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Pressure-induced deep donor level in the chalcopyrite semiconductor alloy $Ag_{0.25}Cu_{0.75}GaS_2$

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We report the appearance of a deep donor in the photoluminescence spectra of the chalcopyrite semiconductor alloy $Ag_{0.25}Cu_{0.75}GaS_2$ under hydrostatic pressures exceeding 5 GPa. The recombination peaks of this deep donor with acceptors exhibit either zero or a small negative pressure coefficient. Our results suggest the existence of a deep donor level which is resonant with the conduction band at ambient pressure.

Alloys of chalcopyrite semiconductors have recently received attention for their role in improving the efficiencies of $CuInSe_2$ solar cells.[1] However, the effect of alloying on defects in these materials is still largely unexplored.[2] One of the most interesting phenomena regarding deep defect centers discovered in the related zinc-blende-type semiconductors in recent years has been the conversion of shallow donors (such as Si) in GaAs to deep donors known as *DX* centers by the application of hydrostatic pressure or by alloying with AlAs.[3] In this paper we report the observation of a deep donor in the photoluminescence spectra of the alloy $Ag_{0.25}Cu_{0.75}GaS_2$ under hydrostatic pressure exceeding 5 GPa. Similar effect has not been observed in either $AgGaS_2$ nor in $CuGaS_2$.

We have grown a series of $Ag_xCu_{1-x}GaS_2$ alloys with $x = 0.25$, 0.5, and 0.75 using the horizontal Bridgman technique. These samples were not intentionally doped. The bulk single crystals were characterized by x-ray diffraction.[4] They were single phased and their crystallographic lattice parameters *a* and *c* were found to depend on the alloy similarly to what has been reported by Matsushita Endo, and Irie.[5] The samples, after cutting into slices, were lapped and polished with syston. High-pressure optical measurements were carried out in a gasketed diamond-anvil cell using a mixture of methanol/ethanol as the pressure medium. The pressure was determined using the ruby fluorescence technique. The entire high-pressure cell was cooled to about 50 K in a closed-cycle He refrigerator. The photoluminescence (PL) measurement was performed using the Ar ion laser as the excitation source. The PL signal was analyzed with a double spectrometer and detected with a photon counting system. Optical-absorption measurement was performed with a standard quartz-halogen lamp and spectrometer setup.

Unfortunately, the PL intensity in most of the $Ag_xCu_{1-x}GaS_2$ alloys is much weaker than those of $AgGaS_2$ and $CuGaS_2$. As a result we have been able to follow the pressure dependence of the emission peaks only in $Ag_{0.25}Cu_{0.75}GaS_2$. The ambient pressure PL spectra in our $Ag_xCu_{1-x}GaS_2$ samples will be presented elsewhere [4] and will not be reproduced here. Figure 1 shows the low-temperature PL spectra of $Ag_{0.25}Cu_{0.75}GaS_2$ at several different pressures. At $P < 5$ GPa they are rather similar to the PL spectrum of $CuGaS_2$ at ambient pressure in that there are only two prominent peaks which we have labeled as *B* and *C* in our previous publications.[6] The peak *B* has been identified as due to recombination of shallow donor-and-acceptor pairs based on its pressure dependence.[6] The peak *C* has been attributed to recombination of deep centers based on its position within the band gap.[6] We notice first that the intensities of both peaks *B* and *C* decrease strongly with *P* and become hardly detectable around 5 GPa. Then new structures appear in the same regions as the peaks *B* and *C* for $P > 5$ GPa. We have labeled the narrower peak which ap-

