During the period of Aug 1, 1990 to Jan 31, 1991, the following research activities have been carried out in studying persistent photoconductivity (PPC) in II-VI mixed semiconductors and related device applications: (1) New Type of Materials, (2) PPC in II-VI Semiconductor Thin Films, (3) Comparison Between II-VI and III-V Semiconductors and (4) PPC Transient Behavior.
Final Technical Report

Project: Persistent Photoconductivity in II-VI Mixed Semiconductors: Related Critical Phenomena and Applications (AFOSR-90-0318)

From: Hongxing Jiang, Department of Physics, Kansas State University

Data: March 26, 1991

During the period of Aug. 1, 1990 to Jan. 31, 1991, the following research activities have been carried out in studying persistent photoconductivity (PPC) in II-VI mixed semiconductors and related device applications:

1. New Type of Materials. We measured PPC in a new type of II-VI mixed semiconductors, Zn_{x}Cd_{1-x}Te. It is very encouraging that strong PPC exists in these materials at room temperatures. The decay time constants of PPC at different temperatures and excitation photon dose have been measured. Furthermore, the PPC behavior has been investigated under different bias voltage, V_{b}. We found for the first time that the decay time constants can be controlled by V_{b}, which is very important for device applications. The sensitivity of optical infrared quenching of PPC under different bias voltage is under investigation.

2. PPC in II-VI Semiconductor Thin Films. It is very important to understand the PPC behavior in semiconductor thin films since eventually all the novel optoelectronic devices utilizing PPC mechanism will be fabricated from thin films. Thin film samples were successfully grown from bulk materials on glass substrates by sputtering and laser ablation methods. The samples we made are Zn_{x}Cd_{1-x}Te and
Cd$_x$Se$_{1-x}$ thin films with thickness about 1 μm. These thin film samples exhibit PPC effect up to room temperatures. The remarkable finding is that the lifetimes of PPC are extremely long in thin film samples which is consistent with our proposed model for PPC and is very important for novel device applications.

3. **Comparison Between II-VI and III-V Semiconductors.** To understand the fundamental properties of PPC in II-VI materials, comparison experiments for II-VI and III-V materials (Al$_x$Ga$_{1-x}$As) are necessary. Many different properties between these two types of materials have been distinguished. Some of the important distinctions are list below:

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<th>II-VI</th>
<th>III-V</th>
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<tr>
<td>Room temperature PPC</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Optical infrared quenching of PPC</td>
<td>Yes</td>
<td>No</td>
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<td>Transition behavior</td>
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4. **PPC Transient Behavior.** For infrared detector or charge storage image device applications, it is important to understand the PPC build-up behavior at room temperatures. In order to find out how fast one could build-up PPC level, we performed build-up experiments under the excitation with the same amount of photon dose but different light intensities. By controlling the timing of an optical shutter, we could build up PPC as fast as a few milliseconds which is the shortest time response we could test because of the response limitation of the apparatus in my laboratory. In order to see the PPC build-up behavior within the time scale as short as microseconds or even nanoseconds, a high intensity fast light source will be needed.
At this stage, we understand better about the fundamental properties of PPC in II-VI semiconductor alloys. We have confirmed that the PPC phenomenon in II-VI semiconductor alloys is both fundamentally and technologically very important and interesting. Physical mechanisms of PPC in II-VI and III-V materials have been distinguished and their behavior were found to be very different. Because of unique properties of PPC in II-VI semiconductor alloys, such as long lifetime, room temperature PPC, and optical infrared quenching, future novel optoelectronic devices utilizing PPC effect in II-VI semiconductor alloys are very promising.

Two papers based on the research results described above are accepted for publications. Several others are under preparations. These results were also presented in conferences. Some relevant materials are also included in this Final Technical Report.
Persistent photoconductivity in II-VI and III-V semiconductor alloys and a novel infrared detector

H. X. Jiang, G. Brown, and J. Y. Lin
Department of Physics, Cardwell Hall, Kansas State University, Manhattan, Kansas 66506-2061

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Persistent photoconductivity (PPC) mechanisms, as well as the similarities and the differences of PPC properties in II-VI and III-V semiconductor alloys have been investigated. The potential applications based on PPC phenomenon in these two kinds of materials are discussed. We have observed that PPC induced in a II-VI mixed crystal by visible (above band gap) illumination can be quenched by long wavelength infrared radiation even at room temperature, which further supports our interpretation that PPC in II-VI mixed crystals is caused by random local potential fluctuations induced by compositional fluctuations. A newly developed infrared detector based on the PPC infrared quenching property of II-VI semiconductor alloys is also reported.

Persistent photoconductivity (PPC) phenomenon observed in a variety of semiconductors is currently under intensive investigation. Most studies on this subject have been concentrated on AlₙGa₁₋₀ₙAs (x > 0.22) in which the defects (DX centers) are a well-known cause of strong PPC effect at temperatures T < 150 K. Hence, PPC is very often taken as an evidence for atomic defect centers in semiconductors which supposedly have unusual properties. Recently, a percolation transition has been observed in II-VI semiconductor alloys in the PPC mode, which demonstrates that the spatial separation between stored charge carriers by random local-potential fluctuations (RLPF) caused by compositional fluctuations is responsible for PPC observed in these materials. In fact, previous work on impurity doped and compensated semiconductors has indicated that microscopic inhomogeneity caused by impurity distribution is the most likely reason for PPC phenomenon. Full understanding of PPC is very important from the point of view of practical applications. The PPC effect can be utilized to optically vary the carrier concentration in a single semiconductor by simply varying excitation photon dose. Because most semiconductors exhibit the PPC effect only at low temperatures (150 K or below), device applications based on PPC phenomenon have not been previously established.

