Supporting Information

ALD Zn(O,S) thin films' interfacial chemical and structural configuration probed by XAS

Anup L. Dadlani,[1] Shinjita Acharya,[2] Orlando Trejo,[2] Fritz B. Prinz[2,3] and Jan Torgersen[2]*

[1] Department of Chemistry, Stanford University, Stanford, CA 94305

[2] Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA

[3] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

Email: jtorgersen@stanford.edu

Experimental Methods

X-ray photoluminescence (XPS) was done using PHI Versa Probe Scanning XPS Microprobe which uses Al (Kα) radiation of 1486 eV in a vacuum environment of $5*10^{-7}$ Torr.

Atomic Force Microscopy (AFM) measurements were done in a JEOL SPM 5200 system, where all images were acquired in AC mode.

ALD of Zn(O,S) films

The substrates were loaded into a customized flow-type ALD system. The substrate temperature was maintained at 160 °C. Diethylzinc (DEZ), distilled H_2O, and a gas mixture of 3.5% H_2S in N_2 were used as precursors to deposit Zn(O,S). The pulse time for all precursors was 0.1 s, their residence time in the reaction chamber was 2 s to ensure complete saturation of the available surface sites. After each precursor pulse, 45 s were allotted for byproduct evacuation. Conventionally, ZnO and ZnS films were deposited in a laminar fashion pulsing DEZ into the reaction chamber before its oxidation with either H_2O or H_2S. Both ALD films are well characterized in literature.[1,2] Zn(O,S) composition was adjusted by employing different ratios of ZnS cycles within the total number of ALD cycles (ZnO+ZnS) as previously reported.[3] In addition to the nanolaminate deposition technique, we propose an alternative diffusion based deposition method (Diffd) employing a set number of H_2S cycles after each ZnO deposition. To differentiate between Zn(O,S) compositions deposited with either method, we refer to the oxidant pulse ratio ($H_2S/(H_2O+H_2S)$) for comparison. Zn(O,S) samples of three different S compositions were fabricated and are described by the H_2S oxidant pulse ratios 33%, 20% and 10%, respectively.

Two types of substrates were used: TiO_2 nanoparticles (NPs) and Si substrates. TiO_2 NPs were prepared on quartz substrates as previously reported.[4] The Si substrates were 500 µm thick p-doped Si <100> (WRS materials). Some substrates were coated with 12 nm of ZnO (60 cycles) prior to the ALD of Zn(O,S) films. On either substrate, 5 pulses of H_2O were employed prior to ALD of ZnO and Zn(O,S) to ensure proper nucleation (and the growth of a native SiO_2 on Si). For ZnS deposition, we pulsed 5 H_2S pulses onto the substrates prior to the deposition.

The sample labels follow the form lettersnumber_cycles, where letters indicate substrate (T for TiO_2 NPs, S for SiO_2 and TZ for 12 nm ZnO coated TiO_2 NPs), number indicates the H_2S to total number of oxidant pulses, and cycles tells the total number of cycles of ALD deposition. In each

case, Zn(O,S) layers were deposited using 10, 20, and 33% of $H_2S/(H_2S+H_2O)$ ALD oxidant pulses

X-ray photoluminescence (XPS) and Atomic Force Microscopy (AFM) was done on Zn(O,S) films to check stoichiometry (main text), film morphology and roughness (Fig. S1) to check for consistency with previous reports.[3,5]

XANES for Sulfur K-edge measurements

At BL 4-3, the samples were positioned at 45° from both the incident x-ray beam and the detector. The energy X-ray slits were approximately set to 1 mm x 10 mm. A Passivated Implanted Planar Silicon (PIPS) detector was used to gather the total fluorescence yield (TFY) data. The samples in the X-ray path were kept under a He environment.

XANES for Oxygen K-edge measurements

Auger electron yield (AEY) and total electron yield (TEY) spectra were gathered at BL 10-1. To measure the sample drain current for the TEY data, all samples were loaded on the sample stick with carbon tape and were electrically grounded with carbon paste.

Oxygen K-edge

The similarities between TEY and AEY spectra justify using the cleaner TEY spectra in the main text. XANES AEY spectra at the O K-edge in thin film Zn(O,S) deposited on silicon is presented in Fig.S4. All spectra were background subtracted and atomically normalized in the energy region from 548 to 560 eV.