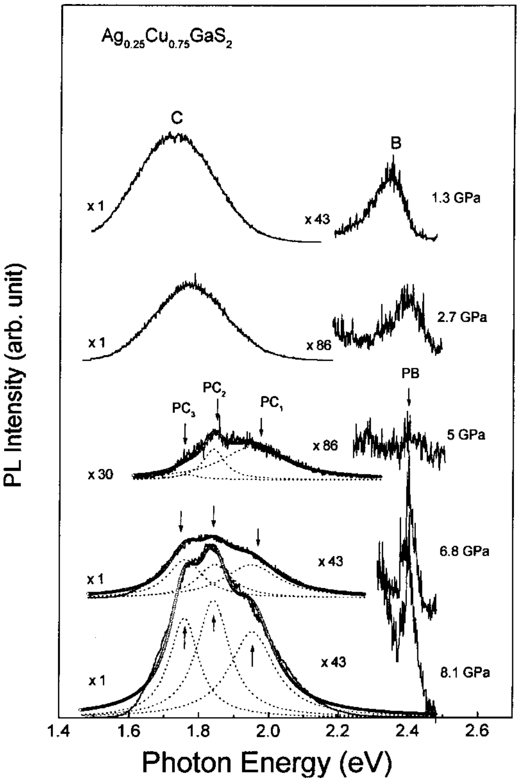

FIG. 1. The photoluminescence spectra of $Ag_{0.25}Cu_{0.75}GaS_2$ for several pressures. The broken curves represent deconvolution of the peak *C* under high pressure into three Gaussian peaks. The open circles represent the sum of the calculated peaks.

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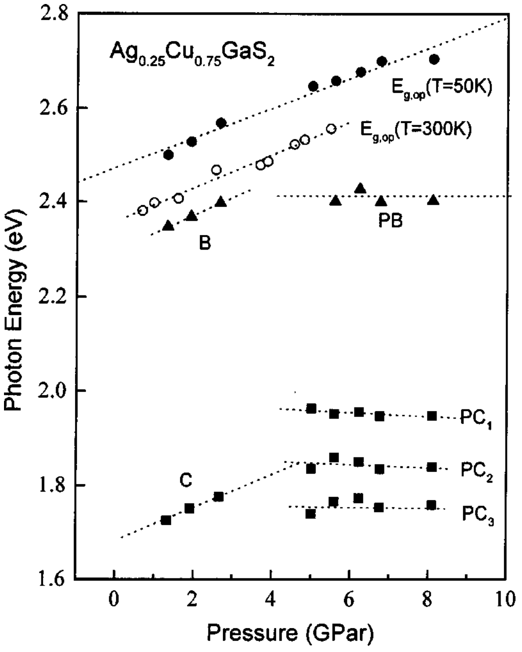

FIG. 2. The pressure dependence of the photoluminescence peak energies compared with that of the band gap $E_{g,\mathrm{op}}$ (measured via absorption) in $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$. The broken lines are fits of the data points to straight lines.

peared in place of peak B as PB. By deconvolution we can resolve the new structure which replaces peak C into three peaks (labeled as PC_1 to PC_3) shown as the broken curves in Fig. 1. In Fig. 2 the pressure dependence of these new peaks are compared with the pressure dependence of the band gap (closed or open circles) determined from the absorption spectra (labeled $E_{g,\mathrm{op}}$). From this plot it is quite obvious that the new peaks have completely different pressure dependence from the peaks B and C. From Fig. 2 we have determined the pressure coefficients of the PL peaks and band gap in $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$. These are compared with the published pressure coefficients of $\mathrm{AgGaS_2}$ and $\mathrm{CuGaS_2}$ (Ref. 6) in Table I. Although the peaks PC_i ($i=1-3$) show almost no pressure dependence in their peak energies, their intensities increase rapidly with pressure for $P>5$ GPa. This is shown more clearly in Fig. 3. We will now discuss separately our results for the two regions: $P<5$ GPa and $P>5$ GPa.

TABLE I. Pressure coefficient of band gap ($E_{g,\mathrm{op}}$), defect emission peaks B, PB, PC_1, PC_2, and PC_3 in $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$ compared with the chalcopyrite compounds $\mathrm{AgGaS_2}$ and $\mathrm{CuGaS_2}$. All units are in meV/GPa.

