

Epitaxial ZnS Thin Films Grown by Single Source Chemical Vapor Deposition

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Deposition and subsequent decomposition of the organometallic precursor zinc diethyldithiocarbamate $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ has been shown to produce ZnS films. On Si(111), these films have been seen to grow epitaxially using X-ray photoelectron diffraction (XPD) as a probe. For film thickness from ~ 5 to 2000 \AA angle-dependent XPD scans, recorded for Zn $2p_{3/2}$ intensity as a function of polar angle θ , resulted in a consistent forward scattering peak at $\theta = 0^\circ$ which indicated that the films have preferred orientation. Detailed analysis of the relative photoelectron intensities (Zn $2p_{3/2}$ and S $2p$) indicated that the films are of cubic structure and [111] oriented. This was despite the total carbon concentration in the bulk remaining at ~ 3 atomic %. This study demonstrates that the relatively simple and low-energy single-source chemical vapor deposition growth technique can be utilized for the production of epitaxial II–VI semiconductor thin films.

Introduction

The single-source chemical vapor deposition (SS CVD) method for making thin films involves the decomposition of a single precursor containing the basic constituents of the desired crystallite material. Much of the work in this area has been in the chemical development of the precursor with in some cases a cursory study of resultant film characteristic.¹ The primary goal in these cases was to deposit, under mild vacuum, an organometallic precursor onto a hot substrate. The precursor subsequently decomposed cleanly (preferably) leaving the desired film constituent at the surface. The unwanted ligands were reacted to form volatile compounds which can be removed from the system.

Recently, SS CVD processes have been refined for the production of device-quality ZnO thin films.^{2,3} In this work the development of film structure was linked to changes in the chemistry of the decomposition with film growth. This resulted in the development of simple SS CVD fabricated optical devices⁴ which incorporated self-textured thin films.

It was of interest to extend this approach to other materials and, in particular, to initially look at the possibility of using SS CVD to form epitaxial films on suitable substrates.

In particular, a consideration in SS CVD is the minimization of by-products occluding within the film. It was of interest therefore to establish whether or not the introduction of a strong structuring-inducing effect (such as a lattice-matched substrate) would have any effect on the amount of occluded by-products.

The material chosen for study is ZnS on a substrate such as Si(111) which has similar lattice constants (lattice mismatch $\sim 0.2\%$) and therefore epitaxial film growth may be possible.⁵

We have previously grown polycrystalline ZnS films on a variety of substrates using single-source chemical vapor deposition (SS CVD) with zinc diethyldithiocarbamate $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ as precursor. The method allows for a low growth temperature and results in highly crystalline and self-textured (ie. one-dimensional ordering) thin films on lattice-mismatched substrates⁶ with carbon contents of the order of 3 atomic %.

Experimental Section

Details of the SS CVD film growth procedure have been described previously.^{2,6} Film growth was carried out utilizing optimal growth conditions with the substrate and source temperature set to 400 and 130°C , respectively.⁶ Zinc diethyldithiocarbamate was sublimed from a resistively heated Knudsen cell. Partial pressure arising from sublimation of the precursor was adjusted at $\sim 2 \times 10^{-6}$ Torr. Film chemistry was monitored using X-ray photoelectron spectroscopy (XPS).⁶ The XPS and angle-dependent XPD experiments were performed using a Kratos XSAM-800 spectrometer with Al $K\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) and electron energy analyzer with a pass energy of 40 eV . The base pressure of the main analysis chamber was $\sim 2 \times 10^{-10}$ Torr. The CVD deposition chamber was attached to the sample preparation chamber of the electron spectrometer. Ion beam etching was performed with a 4 kV Ar^+ ion beam. The energy-dependent XPD experiments were performed using Synchrotron radiation at the undulator beamline ^{13}C of the Photon Factory (Tsukuba, Japan).

