Te antisite incorporation in $\text{ZnS}_{1-x}\text{Te}_x$ thin filmsS. K. Chan,¹ H. J. Liu,^{1,2} C. T. Chan,¹ Z. Q. Zhang,¹ W. K. Ge,¹ and I. K. Sou¹¹*Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*²*Department of Physics, Wuhan University, Wuhan 430072, China*

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We investigate Te-related intrinsic defects in $\text{ZnS}_{1-x}\text{Te}_x$ thin films. First-principles calculations were performed for ZnS with Te as impurity atoms. The results show that the substitutional incorporation of Te in group VI sites cannot form defect states deep in the energy band gap of ZnS. On the other hand, our calculations on both Te antisite and interstitial defects result in deep-level states. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were used to study the chemical structures of three molecular-beam-epitaxy-grown $\text{ZnS}_{1-x}\text{Te}_x$ samples, $x\{0.005, 0.019, 0.026\}$. An asymmetry was detected in the XPS spectra of both Te $3d_{3/2}$ and Te $3d_{5/2}$ core levels, which indicates that a small portion of the incorporated Te atoms is bonded to a more electronegative element. A peak at m/z of 158 was detected in the SIMS depth profiles of these samples and its characteristics match that of TeS components of the lattice matrix. This experimental evidence strongly supports the existence of Te antisite defects in the thin films. We believe that the origin of the highly luminescent centers in $\text{ZnS}_{1-x}\text{Te}_x$ thin films is possibly attributed to the deep-level states generated from Te anti-site incorporation.

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The optoelectronic properties of III-V or II-VI compound semiconductors can be altered by incorporating an element with the same number of valence electrons as one of the host elements. These isovalent semiconductor systems, $AC_{1-x}D_x$, show a continuous change in optical properties when x varies from 0 to 1. $\text{GaP}_{1-x}\text{As}_x$,¹ $\text{ZnSe}_{1-x}\text{Te}_x$,² and $\text{ZnS}_{1-x}\text{Se}_x$ ³ are some of the well-studied systems. In some systems, the impurities form deep-level bound states in the forbidden band gap of the host crystals, which are called isoelectronic centers (IECs). The IECs can be generally treated as point defects which localize the wave function of the carriers. The typical examples include (i) a GaP:N system⁴ in which bound states are attributed to the isolated N atoms or pairs of N atoms with different internuclear pair separation, and (ii) a ZnS:Te system in which bound states were thought to be caused by isolated Te atoms or Te_n ($n \geq 2$) clusters.⁵⁻⁷

In general, IECs form deep-level states within the forbidden band gap due to the difference in electronegativity and atomic size as compared with the replaced host atoms. These centers act as either electron or hole traps for excited carriers. Effective trapped exciton recombination at IECs leads to enhanced luminescence. We recently reported that high-quality $\text{ZnS}_{1-x}\text{Te}_x$ ($0 \leq x \leq 1$) single-crystal alloy films can be grown on GaAs and Si substrates by the molecular-beam-epitaxy (MBE) technique.⁸ Strong photoluminescence in the yellow to blue spectral region, with room-temperature external quantum efficiencies of 2–4 % at an unoptimized excitation wavelength of 365 nm, was observed. In 1972, Baldersch and Hopfield carried out a tight-binding calculation assuming Te isoelectronic substitution on the ZnS:Te system.⁹ By introducing the effect of relaxation of the host crystal into the screened impurity potential of IECs, they predicted the existence of a bound state due to Te IECs based on the pseudopotential theory. The Te atoms were considered to act as isoelectronic hole traps. On the other hand, a number of first-principles calculations have been performed to

study the structural and electronic properties of IECs in III-V semiconductors.

The objective of the present study is to investigate Te related intrinsic defects in $\text{ZnS}_{1-x}\text{Te}_x$ thin films. We started with first-principles calculations for ZnS with possible impurities and defects involved. Our calculated results indicate that substitutional incorporation of Te in an anion site of ZnS will not lead to localized states inside the energy band gap, while antisite and interstitial defects will. Experimental investigations were focused on revealing the electronic and chemical structures of the incorporated Te species in a set of MBE-grown $\text{ZnS}_{1-x}\text{Te}_x$ thin films using x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), respectively. The experimental results strongly support the existence of Te antisite defect in $\text{ZnS}_{1-x}\text{Te}_x$ thin films, which is believed to be a possible origin for the observed strong photoluminescence due to the bound exciton recombination occurring on these carrier traps.

