Sulfur forming an isoelectronic center in zinc telluride thin films

W. K. Ge, S. B. Lam, I. K. Sou, J. Wang, and Y. Wang
Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

G. H. Li, H. X. Han, and Z. P. Wang
National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, China
(Received 1 July 1996)

ZnTe$_{1-x}$S$_x$ epitaxial layers grown on GaAs by molecular-beam epitaxy were studied by photoluminescence (PL) as a function of temperatures, excitation powers, and hydrostatic pressures. A sulfur-related emission peak, labeled as $P_2$, is identified as a deep-level emission by hydrostatic-pressure PL measurement. This indicates that sulfur atoms form isoelectronic centers in a ZnTe matrix. The results qualitatively agree with the theoretical prediction and show experimental evidence of isoelectronic S in ZnTe. A model is proposed to explain the emission mechanisms in the ZnTe$_{1-x}$S$_x$ system with small $x$ values. [S0163-1829(97)01816-X]

I. INTRODUCTION

The optical properties of compound semiconductors can be altered drastically by substitution of host atoms with an element in the same group, i.e., an impurity with the same number of valence electrons as the host atom. Such kinds of isoelectronic substitutions may form extended states, resonance states, or bound states in the band structures of host crystals, depending on the degree of difference between the impurity and the host atom it replaces. In particular, those isoelectronic impurities giving bound states, called isoelectronic centers (IEC’s), can greatly enhance the quantum efficiency of radiative recombination and thus are potentially promising for optoelectronic application. GaP:N (Refs. 1 and 2) and ZnS:Te (Refs. 3 and 4) are the well-known examples of IEC’s in III-V and II-VI compound semiconductors, respectively.

IEC’s are usually characterized by optical techniques, which may show a sharp no-phonon line with a series of phonon replica, or broad emission band in the photoluminescence (PL) spectra, depending mainly on the electron-phonon coupling strength. Theoretical investigation of the binding mechanisms of IEC’s shows that the IEC impurity potential is basically a short-range type, causing bound charges to be highly localized around the IEC, and results in a deep electronic state.5–7 Hence, IEC can be distinguished from the other PL spectral features by applying hydrostatic pressure, under which a deep level will shift in a different rate compared with the shallow and the band-edge states. Theoretical studies also show that electronic polarization to the lattice due to localized charge plays an important role in reducing the binding energy8 and results in electron-phonon coupling features, such as phonon replica or side band, in the PL spectra of IEC.1–4 Several attempts have been made to calculate the binding energy of different IEC systems but the results are still far from satisfying. Recently, Sohn and Hamakawa made a theoretical estimation for the binding energy of simple isoelectronic electron traps in II-VI semiconductors.9 Their results agree with some observed values, such as for ZnTe:O and ZnS:O systems, and explain the nonexistence of the bound state in ZnTe:Se. However, most of the II-VI IEC systems they studied lack experimental data for comparison. Hence, the validity of their model is still debatable and requires further experimental studies.

In this work ZnTe$_{1-x}$S$_x$ is studied, for which it is predicted that sulfur will form an isoelectronic electron trap with a binding energy of about 100–160 meV.9 ZnTe$_{1-x}$S$_x$ is also an interesting system in IEC study since sulfur lies between O and Se in the same group of the Periodic Table, where the former gives a bound state in ZnTe and shows a characteristic phonon side band in the PL spectrum,10 while the latter gives no bound state.12 Hence, examining the ZnTe$_{1-x}$S$_x$ system experimentally—data not available to the knowledge of the present authors—may not only contribute more evidence to compare with Sohn and Hamakawa’s model, but also provide some insights to the trend of IEC properties along the same group of elements doped into a common host crystal.

II. EXPERIMENT

Four MBE (molecular-beam epitaxy) -grown ZnTe$_{1-x}$S$_x$ thin films with $x$ ranging from 0 to 0.16 were studied. A VG V80H MBE system was used to grow the thin films on semi-insulating GaAs substrates oriented in the [001] direction with $2°±0.1°$ off toward [011]. Compound ZnS and ZnTe were used as the sources. All the layers were grown at 300 °C. High-resolution x-ray diffraction technique study confirmed the zinc-blende structure of ZnTe$_{1-x}$S$_x$ epitaxial layer.13 The layer thicknesses of the films measured by optical reflectivity technique range from 1 to 2 μm. Energy dispersive x-ray spectrometry was used to determine the composition of S in ZnTe$_{1-x}$S$_x$.14

PL measurements were carried out at about 10 K for ZnTe$_{1-x}$S$_x$ samples of various S concentrations, and between 7.7 and 80 K in a temperature-dependent study for the sample with $x=0.015$. An Ar$^+$ laser with a beam diameter of 0.1 mm and excitation power of 100 W cm$^{-2}$ was used. The luminescence was analyzed using a Spex 500M mono-
chromator with a 1200 g/mm grating and an R-406 photomultiplier tube.

