Band-tail states in a $Zn_{0.3}Cd_{0.7}Se$ semiconductor alloy probed by persistent photoconductivity

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The distribution of the conduction-band tail states in a $Zn_{0.3}Cd_{0.7}Se$ II-VI semiconductor alloy has been determined experimentally using persistent photoconductivity (PPC) transient measurements, and is confirmed to be exponential. Our results show that the transport properties in II-VI semiconductor alloys are strongly influenced by tail states caused by alloy disorder. A class of transport properties in disordered systems that may be probed by PPC measurements have also been proposed.

Disorder in the crystal can cause a remarkable effect, which is the localization of electronic wave functions in real space, i.e., Anderson localization, which is now recognized as one of the most important problems in condensed matter physics. However, the localization properties (including the distribution of tail states, localized-to-delocalized transition, critical indices, and mobility edges) that are central to the theory of Anderson localization are often not directly accessible experimentally. Substantial advances in our understanding of this subject have been achieved through investigation of the electric transport properties in doped semiconductors in which the localized-to-delocalized transition occurs at low temperatures with increasing impurity concentration.[1−3] Experiments dealing with doped semiconductors usually require very low temperatures, typically $T \sim 1$ K or lower, which makes them difficult. Additionally, it is rather difficult to obtain important parameters through comparison between experimental results obtained from samples with different doping levels because the distribution of tail states may vary from sample to sample. In this paper, we describe a method for investigating carrier transport properties in semiconductor alloys. The method is based on the observation, in II-VI semiconductor alloys, of the phenomenon of persistent photoconductivity (PPC), photoinduced conductivity that persists for a very long period of time after the termination of the excitation light source.[4,5] A distinct advantage of this method is that one can vary the carrier concentration continuously in a single sample through the variation of excitation photon dose.

It was suggested theoretically that alloy disorder can produce fluctuations in band edges and hence energy-band tails in II-VI semiconductor alloys.[6] Experimental techniques such as optical-absorption measurements, dispersive transport analysis, and photoluminescence studies have yielded strong evidence for exponential tails in the density of states (DOS) of doped semiconductors and amorphous materials.[7] The exponential absorption edge of GaAs was found to correlate with transitions involving band tails, which could be controlled by doping.[8] However, the tail states in semiconductor alloys, where potential fluctuations are caused by compositional fluctuations, are less understood. An $|E|^{1/2}$ dependence in the logarithm of the DOS has been suggested previously for II-VI semiconductor alloys.[6] On the other hand, theoretical calculation also indicated that the exponential tail is quite general for

three-dimensional disordered materials.[7] Experimental determination for the distribution of tail states in semiconductor alloys has been lacking. Here, we want to show that the distribution of tail states in semiconductor alloys can be probed by transport measurements utilizing the PPC buildup transient, and from these measurements we confirm experimentally that below the mobility edge, the tail states decrease exponentially. In fact, the PPC buildup transient technique has also been utilized previously for analysis of semiconductor interfaces, such as n-type GaAs thin layers.[9]

The sample used for this study was a $Zn_{0.3}Cd_{0.7}Se$ unintentionally doped semiconductor alloy. Comparison experiments have also been carried out for an $Al_{0.3}Ga_{0.7}As$ epitaxy layer of 2 μm in thickness, doped with 3.3×10^{17} cm^{-3} Si, grown on a semi-insulating GaAs(100) substrate. Experimental details can be found elsewhere.[4] Excitation light intensity for different D values is proportional to 10^{-D}. The typical excitation photon flux used for the measurements is on the order of 10^{13} photons/cm^2s corresponding to $D=0$ for $Zn_{0.3}Cd_{0.7}Se$ and 10^{14} photons/cm^2s corresponding to $D=0$ for $Al_{0.3}Ga_{0.7}As$.

Figure 1 shows the plot of PPC buildup transients obtained for $Zn_{0.3}Cd_{0.7}Se$ at $T=170$ K for three excitation intensities, $D=0.5$, 0.7, and 1.0. The striking feature is that the initial transients show a parabolic dependence on illumination time t. One cannot observe this behavior in materials exhibiting only conventional photoconductivity (PC), which has a typical transient response time on the order of 10^{-6} s and depends only on the light intensity level. Whereas the buildup level of PPC depends on the total excitation photon dose, which is the product of the excitation photon intensity and illumination time.[9] The PPC transient behavior shown in Fig. 1 is a direct consequence of the fact that the conductivity is caused by the transport of photoexcited electrons in the band tail states, as will be shown later.