Peak	$\mathrm{AgGaS_2}$	$\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$	$\mathrm{CuGaS_2}$
$E_{g,\mathrm{op}}(<77\ \mathrm{K})$	37–40.5	33	42
B	58	38	67
C	41	31	24
PB		~ 0	
PC_1		-2	
PC_2		-4	
PC_3		-1	

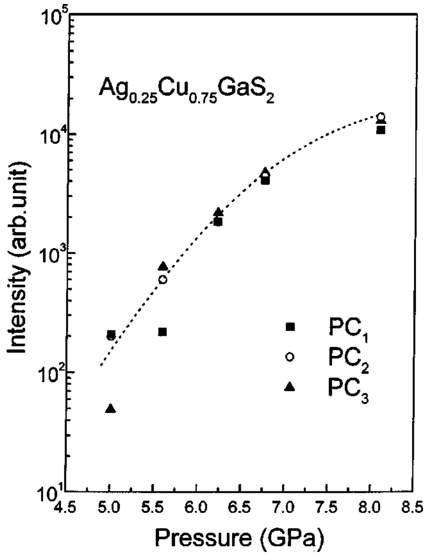

FIG. 3. The pressure dependence of the intensity of the peaks PC_1 to PC_3. The broken curve is for guidance of eyes only.

As we have pointed out earlier, the pressure dependence of the peaks B and C in $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$ is qualitatively rather similar to those of the corresponding peaks in $\mathrm{AgGaS_2}$ and $\mathrm{CuGaS_2}$.[6] The pressure coefficients $\alpha=dE/dP$ of peak B listed in Table I are all *larger* than that of the band gap in the same material while α for peak C is either almost the same as or smaller than that of the band gap. Perhaps the only noteworthy result for the low-pressure range is that α of the band gap in $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$ is *smaller* than that of either $\mathrm{AgGaS_2}$ or $\mathrm{CuGaS_2}$. This is to be contrasted with the alloy $\mathrm{CuIn_xGa_{1-x}Se_2}$ where α was found to vary linearly with the alloy concentration.[7] In the case of $\mathrm{CuIn_xGa_{1-x}Se_2}$ it was pointed out that the linear dependence of α on alloy concentration is an exception rather than the norm. In most chalcopyrite semiconductors α is dominated by the volume deformation potential term:[8]

$$\alpha \sim -(1/B)(\partial E_g/\partial \ln V), \tag{1}$$

where B is the bulk modulus and V is the volume. In most alloys one expects both $1/B$ and $(\partial E_g/\partial \ln V)$ to depend on the alloy concentration x. As a result α should have a nonlinear dependence on x. A nonlinear dependence of the band gap on x is often expressed in terms of a bowing parameter. In case of $\mathrm{Ag_xCu_{1-x}GaS_2}$ this bowing parameter is rather large.[4] In $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$ we have now demonstrated that a bowing parameter also exists for the band-gap pressure coefficient.

For $P \geqslant 5$ GPa the intensity of the peaks B and C has decreased to the point of being almost undetectable while the intensity of new peaks PB and PC_i increases with pressure (see Figs. 1 and 3). We note that the pressures for first-order structural phase transition have been found to be around 4.2 and 16.5 GPa, respectively, in $\mathrm{AgGaS_2}$[9,10] and $\mathrm{CuGaS_2}$.[9,11] However, the corresponding phase-transition pressure in $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$ is not known. Since we have observed no sign of any discontinuous change in the optical-absorption spectra nor in the band gap of $\mathrm{Ag_{0.25}Cu_{0.75}GaS_2}$ up to 8 GPa we suggested that all these changes in the PL are *not* the result of a structural phase transition. Instead, we explain this change in intensity by *the pressure-induced crossing of two* *energy levels* and the subsequent transfer of carriers from the higher energy level to the lower energy one. To determine the pressure at which this levels crossing occurs we can extrapolate the peak *PB* to lower pressure and find that it crosses the peak *B* around 3 GPa. This is consistent with the spectra in Fig. 1 which indicate that the intensity of the peaks *B* and *C* decreases drastically between 2.7 and 5 GPa. Since the peak *B* involves a shallow donor and a shallow acceptor, our result indicates that either the shallow donor or the shallow acceptor crosses a defect level (which we shall denote as *X* for convenience) under pressure. The subsequent transfer of carriers between the shallow levels and *X* produces the drop in the intensity of peak *B*. Furthermore, *X* is most likely a *deep donor* because the peaks *PB* and PC_i produced by *X* exhibit little or no pressure dependence. If a shallow donor were to be still active in these peaks we would expect their pressure dependence to be not too different from that of the band gap. Thus we conclude from the pressure dependence of the PL spectra that *a pressure-induced crossing between a deep donor and shallow donors occurs in* $Ag_{0.25}Cu_{0.75}GaS_2$ >3 GPa. Since the intensity of peaks *B* and *C* behaves quite similarly under pressure we suggest that the peak *C*, like peak *B*, also involves a rather shallow donor which crosses the level *X* at about the same pressure.