A diamond anvil cell (DAC) was used for the hydrostatic-pressure PL measurement. PL was excited with the 4880-Å line from a cw Ar⁺ laser. The PL measurements were performed at 15 K maintained by a closed-cycle He cryostat. PL was collected in a back-scattering manner. Samples with an area of 0.1×0.1 mm² and a thickness of 0.02 μm were encapsulated inside the DAC and pressurized through the medium of solid argon. The pressure was monitored by the spectral shift of the ruby R1 PL line. In this system, desirable hydrostatic pressure up to 3 GPa could be obtained.

III. RESULTS AND ANALYSIS

The PL spectra of the samples with different compositions are shown in Fig. 1. The spectrum of pure ZnTe [see Fig. 1(a)] is dominated by two near-band-edge emission peaks at 2.372 and 2.355 eV that can be assigned as emission from a bound-exciton transition associated with a zinc vacancy and the first LO-phonon replica of a free-exciton transition, respectively. Other broader emission features at the lower-energy region may be due to free-to-bound (FB) transition at acceptors. The 2.328-eV emission is considered to be a FB transition associated with an unknown acceptor, while the one at 2.311 eV can be assigned as a FB transition at As acceptor \((e, As^0)\). The presence of As is possibly due to the out diffusion from the GaAs substrate. ZnTe is well known to be intrinsically \(p\)-type due to self-compensation by Zn vacancy. Hence the unknown acceptor may possibly relate to Zn vacancy also. Since the spectrum is dominated by near-band-edge emission peaks associated with native defects, the quality of the pure ZnTe thin film is high and suitable for comparing with the sulfur-doped samples.

With increasing S concentration in the ZnTe matrix, several new PL features whose relative intensities are composition dependent, appear in the spectra. For the layer with S concentration of 1.5% four emission bands, which are labeled as \(P_1\), \(P_2\), \(P_3\), and \(P_4\) in descending order of energy, can be found [see Fig. 1(b)]. \(P_3\), which is the dominant peak in the spectrum, carries a low-energy tail. \(P_4\), located at about 1.91 eV, is a very broad band with a full width at half maximum of 130–140 meV at 8 K. This emission band resembles that due to IEC of oxygen in ZnTe. Since the behavior of \(P_4\) in PL is made complicated by other deep-level emission features, currently we do not have enough evidence to justify whether \(P_4\) is oxygen related or sulfur related. It is left as an outstanding question for further investigation. Therefore, \(P_4\) is excluded in this study. At higher S concentration the peak positions of \(P_1\), \(P_2\), and \(P_3\) shift to the low-energy side, as shown in Fig. 1(c). The relative intensity of \(P_1\) and that of \(P_2\) change monotonically with increasing S concentration, while the former decreases and the latter increases. In Fig. 1(d), as S concentration reaches 16%, \(P_2\) instead of \(P_3\) is the dominant PL peak in the spectrum, and \(P_1\) is embedded in \(P_2\) and can be resolved only when \(P_2\) is quenched at higher temperature.

The observed peak shift is mainly due to the composition dependence of the band-gap energy \(E_g\) in ZnTe\(_{1-x}\)S\(_x\), where \(E_g\) has the minimum value at about \(x = 30\%\). In Fig. 2, the peak energy versus S composition is plotted and compared with \(E_g\). It can be projected that \(P_2\) converges to the bowing curve of \(E_g\) as \(x\) approaches 30%.

The temperature dependence of the PL spectrum of sample 2 (1.5% S) is shown in Fig. 3. \(P_2\) starts quenching at about 20 K and its peak can hardly be determined after 40 K. Beyond 40 K, \(P_1\) and \(P_3\) are clearly resolved, and it can be seen that \(P_1\) is a Gaussian peak while \(P_3\) is asymmetric. As temperature is increased further, the intensity of \(P_3\) is reduced and all remaining peaks have nearly equal peak intensity at about 60 K. Up to 80 K, only \(P_1\) and \(P_4\) are observed with similar peak intensity.
Further analysis shows that $P_1$ is thermally stable in both peak energy and linewidth while shifting to lower energy with a rate similar to that of the ZnTe band gap after $T \approx 70$ K (Ref. 19) (see Fig. 4). Hence, $P_1$ is likely to be a shallow level originating from a single luminescence center. $P_2$ is harder to characterize in a temperature-dependent PL measurement since it quenches early as temperature increases. Before quenching, $P_2$ seems to shift as slowly as $P_1$. $P_3$ has a sharp change at 40 K in the PL spectrum, whose peak shifts to lower energy rapidly after $T > 40$ K (see Fig. 4). Moreover, the linewidth of $P_3$ is reduced by 8 meV as the excitation level increases, as shown in Fig. 5. Such behavior makes $P_3$ strongly resemble the donor-acceptor pair (DAP). $P_2$ shows an unambiguous relation with sulfur atoms, since its intensity increases with S concentration. Also, the pressure coefficient of $P_2$ obviously deviates from the band gap, which most likely originates from a deep level while compared with the other two peaks.