A comparison experiment has been performed for $Al_{0.3}Ga_{0.7}As$, which also displays the PPC effect below 150 K. It was shown that the alloy disorder effect is much less important in III-V semiconductor alloys than in II-VI semiconductor alloys.[6] Therefore, one would not expect to observe tail states caused by alloy disorder in $Al_{0.3}Ga_{0.7}As$. In this material, deep centers called DX centers that undergo a large lattice relaxation are a well-known cause of PPC.[10] In this model, the DX centers while opti-
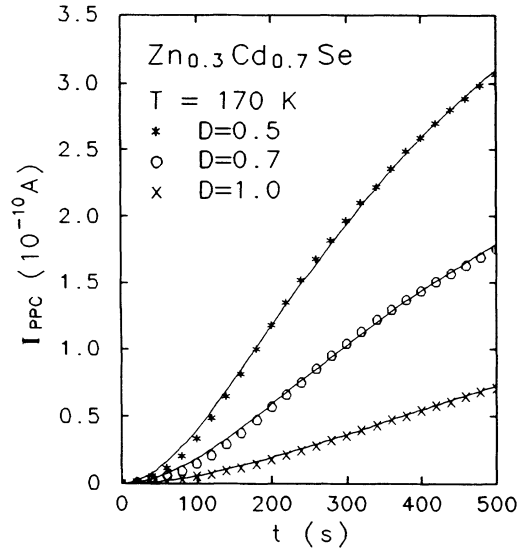
FIG. 1. The kinetics of PPC buildup for $Zn_{0.3}Cd_{0.7}Se$ at $T = 170$ K for three different excitation intensities. Light intensity for different values of D are proportional to 10^{-D}. The solid curves are fits using Eq. (9), $I(t) = I_{max}(1 - e^{-at})^2$.

FIG. 2. The kinetics of PPC buildup for $Al_{0.3}Ga_{0.7}As$ at $T = 60$ K for two different excitation light intensities. The solid curves are fits using Eq. (3), $I(t) = I_{max}(1 - e^{-at})$. Inset: The initial buildup transient from $t = 0$ to 100 s for $D = 1.9$, which exhibits a linear behavior with illumination time t.

cally ionized at low temperatures are very difficult to recapture electrons because of a capture barrier associated with the DX centers, which leads to the PPC effect; the conductivity is induced by electron transport in the conduction band. The PPC buildup kinetics can be easily formulated for $Al_{0.3}Ga_{0.7}As$. Assuming that the photogenerated electron concentration in the conduction band, n, is much smaller than the DX concentration N_{DX} during the illumination, one has[11]

$$dn/dt = g - an .$$ (1)

Here $g = N_{ph}\sigma_{DX}N_{DX}$ is the electron-density generation rate, where N_{ph} is the photon flux and σ_{DX} the photoionization cross section of the DX centers; a is the electron decay rate, which is temperature dependent. The thermal emission of electrons from the DX centers has been neglected, since the emission barrier is twice as large as the capture barrier.[12] From Eq. (1), we then have

$$n(t) = n_{max}(1 - e^{-at}) ,$$ (2)

where $n_{max} = g/a$. With the assumption of the electron mobility μ being independent of electron concentration n, we obtain

$$\sigma(t) = \sigma_{max}(1 - e^{-at}) \text{ or } I(t) = I_{max}(1 - e^{-at}) ,$$ (3)

