Persistent photoconductivity and related critical phenomena in $Zn_{0.3}Cd_{0.7}Se$

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Persistent photoconductivity (PPC) has been investigated for $Zn_{0.3}Cd_{0.7}Se$ mixed crystal. We found that local-potential fluctuations induced by composition fluctuations are responsible for PPC observed here. However, the PPC is observed only above 70 K, in contrast to previous reported results on most materials which exhibit PPC effects predominantly at low temperatures. PPC relaxation shows stretched-exponential decay in temperature region 70 K $< T <$ 220 K. A PPC-related phase transition has been observed, in which the stored charge carriers experienced a transition from localized to delocalized states at temperature T_c ($\approx$ 120 K). Stretched-exponential decay parameters as functions of temperature have been determined.

Light-enhanced conductivity, which persists for anomalously long relaxation times (of the order of minutes to years) after the removal of photoexcitation, has been observed in many semiconductor materials and configurations.[1] In fundamental physics, understanding of the persistent photoconductivity (PPC) phenomena will provide mechanisms for carrier storage and relaxation. The PPC phenomena are also known to be useful for adjusting the density of the electron gas at heterojunction interfaces.[2] The PPC and the undesirable back-gating effects in field-effect transistors may have related origins.

Several mechanisms have been proposed to explain the origin of PPC. In the microscopic random-potential-fluctuation model, the separation of photoexcited carriers by local-potential fluctuations was believed to be the origin of PPC.[1] Nevertheless, a quantitative understanding and conclusive experiments on such systems have not yet been achieved. Queisser and Theodorou have demonstrated for well-defined samples that the spatial separation of photogenerated electrons and holes by built-in electric field from macroscopic potential barrier due to band bending at surfaces or interfaces lead to PPC.[3−5] For artificially constructed layered materials, this model predicts a PPC decay essentially logarithmic in time consistent with experimental observations.[5,6] However, the decay mechanism in bulk semiconductors is not yet well understood and cannot be described by Queisser's formula. The other dominant mechanism involves photoexcitation of electrons from deep-level traps which undergo a large lattice relaxation, namely DX centers.[7,8] The PPC has resulted because recapture of electrons by DX centers is prevented by a thermal barrier at low temperatures. This model explains many PPC features in $Al_xGa_{1-x}As$. Nevertheless, the nature of the DX centers is difficult to understand, and is still being investigated intensively.[9,10] Recently, Zukotynski and Ng suggested that the PPC in Si-doped $Al_xGa_{1-x}As$ is caused by periodic fluctuations in As vs Ga concentration which lead to the shift of the impurity wave function in k space.[11] However, periodic fluctuations are not expected in a real sample. More realistically, the composition fluctuations in mixed crystals are random. Therefore, the mechanisms for creation and relaxation of PPC are still open to questions.

In this paper, PPC phenomena have been investigated in $Zn_{0.3}Cd_{0.7}Se$ mixed crystal throughout the temperature range 8 to 300 K. Experimental results suggest that random-local-potential fluctuations induced by composition fluctuations are responsible for PPC observed here. PPC is observable only above $T > 70$ K, which makes the macroscopic potential barrier or the DX center of large lattice relaxation models unlikely to be the origin of PPC observed in $Zn_{0.3}Cd_{0.7}Se$. This is because these two models lead to the existence of PPC at low temperatures. A PPC-related phase transition occurring at a critical temperature T_c ($\approx$ 120 K) has been observed. PPC decay behavior is also investigated. In the region $T_c < T < 220$ K, the relaxation times of PPC surprisingly decrease with decreasing temperature, which is again unexpected from either macroscopic barrier or DX centers of large lattice relaxation models.