The preparation of “clean” Si(111) surfaces involved three cycles of H-passivation and reoxidization using buffered HF and standard H_2O_2 solution, respectively.^{7,8} The final H-passivation was carried out by immersing Si wafer into 5% HF solution. The wafer was then rinsed thoroughly using absolute ethanol,⁹ immediately inserted into the XPS chamber, and subsequently heated to 350°C for 10 min . This final thermal treatment is aimed at the removal of any adventitious surface contaminants. The chemistry and crystallinity of the Si(111) surface was monitored using XPS and angle-dependent XPD.^{10,11}

Results and Discussion

Figure 1, part 1a–c, shows angle-dependent XPD scans of the Zn $2p_{3/2}$ intensity distribution for SS CVD ZnS films with thickness ranging from ~ 5 to 2000 \AA . For these measurements, the polar angle θ (angle between the electron take-off axis and the surface normal) was varied by tilting the sample. The XPD patterns exhibit an intense and broad peak at $\theta = 0^\circ$. The variation of the background intensities is related to the different

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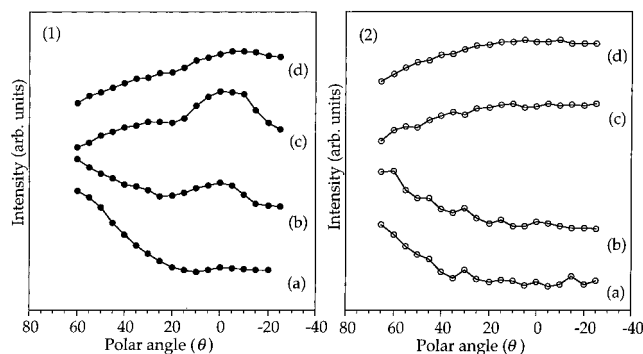


Figure 1. Intensity distribution of (1) Zn 2p_{3/2} and (2) S 2p photoelectrons for ZnS films with thickness at (a) ~5, (b) 12.9, (c) 2000 Å. Figure 1.1(d) and 1.2(d) shows the intensity distribution of Zn 2p_{3/2} and S 2p for the 2000 Å film after Ar⁺ etching.

film thickness.¹² In addition, Figure 1, part 1d, shows the measurement for the 2000 Å film after Ar⁺ ion etching. Due to the sputtering procedure, the surface structure is heavily damaged and the XPD measurement does not indicate significant intensity enhancement. This scan therefore shows the empirical instrument response function which generally exhibits a decrease of photoelectron intensities at high polar angles.¹²

Using the Al K α photon source, the resulting Zn 2p_{3/2} photoelectrons have a kinetic energy (E_k) of approximately 465 eV and forward-scattering predominates at this relatively high energy.^{12,13} In contrast to kinetic energies lower than ~200 eV, back- and multiple-scattering of the emerging photoelectrons are less pronounced and the resulting spectra are less complex.¹³ According to the single scattering model,¹¹ enhanced intensity arises from the forward-scattering of photoelectrons by neighboring atoms along the forward direction. The XPD probe depth for our experiments was 36 Å as estimated using the inelastic mean free path (IMFP) of Zn 2p_{3/2} photoelectrons.¹³ The latter was calculated using the universal IMFP equation that effectively describes mean free paths for high-energy electrons.¹⁴

In ZnS, every zinc atom is surrounded by four sulfur atoms in a tetrahedral arrangement which results in either cubic (sphalerite) or, slightly distorted, hexagonal (wurtzite) structure.¹⁵ Due to the anisotropic crystallographic properties, it is important for applications that the crystallites within the films have preferred orientation (e.g., (111) for cubic and (001) for hexagonal). The enhanced XPD intensities at $\theta = 0^\circ$ (Figure 1, part 1a–c) indicate that already the first monolayers have preferred orientation and the Zn 2p_{3/2} photoelectrons are scattered by the sulfur neighbors perpendicular to the substrate.

