

Metal-insulator transition in semiconductor alloys probed by persistent photoconductivity

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The metal-insulator transition (MIT) caused purely by alloy disorder in a $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}$ semiconductor alloy has been probed by using persistent photoconductivity. Key parameters that describe the MIT, including the critical electron concentration n_c and the energy tail states distribution parameter E_0 , have been determined experimentally. Our results, together with those obtained for impurity-doped and amorphous semiconductors, provide a complete picture of the MIT in different systems.

The transport properties of semiconductors including conductivity, carrier localization, and the metal-insulator transition (MIT), in systems with structure (amorphous), location (impurity), or alloy disorder have been an important subject for many years.^{1,2} The effects of the first two kinds of disorder on the transport properties have been studied extensively, and many important phenomena have been explored. However, effects of alloy disorder on the transport properties in semiconductor alloys have not been extensively studied previously, although it has been known for many years that alloy disorder can have dramatic effects on the optical properties of semiconductors, e.g., it causes exciton localization. This lack of study is partly due to the fact that it is very difficult to probe transport properties affected purely by the alloy disorder. First of all, for undoped (or deep-impurity-doped) semiconductor alloys, there are no measurable charge carriers at room temperature. On the other hand, in shallow-impurity-doped semiconductor alloys, it is very difficult to separate effects due to alloy disorder from those due to impurities. Consequently, the transport properties, including the distribution of tail states, critical carrier concentration, and carrier mobility edges, which are central to the theory of Anderson and Mott MIT, are unknown for semiconductor alloys.

It has been suggested theoretically that alloy disorder can produce fluctuations at the band edges in II-VI semiconductor alloys.³ Photoluminescence measurements on semiconductor alloys have in fact confirmed the existence of the alloy disorder, which causes exciton localization.^{4,5} Recently, we have also demonstrated qualitatively that alloy disorder could affect transport properties and presented strong evidence for an exponential tail in the density of states (DOS) of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}$ alloys.⁶ With the recent development of device applications based on II-VI semiconductor alloys,⁷ an understanding of alloy disorder effects on transport properties is also technically very important. Due to alloy disorder, at $T=0$ photogenerated electrons in the conduction band are localized (or in the band-edge tail states) at low concentrations. As the electron concentration increases to a critical value n_c the electron Fermi level will line up with the electron mobility edge, at which MIT's in semiconductor alloys will occur. Important questions that arise naturally include: What will be the differences between the MIT behaviors

in impurity-doped semiconductors and in semiconductor alloys? What will be the DOS in the localized states due to alloy disorder? What will be the critical concentration n_c in semiconductor alloys and how will this critical concentration be compared with those in impurity-doped semiconductors?

In this paper, we describe a method for probing MIT's caused purely by alloy disorder in semiconductor alloys. Such a method is based on the observation, in II-VI semiconductor alloys, of the phenomenon of the persistent photoconductivity (PPC), photoinduced conductivity that persists for a very long period of time after the termination of the excitation light source.⁸ A distinct advantage of this method is that, in the PPC state, the carrier concentration in the conduction band can be conveniently varied in a single sample with excitation photon dose,⁹ so direct comparisons for different concentrations can be made more easily. Important quantities such as critical carrier concentration n_c and the energy tail states distribution parameter E_0 have been obtained for semiconductor alloys. Previously, the hard gap in the density of states in the In-doped dilute magnetic semiconductors $\text{Cd}_{0.91}\text{Mn}_{0.09}\text{Te}$ was also studied through the use of PPC.¹⁰

The sample used for this study was a $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}$ unintentionally doped semiconductor alloy. Experimental details can be found elsewhere.⁸ The excitation light source was a 100-W white lamp. The excitation intensity was controlled by a set of neutral density filters with different D values and was proportional to 10^{-D} . The typical excitation photon flux used for the measurements was on the order of 10^{13} photons/cm²s corresponding to $D=4$. The electron concentration was measured by the standard Van der Pauw method and calculated from $n_H=(eR_H)^{-1}$, assuming the Hall factor to be 1. The magnetic field for the measurements was 0.46 T. We consider only the electron transport properties here since the hole effective mass in this material is heavier than that of the electron.