The O K-edge XANES total electron yield (TEY) spectra of thin samples (20 cycles) deposited on anatase TiO_2 NPs (Figure 1a) are shown in Fig. S2. A pristine anatase TiO_2 NPs substrate served as our reference. Peaks B_1 and B_2 correspond to transitions from O 1s states to unoccupied hybridized orbitals containing dominantly Ti 3d and O 2p character.[22] Peaks B_3 and B_4 derive from a O 1s excitation to hybridized Ti 4p - O 2p states.[22,23] Samples T33_21 and T20_20 are nearly identical to the reference anatase TiO_2 spectrum except for a change in the B_3/B_4 peak ratio. Feature B_5 results from multiple scattering and is only pronounced in samples where the signal from the anatase substrate is overwhelming. Only T10_20 differs significantly, likely due to the fact it may be more homogeneous than the other two samples in this thickness regime. The highest intensity peak at ~535 eV and the feature past 538 eV are inherent to ZnO.[24]

In general, ultra-thin film Zn(O,S) films did not reveal much at the O K-edge as the majority of the signal stems from anatase TiO_2.

The oxygen K-edge XANES spectra of the thick samples (300 cycles) deposited on a silicon wafer are shown in Fig. S3. As a reference sample, 300 cycles of ALD ZnO were deposited on a silicon wafer. The differences in spectra between the thick and thin film regime samples deposited on Si substrates can be seen in Fig. S5, where a shift in the onset to higher energies is visible in the thinner samples.

The results of the AEY spectra (Fig. S4) for silicon substrate are the same as TEY shown in the main text, which makes sense since it is a planar substrate. In the case of samples deposited on anatase TiO_2, since ALD films can penetrate deeply and the substrate is not flat, the TEY captures a lot of signal from the substrate.

To elaborate on the changes in local bonding environment of O in the buffer layer when deposited on top of 12 nm ALD ZnO (60 cycles) which was deposited on titania and silicon substrates, XANES TEY spectra at the O K-edge are shown in Fig. S7. The same reference has been used, ie. 300 cycles of ALD ZnO deposited on a silicon wafer. All the thin samples, regardless of substrate do not have feature E. The 33% samples most closely resemble the reference because being the thinnest samples, the spectra is predominantly coming from underlying ZnO. The main difference between the samples and the reference is that the B/A ratio decreases as the film thickness increases. The 10% sample, though having the most oxygen, has the lowest B/A ratio because it is thickest and so more signal is a result of the Zn(O,S) film.

Since the TEY of the thin films deposited on ZnO electrode appeared most like ZnO reference, the AEY of films deposited on ZnO on titania is shown in Fig. S8. Samples 10% and 20% start to appear somewhat like the thicker films suggesting a more homogeneous growth of the sulfur poor films. The 33% sample on the other hand, although clearly distorted, still resembles the reference more than the other two stoichiometries.

The TEY of samples deposited on silicon using the alternate deposition strategy that leverages S diffusion is plotted in Fig. S9. The 10% sample looks very similar to 10% plotted in Fig. S4. The 33% has three peaks at the main edge, similar to the thicker 33% sample, however the intensity of these peaks is different, suggesting a great range of tunability for sulfur rich films with thickness. The 50% sample (sulfur rich) resembles 33% from Fig. S4, which may mean that sulfur saturation may have already been achieved.