Because of different mechanisms for PPC observed in II-VI and III-V semiconductor alloys, the potential applications based on these two kinds of materials could be very different. In this communication, we present PPC results for III-V and II-VI semiconductor alloys. We also report the results on a Zn₀.₃Cd₀.₇Se II-VI mixed crystal in which PPC generated by visible (above band gap) illumination can be quenched very effectively by long wavelength (5-18 μm) infrared radiation even at room temperatures. Based on this PPC infrared quenching property, a novel infrared detector could be constructed. A number of advantageous features of this infrared detector will be discussed. The comparison between PPC properties in II-VI and III-V semiconductor alloys will be concentrated on the following three aspects: PPC decay behavior, temperature region for existence of PPC, and the property of optical quenching of PPC.

PPC decay behaviors have been investigated for these materials. In Figs. 1 and 2, we show representative PPC decay curves for Zn₀.₃Cd₀.₇Se and Al₀.₃Ga₀.₇As, respectively. A similar behavior observed here is that PPC decay follows a stretched-exponential function at low temperatures (T < 90 K for Al₀.₃Ga₀.₇As and 70 K < T < 220 K for Zn₀.₃Cd₀.₇Se), $I(t) = I_0 \exp\left(-\left(t/\tau\right)^\beta\right)$, where $\tau$ is the relaxation time constant and $\beta$ the decay exponent. Although the PPC decay in both kinds of materials can be described by stretched-exponential functions, the decay parameters are very different. For II-VI semiconductors, $\beta$ is around 0.8 and $\tau$ is on the order of $10^5$ s. For Al₀.₃Ga₀.₇As, $\beta$ and $\tau$ are on the order of 0.2 and $10^3$ s, respectively, at low temperatures.

Furthermore, the Arrhenius plots, $\tau$ vs 1/T, show two distinctive decay regions for both III-V and II-VI semiconductor alloys, which is caused by different decay mechanisms involved in the high- and low-temperature regions. For Al₀.₃Ga₀.₇As after excitation with certain photon dose, $\tau$ has an activated temperature dependence in the region of $T > 40$ K. This is because at $T > 40$ K, the decay of PPC is caused by thermal activation of electron capture by DX centers and thus the slope of the Arrhenius plot in the region of $T > 40$ K represents the electron capture energy by the DX centers. At low temperatures ($T < 40$ K), the decay of PPC is caused by multiphonon tunneling capture in configurational space according to the large lattice relaxation (Lr) model, or by wavefunction overlap in K-space between the electrons in the L-conduction band and impurities (DX centers) linked to the L-conduction band according to the L-conduction band effective-mass state model. For II-VI semiconductor alloys, the PPC decay is caused by wavefunction overlap between electrons and holes in real space at low temperatures and by electron...
thermal activation from the local potential minima to maxima to recombine with holes at high temperatures; therefore, the thermal barrier approximated from the high-temperature region corresponds to the average energy difference between the local potential minima and maxima.

In Fig. 3, we show a schematic of the real space potential profile at the conduction and the valence band edges of a II-VI mixed crystal. Because of compositional fluctuations, photoexcited electrons (holes) are stored in low potential sites in the conduction (valence) band. Spatially, the low potential sites in the conduction band are separated from those in the valence band leading to very long carrier lifetimes. Consequently, the electron-hole recombination barrier $E_{\text{rec}}$ depends uniquely on the degree of the fluctuation of the sample, which is about 100 meV for Zn$_{0.3}$Cd$_{0.7}$Se and is only about a few meV for a higher quality (lower degree of compositional fluctuations) Cd$_{0.5}$Se$_{0.5}$ sample.7

Furthermore, in Zn$_{0.3}$Cd$_{0.7}$Se, below a certain temperature, $T < 70$ K, the electrons are highly localized and the charge transport becomes negligible and no PPC effect can be observed. As temperature increases, the conductivity is induced either by electron thermal activation hopping between localized sites ($T < T_C$) or by electrons percolating through the network of accessible sites ($T > T_C$), where $T_C$ is a critical temperature at which electrons experience a phase transition from hopping to percolation conduction states.2-4 As temperature increases to an upper limit value, PPC thermally quenches instantaneously. Therefore, there exists an upper temperature limit $T_f$ and a lower temper-
ature limit $T_2$ for the observation of PPC in II-VI mixed crystals. The PPC temperature range as well as $T_C$ are uniquely determined by the degree of the sample compositional fluctuations. Experimentally, $T_C$, $T_U$, and $T_2$ found for Zn$_{0.3}$Cd$_{0.7}$Se are about 120, 300, and 70 K, respectively. For the higher quality CdSe$_{0.5}$S$_{0.5}$ sample, $T_C$ and $T_U$ are about 15 and 150 K, respectively, and PPC is observable down to 8 K. $T_2$ for CdSe$_{0.5}$S$_{0.5}$ has not yet been determined because our current low-temperature system can achieve a lowest temperature of about 8.5 K. For Al$_{0.3}$Ga$_{0.7}$As, there is no lower temperature limit for PPC. Even at temperature $T = 0$, photogenerated electrons still have velocities varying from 0 to Fermi velocity $v_F$ due to the Fermi distribution of electrons in the conduction band. Thus PPC is observed in the entire temperature region of $T < 150$ K. An important fact we would like to indicate here is that from the RLPF model, in II-VI semiconductor alloys, the temperature region for PPC and $E_{\text{rec}}$ can be controlled by varying the degree of fluctuation in the sample, and so one may obtain strong PPC effect at room temperatures. In contrast, the upper limit temperature for PPC in Al$_{0.3}$Ga$_{0.7}$As depends on the electron capture barrier, which is predetermined by the atomic configuration of the DX center, and cannot be changed easily. This is why no PPC can be observed at $T > 150$ K in Al$_{0.3}$Ga$_{0.7}$As, so practical applications based on the PPC phenomenon in Al$_{0.3}$Ga$_{0.7}$As may be limited.