**IV. DISCUSSION**

In this section, the possible origins of $P_1$, $P_2$, and $P_3$ bands are discussed to study the role of sulfur atoms in the emission mechanisms of the ZnTe:S system.

$P_2$ shows an unambiguous relation with sulfur atoms, since its intensity increases with S concentration. Also, the pressure coefficient of $P_2$ obviously deviates from the band gap, which most likely originates from a deep level while compared with the other two peaks. $P_2$ has a sharp change at 40 K in the PL spectrum, whose peak shifts to lower energy rapidly after $T > 40$ K (see Fig. 4). Moreover, the linewidth of $P_3$ is reduced by 8 meV as the excitation level increases, as shown in Fig. 5. Such behavior makes $P_3$ strongly resemble the donor-acceptor pair (DAP). $P_2$ shows an unambiguous relation with sulfur atoms, since its intensity increases with S concentration. Also, the pressure coefficient of $P_2$ obviously deviates from the band gap, which most likely originates from a deep level while compared with the other two peaks.

**IV. DISCUSSION**

In this section, the possible origins of $P_1$, $P_2$, and $P_3$ bands are discussed to study the role of sulfur atoms in the emission mechanisms of the ZnTe:S system.

$P_2$ shows an unambiguous relation with sulfur atoms, since its intensity increases with S concentration. Also, the pressure coefficient of $P_2$ obviously deviates from the band gap, which most likely originates from a deep level while compared with the other two peaks.

$$E(P) = E_0 + \alpha P,$$

where $E_0$ and $E(P)$ are the peak energy under normal and applied pressure $P$, respectively. $\alpha$ is the pressure coefficient of the first order. $P_1$, $P_2$, and $P_3$ have the value of $\alpha$ as 0.081±0.002, 0.076±0.002, and 0.088±0.002 eV/GPa, respectively. They are all smaller than that of ZnTe, which is 0.104 eV/GPa. Although the resolution of the spectra under high pressures is not very good, the data for $P_2$ that become more and more predominant with increasing pressure are reliable. Clearly, $\alpha$ of $P_2$ deviates from the band gap, which most likely originates from a deep level while compared with the other two peaks.

**FIG. 3.** Temperature-dependent PL of sample 2 (1.5% S) excited with a cw Ar$^+$ laser (90 W cm$^{-2}$, $\lambda = 476.5$ nm).

**FIG. 4.** The temperature dependence of $P_1$, $P_2$, $P_3$, and $P_4$ peak energies in sample 2.

**FIG. 5.** Change of linewidth with excitation power density for $P_3$ in sample 2.
where $A^0(k)$ and $E^0(k)$ are the probability amplitude of the $k$ component of $\Psi$ and electron energy of the conduction-band states $|k\rangle$, respectively, under normal pressure. $\beta(k)$ represents the relative change of the $k$ component of $\Psi$ under pressure. For a localized state whose wave function can just be appropriately represented by a set of eigenstates with wide range of $k$, its pressure dependence will not follow the change of only one of the conduction-band valleys with a specific $k$, but a sum of them. Since the pressure dependence of $E_g(dE_g/dP)$ alone is too large to account for the small $\alpha$ of $P_2$, that of $E_{\Gamma}$ and $E_{\bar{X}}$ for ZnTe, which is 0.017 eV/GPa and $-0.017$ eV/GPa, respectively, could also contribute to the pressure coefficient of $P_2$. Thus, $P_2$ is a sulfur-related deep-level emission, showing that sulfur is possibly forming an IEC in a ZnTe system.