AFM

AFM images were obtained on the ultra-thin samples deposited on silicon wafers. The two reference samples which were 300 cycles of ALD were much rougher than the thin films, especially the ZnS sample. AFM was done to check the film morphology and surface roughness (Fig. S1). There was no trend observed in the ultra-thin films, the roughness varying between 2.2 – 2.8 Å.
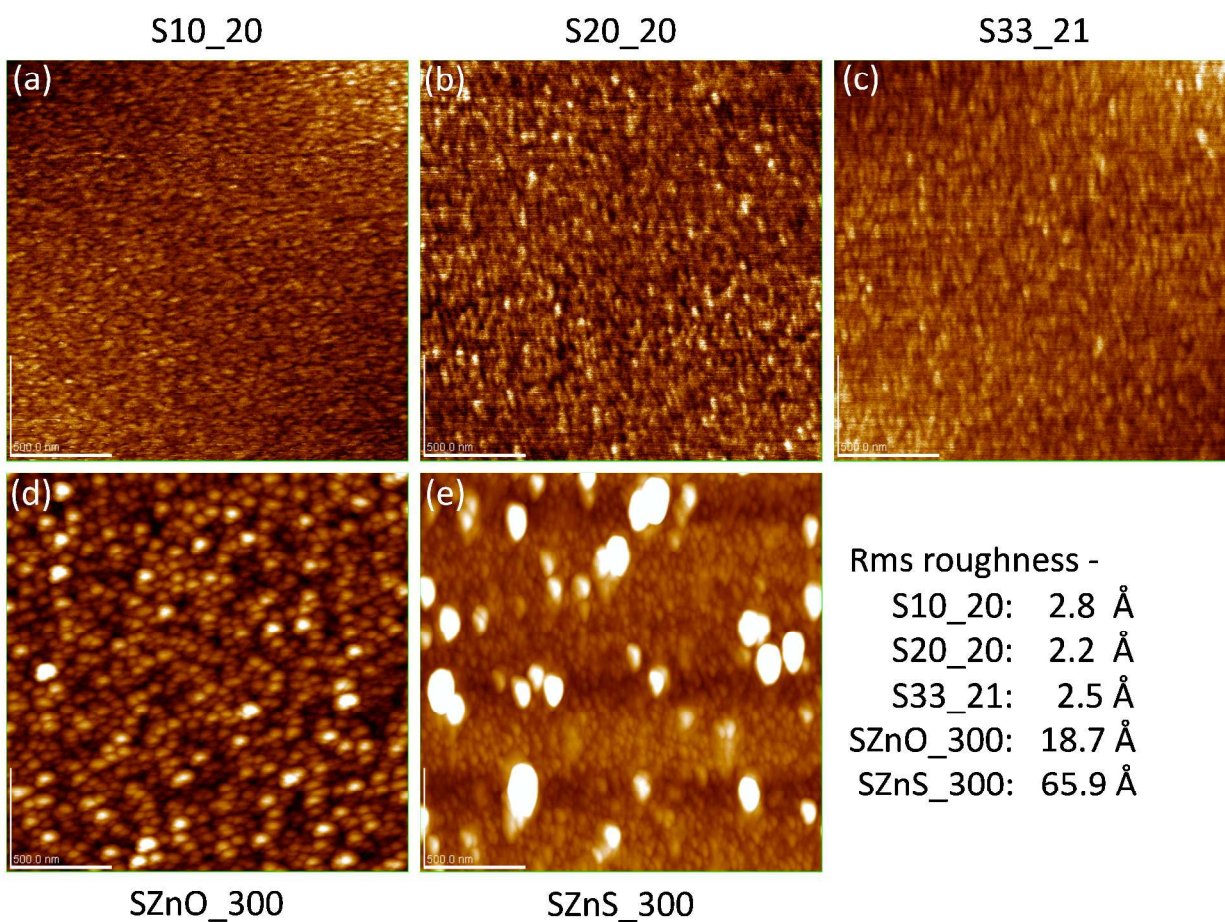

Rms roughness -
S10_20:   2.8 Å
S20_20:   2.2 Å
S33_21:   2.5 Å
SZnO_300: 18.7 Å
SZnS_300: 65.9 Å