An unique property for PPC in II-VI semiconductor alloys is expected—infrared PPC quenching. As indicated in Fig. 3, once charge carriers are stored in potential minima, by illumination with infrared photons whose energy is on the order of $E_{\text{rec}}$, electrons can be transferred to the maximum of the potential height to radiatively recombine with holes, which will result in a quenching of PPC and a stimulation of luminescent emission of photons with energy on the order of $E_r$. Experimentally, we indeed observe in Zn$_{0.3}$Cd$_{0.7}$Se that PPC generated by visible illumination can be optically quenched by infrared radiation. Figure 4 shows experimentally obtained kinetics of the PPC infrared quenching at room temperature. We see that the quenching is evident. Limited by the time response of the detection instrument (digital electrometer), the quenching time shown here is instantaneous. The amplitude of PPC quenching depends on the intensity of the infrared radiation. Experimental observation of infrared quenching of PPC further supports our RLPF model for PPC in II-VI semiconductor alloys. It is well known from earlier work that PPC induced in Al$_{0.3}$Ga$_{0.7}$As cannot be optically quenched, which has also been further experimentally proved recently.

The infrared PPC quenching property makes II-VI mixed crystals a novel room-temperature infrared detector with a number of advantages, including (a) high speed: infrared quenching is a very fast process because infrared excitation and free carrier recombination processes in these materials occur on a sub-nanosecond scale, (b) wider spectral response region: since $E_{\text{rec}}$ can be varied, detectors with different spectral response regions, from a few $\mu$m to about 30 $\mu$m, can be fabricated from II-VI mixed crystals for different application purposes. A room temperature, long wavelength infrared detector is very important in many cases, (c) low cost: the fabrication method of this type of infrared detector is simple and so the cost will be low. Detailed parameters, such as operating spectral region, temperature, and speed of the infrared detector will be investigated further.

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Charge Storage and Persistent Photoconductivity in a CdS$_{0.5}$Se$_{0.5}$ Semiconductor Alloy

A.S. Dissanayake, S.X. Huang†, and H.X. Jiang*
Department of Physics, Kansas State University, Manhattan, KS 66506-2601

and

J.Y. Lin
Department of Physics, University of Northern Iowa, Cedar Falls, IA 50614

ABSTRACT

Relaxation of stored charge carriers in persistent photoconductivity (PPC) mode in a CdS$_{0.5}$Se$_{0.5}$ semiconductor alloy has been investigated. The relaxation time constant of PPC is systematically measured as a function of temperature, and from which the recombination barrier height, $E_{\text{rec}}$, has been determined. Low temperature exciton luminescence has also been investigated and the exciton transition linewidth which is broadened due to the presence of compositional fluctuations is measured. The values of $E_{\text{rec}}$ deduced from the measured exciton linewidth and the localized-to-delocalized transition temperature in PPC mode are consistent with the results obtained from the PPC decay measurements. These experimental results further support our recent interpretation that PPC in II-VI semiconductor alloys is caused by random local potential fluctuations (RLPF) induced by compositional fluctuations.

PACS numbers: 72.20.Jv, 72.60.+g, 72.80.Ey
I. INTRODUCTION

Persistent Photoconductivity (PPC), photo induced conductivity that persists for a very long period of time after the termination of the photoexcitation has been studied for more than two decades. It is one of the most interesting yet not well understood phenomena in semiconductors. PPC has been observed at low temperatures in bulk semiconductors and in various other configurations.\(^1\)\(^-\)\(^4\) Recently, relaxation time constant as long as \(10^{13}\) seconds at 10 K has been observed in \(\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}\).\(^5\) In contrast, decay time constant on the order of \(10^3\) seconds has been found in II-VI semiconductor alloys. Nevertheless, PPC exists up to room temperatures and can be optically quenched by infrared radiation in II-VI semiconductor alloys, which makes them very important materials for device applications, such as novel infrared detectors.\(^6\),\(^7\)

Several mechanisms have been proposed to explain the origin of PPC. PPC could be caused by interface barrier in heterojunction materials.\(^8\),\(^9\) In \(\text{Al}_x\text{Ga}_{1-x}\text{As}\) semiconductors, the DX center is believed to be the origin of PPC.\(^10\),\(^11\) In this model description, PPC is resulted because recapture of electrons by the DX centers is prevented by a thermal barrier at low temperatures. The nature of the DX center is under intensive investigation,\(^12\)\(^-\)\(^15\) with key question focusing on whether it is a deep center with large lattice relaxation (LLR)\(^14\),\(^16\) or simply an effective-mass state impurity of L-conduction band with small lattice relaxation (SLR).\(^15\),\(^17\)\(^-\)\(^19\)

Recently, we have observed that the stored charge carriers in PPC mode in a \(\text{Zn}_{0.3}\text{Cd}_{0.7}\text{Se}\) semiconductor alloy experience a phase transition from a hopping conduction to a percolation transport state at the critical temperature \(T_c\).\(^20\)\(^-\)\(^22\) There are three experimental evidences for this transition: (a) PPC build up level as a function of temperature,\(^21\) (b) PPC decay time constant and decay
exponent as functions of temperature,\textsuperscript{21} and (c) PPC noise level as a function of temperature,\textsuperscript{20} all depict a transition of percolation type near $T_c$. Furthermore, we have shown that $T_c$ is directly correlated to the degree of the compositional fluctuations in II-VI semiconductor alloys. From these experimental results, we proposed that random local potential fluctuations (RLPF) induced by compositional fluctuations are responsible for PPC in II-VI semiconductor alloys. In fact, it has been proposed previously that inhomogeneity in impurity doped and compensated semiconductors caused by impurity doping is the most likely reason for PPC.\textsuperscript{1} In II-VI semiconductor alloys, compositional fluctuations produce concomitant fluctuations in the energy gap. Thus the compositional fluctuations are the cause of the inhomogeneity and impurities may not play an important role. The relaxation of stored charge carriers in PPC mode in II-VI semiconductor alloys was found to follow the stretched-exponential function.\textsuperscript{20-22} At low temperatures, PPC is induced by electron hopping between localized states; as temperature increases to above $T_c$, localized electrons become delocalized and the charge transport occurs via the electrons percolating through the conduction network, while holes remain localized. In these regions, the decay of PPC is caused by wavefunction overlap between electrons and holes in real space. Electrons are localized in the sites or percolating through the network of the potential minima and are spatially separated from the localized holes because the potential minima for electrons are the potential maxima for holes. This leads photo-excited charge carriers to have long lifetimes as well as the effect of PPC. Further increase in temperature would give electrons sufficient thermal energy to transfer to the maximum of barrier height, $E_{\text{rec}}$, to recombine with holes soon after photoexcitation and cause a thermally activated PPC decay behavior.

