



Letter

The interface of SiO₂/ZnS films studied by high resolution X-ray photoluminescenceShinjita Acharya^a, Orlando Trejo^a, Anup Dadlani^b, Jan Torgersen^{a, c, *}, Filippo Berto^c, Fritz Prinz^{a, d}^a Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA^b Department of Chemistry, Stanford University, Stanford, CA 94305, USA^c Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, 7034 Trondheim, Norway^d Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

HIGHLIGHTS

- A clear shift of the S 2p peak with the number of deposition cycles showing that S is present in many different environments at the interface
- The confirmation of the surface confinement of this species as revealed by the XPS measurements at different angles.
- In a depth profile, the shift of the S 2p to higher energy is correlated to the rise of the Si 2p peak giving additional evidence that SO₄²⁻ does not develop upon the exposure of the sample to air but is in fact a species for ZnS nucleation.

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ABSTRACT

Sharp interfaces in optoelectronic devices are key for proper band alignment. Despite its benefits as buffer layer, ZnS deposited via atomic layer deposition (ALD) renders intermixed interfaces to its substrate, which can be detrimental for device performance. Here, we are attempting to elucidate the chemical species deriving from this metal-oxide to metal-sulfide transition studying ultrathin film ZnS on SiO₂ using high resolution X-ray photoluminescence spectroscopy (XPS). Regarding the S 2p spectra after a deposition of only three cycles of ZnS, we discover the many different chemical species in which S is present. These include intermediate oxides such as SO₄²⁻. These species become more obvious as we tilt the sample in the XPS chamber to shallower angles. Comparing the Si 2p and S 2p high resolution peaks in the depth profile, one can clearly uncover the confinement of SO₄²⁻ to the interface of the underlying substrate. This may indicate that SiO₂/ZnS interfaces contain interfacial sulphates that likely alter the electronic configuration of this interface.

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ZnS is an interesting *n*-type II-VI semiconductor with a wide band gap (3.7 eV), low optical absorption in the visible and infrared spectral regions and high refractive index [1, 2]. ZnS films are widely used in optical and electronic systems in flat panels [3], electroluminescent thin film devices [4], infrared windows [5] and ultraviolet light emitting diodes as well as for buffer layers in solar cells [6, 7].

The deposition of ZnS with atomic layer deposition (ALD) is

particularly attractive as this technology provides atomic level thickness [8], and excellent compositional [9] control at relatively low temperatures and mild vacuum conditions. This allows for the precise engineering of the electrical performances of thin films (e.g. recombination [10], resistivity [11], and band alignment [12]). ZnS films can be incorporated in multilayer devices [12, 13] interfacing this metal sulfide to various oxide materials. In such complex architectures proper band alignment is key, which is determined by sharp interfaces [13, 14]. In this aspect, metal-sulfide films present a major challenge due to sulfur's susceptibility to diffusion [15]. Several researchers have

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investigated performance and compositional differences of thin films of various thicknesses deposited employing the same process conditions. They hypothesized that these variations are attributed to changes in the chemical environment in the initial cycles of ZnS ALD [7, 12]. To understand this phenomenon, our group has recently employed the element specific capability of X-ray absorption near edge structure (XANES) to investigate the electronic and geometric configuration of various binary and ternary ALD films interfacing metal-oxide substrates [16-19]. We investigated the O K-, S K-edge as well as Zn K and L-edges of thin film ALD ZnS and $\text{ZnO}_{1-x}\text{S}_x$ of various thicknesses interfacing ZnO thin film electrodes [20, 21]. The results indicated the formation of ZnSO_4 at interfaces, which is known to increase the resistivity and loss in fill factor of the buffer layer [22].

To further understand the importance of this species, we study one particular interface metal-oxide/metal sulfide transition found in $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) based architectures [23]. We investigate the chemical species in the early stages of nucleation on a model substrate (SiO_2) as a first step towards a thorough mechanistic study of the ZnS nucleation on oxide substrates.

We used a customized flow-type reactor described elsewhere [24, 25] for the deposition of ALD ZnS. Diethylzinc (DEZ) (Sigma-Aldrich, USA) and H_2S gas mixture were used as precursors. The latter contained 3.5% H_2S in N_2 , which resulted in a nonflammable gas mixture. DEZ and H_2S were kept at room temperature in 50 cm^3 stainless steel sample cylinders. The substrate temperature was 160°C. The manifold connecting precursors and the chamber was kept at 100°C. Ten sccm of Ar was flowing through the manifold and acted as the carrier gas adjusting the chamber pressure to 0.6 torr (measured by a Pirani gauge, Lesker, USA). Standard pneumatic ALD valves (Swagelok, USA) were used for pulsing precursor vapour into the chamber. The deposition was carried out on a 500 μm thick p-doped Si <100> wafer. Prior to the deposition of ZnS, the oxide was removed and the cleaned wafer was exposed to 10 H_2O pulses inside the ALD chamber (0.1 s pulse, H_2O was kept at room temperature in standard 50 cm^3 cylinders) to ensure the deposition of a 2-3 nm native SiO_2 prior to the deposition of ZnS avoiding exposure of the wafer to atmosphere. The pulse duration for DEZ was 1 s, for H_2S 0.1 s. A growth rate of 0.17 nm/cycle was established (measured by XPS depth profiling and spectroscopic ellipsometry as described in [26, 27]), which was established on this reactor in previous reports [25, 28] and is also reported by others as well within the ALD window [29].