We use $Zn_{0.3}Cd_{0.7}Se$ mixed crystals with dark room-temperature resistivity of about 10^9 Ω cm. Single crystals were grown from a solid solution. The starting materials were purified ZnSe and CdSe powders in appropriate weight proportions. The crystals were grown by using the temperature gradient solution zoning technique. $Zn_xCd_{1-x}Se$ mixed crystals with $0 \leq x \leq 0.4$ were of hexagonal structure.[12] Gold leads were attached to the sample using indium solder and the junctions were carefully tested for Ohmic contacts. PPC measurements are performed in a closed-cycle He refrigerator. Our sample was attached to a copper sample holder with care taken to ensure good thermal contact yet electrical isolation. A mercury lamp was used along with appropriate filters, so two lines at 435.8 and 546.1 nm dominated the output of the excitation source. The data at different temperatures were taken in such a way that the system was always warmed up to room temperature after a measurement and allowed to relax to equilibrium, then cooled down in darkness to the desired temperature of measurements. This is to ensure that the data obtained for each temperature has the same initial condition. Additionally, at a given temperature, the relaxation times of PPC are found to be increasing with increasing the illumination dose.[13] Therefore, decay of PPC at different temperatures is obtained by illuminating the sample by exactly the same amount of photon dose at every temperature of decay measurements. The photon dose is about 2×10^{13} photons/cm^2 per second.
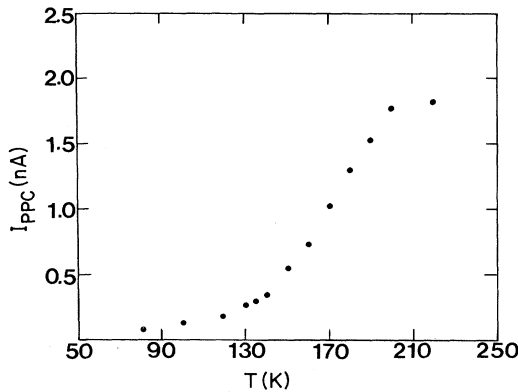
FIG. 1. Buildup levels of persistent photoconductivity in $Zn_{0.3}Cd_{0.7}Se$ mixed crystal as a function of temperature. Illumination time is 1000 s, and photon dose is about 2×10^{13} photons/cm^2 per second. Dark current has been subtracted out. Notice a sharp increase near $T = 120$ K.

FIG. 3. Plot of $\ln[\ln I_{PPC}(0) - \ln I_{PPC}(t)]$ vs $\ln(t)$ for three selective temperatures. Linear curves indicate that the PPC decays according to the stretched exponential, $I_{PPC}(t) = I_{PPC} \times (0)\exp[-(t/\tau)^\beta]$.

Figure 1 shows PPC buildup levels as a function of temperature for 1000 s of light illumination. We see that PPC increases slowly in the temperature region of 70 to 120 K and then increases sharply near 120 K. As temperature becomes lower than 70 K, virtually no PPC (nor photoconductivity) could be observed. Similar results have been observed previously in doping-modulated amorphous silicon superlattices in which no PPC could be induced at temperature $T < 80$ K.[14] The authors proposed deep traps of acceptorlike AX centers to be the origin of PPC. In this model, the AX center is analogous to the DX center yet it implies a thermal barrier against the creation of PPC at low temperatures. However, the high-temperature annealing effects on PPC observed in such systems ruled out the mechanism requiring deep traps.[15] To date, there is no reported results on any other materials which show the similar PPC effect.

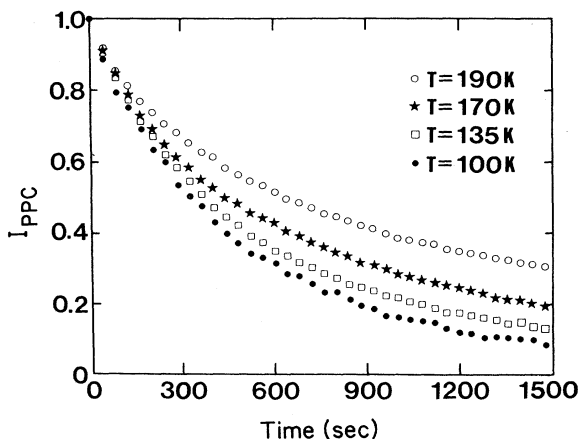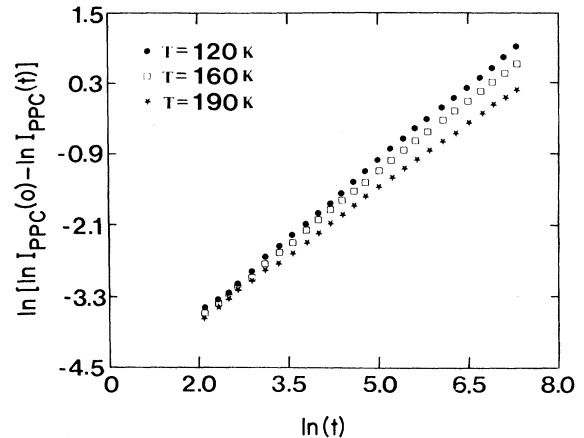Figure 2 shows PPC decay curves for four different

FIG. 2. PPC decay curves for four selective temperatures. Each decay curve is normalized to a unity at $t = 0$. Experimental conditions are the same as those in Fig. 1.