In contrast, the pronounced forward scattering peaks at $\theta = 0^\circ$ were not observed in the polar scans of the S 2p intensity distribution (S 2p $E_k \sim 1326$ eV) for corresponding films, as shown in Figure 1, part 2a–c. The forward scattering enhancement shown in Figure 1, part 1a–c is related to the structure of ZnS films and measurement geometry. These results together with those shown in Figure 1, part 2 indicate that SS CVD ZnS films are of cubic structure, and that the film crystallites have preferred [111] orientation as will be discussed below. Figure 2 shows a cross-section of the cubic ZnS structure, in which sulfur atoms are arranged in layers according to cubic close-packed (ccp) ABC stacking sequence.¹⁵ Due to the ABC sequence, S photoelectrons originating from layers B and C are not forward-scattered along the [111] direction by next-nearest neighbors. Scattering occurs, however, for S photoelectrons from layer A by Zn atoms in layer C with a distance of approximately 6.9 Å. For Zn photoelectrons, forward scattering involves the S atoms along the [111] direction (the corresponding Zn–S

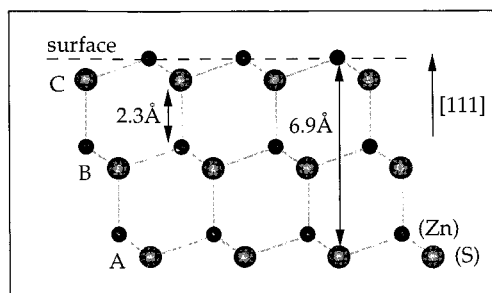


Figure 2. Cross-section of the cubic ZnS structure showing the geometry of forward-scattering along the [111] direction.

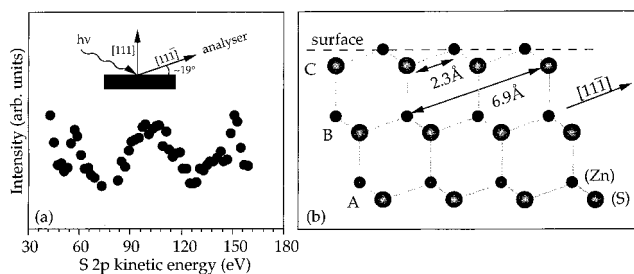


Figure 3. (a) Intensity distribution of S 2p measured along [111] direction for the 2000 Å film. (b) Cross-section of the cubic ZnS structure showing the geometry of forward-scattering along [111] direction. The upper inset shows the geometry of measurements.

distance is of ~2.3 Å¹⁵). Since the scattering amplitudes vary with the distance r of scatterers as $1/r^2$,¹⁵ the S 2p polar scans result in much smaller forward-scattering signals at $\theta = 0^\circ$ than those of Zn 2p photoelectrons. In addition the crystallographic quality of the bulk was analyzed using X-ray diffraction (XRD). The XRD pattern of the 2000 Å film has indicated a strong (111) reflection at the diffraction angle (2θ) of ~28.7° (FWHM ~0.8°).¹⁶

Forward-scattering measurements are useful for analyzing the out-of-plane preferred orientation at the interface. The XPD signals should also be influenced by preferred in-plane orientation of the ZnS molecules (possible forward-scattering along other atomic direction, photoelectron diffraction peaks). These features, however, would have significantly less intensity than the peak at $\theta = 0^\circ$ ^{17,18} and, especially for the ultra-thin film measurements (Figure 1, part 1a,b), would probably be below the detection limit.