Figure 1 shows the plots of PPC buildup transients obtained for $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}$ at three different conditions: (a) $T=171$ K, $D=4.4$, (b) $T=171$ K, $D=4.6$, and (c) $T=201$ K, $D=4.4$. The asterisks are experimental results. The striking feature is that the initial transients show a parabolic dependence on illumination time t , fol-

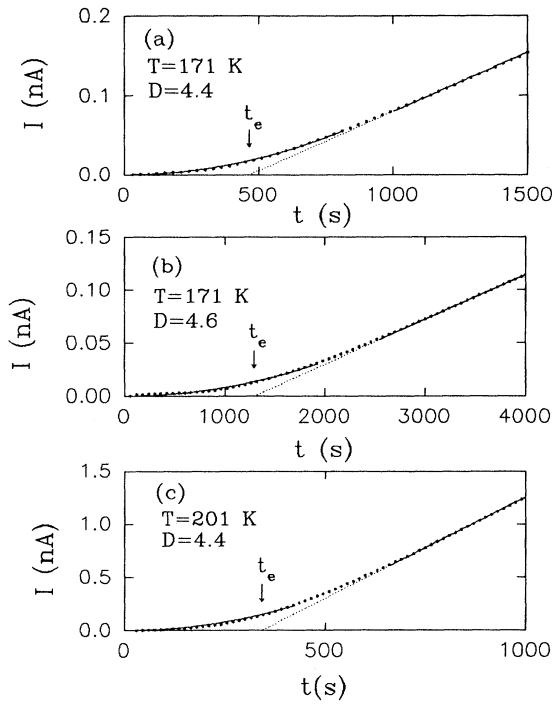


FIG. 1. PPC buildup transients at three different conditions: (a) $T=171$ K, $D=4.4$, (b) $T=171$ K, $D=4.6$, and (c) $T=201$ K, $D=4.4$. The asterisks are experimental results and the solid lines are theoretical fittings by using Eqs. (1) and (2). The extrapolation of the linear fitting to the time axis (dashed lines) defines the critical illumination time t_e , at which the free electron transport becomes important.

lowed by a linear dependence on illumination time. Such a behavior has been observed previously by us, and was attributed to the fact that the conductivity of the initial buildup is due to the transport of photoexcited electrons in the band-edge tail states.⁶ The concentration of the photogenerated electrons in the conduction band is linearly dependent on the illumination time in the entire transient regions for all three different conditions.¹¹ However, the conductivity contributed by the tail states varies parabolically with electron concentration or illumination time. As the electron concentration increases to a certain level, above which the electron transport in the extended states (or the free electron transport) becomes important, the conductivity then becomes linearly dependent on the total electron concentration (or illumination time). At $T=0$, the initial transient of the photocurrent can be written as⁶

$$I(t) = I_0(1 - e^{-\alpha t})^2 \approx At^2 \quad (\alpha t \ll 1, E_F < E_m). \quad (1)$$

When the electron Fermi level is above the mobility edge E_m , the photocurrent can be written as

$$I(t) = I_1(1 - e^{-\alpha t}) \approx Bt \quad (\alpha t \ll 1, E_F > E_m). \quad (2)$$

The parameter α in Eqs. (1) and (2) is the electron decay rate due to the decay of PPC. Experimental data in Fig.