Figure S1: AFM of films deposited on silicon and imaged in acoustic mode. Each images is a scan of 2 x 2 um^2. Scale bar is 500 nm for all images. **(a)** S10_20 **(b)** S20_20 **(c)** S33_21 **(d)** reference sample, SZnO_300, and **(e)** reference sample SZnS_300. The root mean square (Rms) roughness of each of the samples is given, where ZnS is roughest and all the thin films are nearly similar in roughness.
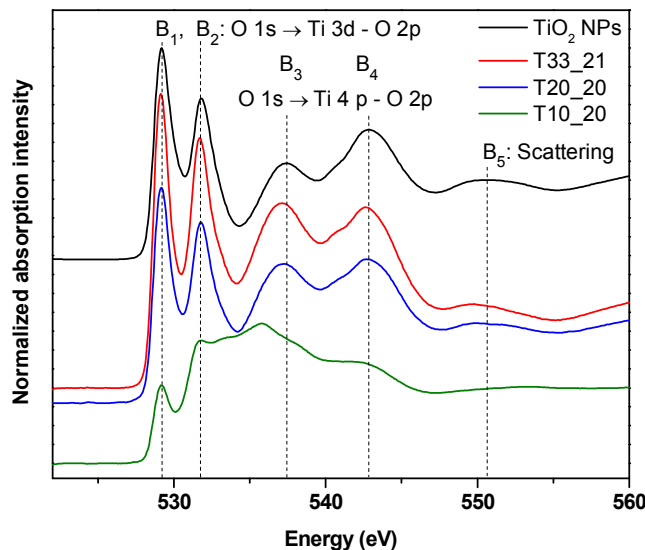
Figure S2: O K-edge TEY spectra of 20 cycles Zn(O,S) with 10% (green), 20% (blue) and 33% (red) $H_2S/(H_2S+H_2O)$ cycle ratios grown on TiO_2 NPs (black reference). Peaks B_1 and B_2 derive from a O 1s to Ti 3d − O 2p hybridized orbital transition, while peaks B_3 and B_4 stem from O 1s to Ti 4p − O 2p transition and B_5 arises from multiple scattering.
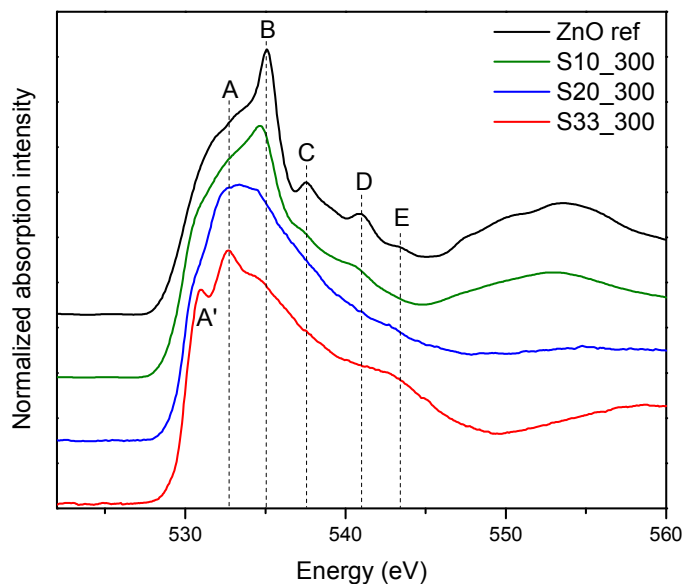

Figure S3: The O K-edge XANES TEY spectra of thick samples (300 cycles) deposited on silicon substrates. As a reference sample, 300 cycles of ALD ZnO were deposited on a silicon wafer. O K-edge spectra were background subtracted and atomically normalized in the energy region from 548 to 560 eV.
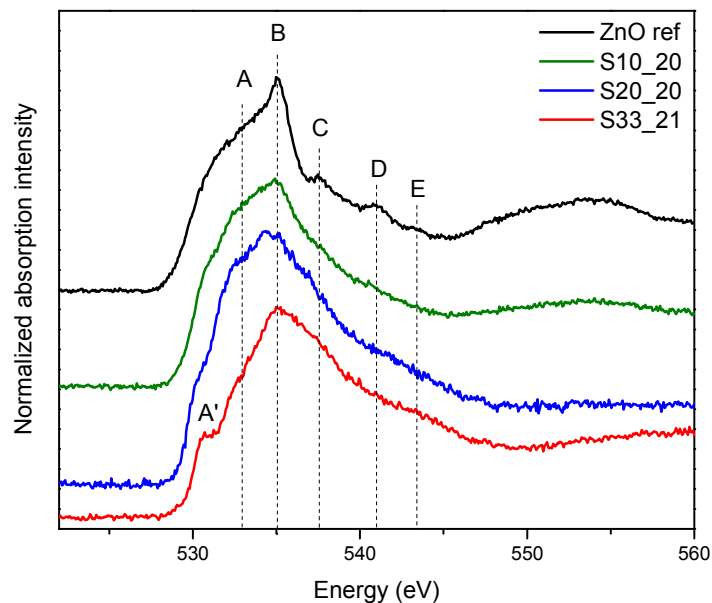
Figure S4: The O K-edge XANES AEY spectra of ultra-thin samples (20 cycles) deposited on silicon substrates. As a reference sample, 300 cycles of ALD ZnO were deposited on a silicon wafer.
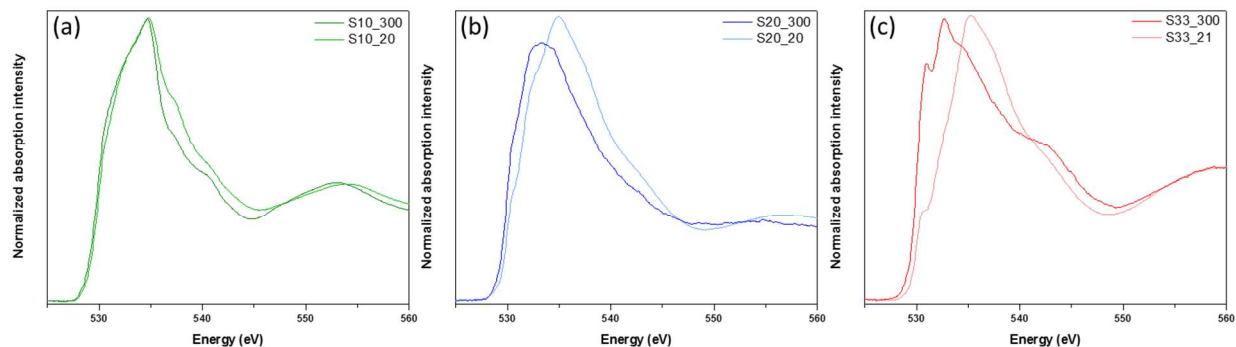

