Atomic Layer Deposition of Zn(O,S) Alloys Using Diethylzinc with H$_2$O and H$_2$S: Effect of Exchange Reactions

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ABSTRACT: Zn(O,S) thin films have a tunable band gap and are useful as conduction and valence band buffers in various types of solar cells. Previous growth of Zn(O,S) thin films by atomic layer deposition (ALD) has utilized alternating cycles of ZnO ALD and ZnS ALD. Controlling the composition of the Zn(O,S) alloys using alternating cycles is complicated because of an efficient exchange reaction between ZnO and gaseous H$_2$S given by ZnOH* + H$_2$S → ZnSH* + H$_2$O. This facile exchange reaction leads to a higher than expected sulfur content in the Zn(O,S) films. In this study, the effect of this exchange reaction on the composition of Zn(O,S) films was examined by varying the reaction conditions. For growth using alternating cycles, the Zn(O,S) film composition was strongly affected by the temperature and the size of the H$_2$S exposure. An alternative method that avoids alternating cycles of ZnO ALD and ZnS ALD was also employed to grow Zn(O,S) thin films. This alternative method uses codosing of H$_2$O and H$_2$S at 100 °C. Codosing allows the composition of the Zn(O,S) film to be controlled by the mole fraction of the dosing mixture. The relative magnitudes of the exchange reaction rate ($k_i$) for ZnOH* + H$_2$S → ZnSH* + H$_2$O and the competing exchange reaction rate ($k_j$) for ZnSH* + H$_2$O → ZnOH* + H$_2$S could be estimated using this method. Through the study of the composition of the Zn(O,S) films for different H$_2$O and H$_2$S partial pressures during codosing, the ratio of the exchange reaction rates, $k_i/k_j$, was determined to be 71–231. Band gaps were measured for the Zn(O,S) thin films grown using the alternating cycle method and the codosing method. The band gaps could be correlated with the most control by varying the mole fraction of H$_2$S in the H$_2$S/H$_2$O codosing mixture.

1. INTRODUCTION

Zn(O,S) alloys have received considerable interest because they have tunable band gaps and are useful as conduction and valence band buffers in solar cells. The band gap of Zn(O,S) is tunable from 2.6 to 3.6 eV. For Cu(In, Ga)Se$_2$ solar cells, Zn(O,S) alloys are a potential replacement for the toxic CdS buffer layer. For dye-sensitized solar cells, Zn(O,S) alloys can serve as a conduction band buffer between the excited dye molecule and the TiO$_2$ electron transport layer. The utility of Zn(O,S) alloys depends on the ability to control their composition to tune their band gap and band positions. There are a number of advantages to growing Zn(O,S) alloys using atomic layer deposition (ALD) techniques. Ternary alloys can be grown using ALD by alternating the ALD cycles used to grow the pure compounds. The composition of the alloy is controlled by varying the ratio of the ALD cycles used to grow the pure compounds. This alternating cycle method of controlling the composition of ternary alloys is normally very effective. However, there is vast disagreement among the many groups that have studied the relationship between the alloy composition and the ratio of the ZnO/ZnS ALD cycles. The results for the %ZnS in the Zn(O,S) films versus the fraction of ZnS ALD cycles are shown in Figure 1a. Although there is disagreement between the various results, the ALD growth of Zn(O,S) alloys typically produces films containing far more sulfur than would be predicted by the fraction of ZnS cycles. This higher sulfur content is believed to result from the exchange reaction between H$_2$S and ZnO.

H$_2$S can react with the ZnO surface according to

\[ \text{ZnOH}^* + \text{H}_2\text{S} \rightarrow \text{ZnSH}^* + \text{H}_2\text{O} \]  

(1)

The asterisks indicate the species on the surface. This reaction is similar to the bulk reaction between ZnO and H$_2$S given by

\[ \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \]  

(2)

Thermochemistry predicts that this bulk reaction is exothermic. The standard enthalpy change and standard free energy change are nearly constant at $\Delta H^\circ = -17.5$ kcal and $\Delta G^\circ = -17.5$ kcal, respectively, over a wide temperature range. $\Delta G$ predicts a spontaneous reaction until the reaction system reaches an extremely large equilibrium constant of $K = 1.8 \times 10^{10}$ at 100 °C. The reaction of H$_2$S with ZnO has been well-studied by many previous investigations. ZnO is used as an industrial sorbent for hydrogen sulfide. There are many studies on the kinetics and mechanism of this reaction.