1 have been fitted by Eqs. (1) and (2) for the two different regions, which are shown as solid lines in Fig. 1. Very good agreements have been obtained between experimental results and calculations. Since the experiments were done at $T > 0$ K, electron concentration in the extended states will have approximately a linear dependence on the total electron concentration (or illumination time) even when the electron Fermi level is below the mobility edge. The extrapolation of the linear fit to the time axis defines the critical illumination time t_e (or electron concentration), above which the electron transport in the extended states becomes important. By comparing Fig. 1(a) with Fig. 1(b), we can see that at a fixed temperature, t_e increases as excitation light intensity decreases (D increases) as we expected, since a longer illumination time is needed under lower excitation intensities for the electron concentration to reach the critical value. By comparing Fig. 1(a) with Fig. 1(c), under the same excitation intensity, we see that the critical illumination time t_e decreases with an increase of temperature, which is again as we expected. Under the same excitation intensity, the concentration of the photoexcited electrons in the conduction band is the same, but more electrons will be thermally activated into the extended states at higher temperatures. Experimentally, this would show up as a shorter illumination time required in order to observe the electron transport in the extended states. The detailed calculation for the temperature dependence of t_e will be discussed later. A comparison PPC buildup experiment has been performed also for $\text{Al}_x\text{Ga}_{1-x}\text{As}$, which also exhibits the PPC effect below 150 K. In this material, deep centers called DX centers that undergo a large lattice relaxation are a well-known cause of PPC and the PPC buildup transients measured at different temperatures and intensities always follow Eq. (2) and the behavior of Eq. (1) was never observed.⁶ Comparison experiments have also been carried out for doped and undoped II-VI semiconductor alloys.¹² These results indicate that transport properties of undoped $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}$ are strongly affected by the alloy disorder.

Figure 2(a) is the plot of the slope of the linear dependence part of the PPC buildup transient, $B (=I_1\alpha)$ in Eq. (2), versus the relative light intensity 10^{-D} . A linear behavior is evident, as we expected, since $I_1 \propto$ light intensity $\propto 10^{-D}$. One of the key parameters that determines the transport properties in a disordered system is n_c , the critical electron concentration of the MIT at $T=0$. n_c in impurity-doped semiconductors has been studied extensively both theoretically and experimentally. Very good agreement between experiments and theory has been achieved. However, the existence of n_c caused by alloy disorder in semiconductor alloys has never been addressed. Another important parameter is E_0 , which determines the distribution of the tail states. In the following, we will discuss how to obtain these two parameters in semiconductor alloys. The DOS in the tail states in semiconductor alloys can be described by an exponential function,^{6,13}

$$g(E) = (N_0/E_0) \exp[(E - E_m)/E_0] \quad (E < E_m), \quad (3)$$

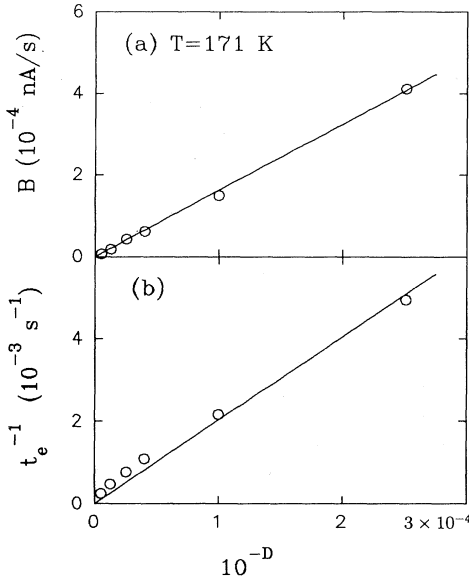


FIG. 2. (a) Parameters $B = I_1 \alpha$ in Eq. (2) and (b) inverse of the critical time t_e^{-1} versus the relative light intensity 10^{-D} at $T = 171$ K. The straight lines are the least-square fit to the data.

where E_0 is the slope of the distribution of the conduction band-edge tail states, which is directly correlated with the energy fluctuation in the tail states, and N_0 is the total density of states in the tail. We obtain at $T=0$, $N_0 = n_c = \int g(E) dE$, where n_c or N_0 depends on the inherent properties of semiconductor alloys. With a total electron concentration in the conduction band being n_c , the electron Fermi level will line up with the mobility edge ($E_f = E_m$). However, at $T > 0$ K, most electrons will remain in the localized states, but some fraction will be thermally activated into the extended states. In order to calculate the electron concentration in the extended states, we have to know the temperature dependence of the Fermi level E_f . We can calculate this dependence based on the fact that the total electron concentration remains as n_c ,