Figure S5: The O K-edge XANES TEY spectra of thick (300, dark) and ultra-thin samples (20 cycles, light) deposited on silicon substrates **(a)** 10% **(b)** 20% **(c)** 33%. In all cases, the thinner samples have a slightly later onset compared to the thick films.
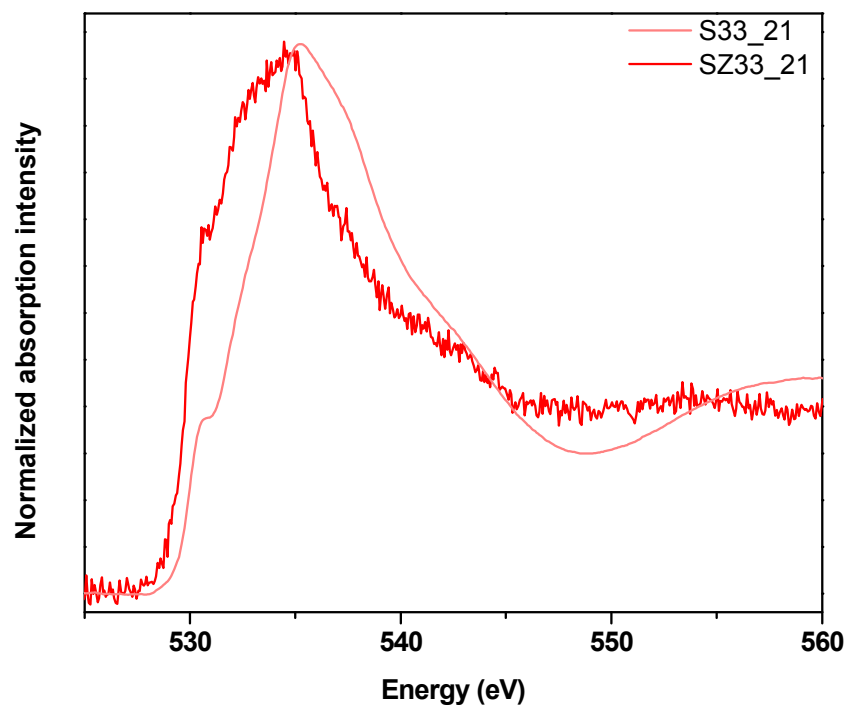
Figure S6: The O K-edge XANES spectra of 33% films grown on ZnO (AEY dark) and directly on Si substrate (TEY light). The two curves have been replotted from the main text in order to show the redshift of the XANES spectrum for the film grown on ZnO.
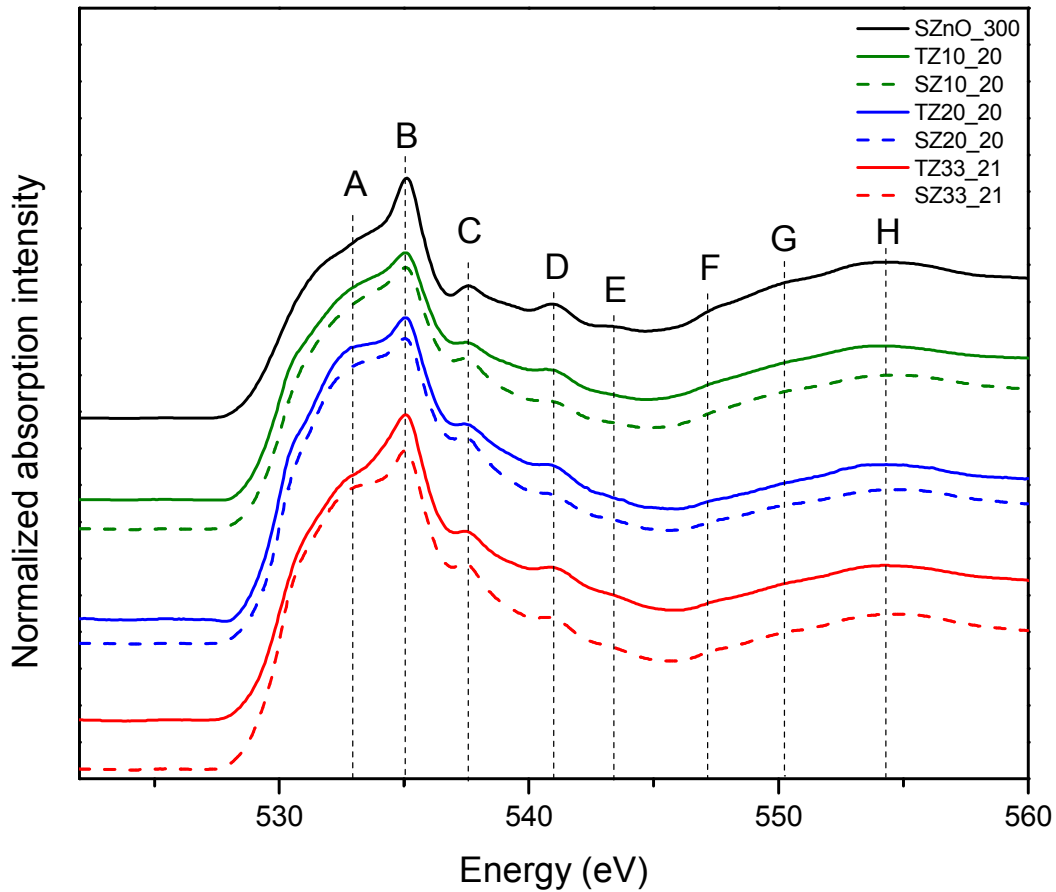