Our first-principles calculations were performed using the density-functional theory within the framework of the local-density approximation (LDA),^{10,11} as implemented in the VASP package.¹² The ultrasoft pseudopotentials¹³ were used for Zn, S, and Te, and a plane-wave cutoff of 20 Ry was used. A 64-atom supercell, with atoms arranged in zincblende structure, was used to model the system with a nominal formula of $\text{Zn}(32)\text{S}(32)$. All atomic positions and cell volume are fully relaxed, and multiple initial positions (including off-symmetry positions) were tried when Te is introduced, and the final relaxed state is found to be independent of initial positions.

We first considered the substitutional incorporation of Te in an anion site by replacing one S atom with a Te atom in the 64-atom $\text{Zn}(32)\text{S}(32)$ matrix. The resulting supercell is $\text{Zn}(32) \sim \text{S}(31)\text{Te}(1)$. Here the sign “ $\sim$ ” is used to separate the cation and anion parts. Figure 1 shows the calculated

FIG. 1. Calculated total DOS for Te substituting an S atom for 64-atom (solid line) and 216-atom (dashed line) unit cells.

total density of states (DOS) for $\text{Zn}_{32}\sim\text{S}_{31}\text{Te}_{1}$. One can see that no impurity state appears inside the band gap. The states introduced by Te have strong amplitude on the Te site, but the localization is not strong enough to induce a split-off state in the gap, so that they form a shoulder in the DOS that merges with the valence-band maximum, rather than splitting off to form a clearly identifiable defect state in the gap. The DOS calculated with a 216-atom unit cell gives the same result. When more S atoms are substituted, the Te atoms can form pairs or clusters in the ZnS matrix. However, their calculated DOSs lead to the same result that no energy state is formed inside the band gap as in the case of single Te substitution. It is thus unlikely that substitutional Te can give a straightforward account for the strong photoluminescence observed in this system. We next considered Te as antisite defects in the system. Figure 2 displays the calculated DOS for $\text{Zn}_{31}\text{Te}_{1}\sim\text{S}_{32}$, where a single Te atom replaces one of the Zn atoms in the ZnS matrix. In contrast with Fig. 1, a peak obviously appears inside the band gap indicating the existence of a defect level. We have also examined the DOS for interstitial Te incorporation, which also shows a defect state inside the band gap. However, we note that it is energetically very unfavorable for Te atoms to stay in the interstitial sites of ZnS because of the large size of Te. We should emphasize that single-particle LDA calculations based on periodic “supercells” cannot provide definitive answers for luminescence phenomena. But it is fair to say that the results do not provide straightforward support for a substitutional isocenter being the origin for the high luminescence, while antisite centers may be a possibility. The judgment should come from experiments, which were performed explicitly to look for antisite centers. The samples used for our experimental studies were grown by the molecular-beam-epitaxy (MBE) technique in a VG V80H system on either semi-insulating GaAs (100) or GaP (100) substrates. $\text{ZnS}_{1-x}\text{Te}_x$ thin films were grown using compounds ZnS and ZnTe sources contained in separate effusion cells. The Te composition was controlled by adjusting the cell tempera-

FIG. 2. Calculated total DOS for Te substituting a Zn atom for a 64-atom unit cell. The Fermi level is at 0 eV.

tures. The optimal growth temperature was found to depend strongly on the desired Te composition of the alloys. The details of growth conditions were reported elsewhere.¹⁴ The Te composition of $\text{ZnS}_{1-x}\text{Te}_x$ thin films was obtained in XPS studies after removing the surface-contaminated layer by 8-min sputtering. The data showed that the three $\text{ZnS}_{1-x}\text{Te}_x$ thin films in this study have the Te compositions of 0.5%, 1.9%, and 2.6%.

Two surface analysis experiments were conducted in this work. XPS analysis was performed using a Physical Electronics PHI 5600 multitechnique system with a Mg $K\alpha$ x-ray source ($h\nu=1253.6$ eV). Ar^+ sputtering was used to remove hydrocarbon and other contamination on the sample surface prior to analysis. TOF-SIMS depth profiling was carried out using a Physical Electronics 7200 TOF-SIMS spectrometer with a base pressure of 10^{-10} Torr. Cs^+ cations of 8 keV were used as a primary ion source to bombard the sample surface.