temperatures. For comparison, each curve is normalized to a unity at time $t = 0$, dark current has been subtracted out. As we see that PPC decays faster as temperature decreases. This is unexpected from the present existing PPC models. However, as temperature increases to above 220 K, PPC shows the usual decay behavior, i.e., PPC decays more rapidly as temperature increases. PPC still exists up to room temperature but with shorter relaxation times. Furthermore, the PPC relaxation shows stretched-exponential behavior. In the full time range, at $T < 220$ K, actual current (I_{PPC}) decay curves in Fig. 2 fit with the Kohlrausch expression,[16]

$$I_{PPC}(t) = I_{PPC}(0)\exp[-(t/\tau)^\beta] , \qquad (1)$$

where τ and β are two decay parameters. Figure 3 shows representative plots of $\ln[\ln I_{PPC}(0) - \ln I_{PPC}(t)]$ vs $\ln(t)$ for three different temperatures. The perfect linear behavior of the plots demonstrates that the PPC decay is well described by Eq. (1). Stretched-exponential relaxation reveals similarities of the present system to the disordered systems,[16] and thus implies that the microscopic random-potential fluctuations are the origin of the observed PPC phenomena. β and τ for different temperatures can be determined from a least-squares fit with experimental data. We have obtained β and τ as functions of temperature in Fig. 4. The value of β is about 0.85 ± 0.03 below 120 K, and depicts a clear decrease near 120 K. The characteristic decay time constant τ also shows a transition at 120 K. At temperatures above 220 K, the decay of PPC is no longer well described by the stretched exponential. The PPC relaxation rate increases as temperature increases in the region of $T > 220$ K.

Experimental results on temperature-dependent PPC buildup levels and PPC decay clearly depict percolation behavior. This leads us to interpret the observed PPC in terms of the spatial separation of photoexcited carriers by electric fields of local-potential fluctuations induced by
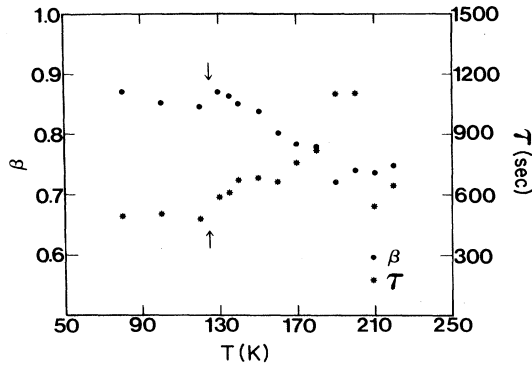
FIG. 4. Decay parameters β (●●●) and τ (✱✱✱) vs temperature. Notice large changes near 120 K indicated by arrows.

composition fluctuations. In mixed crystals large composition fluctuations are well known, which causes local-potential barriers in band edges.[17,18] In temperatures at which carriers hardly overcome the recombination barriers, $T < 220$ K, present system behaviors similar to the disordered systems. Thus, the relaxation can be well described by the stretched exponential which is known as a universal function describing disordered systems towards equilibrium. At temperatures below 70 K, photoexcited carriers are strongly localized and immobile, and activated hopping processes are negligible. Thus, PPC effects are not observed in this temperature region. In the region of 70 K $< T < 120$ K, our system is in the lower conductivity state, in which case PPC is contributed by activated electron hopping between localized states. However, at temperatures above the percolation threshold $(T > 120$ K), extended electron states contribute to percolation conductance, while holes still remain localized. Therefore, two PPC states are expected. Experimentally, a phase transition near 120 K is indeed observed in Figs. 1 and 4.

We expect that results in Fig. 1 can be rationalized using a percolation approach. When the system is in the percolation state, $T > T_c$, temperature-dependent PPC is expected to have the following expression:

$$I_{\text{PPC}}(T) = a(T - T_c)^\nu, \quad (T > T_c), \quad (2)$$

where ν is the conductivity exponent. Experimental data obtained in the region 130 K $< T < 200$ K fit equation (2) very well and yield $\nu = 1.30 \pm 0.05$ and $T_c = 118 \pm 2$ K. We also fit $I_{\text{PPC}}(T)$ in the same region using exponential temperature dependence $I_{\text{PPC}}(T) = A\exp(-E/kT)$, and the fit is not as good as the percolation approach. To date, the conductivity exponent has not yet been settled for the lattice problem, and values from 1.6 to 2.2 have been reported for three-dimensional lattices.[19,20] Our sample represents a whole new system of percolative semiconductors, which is quite different from the pure lattice problem.