Figure S7: The O K-edge XANES TEY spectra of ultra-thin samples (20 cycles) deposited with 12 nm of ZnO (60 cycles) sandwhiched between the buffer layer and silicon substrate (dashed lines) and TiO$_2$ NPs (solid lines). As a reference sample, 300 cycles of ALD ZnO were deposited on a silicon wafer.
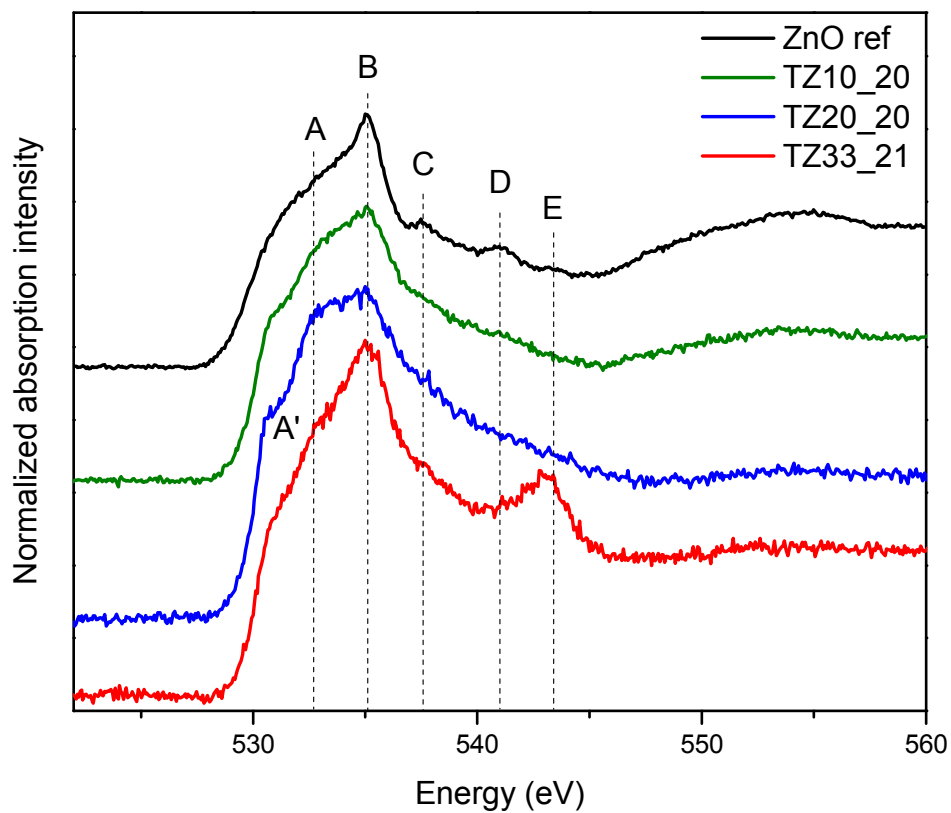
Figure S8: The O K-edge XANES AEY spectra of ultra-thin samples (20 cycles) deposited with 12 nm of ZnO (60 cycles) sandwhiched between the buffer layer and TiO_2 NPs. As a reference sample, 300 cycles of ALD ZnO were deposited on a silicon wafer.
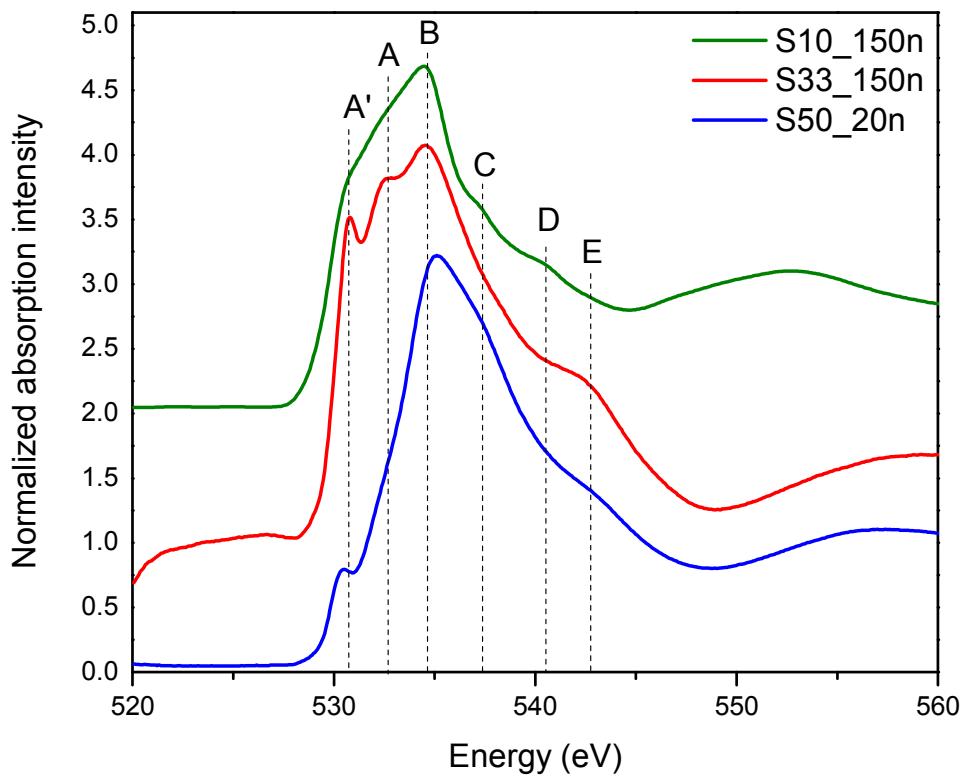
Figure S9: The O K-edge XANES TEY spectra of Zn(O,S) films of varying S composition deposited using our diffusion facilitated deposition method (Diffd), demarcated by "n" on a