In this paper, we study the PPC decay process in a CdS$_{0.5}$Se$_{0.5}$ semiconductor
alloy. The decay time constants are measured systematically in entire PPC temperature region, and from which we obtained the recombination barrier height, $E_{rec}$, which represents the average energy difference between the potential minima and maxima of the fluctuating potentials in the conduction band. Low temperature exciton luminescence is also investigated for CdS$_{0.5}$Se$_{0.5}$. The exciton transition linewidth predominantly caused by compositional fluctuations in the sample is measured and from which we deduced the energy fluctuation parameter for electrons of excitons. The result is compared with that obtained from PPC data. Our experimental results further support our recent interpretation that PPC in II-VI semiconductor alloys is caused by RLPF induced by compositional fluctuations.

II. EXPERIMENTAL

The samples used for this study was a CdS$_{0.5}$Se$_{0.5}$ semiconductor alloy supplied by Cleveland Crystals, Inc. of size about 5 x 10 x 1 mm$^3$ with dark room temperature resistivity of about $10^9$ Ω.cm. Gold leads were attached to the sample using indium solder and the junctions of 1 mm in diameter about 5 mm apart on the sample surface are carefully tested for ohmic contacts. The c-axis is perpendicular to the sample surface. The sample was attached to a copper sample holder, which is inside a closed-cycle He refrigerator, 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 obtained at different conditions were taken in such a way that the system was always allowed to warm up to 300 K and relaxed to equilibrium after each measurement, then cool down in darkness to the desired temperature of measurements. This is to ensure that each set of data has the same initial condition. Measurements of PPC build up and decay at different
photon dose conditions are taken by illuminating the sample for different time intervals while keeping the same intensity at different temperatures. The PPC build up levels depend on excitation photon dose. The typical excitation photon flux used for the measurements is on the order of $10^{13}$ photons/cm$^2$·s. The current is measured by a Keithley digital electrometer (model 617), which is interfaced with a computer. A 1.5-V bias is supplied by a battery.

Photoluminescence data were collected in a reflecting mode. Excitation pulses of about 7 ps in duration at a repetition rate of 1 MHz were provided by a cavity-dumped ultrafast dye laser (Coherent 702-2CD) which was pumped by a YAG laser (Quantronix 416) with a frequency doubler. The lasing photon energy was 2.125 eV with a spectral width of about 2 meV corresponding to a band to band excitation. The average power density is about 100 mW/cm$^2$. The detection system consists of a time-correlated single-photon counting system and a double monochromator with a spectral resolution of 1 meV.

III. RESULTS AND DISCUSSIONS

PPC decay curves for CdS$_{0.5}$Se$_{0.5}$ at two representative temperatures, T=8.6 K and T=40 K, are shown in Fig. 1. PPC are normalized to unity at t=0, the moment of excitation light being terminated. The dark current has been subtracted. These two curves show that PPC decays faster at T=40 K than at T=8.6 K. At T=8.6 K, PPC level is about 6% of its initial level after 1000 seconds decay. Just as in Zn$_{0.3}$Cd$_{0.7}$Se, the decay of PPC in CdS$_{0.5}$Se$_{0.5}$ can be approximated by a stretched-exponential function, a behavior frequently observed in disordered systems.

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

(1)
where $r$ is the decay time constant and $\beta$ is the decay exponent. This has been demonstrated by the plot of $\ln[\ln I_{ppc}(0) - \ln I_{ppc}(t)]$ as a function of $\ln(t)$ for PPC decay curves obtained at these two temperatures. An approximated linear behavior can be observed in Fig. 2. From these curves we can obtain $r$ and $\beta$. The stretched-exponential decay approximation shown in Fig. 2 for PPC relaxation in CdS$_{0.5}$Se$_{0.5}$ is not as good as in Zn$_{0.3}$Cd$_{0.7}$Se.\textsuperscript{21} This is believed due to the fact that the degree of the fluctuations in CdS$_{0.5}$Se$_{0.5}$ is not as large as that in Zn$_{0.3}$Cd$_{0.7}$Se, which is consistent with the experimental observation that the transition temperatures $T_c$ is 120 K for Zn$_{0.3}$Cd$_{0.7}$Se and 15 K for CdS$_{0.5}$Se$_{0.5}$.\textsuperscript{20} In any case, such an approximation enables us to measure the effective relaxation time constant $r$ systematically as a function of temperature, which can provide important information.

Figure 3 is the plot of the decay-time constant $r$ as a function of temperature for CdS$_{0.5}$Se$_{0.5}$. We can see that PPC decays slower near 15 K than at temperatures lower than 15 K, which is very similar to the behavior exhibited by Zn$_{0.3}$Cd$_{0.7}$Se. The Arrhenius plot, $\ln r$ vs $1/T$ in Fig. 4 shows two distinctive temperature regions. At high temperatures ($T > 20$ K), PPC decay is caused by electrons thermally activated into the potential maximum regions to recombine with holes; therefore, $r$ is thermally activated and a linear behavior in this temperature region ($T > 20$ K) is evident. At low temperatures, $r$ is weakly dependent on temperature, and PPC decay is caused by wavefunction overlap between electrons and holes in real space. The observed larger values of $r$ near 15 K than at $T < 15$ K can be accounted for by that PPC decays slower at the percolation state than in hopping conduction state due to the electron redistribution effect as discussed previously.\textsuperscript{21}

Dependence of the PPC relaxation behavior on excitation photon dose is also
investigated for CdS$_{0.5}$Se$_{0.5}$. Fig. 5 shows the decay curves obtained at 8.4 K after excitation with three different light illumination times. Similar to the behavior exhibited by Zn$_{0.3}$Cd$_{0.7}$Se, at a constant temperature and prior to the PPC saturation, the relaxation of PPC proceeds faster with decrease of excitation photon dose as depicted in Fig. 5. This behavior can also be explained qualitatively in terms of our model description. As the electron quasi-Fermi level (or carrier concentration) increases, the charge transport is affected more pronounced by means of percolation. Since PPC decays slower in percolation state than in hopping transport state due to the electron redistribution effect discussed previously, $\tau$ increases with increase of the quasi-Fermi level or excitation photon dose. At very low excitation photon dose region, a different behavior is observed. Further experimental and theoretical investigations are required to explain the temperature and excitation photon dose dependent PPC relaxation behavior in percolation and hopping transport regimes quantitatively.

