RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 56, NUMBER 8 15 AUGUST 1997-II

Observation of metastable deep acceptor states in $AgGaS_2$ from donor-acceptor pair-emission spectra

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(Received 2 June 1997)

We report the discovery of photoinduced quenching of donor-acceptor pair-emission peaks in $AgGaS_2$ crystals at liquid-He temperatures. From previous high-pressure studies [Phys. Rev. B **55**, 9642 (1997)] these peaks have been attributed to radiative recombination between shallow donors and *deep acceptors*. We explain our results by the optical capture of the deep neutral acceptors into optically inactive metastable states. At low temperatures the capture time is found to be $\leqslant 10^2$ s while the emission time is of the order of 10^3 s. The thermal capture barrier height of the metastable states is determined to be about 2 meV. [S0163-1829(97)52932-8]

INTRODUCTION

Within the last two decades, a number of deep centers in semiconductors have been found to exhibit the phenomenon of metastability.[1] The metastable states that have been studied so far in GaAs and related alloys are all deep donors, such as the DX (Ref. 2) and the $EL2$ (Ref. 3) centers. On the other hand, it has been proposed by Park and Chadi[4] that deep acceptors (labeled as AX centers) with properties similar to the DX centers may occur in large band gap II-VI semiconductors and, furthermore, they may contribute to the difficulty in achieving p-type conductivity in semiconductors such as ZnSe. There is much similarity between the chalcopyrite family of semiconductors and those with the zinc blende structure.[5] For example, the large band gap chalcopyrite semiconductor $AgGaS_2$ can be considered to be the analog of the II-VI zinc blende semiconductor $Cd_{0.5}Zn_{0.5}S$. Similar to the large band gap II-VI materials it tends to be insulating or to exhibit very poor p-type conduction as a result of deep acceptors.[9] In this paper we report the observation of metastable deep acceptor states in $AgGaS_2$ via quenching of its donor-acceptor pair-emission spectra.

EXPERIMENTAL DETAILS

The $AgGaS_2$ bulk single crystals used in this experiment were grown by the horizontal Bridgman method using a tubular two-zone furnace. Most of the crystals are not intentionally doped. Only one sample has been doped with Cd. Details of the crystal-growth process have been described before[6] and will not be repeated here. The as-grown crystals, even when undoped, typically show variations in color from one end to the other because of the different concentrations of defects in them. We note that the phenomenon reported here is most prominent in crystals which are lighter in color. The samples were cooled to low temperature in a variable-temperature optical dewar and the photoluminescence excited by the 442.0 nm line of an He-Cd laser. The optical setup for detecting the emission has been described elsewhere.[6] To minimize heating effects the size of the focal spot on the sample is typically about 450 μm.

EXPERIMENTAL RESULTS

The photoluminescence (PL) spectra of $AgGaS_2$ bulk single crystals have been studied by many groups already (see Ref. 6 and references therein). Typically, one finds that the PL spectrum is dominated by a strong ‘‘green emission peak’’ (labeled as B in Ref. 6) below the band gap and centered around 496.8 nm (or photon energy of 2.50 eV). This peak has usually been identified with donor-acceptor pair recombination. In some samples a weak structure may also be observed at 2.70 eV and is attributed to emission from free excitons (labeled as EX in Ref. 6). In studying some $AgGaS_2$ samples which are very light in color and presumably very much purer than crystals previously studied, we found that their PL intensity decreases continuously with time under constant exposure to the laser light. As an example, we show in Fig. 1 two PL spectra from the sample labeled as AGS#510 (the labeling of samples in this paper is identical to our previous publication[6] for comparison purposes) obtained at 3.4 K when (a) the sample was exposed to the He-Cd laser light for the first time and (b) after more than 10 min of exposure. Figure 2(a) shows the time dependence of the peaks labeled B and EX in Fig. 1(a) during constant laser excitation. While the intensity of peak EX decreases by less than a factor of 2 the peak B decreases by *a factor of more than 50* in about 10 min. Because of the fast decay in peak B the spectrum in Fig. 1(a) has to be obtained in small ‘‘increments.’’ The sample is exposed to laser light for about 10 s to obtain one segment of the spectrum. A scan rate faster than normal is used while the slit width is also increased. It is then allowed to recover in the dark before the next segment is measured. To average out the change in the intensity during the laser exposure, each segment is measured twice. The first time, the spectrometer is scanned from