The measurement on T_c yields some information on the composition fluctuations in the sample. Assuming the composition fluctuations of the sample are random and obey Gaussian distribution,

$$P(x) = P_0\exp[-(x - x_0)^2/2\sigma^2], \quad (3)$$

where $x_0 = 0.3$, is the mean composition of Zn for our sample, P_0 can be determined by normalization condition $\int_0^1 P(x)dx = 1$, and σ is the fluctuation parameter. It is known that the band gap varies linearly[21] with x from 1.84 eV $(x = 0$, CdSe) to 2.8 eV $(x = 1$, ZnSe) for $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$.[22] Using the value of critical filling electron states p_c (≈ 0.25) obtained from computer simulation on three-dimensional lattices,[19] and the experimental value of T_c ($= 120$ K), we obtain $\sigma = 0.027$.[13] This gives an estimated value for composition fluctuations in the sample. The composition fluctuation parameter derived from exciton luminescence linewidth is about 0.023, which is in reasonable agreement with the above calculated value. In the local-potential-fluctuation model, T_c and σ have a one-to-one relationship. We expect that for mixed crystals with larger composition fluctuations, the critical temperature T_c as well as the temperature region for stretched-exponential decay behavior will exist in a higher-temperature region. Thus, PPC provides an additional method for determining composition fluctuations in mixed crystals. On the other hand, the temperature region for existence of well characterized PPC can be controlled by varying σ, which is very important for device applications.

Furthermore, we found that the critical temperature T_c depends slightly on the excitation photon dose. However, in the temperature region 130 K $< T < 220$ K, β is independent of excitation photon dose at the same temperature. Therefore, at a given temperature within the above-mentioned region, the decay of PPC created by different levels of photon dose can be scaled by the same formula,

$$I_{\text{PPC}}(t') = I_{\text{PPC}}(0)\exp(-t'^\beta), \quad (4)$$

with t' being t/τ and τ depending on the photon dose. Detailed investigation concerning this point will be published in a forthcoming paper.[13] Stretched-exponential decay implies an average relaxation time of the system to be

$$\langle\tau\rangle = \int_0^\infty \exp[-(t/\tau)^\beta]dt = \beta^{-1}\tau\Gamma(\beta^{-1}), \quad (5)$$

with Γ being the γ function. At $T < T_c$, we obtain $\langle\tau\rangle$, the average relaxation time, to be about 530 s. In the temperature region $T_c < T < 200$ K, β decreases and τ increases with increasing T. As a result $\langle\tau\rangle$ increases even more drastically than the characteristic decay time constant τ. At the temperature of the slowest relaxation, $T = 200$ K in Fig. 4, with $\beta = 0.74$ and $\tau = 1107$ s, we obtain $\langle\tau\rangle = 1330$ s.

Previous reported results on other materials are usually that relaxation time of PPC decreases with increasing temperature. This has been interpreted in terms of the fact that the probability for carriers to overcome the capture barrier increases with increasing temperature. Therefore, our results are unexpected from other models. Qualitatively, we can explain the temperature-dependent decay behavior as follows: The decay of PPC depends on the distribution of charge carriers and the conductivity states. For $T < T_c$, since PPC is contributed by activated hopping between localized states, the effect of redistribution among the localized states with time is negligible. Thus, the decay is only determined by the initial distribu-

tion of charge carriers, and the decay rate depends on the wave-function overlap between electrons and holes. We believe that the PPC decay mechanism in this temperature region should be similar to that of the donor-acceptor pair (DAP) transition, in which case electrons and holes are respectively bounded to donors and acceptors, and the transition rate is determined by wave-function overlap between bounded electrons and holes.[23−25] At $T > T_c$, electrons are in the percolation states, the effect of electron redistribution in real and momentum spaces plays an important role. Electrons redistribute in such a way that they always prefer to occupy the sites of minimum potential energies. In percolation description, conductivity is contributed by electrons percolating through the network of accessible sites (locations of low potential energy). The time duration of an electron on each accessible site depends on the potential depth of the site and thus depends on composition x at each site. It is easy to understand that the probability for finding an electron at the site of minimum potential is highest compared to other sites because, relatively, electrons tend to spend more time on such a site. Since holes remain localized and immobile, the recombination becomes spatially less possible with increase of time because of the lack of holes around these

sites (nearby holes have been recombined with electrons in earlier time stages). As temperature increases, the redistribution effect becomes more pronounced, thus an increase in τ is observed. Quantitative understanding of the relaxation process of stored charge carriers is under investigation.

In conclusion, PPC phenomena in $Zn_{0.3}Cd_{0.7}Se$ mixed crystal have been investigated. Experimental results suggest that the random-local-potential fluctuations induced by composition fluctuations are responsible for PPC. Two PPC states have been observed. PPC is contributed by electrons in percolation states above T_c (≈ 120 K), and is due to activated electron hopping between localized states below T_c. In full time range, relaxation of PPC is well described by a stretched-exponential decay in the temperature region 70 K $< T <$ 220 K. Decay parameters are determined, and depict transition behavior near T_c. Our results show that mixed crystals represent a model system to study percolative semiconductors. Additionally, the PPC phenomena in these types of samples can be well characterized and exist in high-temperature regions, which are extremely important to fundamental physics and device applications.

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