The analysis was conducted in a PHI-Versaprobe (Physical electronics, USA) using Al $K\alpha$ radiation (1486 eV) in vacuum (5×10^{-10} torr). The instrument was equipped with Ar ion sputter guns for surface cleaning and depth profile analysis. The sample stage could be tilted to increase the surface sensitivity of the analysis.

Figure 1 shows the high resolution XPS peak of S 2p after three complete ALD cycles of DEZ and H_2S on a Si<100> wafer with native SiO_2 surface. The sulfide peaks at 161.2 and 162.2 eV are the binding energies (BE) of ZnS. Due to low signal, it is unclear whether there is spin orbit coupling (fitted like this in Fig. 1) or there are indeed 2 species present, where both can be rationalized. At the higher binding energies, there are also 2 peaks fitted, where it is believed that both sulfate and either an intermediate oxidative species or simply noise are present. The presence of interfacial sulfates and intermediate oxidant species is

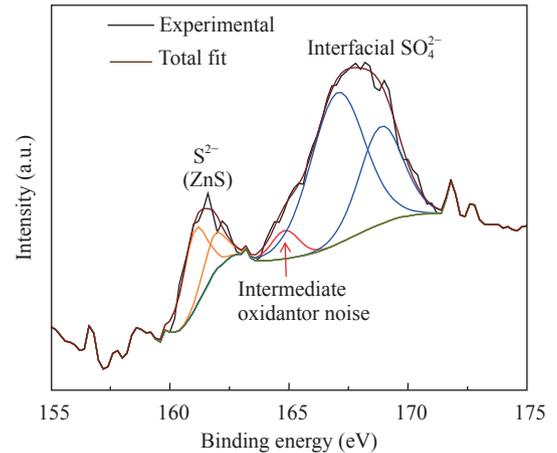


Fig. 1. XPS of S 2p of three complete ALD cycles of H_2S and DEZ deposited on Si wafer. It is clearly seen that there are many species present on the surface of the silica. There is sulfur bonded to zinc (ZnS) at the lower binding energies. At the higher energies, it appears as if there are some intermediate oxidants, but mostly interfacial sulfates. The broadness of the higher energy peak suggests that due to amorphous nature of the underlying native oxide, the sulfur is present in many different chemical environments, which may also explain the presence of intermediate oxidant species.

possible because SiO_2 is flexible in rearranging the surface atoms, which might be more difficult than for other oxide substrates as indicated for TiO_2 previously [19, 20]. The peaks are also quite broad due to the amorphous nature of the native oxide layer, creating several environments that sulfur is present in.

High resolution XPS (Fig. 2) was also done on a Si wafer that had five complete ALD cycles of H_2S and DEZ deposited. The spectra were obtained at different sample mounting angles in order to probe different depths within the sample. At shallow angles, the surface was probed where it is seen that only sulfide species are present. As the angle is increased, the appearance of a sulfate species appears, indicating that the sulfate is located closer to the interface. At an angle almost normal to the analyser (85°), the sulfate species is equal in intensity to the sulfide species, where we are predominantly probing at the interface of the substrate and the ALD ZnS film.

We also conducted a high resolution XPS depth profile of the S 2p peak to further evaluate the confinement of the sulfate species to the interface to the SiO_2 substrate and that the occurrence of the sulfate species is not a matter of exposure of partly exposed substrate to ambient air. This is of particular importance since ZnS and other metal sulfide ALD films exhibit exceptionally strong Volmer-Webber nucleation [28]. When DEZ is introduced, unconnected islands of approximately 5 nm in diameter and a few angstroms in height nucleate over a period of two or three cycles before they coalesce into a continuous film [26]. To ensure that the film was continuous before its exposure to air and to rule out the formation of sulfate species upon exposure to air, a ~170 nm thick ZnS film was grown (100 cycles) and analyzed. The depth profile was done by taking each spectrum after 12 additional seconds of sputtering in succession. Sulfide is only present when no sputtering is done (at top of film). Even after 12 s of sputtering only sulfide is there. After 24 s, we see a sharp decrease in the sulfide peak and a sulfate peak begins to appear.