$$n_c = \int_{-\infty}^{+\infty} f(E) g(E) dE, \quad (4)$$

where $f(E) = \{1 + \exp[(E - E_f)/kT]\}^{-1}$ is the Fermi distribution function of electrons. In order to calculate Eq. (4), we need information concerning $g(E)$ above the mobility edge E_m . This has been discussed previously by Redfield.¹⁴ However, the use of a more accurate form of $g(E)$ by Redfield for the case of $E > E_m$ introduces two more fitting parameters. As an alternative method, one could approximate $g(E)$ by Eq. (3) if $E_0 \gg kT$. In this case, $\exp[(E - E_f)/kT]$ in the denominator of $f(E)$ will be much larger than $\exp(E/E_0)$, leaving the integration in Eq. (4) relatively unaffected. We have confirmed this with numerical calculations by using the form of $g(E)$ for $E > E_m$ proposed by Redfield compared with that of Eq. (3) in the temperature region of the experiments. From Eqs. (3) and (4), we obtain $\exp[(E_m$

$-E_f)/E_0] = 1/I$, where $I = \int_{-\infty}^{+\infty} [e^y/(1 + e^{\alpha y})] dy$ and $\alpha = E_0/kT$.

With the total electron concentration in the conduction band being n_c , the electron concentration in the localized states ($E < E_m$) at a finite temperature can be calculated as,

$$n(T) = \int_{-\infty}^{E_m} \frac{(N_0/E_0) \exp[(E - E_m)/E_0]}{1 + \exp[(E - E_f)/kT]} dE. \quad (5)$$

From Eq. (5), we obtain

$$n(T)/n_c = \int_{-\infty}^0 \frac{e^y}{1 + (Ie^y)^\alpha} dy. \quad (6)$$

The electron concentration in the extended states is thus $\Delta n = n_c - n(T)$.

Equation (6) can explain our experimental results presented in Fig. 1. We can also deduce important quantities n_c and E_0 by comparing Eq. (6) with experimental results. The excitation light intensity dependence of the critical illumination time t_e is presented in Fig. 2(b), which shows a linear dependence. This can be easily explained from the above calculation. With the condition of $\alpha t \ll 1$, the total electron concentration n in the conduction band is proportional to the total excitation photon dose, i.e., $n = C 10^{-D} t$, where C is a proportionality constant and t is the illumination time. If $\Delta n [= n_c - n(T)]$ is the critical electron density in the extended states above which the electron transport in the extended states becomes significant (where photocurrent increases linearly with illumination time), then $n(T) = C 10^{-D} t_e$, which gives, $t_e^{-1} = S_1 10^{-D}$, where $S_1 = C/n(T)$. Since $n(T)$ is a constant at a fixed temperature, a linear dependence of t_e^{-1} on 10^{-D} is expected, which is exactly what we have observed in Fig. 2(b). By substituting $n(T) = C 10^{-D} t_e$ into Eq. (6), we thus obtain

$$t_e = S_2 \int_{-\infty}^0 \frac{e^y}{1 + (Ie^y)^\alpha} dy, \quad (7)$$

where $S_2 = (10^D n_c / C)$.

Figure 3 is the experimental results of t_e as a function of temperature under two different excitation intensities $D = 4.4$ (●) and $D = 4.7$ (○). t_e decreases as temperature increases. The solid lines in Fig. 3 are the least-squares fit of data with Eq. (7). A perfect agreement between experimental results and calculation is obtained and the fitted values are $E_0 = 20.8$ and 20.1 meV and $S_2 = 1.03 \times 10^3$ and 2.20×10^3 s for $D = 4.4$ and 4.7 , respectively. E_0 obtained for two different D values are consistent with each other as it should be and is also very reasonable by comparing with the linewidth of localized exciton emission band which is usually between 10–100 meV, depending on materials. Assuming a Gaussian compositional distribution, E_0 obtained here corresponds to a mean composition $x_0 = 0.3$ and a distribution width $\sigma = 0.026$. This value can also be calculated from the energy gap difference between ZnSe and CdSe (=960 meV) by assuming a conduction-band offset parameter of 80%.¹⁵ The value of this width obtained here also agrees perfectly with that obtained earlier from a percolation model