where $\sigma_{max} = eg\mu/a$ and I_{max} represents the saturation level of PPC at a given level of photon flux. The PPC buildup transients for $Al_{0.3}Ga_{0.7}As$ have been measured at different intensity levels. The results are shown in Fig. 2 in which the solid curves are fits using Eq. (3) with fitting parameters $I_{max} = 1.8$ mA, $a = 7.0 \times 10^{-4}$ s^{-1} for $D = 1.7$ and $I_{max} = 1.5$ mA, $a = 5.1 \times 10^{-4}$ s^{-1} for $D = 1.9$. We see that the experimental results are well described by Eq. (3), which implies that the assumption of electron mobility being independent of carrier concentration is valid for
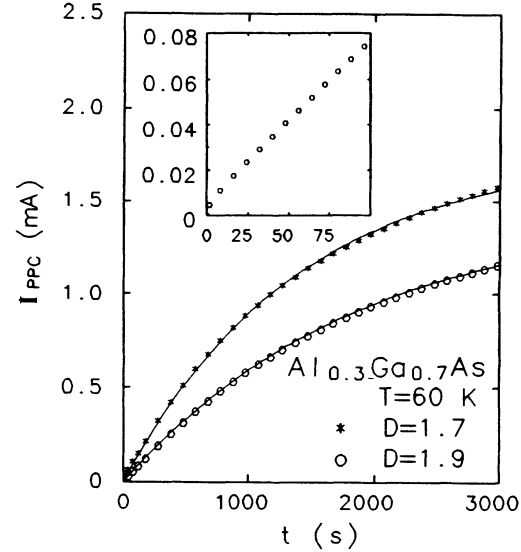
$Al_{0.3}Ga_{0.7}As$ because the fluctuations in the conduction-band edge is negligible. Buildup transients measured at different conditions always follow Eq. (3). Equation (3) also shows that the initial PPC level increases linearly with increasing t. In the inset of Fig. 2, we expand the PPC initial transient in the time regime from $t = 0$ to 100 s for $D = 1.9$, which clearly shows a linear dependence of PPC on t. The initial parabolic transient behavior exhibited by $Zn_{0.3}Cd_{0.7}Se$ has never been observed in $Al_{0.3}Ga_{0.7}As$.

Our previous experimental results suggested that PPC in $Zn_{0.3}Cd_{0.7}Se$ is generated by a band-to-band excitation.[4,5] However, the photoexcited electron concentration $n(t)$ in $Zn_{0.3}Cd_{0.7}Se$ is still described by Eq. (2) with g being replaced by $g = N_{ph}a'\eta$, where a' is the photon absorption coefficient and η is the quantum efficiency. Therefore, the PPC transient in $Zn_{0.3}Cd_{0.7}Se$ should also follow Eq. (3) if the mobility in $Zn_{0.3}Cd_{0.7}Se$ is also independent of carrier concentration n or electron quasi-Fermi level. However, experimental results shown in Fig. 1 obviously deviate from Eq. (3). This is due to the existence of potential fluctuations in II-VI semiconductor alloys, which has been indicated by the observation of exciton localization by alloy disorder.[13] It is the larger values of variation of energy gap E_g with composition x, dE_g/dx, that permits considerably greater potential fluctuations in II-VI semiconductor alloys compared to III-V semiconductor alloys.[6] Such a fluctuating potential can cause tail states in the gap and localization of charge carriers at low temperatures. As a consequence, the electron mobility in this case is no longer independent of electron concentration or energy and the conductivity of $Zn_{0.3}Cd_{0.7}Se$ is now described by[14]

$$\sigma = -\int (\partial f/\partial E)\sigma(E)dE ,$$ (4)

where $f(E)$ is the Fermi distribution function for electrons and $\sigma(E)$ is the conductivity at energy E which depends on electron concentration or illumination time. For simplicity, conductivity caused by hole transport has been neglected because of their heavier mass. In the low carrier-concentration regime where the electron quasi-Fermi level E_F is below the mobility edge E_m, the conductivity is contributed by electron hopping in localized states and the electron mean free path is determined by elastic collisions in the nonperiodic fields induced by alloy disorder. According to the Kubo-Greenwood formula, at energy E and temperature T, the electron conductivity $\sigma(E)$, is given by[14]

$$\sigma(E) = (2\pi e^2 \hbar^3/m^2)|D_E|^2_{av}[N(E)]^2 , \tag{5}$$

where m is the electron effective mass, D_E the matrix element, and $N(E)$ the DOS at energy E. The suffix av means an average over all states of the same energy E. For the case of $E_F < E_m$, most electrons occupy the deep tail states; to the first-order approximation, the Fermi distribution can be approximated by a step function. Assuming $|D_E|^2_{av}$ is independent of energy E and substituting Eq. (5) into (4), we have

$$\sigma = \sigma(E_F) = C[N(E_F)]^2 , \tag{6}$$

where $C = (2\pi e^2 \hbar^3/m^2)|D_E|^2_{av}$. Assuming that the DOS in the tail states is exponential, then