There is also a competing surface reaction where H$_2$O reacts with ZnSH* according to

\[ \text{ZnSH}^* + \text{H}_2\text{O} \rightarrow \text{ZnOH}^* + \text{H}_2\text{S} \]  

(3)

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The alternating cycle method is performed with only H$_2$O in the gas phase. Some H$_2$O surface reactions will occur to produce a free energy change of $\Delta G^\circ = +17.5$ kcal and a standard enthalpy change of $\Delta H^\circ = +17.5$ kcal.$^{22}$ These positive $\Delta H^\circ$ and $\Delta G^\circ$ values suggest that this reverse reaction is not favorable. However, the H$_2$O surface reaction during the alternating cycle method is performed with only H$_2$O in the gas phase. Some H$_2$O surface reactions will occur to produce a small finite H$_2$S pressure because $\Delta G$ is negative when there is no H$_2$S partial pressure. The H$_2$O surface reaction also occurs with ZnSH* surface species and may be very different than the bulk reaction.

There is also a wide variation of band gaps versus the %ZnS in the film reported for Zn(O,S) alloys grown by ALD using the alternating cycle method.$^{14,16−21}$ These results are shown in Figure 1b. The reasons for these differences are not clear. Perhaps the various growth strategies produce slightly different film structures. The possible nanolaminate nature of the Zn(O,S) films may be an issue.$^{31}$ ZnO, ZnS, and Zn(O,S) alloy films grown by ALD are generally reported to be polycrystalline. The Zn(O,S) films are no longer crystalline when the O/S ratio is $\sim 3/1$.$^{18,32}$

In this paper, the growth of Zn(O,S) alloys was examined using in situ quartz crystal microbalance (QCM) to measure the growth rate and ex situ X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) techniques to characterize film composition and growth rate. These studies reveal that controlling the composition of Zn(O,S) films using the alternating cycle method is difficult. The temperature, exposure time, and ratio of ZnO/ZnS ALD cycles can strongly affect the composition of the alloy. Zn(O,S) alloys were also grown by codosing the H$_2$O and H$_2$S. This alternative growth method is shown to yield more reproducible results for the band gaps than the alternating cycle method. The ratio of the H$_2$S and H$_2$O surface exchange reaction rates was also quantified using codosing experiments.

II. EXPERIMENTAL SECTION

Zn(O,S) thin films were grown in a hot-walled viscous flow ALD reactor.$^{33}$ The reactor consisted of a stainless steel tube that is 45 cm in length with an inside diameter of 3.5 cm. Two gas lines flowing 75 sccm nitrogen (UHP Airgas) were attached to the front of the reactor. The back of the reactor contained a capacitance manometer pressure gauge and a mechanical pump. Using the nitrogen flow and pumping with the mechanical pump, the pressure in the reactor was $\sim 1$ Torr.

Three precursors were used to grow Zn(O,S) thin films: diethyl zinc (DEZ, Sigma-Aldrich), deionized water, and hydrogen sulfide gas (Sigma-Aldrich 99.5% pure). The dose pressure of each precursor, all kept at room temperature, was controlled through a combination of metering valve and two computer-controlled pneumatic valves. Precursors were introduced directly into one of the two nitrogen gas lines and were carried by the N$_2$ flow into the reactor. During growth using the alternating cycle method, an in situ quartz crystal microbalance was used to monitor the mass of Zn(O,S) thin films.

For ex situ XPS and XRR measurements, thin films were grown on silicon wafers (MEMC, arsenic-doped). For ex situ band gap measurements, Zn(O,S) thin films were deposited on soda-lime glass slide covers (VWR micro cover glass). Prior to deposition, the samples were sonicated in acetone for at least 10 min, rinsed with isopropyl alcohol or methanol, then dried using nitrogen.

Using the alternating cycle method, ZnO, ZnS, and Zn(O,S) thin films were grown using 0.3 s reactant doses followed by 30 s purges. Alloys of ZnO and ZnS were grown by varying the numbers of growth cycles for ZnO ALD using DEZ/H$_2$O with one cycle for ZnS ALD using DEZ/H$_2$S. Films grown in this manner were labeled by the ratio of the ZnO/ZnS cycles or by the fraction of ZnS cycles. For example, a 3:1 film was grown using three cycles of ZnO ALD followed by a single cycle of ZnS ALD. A 3:1 film has a ZnS cycle fraction of 0.25.