At thermally activated region, the decay time constant $\tau$, can be expressed as

$$\tau = \tau_0 \exp(\frac{E_{\text{rec}}}{kT}),$$

(2)

where $E_{\text{rec}}$ is the recombination barrier height, $k$ is the Boltzmann constant. the potential barrier, $E_{\text{rec}}$, obtained from the high temperature region shown in Fig. 4 is 6.6 meV. This value indicates a small degree of potential fluctuations of the CdS$_{0.5}$Se$_{0.5}$ sample. We believe that this is the first experimental observation of such a small recombination barrier that leads to the PPC effect.

The amplitude of the fluctuating potentials in the conduction band, or equivalently, the recombination barrier height in different samples $E_{\text{rec}}$, is uniquely determined by the compositional fluctuations in the samples. On the
other hand, the transition temperature $T_c$ observed in PPC mode for different samples is also correlated to the compositional fluctuations in the sample. Therefore, we can deduce the value of $E_{\text{rec}}$ from the measured value of $T_c$. Since the growth of the samples is a random process, the composition should be fluctuated around the mean composition value $x_0$. The probability of lattice sites with composition $x$ thus follows a Gaussian distribution and can be written as

$$P(x) = P_0 \exp\left[-\frac{(x-x_0)^2}{2\sigma_x^2}\right],$$

where $P_0$ is determined by normalization condition $\int P(x)dx = 1$ and $\sigma_x$ is the compositional fluctuation parameter. In general, the energy gap of II-VI semiconductor alloys $A_xB_{1-x}C$, $E_g(x)$, depends linearly on the composition,

$$E_g(x) = E_g(x=0) + \alpha x.$$  

From these considerations, we have established the correlation between $T_c$ and $\sigma_x$. For CdS$_x$Se$_{1-x}$, $E_g(x=0)=1.84$ eV and $E_g(x=1)=2.58$ eV, and so we have $\alpha=740$ meV. The average recombination barrier height, $E_{\text{rec}}$, for different samples can be obtained from the following approximation,

$$\langle E_{\text{rec}} \rangle = E_g(x_0+\sqrt{2}\sigma_x) - E_g(x_0-\sqrt{2}\sigma_x) = 2\sqrt{2}\alpha \sigma_x.$$  

For CdS$_{0.5}$Se$_{0.5}$, the observed $T_c$ is 15 K, and from which we deduced a value of $\sigma_x$ of about 0.0035. Based on these values, we calculate $E_{\text{rec}}$ from Eq. (5) to be 7.3 meV, which is in reasonable agreement with the result obtained from the plot.
of $\ln r$ vs $1/T$ shown in Fig. 4. In fact, the recombination barrier height, $E_{\text{rec}}$, also depends on the stored charge carrier concentration because it is measured from the quasi-Fermi levels. These results further support our interpretation that PPC in II-VI semiconductor alloys is caused by conduction of charge carriers stored in random-local potential wells induced by compositional fluctuations.

It is also well known that the properties of photo-generated electron-hole pairs (or excitons) is strongly influenced by compositional fluctuations. In semiconductor alloys, excitons exhibit an important feature, i.e. the exciton localization in the random potential wells induced by compositional fluctuations. Recently, by studying the time resolved photoluminescence of exciton transition in CdSe$_{0.5}$S$_{0.5}$, we found the Mott-Anderson type of localization just below the mobility edge for excitons from their lifetime measurements, which is consistent with the characteristics exhibited in PPC mode. Fig. 6 shows the low temperature (8.4 K) photoluminescence of localized exciton transition line in CdS$_{0.5}$Se$_{0.5}$. Two peaks at 2.075 eV and 2.041 eV are ascribed, respectively, to the radiative recombination of localized exciton and its one-phonon replica. The measured full width at half maximum (FWHM) of the localized exciton line is about 11.3 meV compared with about 0.2 meV in good crystal of CdS or CdSe. The linewidth broadening is predominantly caused by compositional fluctuations. Because the linewidth of the exciton transition is caused by energy fluctuations in both the conduction and the valence bands, we can assume that the energy fluctuations for the electrons of the excitons in the conduction band is about half of that 11.3 meV. Therefore, the exciton transition linewidth measurement gives a value for energy fluctuations in the conduction band to be 5.7 meV, which is smaller than the value of $E_{\text{rec}}$ obtained from the PPC measurements. This is what we expected. For localized excitons, their electrons cannot distribute in those sites with
energies as high as the potential maximum (see Fig. 1 of Ref. 22). Thus half of
the FWHM of the localized exciton transition line should be smaller than $E_{\text{rec}}$. These results further explore the alloy disorder effect and again support our interpretation for PPC in II-VI semiconductor alloys.