$$N(E) = (N_0/E_0)\exp(-E/E_0), \quad E < E_m , \tag{7}$$

where energy E is measured from the mobility edge E_m into the gap, E_0 is the slope of the distribution of the conduction-band tail-states, and N_0 is the total DOS below the mobility edge and $N_0 = \int N(E)dE$. Notice that $n(t)$ is still described by Eq. (2). On the other hand, photoexcited electrons are under quasi-equilibrium in the PPC mode, so we also have $n(t) = \int N(E)f(E)dE = N_0\exp(-E_F/E_0)$, $E_F < E_m$. Therefore, we obtain $N(E_F) = (N_0/E_0)\exp(-E_F/E_0) = n(t)/E_0$. From Eqs. (6) and (2), we then have

$$\sigma(t) = (C/E_0^2)n^2(t) = (Cn_0^2/E_0^2)(1 - e^{-at})^2 , \tag{8}$$

or

$$I(t) = I_{max}(1 - e^{-at})^2 . \tag{9}$$

Equation (9) has been used to fit the experimental results in Fig. 1 shown as solid curves. Fitted values of I_{max} are 0.44, 0.31, and 0.19 nA for $D=0.5$, 0.7, and 1.0, respectively; a are 3.6×10^{-3} s^{-1}, 2.9×10^{-3} s^{-1}, and 2.0×10^{-3} s^{-1} for $D=0.5$, 0.7, and 1.0, respectively. We see that Eq. (9) describes well the experimental data. Notice that Eq. (9) is derived for low electron concentration. For small t, $n(t)$ is proportional to t, Eq. (9) implies a parabolic dependence following $I(t) = I_{max}a^2t^2$, contrary to the linear dependence observed in $Al_{0.3}Ga_{0.7}As$ without tail states. Therefore, our results show that the transport properties in II-VI semiconductor alloys at low carrier concentration are governed by the exponential tail of states, and the conductivity strongly depends on carrier concentration or the quasi-Fermi level.

Equation (9) is derived with the assumption of the ex-

ponential tail of states in the conduction-band edge. In fact, any other distribution of tail states that gives the result of $N(E_F) \propto n(t)$ can also lead to Eq. (9). Many different forms of tail states in DOS have been proposed,[15] which can be written as $N(E) = KE^n\exp(-|E/E_0|^\beta)$, $\frac{1}{2} \leq \beta \leq 2$, where K is a constant. It is easy to prove that the linear dependence of $N(E_F)$ on $n(t)$ cannot be obtained except for $\beta = 1$ and $n = 0$. Thus the exponential tail of states in II-VI semiconductor alloys is confirmed. Our results obtained for $Zn_{0.3}Cd_{0.7}Se$ here together with previous results obtained for doped semiconductors and amorphous materials indicate that exponential tail of states is universally independent of the origin of the disorder, which is consistent with the theoretical argument.[7]

The conductivity is expected to be described by Eq. (9) in the low carrier-concentration regime where $E_F < E_m$, which is the condition for Fig. 1. As the quasi-Fermi level increases to above E_m, the conductivity of the system is induced by electron transport through the conduction network constructed by local potential minima[4] and the electron mobility becomes almost independent of carrier concentration as in $Al_{0.3}Ga_{0.7}As$; we expect the PPC transient to be described by Eq. (3). Combining these facts, we can write for II-VI semiconductor alloys

$$\sigma(E) \begin{cases} = C[N(E)]^2, & E < E_m, \tag{10a} \\ \geq C[N(E_m)]^2, & E \geq E_m. \tag{10b} \end{cases}$$

It should be noted that Eq. (10b) includes the following two cases: If $\sigma(E_m) > C[N(E_m)]^2$, a sharp transition in the PPC buildup transient is expected; on the other hand, if $\sigma(E_m) = C[N(E_m)]^2$, a continuous increase in conductivity will be observed. It is interesting to compare Eq.
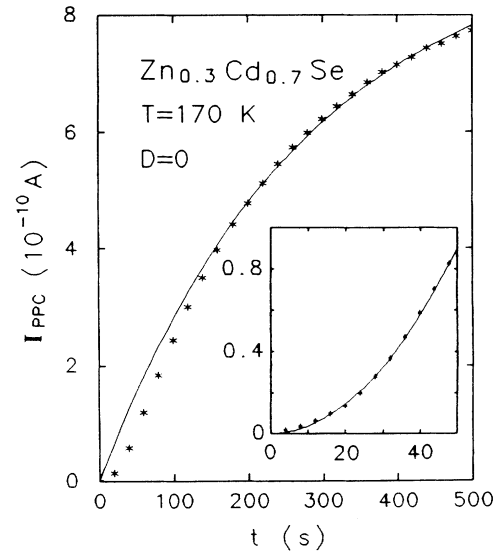