Having established that shallow donors are involved in the peaks *B* and *C* while a deep donor is involved in the peaks *PB* and PC_i in $Ag_{0.25}Cu_{0.75}GaS_2$ we can determine the pressure coefficients of the *acceptors* in these peaks from Table I. If we assume that the shallow donors have the same pressure coefficient as the conduction band then the pressure coefficient of the acceptor involved in *B* (which we shall abbreviate as $\alpha_{\text{acceptor}B}$) relative to that of the valence band (to be abbreviated as α_{Valence}) is equal to the *difference* in the pressure coefficients of the band gap and peak *B* in Table I. In this way we obtain

$$(\alpha_{\text{acceptor}B}-\alpha_{\text{Valence}})=-5\ \text{meV/GPa}.$$

Similarly we can deduce the pressure coefficient of the acceptor involved in *C* as

$$(\alpha_{\text{acceptor}C}-\alpha_{\text{Valence}})=2\ \text{meV/GPa}.$$

Each of these pressure coefficients have error bars of about 2 meV/GPa. The energy of peak *PB* has essentially no pressure dependence. Hence if we assume that peaks *B* and *PB* involve the same acceptor, then we find that *the pressure coefficient of the deep donor* $X(\alpha_X)$ *is equal to* $\alpha_{\text{acceptor}B}$ within uncertainties of about 3 meV/GPa. Based on this result we can estimate the pressure coefficients of the acceptors involved in the peaks PC_1 to PC_3. By taking the difference between the pressure coefficients of these peaks and *PB* we find that

$$\begin{aligned}\alpha_{\text{acceptor}PC1}-\alpha_{\text{Valence}}&=(\alpha_{\text{acceptor}PC1}-\alpha_{\text{acceptor}B})\\&\quad+(\alpha_{\text{acceptor}B}-\alpha_{\text{Valence}})\\&=-(\alpha_X-\alpha_{\text{acceptor}PC1})+(\alpha_X\\&\quad-\alpha_{\text{acceptor}B})+(\alpha_{\text{acceptor}B}-\alpha_{\text{Valence}})\\&=-(-2)+0+(-5)\ \text{meV/GPa}\\&\sim-3\ \text{meV/GPa}.\end{aligned}$$

Similarly we find that the coefficients $\alpha_{\text{acceptor}PC2}-\alpha_{\text{Valence}}$ ~-1 meV/GPa and $\alpha_{\text{acceptor}PC3}-\alpha_{\text{Valence}}\sim-4$ meV/GPa. Note that in all cases the experimental uncertainties in these pressure coefficients are $\sim$ 3 meV/GPa.