The behavior of decay time constant as a function of temperature shown in
Fig. 4 seems similar to that of a same plot for $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$. However, we believe
that different PPC mechanism are involved in II-VI and III-V semiconductor
alloys. For $\text{Al}_x\text{Ga}_{1-x}\text{As}$, the capture barrier obtained from the Arrhenius plots has
a smallest value on the order of 200 meV at $x=0.3^{27}$ Furthermore, the PPC decay
behavior at low temperatures in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ can be accounted for by the multiphonon
tunneling model for DX centers of lattice relaxation, although it did not
exclude the possibility of that the decay is due to the wavefunction overlap
between the conduction electrons with the DX centers in k-space. In contrary,
the recombination barrier height $E_{\text{rec}}$ obtained from Fig. 4 is only 6.6 meV, which
implies that the PPC in $\text{CdS}_{0.5}\text{Se}_{0.5}$ is not likely caused by defect centers such
as DXs. Thus we believe that the weakly temperature dependent behavior of $\tau$ at
low temperature region for $\text{CdS}_{0.5}\text{Se}_{0.5}$ is caused by wavefunction overlap between
randomly distributed electrons and holes in real space.

IV. CONCLUSIONS

Charge storage and PPC phenomena in a $\text{CdS}_{0.5}\text{Se}_{0.5}$ semiconductor alloy have
been studied. The observed behavior of the PPC decay time constant as a function
of temperature shows that the decay of the stored charge carriers is dominated
by thermal activation at temperatures $T > 20$ K for $\text{CdS}_{0.5}\text{Se}_{0.5}$; the decay at low
temperatures is caused by wavefunction overlap between the randomly distributed
stored electrons and holes in real space. The recombination barrier height
obtained from the PPC decay time measurements is consistent with the results obtained from the PPC transition temperature and the exciton transition linewidth measurements. These experimental results further support our recent model that the random local potential fluctuations (RLPF) induced by the compositional fluctuations are responsible for PPC in II-VI semiconductor alloys.

Acknowledgements

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REFERENCES

+. Present and permanent address: Department of Physics, Hua Chiao University, Fujin, P. R. China.

*. To whom all the correspondence should be addressed.

Figure Captions:

Fig. 1. Normalized PPC decay curve of CdS$_{0.5}$Se$_{0.5}$ at two representative temperatures, T=8.6 K and T=40 K, after 500 seconds of light illumination. The dark current has been subtracted out. The excitation light intensity used is on the order of $10^{13}$ photons/cm$^2$·s.

Fig. 2. Plot of ln[lnPPC(t)] as a function of ln(t) for two selective temperatures, T=8.6 K and T=40 K. Approximated linear behavior indicates that the PPC decays according to the stretched-exponential function, $I_{PPC}(t) = I_{PPC}(0) \exp[-(t/t)^\beta]$.

Fig. 3. Plot of the PPC decay-time constant $\tau$ as a function of temperature for CdS$_{0.5}$Se$_{0.5}$. Experimental conditions are the same as those in Fig.1.

Fig. 4. Semi-logarithmic plot of decay-time constant as a function of $1/T$ for CdS$_{0.5}$Se$_{0.5}$.

Fig. 5. $I_{PPC}$ (normalized) vs decay time $t$ for different illumination times.

Fig. 6. The low temperature (T=8.4 K) exciton photoluminescence of a CdS$_{0.5}$Se$_{0.5}$ semiconductor alloy. The excitation energy was 2.125 eV with an average power density of about 100 mW/cm$^2$.\textsuperscript{2}
CdS$_{0.5}$Se$_{0.5}$

$T_T=8.6K$

$T=45K$

$\tilde{\gamma}$ vs. $t$ (s)

$\tilde{\gamma}$ (Normalized)
Fig. 2

\[ \ln(\ln(\langle t=0 \rangle_{PP}(t))) \]

\[ \text{CdS}_{0.5}\text{Se}_{0.5} \]

* T=8.6 K

o T=45 K
Cd$_{0.5}$Se$_{0.5}$

$T=8.4 \text{ K}$

Metal-free Phthalocyanine (H2Pc) and Copper Phthalocyanine (CuPc) single crystals were grown by vacuum sublimation. The wavelength dependency and the temperature dependency of photocurrent (Iph) of these single crystals were investigated. The spectra of Iph vs. \( \lambda \) reveal maxima at 1.14, 1.56, and 2.46 \( \text{eV} \) for H2Pc and at 1.14, 1.77, 2.04, and 2.31 \( \text{eV} \) for CuPc. The absorption spectra of H2Pc and of CuPc in \( H_2S_4 \) solution correspond to the respective Iph spectra. The temperature dependency of Iph and that of dark current (Id) are of the form \( I = I_0 \exp(-E_a/kT) + C \). The thermal activation energy of the Iph for H2Pc at all three maxima is 0.3 \( \text{eV} \), while for the Id it is 0.5 \( \text{eV} \). These observations are interpreted to indicate that the existence of three valence bands from which electrons are excited to a single trap level lying 0.2 \( \text{eV} \) below the conduction band. Conduction, then, is by free holes. The Id activation indicates the presence of a fourth valence band lying 0.2 \( \text{eV} \) below the trap level.

SESSION E16: DEFECTS IN III-IV COMPOUNDS

Tuesday morning, 19 March 1991
Room 230 at 8:00
G. Neumark, presiding

8:00

Dynamics of Persistent Photoconductivity (PPC) in AlGaAs. A. J. Lin, The Univ. of Northern Iowa; A. Dissanayake, G. Brown, and H. X. Jiang, Kansas State University. Relaxation of Persistent Photoconductivity (PPC) in AlGaAs has been investigated. The relaxation time constant, \( \tau \), as a function of the conduction electron concentration, \( n_e \), is expressed in the form \( \tau = T \alpha n_e \) at 77 K. Two distinct regions corresponding to degenerate and nondegenerate regimes have been observed for the first time. In the nondegenerate regime, \( \tau \) decreases with an increase of \( n_e \) and the relaxation of PPC is predominantly caused by activation capture of electrons at DX centers. In the degenerate regime, \( \tau \) increases with an increase of \( n_e \) and the relaxation of PPC is predominantly caused by tunneling capture via multiphonon emission. Excitation photon dose required for the transition from nondegenerate to degenerate regime is observed to occur increases with an increase of temperature. Behavior of PPC observed in AlGaAs is compared to that in InGaAsP [2].

* Supported by a AFOSR research grant.