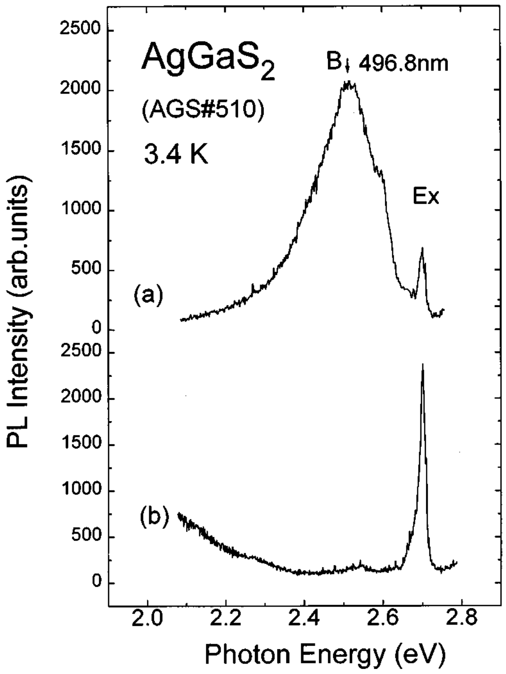

FIG. 1. Photoluminescence spectra of AgGaS$_2$ sample AGS#510 obtained at liquid-He temperature. a: obtained immediately after the sample was exposed to the excitation light, and b: after the sample was exposed to the laser light for about 15 min.

high photon energy to low photon energy, while in the second run the spectrometer scanning direction is reversed. The average of these two spectra is used to reconstruct Fig. 1(a).

The decay of the peak B with time is essentially exponential and follows the simple expression

$$I(t)=I(0)e^{-t/\tau}+I(\infty), \tag{1}$$

where $I(0)$ is the initial intensity, τ is the decay time, and $I(\infty)$ is the time-independent background. As shown in Fig. 2(b) the sample "recovered" in about 15 min when the laser was blocked and the sample was left in the dark.

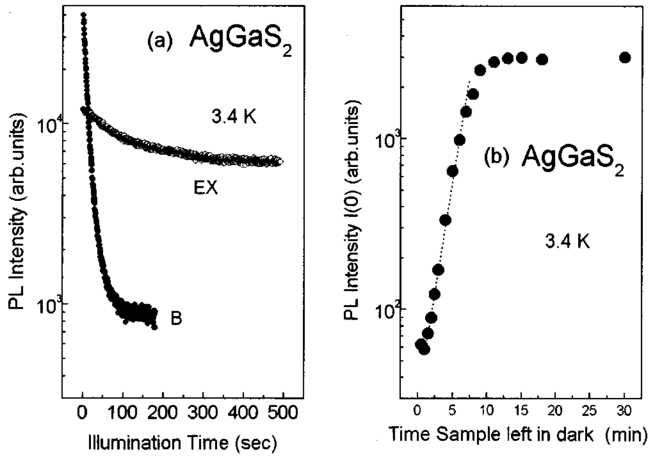

FIG. 2. (a) The time-dependent decay of the intensity of the green emission peak B in sample AGS#510 compared with that of the excitonic peak EX. (b) The "recovery" of the initial peak intensity of peak B after the sample was left in the dark for different time durations.

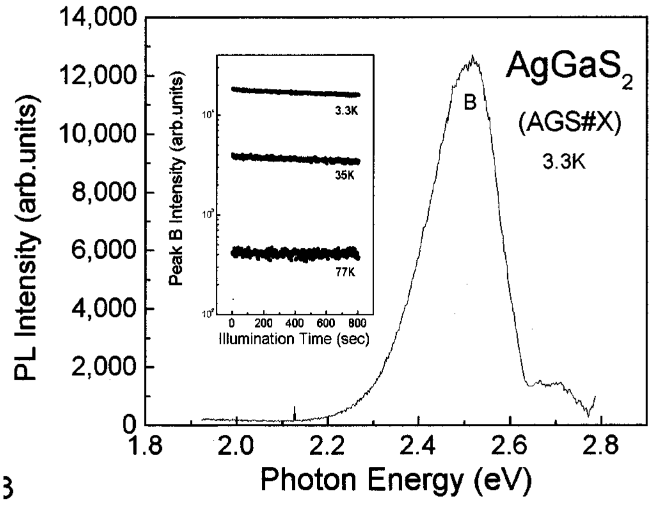

FIG. 3. The emission spectrum of another AgGaS$_2$ sample (AGS#X) which does not exhibit any time dependence in its photoluminescence. The inset shows the intensity of peak B as a function of time at several different temperatures. Note that while the intensity of peak B decreases rapidly with an increase in temperature, there is no change in its intensity with prolonged exposure to the laser showing that the laser irradiation is not producing any heating effect.