silicon wafer. The 10% sample looks very much like thick samples grown the conventional way (Figure S3). The 33% sample which is only half as thick as the thick samples contains A', A, and B peaks but with different intensities. It appears the S rich films have a wide range of tunability. The 50% thin sample looks similar to 33% thin film grown by either deposition strategy.
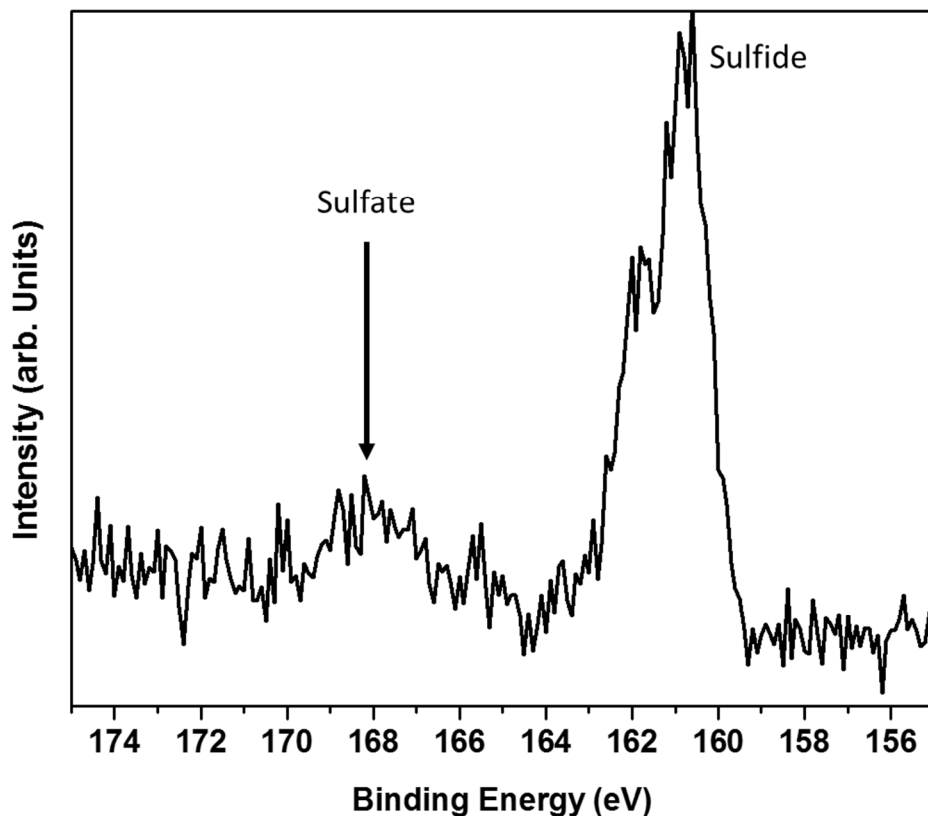
Figure S10: XPS S 2p high resolution spectrum of S33_21n film synthesized employing the Diffd method. The formation of a sulfate peak at ~168 eV can be observed indicating that sulfate forms at the SiO_2 interface. Sulfate formation is not prevented by employing the Diffd method.