In Fig. 1 we notice that the pressure-induced peaks *PB* and PC_i are sharper than the peaks *B* and *C* which disappear under pressure! While the peaks PC_i are much broader than the peak *PB* they are still sharp enough to allow three peaks to be resolved. The widths of peaks *B* and *C* are usually understood to be dominated by inhomogeneous broadening. Since these peaks involve recombination between pairs of donors and acceptors, the emitted photon energy depends on the distance *R* between the donor and acceptor via the Coulomb energy $-e^2/\varepsilon R$ where *e* is the electronic charge and ε is the dielectric constant. Since most chalcopyrites are compensated there is usually a range of distances *R* between donors and acceptors and hence the donor-acceptor pair emission peaks are usually quite broad. The fact that the peaks *PB* and PC_i are *narrower* than the corresponding peaks *B* and *C* suggests that the distribution of the deep donors *X* is different from those of the shallow donors responsible for *B* and *C*. One possibility is that they form complexes with the acceptors resulting in a narrower distribution of the separation *R*. In addition, the fact that the three PC_i peaks have slightly different pressure coefficients suggests that there are more than one deep acceptors involved in the peak *C*. That these peaks are broader than peak *PB* can be explained by the fact that they involve deep acceptors whose emissions can be broadened by strong coupling with phonons.

Finally, although we cannot pinpoint the identity of the deep donor level *X* in our experiment, we like to address the question why deep donor levels appear in the alloy $Ag_{0.25}Cu_{0.75}GaS_2$ but not in $AgGaS_2$ and $CuGaS_2$. In the zinc-blende-type semiconductors, it is known that the conduction minima at the *X* points of the Brillouin zone (X_c) have small and negative pressure coefficients (~-10 meV/GPa).[12] In semiconductors such as GaAs about 4 GPa of pressures will lower X_c below the minimum at zone center (Γ_c) and thus convert GaAs from a direct into an indirect band-gap semiconductor.[13] Such drastic change in the nature of the conduction-band minimua is expected to alter the nature of donor levels. It is now generally accepted that the pressure induced change in band structure in GaAs is responsible for the conversion of shallow donors to deep donors known as the *DX* centers.[3] In addition, this crossover from direct to indirect band gap in GaAs can be facilitated by alloying with AlAs. It has been shown that an alloy concentration of 1% of Al is equivalent to about 0.1 GPa as far as the conversion of shallow donors to *DX* centers is concerned.[14] However, this does not seem to be the case in $Ag_{0.25}Cu_{0.75}GaS_2$. Our absorption measurements suggest that $Ag_{0.25}Cu_{0.75}GaS_2$ remains a direct gap material under pressure. To our knowledge, band extrema with negative pressure coefficients and pressured induced Γ_c-X_c crossover similar to those found in GaAs have not been reported in chalcopyrite semiconductors. A possible reason for this is that I-III-VI$_2$ chalcopyrite semiconductors are analogs of II-VI zinc-blende semiconductors (like CdS and ZnSe) whose X_c minima are typically too high in energy above the Γ_c minima for pressure to induce a crossover before structural phase transitions occur. Another way to explain our results is to invoke deep donors which are resonant with the conduction band at ambient pressure. It has been known for some time now that N in GaAs forms a resonant level above the Γ_c minimum.[15] Such deep and localized centers have much smaller pressure dependence than Γ_c whose pressure coefficient is ~100 meV/GPa.[12] As a result a deep level resonant with the conduction band can be brought into the band gap under sufficient pressure. Alloying has been known to lower the pressure necessary to induce such crossing of a resonant deep level and the Γ_c band minima by increasing the band gap. Examples of such cases include N in $Ga_xAs_{1-x}P$ (Ref. 15) and Te in $Ga_xAl_{1-x}As$.[14] More recently, oxygen in wurtzite GaN has been shown to form resonant deep levels which can be brought into the band gap by pressure where they freeze out carriers.[16] Thus we suggest that deep donor levels may also be resonant with the conduction band of $Ag_xCu_{1-x}GaS_2$ alloys. These deep donors can be lowered into the band gap by pressure. It is also quite possible that this process can be facilitated by alloying Cu with Ag. Such possibility is currently under investigation.

In conclusion, we have measured the pressure dependence of defect emission peaks in the chalcopyrite alloy $Ag_{0.25}Cu_{0.75}GaS_2$ and found evidence of a deep donor level which is resonant with the conduction band at ambient pressure but can be brought into the band gap by pressure exceeding 5 GPa.

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