It is reasonable to question whether the observed time-dependent effects are caused by laser-induced heating of the sample. In our previous studies (see Ref. 6) we have found that as the temperature (T) is increased the intensity of peak B decreases with an activation energy of about 27 meV (Ref. 6) associated with the thermal ionization of shallow donors. In contrast to peak B, the intensity of the free exciton emission peak at 2.70 eV increases with T.[10] Thus, the time-dependent behavior of peak B may be explained by laser-induced heating. However, the time dependence of peak EX may not. To demonstrate that this is not a heating effect we show in Fig. 3 the PL spectrum of another AgGaS$_2$ sample (AGS#X) measured under similar conditions. The inset of this figure shows the time dependence of peak B for three different temperatures. While the PL intensity of this sample has the same strong activated temperature dependence, it does not show any time dependence. These results have convinced us that the observed effect in sample AGS#510 is not simply due to laser-induced heating.

While we have found other AgGaS$_2$ samples which exhibit time-dependent PL decay, we shall concentrate on sample AGS#510 in the rest of this paper. Its decay time τ is found to depend strongly both on the excitation laser power P (see Fig. 4 and its inset) and on T (shown in Fig. 5). The dependence of τ on power appears to be inversely proportional to P, while the dependence on T seems to be activated. We have fit the temperature dependence of τ with the following expression:

$$\tau(T)=\frac{\tau_0}{(1+\alpha e^{-E_a/kT})}, \tag{2}$$

where the three parameters τ_0, α, and E_a are treated as adjustable parameters and k is the Boltzmann constant. The

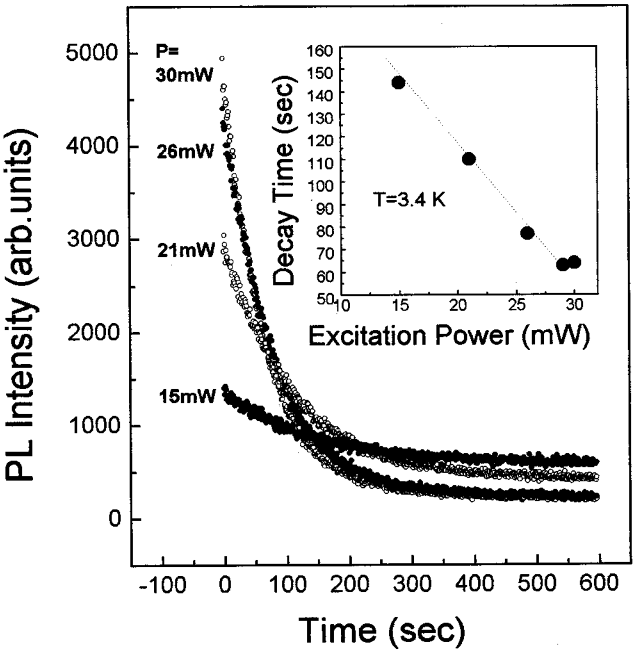

FIG. 4. The time-dependent decay of the peak intensity of the green emission peak at 496.8 nm [labeled B in Fig. 1(a)] in sample AGS#510 at 3.4 K for several different laser powers. The dependence of the decay time constant on the excitation laser power is shown in the inset.

solid curve in Fig. 5 is obtained with τ_0 (the decay time at $T=0$) $=57.4$ s; $\alpha=1.27$, and the activation energy E_a ~ 2 meV.