FIG. 3. The kinetics of PPC buildup for $Zn_{0.3}Cd_{0.7}Se$ under the illumination with a higher excitation intensity ($D=0$) at $T=170$ K and the solid curve is a fit using Eq. (3), $I(t) = I_{max}(1 - e^{-at})$. Inset: The initial buildup transient from $t=0$ to 50 s, which follows Eq. (9), $I(t) = I_{max}(1 - e^{-at})^2$ shown as a solid curve.

TABLE I. A list of some fundamentally important transport properties in disordered systems that may be studied in semiconductor alloys in the PPC mode.

$E_F < E_m$	$E_F \sim E_m$	$E_F > E_m$
Carrier localization	Localized-to-delocalized	Electron-hole recombination
Hopping conduction	transition	in a random potential
Tail states	Localization parameters	Electron conduction network

(10), which is valid for temperature $T > 0$, with the original definition of mobility edge for $T=0$,[14]

$$\sigma(E) \begin{cases} =0, & E < E_m, \\ > 0, & E > E_m. \end{cases} \quad (11)$$

The exact energy dependence of $\sigma(E)$ is more complicated than Eq. (10), which has been discussed previously.[16]

From Eq. (10), one would expect to observe the PPC transient behavior changing from Eq. (9) to Eq. (3) as the quasi-Fermi level crossing over the mobility edge. The PPC buildup transient has been obtained for $Zn_{0.3}Cd_{0.7}Se$ under the illumination of a higher excitation intensity ($D=0$) at 170 K and the above-described change in PPC buildup transient has indeed been observed as shown in Fig. 3, where the solid curve is a fitting using Eq. (3). We see that Eq. (3) fits quite well for entire time range except the initial transient. In the inset of Fig. 3, we have replotted the initial PPC transient in the 0 to 50 s time regime corresponding approximately to the region of 0 to 500 s for $D=1$, which clearly follows Eq. (9), shown as a solid curve. This clearly demonstrates that $\sigma(E)$ depends on energy at $E < E_m$ and is almost independent of energy at $E \geq E_m$ as described by Eq. (10). However, we did not observe a sharp transition in the PPC buildup transient, which implies that our experimental situation corresponds to the case of $\sigma(E_m) = C[N(E_m)]^2$ in Eq. (10b). The above discussions also imply that there is a photon flux dependent PPC buildup time limit at which Eq. (9) can no longer describe well the experimental data obtained for $Zn_{0.3}Cd_{0.7}Se$. The fit between Eq. (9) and the actual PPC

buildup transients in $Zn_{0.3}Cd_{0.7}Se$ is expected to be better for lower excitation intensity levels (or larger D values) due to the fact that the crossover between E_F and E_m occurs later at lower excitation intensity levels, which is indicated by experimental data shown in Fig. 1.

It can be seen from the results presented above that PPC is quite sensitive to potential fluctuations caused by disorder because PPC is a direct measure of electron transport in the conduction band. Additionally, in the PPC mode, stored charge carriers are under quasiequilibrium after photoexcitation and one can vary the carrier concentration continuously in a single sample through the variation of the excitation photon dose, which cannot be achieved by any other methods. Thus many fundamental properties may be studied more easily in the PPC mode. Therefore, the observation of the PPC phenomenon in II-VI semiconductor alloys not only provides a tool for finding the distribution of tail states but may open another avenue for investigating fundamentally important transport properties in disordered materials. In Table I, we summarize some fundamental properties that may be studied in the PPC mode.

In conclusion, we have shown that the carrier transport properties in $Zn_{0.3}Cd_{0.7}Se$ are strongly influenced by tail states caused by alloy disorder. The distribution of the tail states has been probed experimentally utilizing the PPC buildup transient measurements and is confirmed to be exponential. It can be seen from this work that PPC is a unique phenomenon that can be utilized to study fundamentally important transport properties in systems with a certain degree of disorder.

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