Due to the fact that the samples were exposed to the air before being loaded into the XPS system, a thin oxide layer is expected on their surfaces. The XPS spectra obtained from the surface of the as-grown samples contain two characteristics peaks located at 577.2 and 587.8 eV near the tellurium $3d_{5/2}$ and $3d_{3/2}$ core-level peaks, respectively, which are attributed to the well known oxidized tellurium features. The characteristic peak of the $1s$ core level of oxygen at 531.0 eV was also detected in these spectra. Prior to our quantitative XPS analysis, Ar sputtering was performed on these samples to remove the surface oxide to the extent that both the two tellurium oxide related peaks and the oxygen $1s$ core-level peak are below the detection limit. The XPS spectra of the Te $3d_{5/2}$ core level at binding energy near 572.8 eV obtained from the sputtered $\text{ZnS}_{1-x}\text{Te}_x$ samples under investigation are shown in Fig. 3. It reveals that a higher shoulder consistently appears at the high-energy side in the spectra of the Te $3d_{5/2}$ core level. This spectral asymmetry can be attributed to the superposition of two Te-related characteristic peaks. Each of these two spectra can be fitted by two Gaussian functions.

FIG. 3. Measured XPS Te 3d_{5/2} spectra and fitted curves of ZnS_{1-x}Te_x samples with Te composition of (a) 2.6%, (b) 1.9%, and (c) 0.5%.

As shown in Fig. 3, the dominant and minor peaks of the Te 3d_{5/2} lie at about 572.8 and 574.3 eV, respectively, with a difference around 1.5 eV in binding energy. A similar asymmetry was also detected in the measured XPS spectra of Te 3d_{3/2} core-level peaks with a difference in binding energy very similar to the Te 3d_{5/2} core-level peaks. Table I lists the fitted peak values and area percentage for the dominant and minor peaks of both Te 3d_{5/2} and 3d_{3/2} core levels of these three samples. It is worth pointing out that the binding energy of a Te 3d_{5/2} electron in pure Te is around 573.1 eV and that of telluride compounds lies at a lower energy ranging from 572.2 to 572.8 eV.¹⁵ So the two dominant peaks of the observed Te 3d spectra are likely contributed by those Te atoms incorporated substitutionally in anion sites surrounded by Zn atoms.

It is well known that the binding energy of the core electrons of an element is enhanced if it is bonded with a more

electronegative element, such as the cases of oxidized tellurium. The appearance of the minor peaks centered at higher binding energies shown in Fig. 3 indicates that some of the incorporated tellurium atoms are bonded with atoms which are more electronegative than tellurium. Since the binding energies of these two minor peaks are substantially lower than those of the commonly observed TeO₂ (3d_{5/2} E_b=575.8 eV) and TeO₃ (3d_{5/2} E_b=576.7 eV), plus the fact that the oxygen content in the sputtered samples is below the XPS detection limit, it is very unlikely that these two minor peaks are caused by oxidized tellurium. On the other hand, sulfur, one of the major host components in the ZnS_{1-x}Te_x matrix, owns an electronegativity between those of oxygen and tellurium. Therefore, it is reasonable to relate the two observed minor peaks with part of the incorporated tellurium atoms that are located in antisites surrounded by sulfur atoms.

TABLE I. Fitted peak values and area percentage for the dominant and minor peaks of both Te 3d_{5/2} and 3d_{3/2} core levels of the three ZnS_{1-x}Te_x thin film samples.

Characteristic peak of Te	Sample with Te composition, x(%)	Dominant peak		Minor peak	
		Binding energy (eV)	Area percentage (%)	Binding energy (eV)	Area percentage (%)
3d _{5/2}	0.5	572.76	78.2	574.27	21.8
	1.9	572.85	76.0	574.28	24.0
	2.6	572.78	81.7	574.19	18.3
3d _{3/2}	0.5	583.18	76.5	584.70	23.5
	1.9	583.28	76.5	584.78	23.5
	2.6	583.17	77.7	584.58	22.3

FIG. 4. Measured TOF-SIMS depth profiles for the ion species of $^{126}\text{Te}^{16}\text{O}$, $^{126}\text{Te}^{16}\text{O}_2 + ^{126}\text{Te}^{32}\text{S}$, and $^{126}\text{Te}^{16}\text{O}_3$ oxide of the $\text{ZnS}_{1-x}\text{Te}_x$ sample with x of 2.6%. The inset shows that of ^{16}O and $^{64}\text{Zn}^{16}\text{O}$.