8:12

Magneto-optical properties of the DX center in AlGaAs:Te. E. R. Peale, H. J. Sun and G. D. Watkins, Lehigh University.* and Y. Mochizuki, NEC Corpor. Magneto-optical absorption spectra of 0.4 mm thick, single-crystal AlGaAs:Te give evidence for two bleachable absorptions, one of which is identified as the DX center. The bleach-state absorption coefficient and magnetic circular dichroism (MCD), measured from 0.66 to 2.2 \( \mu \text{m} \) at 1.7 K, are adequately described by the Drude free-electron model, in terms of which a value for the electron effective mass is obtained. Cooling the sample in darkness leads to transmission transients, from which ground-state absorption coefficients and optical-conversion cross sections for the bleachable absorptions are derived. The conversion threshold is 0.6 eV for the DX and 1.5 eV for the second bleach, and the recovery barrier is significantly different for the two. The MCD at the beginning of each transient is identified with the ground state of each absorber, and temperature dependence reveals that the bulk of the initial MCD has a non-paramagnetic origin. We conclude that the paramagnetic MCD from the DX ground state is very small, being less than 0.004% of its absorption coefficient.

*Supported by National Science Foundation Grant No. DMR-89-02572

8:24

Uniaxial Stress Dependence of the Properties of the DX Center in Si-Doped AlGaAs:Te. Zhiguo Wang, K. Chung, T. Miller, G. Brown, M. J. Nathan, University of Minnesota. We have used LDT measurements as a function of externally applied uniaxial stress to study the properties of the DX center in AlGaAs:Te. No splitting of the peaks from the DX center has been observed up to 15 kbar for uniaxial stresses along [100] and [110] directions. The thermal activation energy, \( E_a \), decreases monotonically with stress along both directions. The capture energy, \( E_c \), increases with stress along these two directions after the crossover between the \( \Gamma \) and \( L \) bands for [111] stress. The rates of change of \( E_a \) and \( E_c \) with stress along [100] and [111] directions are about same. The thermal activation energy, \( E_a \), is given by \( E_a = (E_p + E_c)/2 \). A reasonable agreement between the experimental results and the negative-U model is found.

* Supported by NSF grant NSF/ECSE-8803928


8:36

Uniaxial Stress Dependence of DLTS Spectra of DX Centers in GaAs. K. P. Li and P. Y. Yu, U.C. Berkeley; R. Bauer, MPB—The effects of uniaxial stress on DX centers in GaAs have been studied in DLTS by applying stress along the [100], [110] and [111] directions. No splitting nor broadening of the DLTS peaks for the three stress directions was observed up to 10 kbars. However, the peaks were observed to shift very nonlinearly with stress. The stress dependence being different for the three stress directions. Furthermore, the intensity of the peaks decreased with stress, very strongly only for stress along the [100] direction. The results will be compared with predictions of both large relaxation and small relaxation models of the DX center.

8:48

Local Vibration Mode Spectroscopy of DX Centers in Si-Doped GaAs Under Hydrostatic Pressure. J. A. Wolk and E. Hailer, Lawrence Berkeley Laboratory and Univ. of Calif. at Berkeley. M. B. Kruger, R. Jeantoz, and J. N. Heyman, Univ. of Calif. at Berkeley, W. W. Walukiewicz, Lawrence Berkeley Laboratory. We report the observation of a new local vibrational mode (LVM) in hydrostatically stressed, Si-doped GaAs. The corresponding infrared peak is distinct from the SiO2 shallow donor LVM peak, which is the only other LVM peak observed in our samples, and is assigned to the DX center. The shift of LVM frequency with pressure has been measured for both the SiO2 shallow donor and the DX center. These shifts are linear over the pressure range 0-40 kbar and are given by \( d\nu_{\text{LVM}}/dp = 0.66 \pm 0.03 \text{ cm}^{-1}/\text{kbar} \) and \( d\nu_{\text{SiO2}}/dp = 0.61 \pm 0.04 \text{ cm}^{-1}/\text{kbar} \). The relative intensities of the Si DX LVM and the SiO2 shallow donor LVM and photoconductive behavior of the sample are consistent with the appearance of a defect which binds two electrons as it undergoes a lattice relaxation at approximately 23 kbar. This is the first experiment in which Fourier transform LVM spectroscopy of semiconductors has been performed using samples mounted in a diamond anvil cell.

* Work supported by US DOE under Contract DE-AC03-76SF00098

9:00

Observation of a Tetrahedral Spin = 5/2 Defect in InP:Sn by ODMR and ODDENDOR. H. J. Sun, R. E. Peale, and G. D. Watkins, Lehigh University. An optically-detected magnetic resonance (ODMR) peak is found in as-grown Sn-doped InP while monitoring the magnetic circular dichroism at 1.38 eV. The

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parameters. The energy gap varies linearly with composition $x$ in the range studied. The temperature variation of the energy gap can be well fitted by the empirical Varshni relation. The determined non-linear components of this dependence do not vary significantly with composition. At low temperatures, the broadening is primarily produced by random distribution of Fe and Cd atoms. For $T > 100 K$, the broadening parameter increases with temperature due to the scattering of excitons by phonons.

1 Y. P. Varshni, Physica 34, 149 (1967).

Tuesday Morning

9.12

E15 7 Relaxation of Stored Charge Carriers in II-VI Semiconductor Alloys. A. Disanayake, G. Brown, J. Y. Lin and H X. Jiang, Kansas State Univ.—Relaxation of stored charge carriers in persistent photoconductivity (PPC) mode in Cd$_{1-x}$Se$_x$, $S_{1-x}$, and Zn$_{0}$Cd$_x$Se II-VI semiconductor alloys are investigated. The kinetics of PPC build-up behavior at different conditions are studied. The decay of PPC follows the stretched-exponential function. The experimental results further support our recent interpretation that PPC in II-VI semiconductor alloys is caused by random local potential fluctuations (RLPF) induced by compositional fluctuations. Reorganization barrier heights between the potential minima (locations of allowed modes) and maxima (locations of asper holes) of the random fluctuating potentials have been determined for Cd$_{0.365}$Se$_{0.635}$ and Zn$_{0.365}$Cd$_{0.635}$Se. Low temperature exciton transition linewidth which is predominantly caused by compositional fluctuations has been measured and the results are compared with the PPC data.