DISCUSSIONS

As mentioned earlier, the peak B in $AgGaS_2$ is usually identified with recombination of donor and acceptor pairs. In particular, the dependence of its peak intensity on temperature suggests an activation energy of ~ 27 meV which agrees with the shallow donor binding energy.[6] Its pressure dependence was found to be unusual in that it is *larger* than that of the band gap and the exciton in $AgGaS_2$.[7] Based on these results the acceptors involved in peak B have been identified as *deep acceptors*.[8] Thus it is reasonable to attribute the photoquenching of peak B to the *excitation of the deep acceptors into some metastable states.*

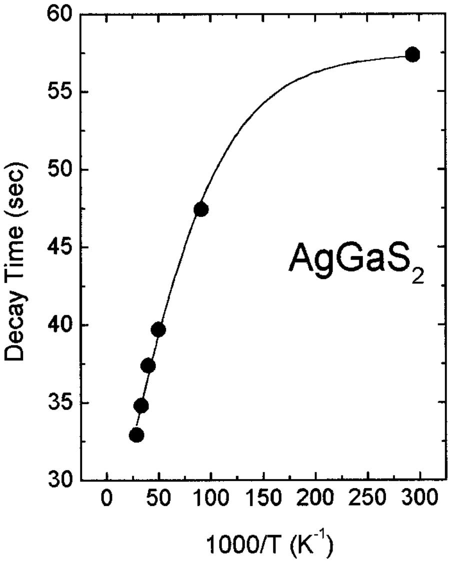

FIG. 5. The temperature dependence of the decay time constant on temperature exhibited in an Arrhenius plot. The excitation laser power is maintained constant at ~ 30 m W. The solid curve is a fit of the experimental points with Eq. (2) by adjusting the parameters: τ_0, α, and E_a as discussed in the text.

Since our $AgGaS_2$ samples are highly compensated we assume that there are no neutral acceptors at low temperature before laser excitation. The laser excites free electrons and holes which are trapped, respectively, on the donors and acceptors before recombination. This picture of bimolecular recombination is consistent with the *quadratic* dependence of the initial intensity I_0 on P that we have deduced from spectra similar to those shown in Fig. 4. Under steady-state illumination, these neutral acceptors can also be optically excited into higher-energy states. We propose that these excited holes can then be captured into optically inactive metastable states. The lifetime of these metastable states is of the order of 10^3 s as estimated from the ''recovery time'' in Fig. 2(b). They are presumably not optically active since no new emission peaks appear. As a result, the intensity of the donor-acceptor pair emission decreases steadily with time as the neutral acceptors are converted into these ''dark'' states. The observed almost linear dependence of the decay time on the laser power P is consistent with this optical excitation mechanism.

The capture time into the metastable state can be deduced from the decay time of peak B. Note that the measured decay time represents the lifetime of the neutral acceptor population and is therefore inversely proportional to the laser power. The capture time for one acceptor is given by the decay time in the limit of $P \rightarrow 0$. From the inset in Fig. 4 we find a capture time of ~ 230 s at $T=3.4$ K. The temperature dependence of the decay time shown in Fig. 5 indicates that the neutral acceptors can also be thermally excited into the metastable state. The activation energy as determined by fitting the experimental points in Fig. 5 is quite small, only ~ 2 meV. At low temperatures, optical capture can be much more efficient than thermal capture. However, at $T>50$ K the reverse is true.

While we cannot make a definitive identification of the metastable acceptor state, we note its following properties. Since no new emission peaks appear as a result of the disappearance of peak B, this suggests that the metastable state may no longer contain a hole as in the neutral acceptor. The absence of any sign of enhancement in the free exciton emission suggests that there is no increase in the population of free holes, i.e., if the photons ionize the neutral acceptors, then the photoexcited holes do not remain free for very long. One possibility (although not the only one) is that these free holes are trapped on neutral acceptors to form doubly charged A^+ states. While such A^+ states have been proposed to exist in large band gap II-VI semiconductors,[4] there are not enough results to either prove or disprove their existence in the chalcopyrite compounds. We note that photoexcited states of DX centers have been detected and studied in $Al_xGa_{1-x}As$ alloys,[11] but the properties of metastable acceptors in the chalcopyrite compounds are quite different from those of the *DX* centers. However, the similarity between the two families of materials suggest that photoinduced quenching of deep acceptor related emission may also exist in large band gap II-VI semiconductors.

CONCLUSIONS

We have observed photoinduced quenching of a shallow donor-to-deep acceptor transition in $AgGaS_2$ crystals. We have explained this behavior as a result of excitation of the deep acceptors into optically inactive metastable states with lifetimes of about 10^3 s. The thermal barrier for capture into these metastable states has been deduced to be around 2 meV.

ACKNOWLEDGMENTS

The part of this work performed in Korea was supported by the Chung-Ang University Special Research Grants in 1997. The work at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. I.H.C. also acknowledges financial support, from the Korea Research Foundation (nondirected research fund).

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