Through analyzing the XPS results described above, it is believed that there is a portion of the incorporated Te atoms in the $\text{ZnS}_{1-x}\text{Te}_x$ samples acting as antisite defects. SIMS is an ideal technique to test this hypothesis because it has the capability to determine whether TeS species, which are strong evidence of the formation of Te antisites, exist in the $\text{ZnS}_{1-x}\text{Te}_x$ matrix. Te has various isotopes of which ^{126}Te is of special importance in this study, because of its 18.8% abundance and uniqueness that no cluster formed by a combination of O, S, and Zn atoms can have the m/z ratio of 126. The SIMS depth profiles of different ion species obtained from the $\text{ZnS}_{1-x}\text{Te}_x$ thin film with Te composition of 2.6% are shown in Fig. 4. SIMS studies on two other $\text{ZnS}_{1-x}\text{Te}_x$ thin films with Te composition of 0.5% and 1.9% provided similar results (not shown in this paper). In performing the depth profiles shown in Fig. 4, five ion species with an oxygen constituent were monitored. They are oxygen at m/z of 16, ZnO at m/z of 80, TeO at m/z of 142, $\text{TeO}_2 + \text{TeS}$ at m/z of 158, and TeO_3 at m/z of 174. In particular, the contribution at m/z of 158 is limited to TeO_2 and TeS. Therefore, it is expected that a careful inspection of the characteristics of this m/z peak could confirm whether or not TeS clusters exist in $\text{ZnS}_{1-x}\text{Te}_x$ thin films.

The ion intensities of pure oxygen and zinc oxide of the $\text{ZnS}_{1-x}\text{Te}_x$ thin film with a Te composition of 2.6% are plotted as a function of sputtering time in the inset of Fig. 4. It can be seen that both oxygen and zinc oxide signals have a significant drop at sputtering time of 1 min as compared to the initial data taken at the onset of sputtering, and then decrease slightly throughout the sputtering process afterwards. It implies that there is less of a possibility for the formation of the oxide-related secondary ions in the interior of the samples. It is usually expected that oxygen contami-

nation is more serious at the surface as compared with the interior of the thin films. More oxide would then be formed on the surface of the thin films. Therefore, the intensity of any oxide-related ion should drop following the trend of pure oxygen. In Fig. 4, one can see that both TeO and TeO_3 signals basically follow these trends. On the other hand, the depth profiles of m/z at 158 in all three samples show a sharp increase at sputtering time of 1 min and then maintain at a higher level as compared to the initial value taken at the onset of sputtering. Since this characteristic is obviously opposite to that of oxygen and other oxides as described above, we believe that the depth profiles of m/z at 158 in all three samples are dominantly contributed by TeS species.

A similar SIMS study of a ZnTe thin film sample, which should be free of TeS clusters, was conducted for strengthening our conclusion on the existence of Te antisite defects. This study reveals that the dominant oxide is TeO among the three possible tellurium oxides in the thin film. This result further supports that the detected signal of m/z at 158 for the three $\text{ZnS}_{1-x}\text{Te}_x$ samples is mainly contributed by TeS rather than TeO_2 species.

In conclusion, we have carried out both theoretical and experimental studies on Te-related intrinsic defects in $\text{ZnS}_{1-x}\text{Te}_x$ thin films. The results of our local-density-functional theory show that substitutional incorporation of Te in group VI sites does not form defect states that noticeably split off from the valence-band maximum of ZnS. This is in strong contrast to the previous reports based on other theoretical approaches. On the other hand, our calculations on Te antisite and interstitial defects both result in deep-level states in the energy band gap, with Te antisite defects being more energetically favorable. Experimental studies were carried out on three MBE-grown $\text{ZnS}_{1-x}\text{Te}_x$,

$x=\{0.005, 0.019, 0.026\}$, thin films using both XPS and TOF-SIMS techniques. An asymmetry was detected in the XPS spectra of both Te $3d_{3/2}$ and Te $3d_{5/2}$ core levels. Detailed analysis of these spectra seems to indicate that a small portion of the incorporated Te atoms are bonded to a more electronegative element. The SIMS depth profiles obtained from the same set of samples show a peak at m/z of 158, which owns characteristics of TeS components of the lattice matrix. These experimental findings strongly support the existence of Te antisite defects in these $\text{ZnS}_{1-x}\text{Te}_x$ thin films. The results of this study lead us to believe that the origin of the highly luminescent centers in $\text{ZnS}_{1-x}\text{Te}_x$ thin films is

possibly attributed to the deep-level states generated from Te antisite incorporation.

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