* Supported by a AFOSR research grant.


9.12

E15 8 Dynamics of Exciton Localization In a CdSe$_{0.5}$S$_{0.5}$ Semiconductor Alloy. H. X. Jiang, L Q. Zu and J Y. Lin, Kansas State Univ.—Dynamic processes of exciton localization in a CdSe$_{0.5}$S$_{0.5}$ semiconductor alloy have been studied by time-resolved photoluminescence. We found experimentally that the exciton transfer rate departs a power-law behavior near the mobility edge $E_m$. This is caused by the fact that near $E_m$, the exciton localization length $\xi$ diverges according to the power law $\xi(E) \sim (E_m-E)^{-1}$. Such a behavior is analogous to the classical behavior of the carriers in the Anderson localization model with $\xi$ being 2/3. Experimentally measured value of $s$ is about 0.7, which demonstrated that the Anderson model for charge carriers can well describe the system of localized excitons in semiconductor alloys.

* Present address: Dept. of Physics, The Univ. of Northern Iowa, Cedar Falls, Iowa 50614.


9.16

E15 9 Raman Study of the diluted magnetic semiconductors Zn$_{0.9}$Co$_{0.1}$Se and Zn$_{1-x}$Fe$_x$Se. C L. Mak, and R. Sooryakumar, The Ohio State University, Columbus, O H. B. T. Jonker, and G. A. Prins, Naval Research Laboratory, Washington, D.C. — We report on a Raman study of the diluted magnetic semiconductors Zn$_{0.9}$Co$_{0.1}$Se and Zn$_{1-x}$Fe$_x$Se. The concentration $x$ varies between 0.76 and 9.4% for Co and between 2.7 and 22% for the Fe dopants. The single crystalline films were grown by MBE to thickness of about 1 $\mu$m with the Co and Fe being incorporated in a random, substitutional manner. Both alloys possess a homogeneous crystal phase having the zinc-blende structure.

The observed dependence of the first order phonon spectrum on $x$ follows the "one-mode" behavior and can be described by the modified random element isodispacement model (MREI). Low-frequency disorder-induced one-phonon density-of-state features are also evident in the Raman spectra and will be discussed.

Work at Ohio State University is supported by the NSF under Grant DMR 90 01647 and at NRL by the Office of Naval Research.

9.48

E15 10 Multi-Mode Behavior in Cd$_{1-x}$Zn$_x$Mn$_y$Te: A Raman Scattering Study. *Eunsook Oh, R. G. Alonso, I. Miodkowski, A K Ramdas, Purdue U — We report Raman scattering from optical phonons in the ternary Cd$_{1-x}$Zn$_x$Te and in the quaternary Cd$_{1-x}$Zn$_x$Mn$_y$Te grown by the Bridgman method. Variation of the frequency of the zone-center optical phonons as a function of composition $x$ in Cd$_{1-x}$Zn$_x$Te shows a "two mode" behavior. We observe three distinct LO phonons in Cd$_{1-x}$Zn$_x$Te due to the additional impurity mode associated with manganese. The extension of the modified random-element isodispacement model to quaternary compounds explains the frequency of the optical phonons as a function of $x$ and $y$. We also report the Raman electron paramagnetic resonance of Mn$^{2+}$ and the pronounced magnetic field dependence of photoluminescence in these quaternary diluted magnetic semiconductors.

*Supported by NSF (DMR 88-17106).

10:00

E15 11 A New Type of Spectroscopy for Impurity or Defect Levels of Narrow Gap Semiconductors: Application to n-HgCdTe. D. G. SETZER, J. R. LOWNRY, National Institute of Standards and Technology, G. L. LITTLER, T. T. YOON, M. R. LIDOEK, University of North Texas. — We report on a new type of spectroscopy for impurity or defect levels in the energy gap of narrow gap semiconductors based on near band-gap photon energies and high-magnetic fields. This spectroscopy is done under the conditions of intense laser photoexcitation and is associated with the relaxation processes of hot electrons by impact ionization of valence electrons into impurity or defect levels. Hot electrons were photoexcited into the conduction band by sequential absorption of intense CO$_2$ laser radiation. We observe wavelength-independent structure in the magnetic-field dependence of the photoconductive response in samples of Hg$_{1-\delta}$Cd$_{\delta}$Te with $\delta=0.22$ and 0.24. This structure arises from resonances that occur when the energy difference between Landau level of hot electrons and a valence electron Landau level is equal to the energy required to impact ionize valence electrons into impurity or defect levels in the gap. For the sample with $\delta=0.22$ and an energy gap of 95 meV, three levels are found at 15, 45, and 59 meV above the valence band. A level at 61 meV is found for the sample with $\delta=0.24$ and a gap of 122 meV.

10:12

E15 12 Resonance Raman Study of Single Crystal PdO. J. R. McBRIIDE and W. H. WEBER, Ford Motor Company. — Vapor transport techniques were used to grow mm-size single crystals of PdO. The allowed Raman modes, $B_{1g}$ at 650 cm$^{-1}$ and $E_{2g}$ at 445 cm$^{-1}$, were observed by Lowery studies on oriented crystals. The excitation spectra of both modes exhibit a strong resonance near 2.5 eV. This resonance appears to be associated with an O(2p)-Pd(4d) charge transfer excitation, which also produces a peak at $\sim 2.5$ eV in the Im($e$) spectrum. In addition to the allowed modes, numerous first order forbidden Raman lines also appear in the spectra. These features cannot be due to impurities, since spectra from oxidized Pd foils and sputtered films are virtually identical to those from the single crystals. Films of Pd$_8$O$_{18}$ were grown to help identify some of the second order features. Tentative assignments for these features and correlations of the resonance data with preliminary band structure calculations will also be discussed.