The peak energy trend of $P_2$ with the change of sulfur concentration also supports that $P_2$ is an IEC emission peak. Experimentally, the binding energy can be roughly estimated by the optical depth of $P_2$ with respect to the band gap, provided that the lattice relaxation is not too large. The strength of electron-phonon coupling of an emission center can be qualitatively described according to the line shape. Unfortunately, $P_2$ in sample 2 is seriously obscured by its neighboring peaks. It is, however, possible to postulate the line shape according to the peak shape of $P_2$ in sample 4 [see Fig. 1(d)], where $P_2$ is predominant. It can be seen that $P_2$ has a rather sharp peak, which implies that it is not broadened significantly by electron-phonon interaction. Therefore, it is reasonable to assume that the total binding energy associated with $P_2$ emission can be estimated by the optical depth of $P_2$. In Fig. 2, the optical depth of $P_2$ is shown to be generally decreased with increasing sulfur concentration. The same observation can also be found in the ZnSe$_{1-x}$Te$_x$ system. This trend is reasonable due to the fact that when the concentration of IEC increases, the doped system becomes less and less host-crystal-like, but rather remains in a state of alloy that has the physical properties between the host crystal and the substitutional sublattice. The binding energy should be reduced to zero due to the delocalization of excitons when the wave function of the largely populated IEC bound states overlap sufficiently with each other. Therefore, the composition dependence of peak energy also supports that $P_2$ is an emission from a sulfur-related IEC bound state. This and the bowing effect of $E_g$ due to the incorporations of S into ZnTe indicate that S plays both roles as a component of the alloy as well as an IEC impurity, similar to the case of Te in ZnS.

Both $P_3$ and $P_1$, having the pressure behavior similar to the band gap, are expected to originate from the emission of shallow levels. The $P_1$ emission peak is most likely from free-to-bound transitions associated with Zn-vacancy-related acceptors. In the temperature-dependence study, $P_1$ shows a redshift after 60 K with a rate similar to that of ZnTe band gap, showing that $P_1$ is associated with a shallow level. Due to the tendency of “self-compensation” by forming a Zn vacancy" and low-ionization energy of donors (−20 meV)\textsuperscript{26} in ZnTe, the shallow level responsible for $P_1$ emission is not likely to be due to the donor. Comparing the PL spectrum of pure ZnTe with sample 2 (1.5% S), $P_1$ and $(e,A^0)$ emission peaks have the same optical depth of about 54 meV below the band gap. Hence, it is reasonable to assign $P_1$ as an
acceptor emission peak that is possibly related to a Zn vacancy. \( P_3 \) showing a decrease in linewidth with increasing excitation level can be interpreted as a DAP emission. The narrowing of the spectral line is due to the saturation of distant pairs with a large amount of free carriers created under high excitation power. While the origin of the DAP is distant pairs with a large amount of free carriers created un-

The increase in relative intensity of \( P_2 \) in the expense of \( P_3 \) under pressure seems to be related to the capture of excitons released from \( P_1 \) and \( P_3 \) by \( P_2 \). The release of excitons from \( P_1 \) and \( P_3 \) is due to a higher probability of those centers to collide with nonradiative centers under pressure. On the other hand, this probability is low for defect centers with short-range potential, such as \( P_2 \).

A model for the three radiative recombination processes resulting in \( P_1 \), \( P_2 \), and \( P_3 \) emissions based on the above discussion is proposed. In the model, \( P_2 \) is the radiative recombination of an exciton bound to isoelectronic sulfur. The total binding energy of \( P_2 \) (73 meV) is contributed by two parts, namely, the energy of tight binding an electron to a sulfur atom, \( E_i \), and the loosely binding energy of a hole. \( E_i \) can be estimated as 60–70 meV. Compared with the calculated result,\(^9\) the experimental value of \( E_i \) is somewhat lower than expected. \( P_1 \) is interpreted as a FB transition associated with an acceptor, whose energy level \( E_A \) is 54 meV above the valence band, while \( P_3 \) is due to DAP emission in which the acceptor is in common with that associated with \( P_1 \).

V. CONCLUSION

ZnTe\(_{1-x}\)S\(_x\) epitaxial thin films with \( x \) ranging from 0 to 0.16 are studied in PL measurement as a function of temperatures and excitation intensities, as well as hydrostatic pressures. A sulfur-related emission peak labeled as \( P_2 \) is identified as a deep-level emission in PL study under hydrostatic pressure. This peak is assigned as the IEC emission due to sulfur atoms in ZnTe. This evidence of isoelectronic S in ZnTe, agrees qualitatively with the theoretical prediction by Sohn and Hamakawa.\(^3\) A model is proposed to explain the above emission mechanisms.

ACKNOWLEDGMENTS

The work done at The Hong Kong University of Science and Technology was supported by Grant No. CPDG 94/ 95.SC08 and HKUST 615/95P.

---