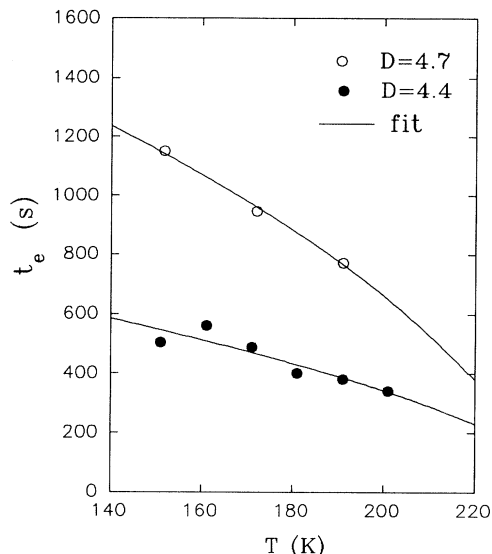


FIG. 3. The critical illumination time t_e as a function of temperature under two different light intensities, $D=4.4$ (●) and $D=4.7$ (○). The solid lines are the least-squares fit of data to Eq. (7). The fitted values are $E_0=20.8$ and 20.1 meV, $S_2=1.03 \times 10^3$ and 2.2×10^3 for $D=4.4$ and 4.7 , respectively.

calculation.¹⁶ The ratio of $S_2(D=4.7)/S_2(D=4.4)$ from fitted values is 2.14 and from Eq. (7) is $10^{D_1-D_2}=10^{0.3}=2.0$, which again agrees very well.

We have also measured electron concentration by the Hall measurements. No electron concentration was measurable in the dark state even up to room temperature. One thing we have to indicate here is that the Hall concentration measures only the electron concentration in the extended states (free electron concentration), whereas electrons in the localized states are not measurable by the Hall measurements. We found that the measured Hall concentration n_H versus illumination time has approximately a linear relation. However, no electron concentration is measurable at the first few hundreds of seconds, since all electrons are in the tail states. n_H can be approximated by

$$\begin{aligned} n_H &\approx n \exp[(E_f - E_m)/kT] \\ &= C10^{-D}t \exp[(E_f - E_m)/kT]. \end{aligned} \quad (8)$$

n_H versus illumination time t has been measured at five different temperatures, $T=161, 171, 181, 191,$ and 201 K for $D=4.4$. The slopes of n_H versus t , $S_3 (=C10^{-D}\exp[(E_f - E_m)/kT])$, were then measured for these temperatures. We then plotted $\ln S_3$ versus $1/T$, which gives $C10^{-D}=9.1 \times 10^{13} \text{ cm}^{-3} \text{ s}$. From $S_2 = n_c 10^D/C = 1.03 \times 10^3$, we thus have $n_c = C10^{-D}S_2 = 9.1 \times 10^{14}/\text{cm}^3$. We have, therefore, demonstrated the existence of n_c in semiconductor alloys caused purely by alloy disorder. Furthermore, our results indicate that the critical concentration of MIT caused by alloy disorder is about two orders of magnitude smaller than that in impurity-doped semiconductors, which is of the order of $10^{17}/\text{cm}^3$. Another feature of utilizing PPC in semiconductor alloys to study transport properties is that we can perform experiments at relatively higher temperatures instead of very low temperatures, as for impurity-doped semiconductors. In impurity-doped semiconductors, the electron transport occurs in the impurity band, which has a fluctuation parameter E_0 of the order of 1 meV. Here, in $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ semiconductor alloys, the electron transport occurs in the conduction band with E_0 of about 20 meV. Due to this large fluctuation in the tail states of the sample studied here, we cannot detect any photocurrent at temperatures below 120 K even with our instrumental limitation being ~ 0.1 pA. Additionally, we observe that PPC increases exponentially with temperature at $T > 120$ K, which is consistent with the above described picture of MIT in semiconductor alloys.

In conclusion, we have studied, by using PPC, the electron transport properties in $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}$ due to purely alloy disorder. Key parameters for describing transport properties, n_c and E_0 , have been determined. It can be seen that the observation of PPC phenomenon in II-VI semiconductor alloys not only provides a tool for studying MIT but also opens an avenue for investigating fundamentally important transport properties in semiconductor alloys. The results presented here are also important for device applications based on semiconductor alloys.

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