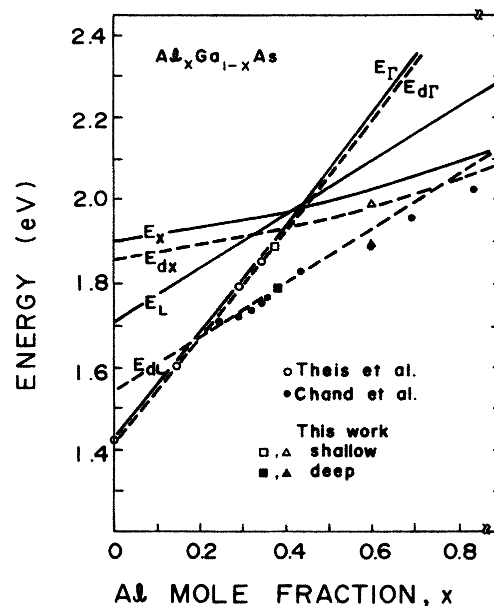

FIG. 5. Experimental data of activation energies for the shallow and deep *DX* states for sample A and for $x=0.38$ sample plotted along with the conduction-band energy as a function of alloy composition. Dotted lines indicate the donor state derived from each conduction band (see text). Reported data of thermal depth of the deep *DX* state [by Hall measurement, Chand *et al.* (Ref. 11)] and those of the shallow *DX* level [by far-infrared absorption, Theis and co-workers (Refs. 15 and 16)] are also plotted.

the D^- state depends on the intensity of the illuminating light which excites to directly produce the D^- state and/or to produce free electrons to be captured by the neutral shallow *DX* center. Since in this study we did not carefully monitor the intensity and energy of the light to induce the PPC, further discussion here is too speculative. We presently plan to investigate this problem further.

In Fig. 5 we plot the activation energies for sample A as well as the results for the $x=0.38$ sample with respect to the alloy dependence of the band structure. Also plotted are the thermal depth of the deep *DX* state reported by Chand *et al.*[11] and the $1s-2p$ optical absorption energy for the shallow *DX* states as reported by Theis *et al.*[15,16] In this figure, the donor level associated with each conduction band is plotted by the dotted line ($E_\Gamma - E_{d\Gamma} = 5$ meV, $E_L - E_{dL} = 150$ meV, $E_X - E_{dX} = 40$ meV).[19,20] As clearly seen in the figure, data for the deep and shallow *DX* states are well described by the *L*-derived and Γ-derived donor states, respectively, in the direct-gap region. It is also noted here that the shallow *DX* state in the indirect region is fairly well interpreted by the *X*-derived effective-mass state. Therefore, the alloy dependence of the PPC magnitude is clearly understood by these changes in depth of the shallow *DX* level together with the height of capture barrier to the deep *DX* state. The reported sudden drop in the PPC magnitude near $x=0.4$ probably indicates further deepening of the shallow *DX* state due to mixing of Γ-derived and *X*-derived states.

In summary, we observed the simultaneous existence of the shallow and deep *DX* states in the indirect $Al_xGa_{1-x}As$ alloy. The shallow *DX* states are well described by the Γ-derived and *X*-derived effective-mass states in the direct- and indirect-gap regions, respectively. Deepening of the shallow *DX* state in indirect-gap region was found with respect to the depth of the shallow state in the direct-gap region and this is one of the reasons for the small magnitude of an observable PPC as reported previously.

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