To probe the in-plane orientation of the film molecules, we employed energy-dependent XPD, which measured the S 2p photoemission intensity for a fixed geometry along [111] direction of the [111] oriented films (see Figure 3a for illustration). Due to this geometry the measurement was sensitive to the in-plane ordering. The XPD features shown in Figure 3a are the results of various scattering effects for S 2p in the ZnS atomic network, including forward-scattering by nearest Zn atoms along the [111] direction (Figure 3b). The observation of these diffraction peaks demonstrates that the film crystallites have a well-defined in-plane orientation. Together with the angle-dependent XPD results discussed above, this would demonstrate that the films are epitaxial. The energy-dependent XPD studies were performed for a film with 2000 Å thickness but the consistent angle-dependent XPD results (Figure 1, part 1a–c) would indicate that the thinner films are of analogous crystallographic quality.

Enhanced forward-scattering can significantly alter photoelectron intensities in XPD experiments.¹¹ Figure 4a shows the energy-dependent XPD for a cubic ZnS single-crystal reference, which measured S 2p photoemission along [110] direction. Due

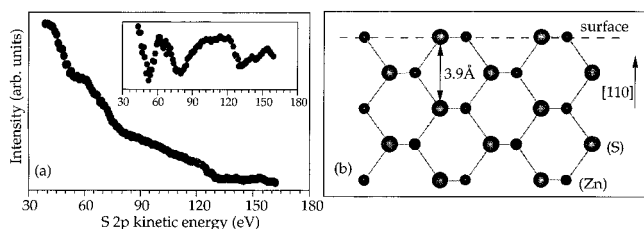


Figure 4. (a) Intensity distribution of S 2p measured along [110] direction for the cubic ZnS single crystal. The inset shows the normalized intensity. (b) Cross-section of the cubic ZnS structure showing the geometry of forward-scattering along [110] direction.

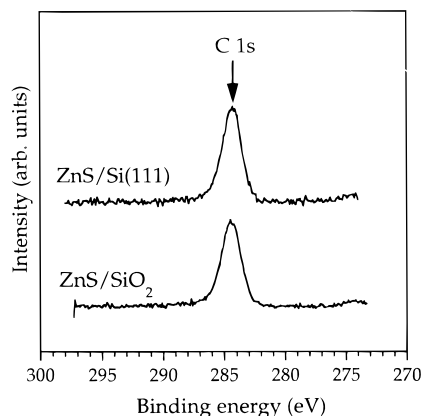


Figure 5. C 1s XPS scans for ZnS films grown on Si(111) and SiO₂.

to this measurement geometry, forward-scattering of the emerging S photoelectrons is only a weak effect (the next nearest neighbor of S atoms in [110] direction has a distance of approximately 3.9 Å, as shown in Figure 4b). As a result, the diffraction intensity from this single-crystalline reference is smaller than that of the films (Figure 3). The observed very large diffraction intensity of the film measurements however, is another indication for the crystallographic quality of the ZnS thin films.

Figure 5 shows the C 1s XPS region scans for the 2000 Å thick epitaxial film and a self-textured film grown on SiO₂ under identical conditions. These films exhibited the same out-of-plane orientation. It is interesting to note that these films also consisted of similar carbon concentration which varied between 2 and 4 atomic %. In addition, it has been observed that film crystallinity was varied significantly with the carbon concentration² and the results here seem to suggest that below a certain carbon concentration, film crystallinity is independent of this, but primarily depends upon the substrate structure.

Conclusion

In summary, this paper examined the crystallographic quality of SS CVD ZnS thin and ultra-thin films on Si(111). Angle-

dependent XPD indicated that the films are of cubic structure and film crystallites have (111) out-of-plane orientation already at the interface. The Zn and S 2p diffraction patterns are consistent with cubic stacking geometry, which resulted in enhancement of Zn 2p intensity and substantially suppressed S 2p intensity at $\theta = 0^\circ$. The energy-dependent XPD results have shown that the ZnS molecules also have well-defined long range in-plane orientation. The concentration of carbon was approximately 3% and independent of the substrates used. The restrictive epitaxial forces are perhaps more important in determining film structure than the impurity status of the evolving films. This study has demonstrated that single-source chemical vapor deposition is an alternative technique for fabrication of epitaxial II–VI semiconductor thin films.

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