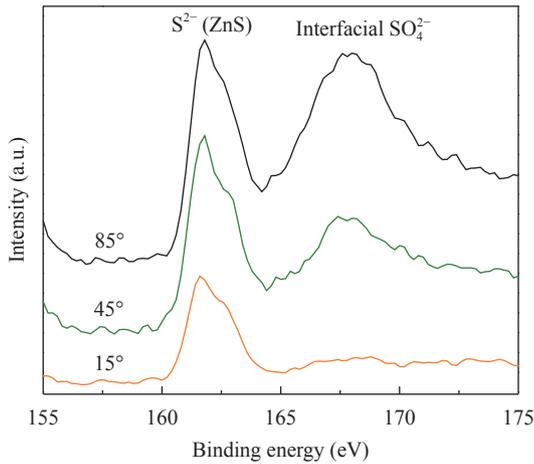


Fig. 2. High resolution XPS of S 2p of five complete ALD cycles of H₂S and DEZ deposited on Si wafer. It is clearly seen that as we probe the electrons ejected at shallower angles, the only species visible is the sulfide (ZnS). As the angle is changed to 45°, we see the appearance of a sulfate species, indicating that it is closer to the substrate interface. Almost normal to the surface (85°), the sulfate peak is at a similar intensity as the sulfide species. The increase in intensity as the angle becomes more normal to the surface means that the sulfate is predominantly at the interface.

After 36 s and up to 1 min of sputtering, the sulfide peak is practically gone and there is an unmistakable sulfate peak.

In addition to the S 2p peak that revealed the interfacial presence of sulfate species, the Si 2p peak was tracked in order to find out when the interface was reached. This way, it can be confirmed that the relative intensity of the sulfate species increases (Fig. 3) as the Si signal increases towards the interface (Fig. 4). Indeed, this trend is clearly visible further strengthening the hypothesis that the sulfate species is confined to the interface.

Using standard high resolution XPS, we have shown that an intermediate sulphate is formed upon the exposure of SiO₂ to the initial cycles of ALD ZnS deposition. Changing the measure-

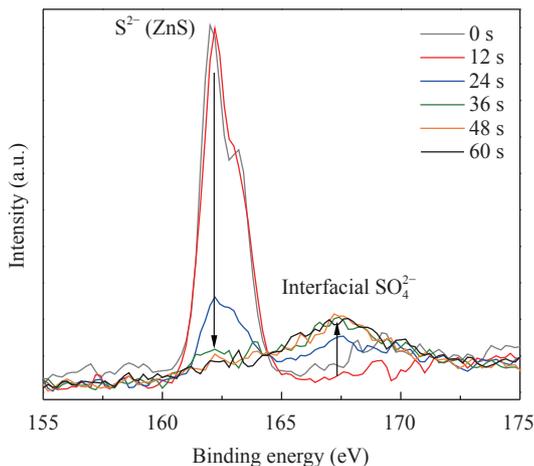


Fig. 3. High resolution XPS of S 2p of 100 complete ALD cycles of H₂S and DEZ deposited on Si wafer. A thick sample was necessary to make sure there was no exposed Si interface that when exposed to the environment would result in the formation of a sulfate species.

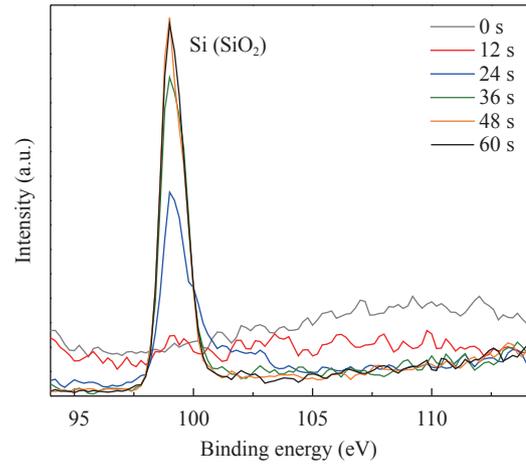


Fig. 4. High resolution XPS of Si 2p of 100 complete ALD cycles of H₂S and DEZ deposited on Si wafer.

ment angle of the XPS setup and investigating depth profiles of 170 nm thick ALD films, we rule out the formation of this species resulting from the sample's exposure to air. Rather, this intermediate species seems inherent to the deposition mechanism. This clearly indicates the need for further studies on application-relevant oxide substrates and extensive mechanistic studies for the fundamental investigation of nucleation mechanism of ZnS and other metal-sulfide ALD processes on oxide substrates, a process that is crucial for many applications in various fields of optoelectronics, where respective thin films are rapidly increasing in popularity.

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