References

(1)   Boichot, R.; Tian, L.; Richard, M.-I.; Crisci, A.; Chaker, A.; Cantelli, V.; Coindeau, S.; Lay, S.; Ouled, T.; Guichet, C.; Chu, M. H.; Aubert, N.; Ciatto, G.; Blanquet, E.; Thomas, O.; Deschanvres, J.-L.; Fong, D. D.; Renevier, H. *Chem. Mater.* **2016**, *28* (2), 592–600.

(2)   Stuyven, G.; De Visschere, P.; Hikavyy, A.; Neyts, K. *J. Cryst. Growth* **2002**, *234* (4), 690–698.

(3)   Platzer-Björkman, C.; Törndahl, T.; Abou-Ras, D.; Malmström, J.; Kessler, J.; Stolt, L. *J. Appl. Phys.* **2006**, *100* (4), 044506.

(4)   Trejo, O.; Roelofs, K. E.; Xu, S.; Logar, M.; Sarangi, R.; Nordlund, D.; Dadlani, A. L.; Kravec, R.; Dasgupta, N. P.; Bent, S. F. *Nano Lett.* **2015**.

(5)   Bakke, J. R.; Tanskanen, J. T.; Hägglund, C.; Pakkanen, T. A.; Bent, S. F. *J. Vac. Sci. Technol. A* **2012**, *30* (1), 01A135.