Most of the Zn(O,S) alloy films were grown at 100 and 150 °C. A few Zn(O,S) alloy films were grown at 225 °C. The precursor exposures were determined from pressure measurements. The peak precursor pressures during the exposures were 60−70 mTorr for H$_2$O, 30−50 mTorr for H$_2$S, and 45−55 mTorr for H$_2$S.
mTorr for DEZ. The precursor exposures were 0.4–0.5 Torr·s for \( \text{H}_2\text{O} \), 0.4–0.5 Torr·s for \( \text{H}_2\text{S} \), and 0.55–0.65 Torr·s for DEZ. All of these exposures are known to grow either ZnO ALD or ZnS ALD at normal growth rates of approximately 2 Å/cycle for ZnO ALD and 1 Å/cycle for ZnS ALD.\[^{34,35}\] Although DEZ decomposition could be a problem at 225 °C with large DEZ exposures, the decomposition is much slower than the ALD reaction.\[^{36}\] At the small DEZ exposures used in these experiments, there was no evidence of DEZ decomposition. XPS analysis did not show any carbon or metallic zinc in the Zn(O,S) alloy films grown at 225 °C. In addition to the alternating growth method, Zn(O,S) films were also grown using the codosing method. The codosing method has also been employed recently to grow Zn(O,S) alloy films using spatial ALD techniques.\[^{37}\] Codosing replaces the alternating ZnO/ZnS ALD cycles with a single DEZ dose and a combined \( \text{H}_2\text{O}/\text{H}_2\text{S} \) dose. These films were grown using a quasi-static approach. For these growth experiments, a valve was inserted between the mechanical pump and the reactor that allows for static growth conditions. The reactor was first pumped down to base pressure. The reactor was then isolated from the mechanical pump and exposed to 400–500 mTorr DEZ and held for 5 s. The reactor was then reevacuated to base pressure and purged with 150 sccm \( \text{N}_2 \) for 35 s.

The substrate was then exposed to the combined \( \text{H}_2\text{O}/\text{H}_2\text{S} \) dose with the \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) at predetermined pressures. The \( \text{H}_2\text{S} \) mole fraction, \( X_{\text{H}_2\text{S}} \), was determined from initial partial pressures of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) by assuming that the gases behave ideally at these low pressures typically less than 1.5 Torr. The \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) pressures were a minimum of 458 mTorr of \( \text{H}_2\text{O} \) and 56 mTorr for \( \text{H}_2\text{S} \). The precursors were codosed into the reactor and held for 30 s without pumping. To investigate the effect of the initial surface coverage on the final composition and band gap, codosed films were also grown using a slightly different method. A 2 s delay was implemented between the introduction of one of the codosed precursors into the reactor and the second codosed precursor. The delay between the \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) precursors allowed one reactant to react before the other.

Film composition was determined by XPS using a PHI 5600 XPS spectrometer equipped with an Al Kz source. For calibration, four samples were grown using the alternating growth method on glassy carbon substrates. These samples consisted of 1:1, 3:1, 6:1, and 9:1 films. These samples were then analyzed by Rutherford backscattering (RBS) (University of Minnesota Characterization Facility). The RBS calibration determined that the percentage of zinc in the films obtained by the \( \text{Zn}3s \) and \( 3p \) XPS peak was not reliable. As a result, the % ZnS was determined from XPS analysis using the comparison of the O 1s and S 2s peaks. The film composition determined from the O 1s and S 2s XPS peaks agreed with the RBS analysis for all four films.

X-ray reflectivity was used to determine the thickness of films (Bede D1, Jordan Valley Semiconductors). Band gaps of the films were determined from ultraviolet–visible (UV–vis) transmission measurements using an Ocean Optics ISS-UV/vis. For these measurements, a minimum of 500 cycles yielding film thicknesses of 50–120 nm were grown on soda-lime glass substrates. The band gaps were calculated for direct transitions except for amorphous films where indirect band gaps were determined following standard procedures.\[^{32}\] Thicker samples were more accurate because there was a persistent optical interference background for thin samples that coincided with the onset of absorption from the band gap.

### III. RESULTS AND DISCUSSION

#### A. Alternating Cycle Method.

Figure 2 shows the mass changes monitored by the in situ QCM measurements during the deposition of three Zn(O,S) thin films. These films were grown by alternating cycles with ZnO:ZnS ratios of 9:1, 3:1, and 1:1 at 150 °C. Each of the three alloys has a unique growth pattern. The mass changes reflect the underlying surface reactions occurring during each reactant exposure. In particular, the three alloy films consistently show a larger mass gain for the first \( \text{H}_2\text{S} \) exposure after ZnO ALD cycles than the mass gain for \( \text{H}_2\text{S} \) exposures during steady-state ZnS ALD growth.

The size of the \( \text{H}_2\text{S} \) mass increase also depends on the number of preceding ZnO cycles. Figure 2 shows that the \( \text{H}_2\text{S} \) mass increases for the first \( \text{H}_2\text{S} \) exposure after the ZnO ALD cycles are 8 ng/cm² for the 1:1 film, 27 ng/cm² for the 3:1 film, and 30 ng/cm² for 9:1 film. In comparison, the mass gains for the DEZ exposures following each \( \text{H}_2\text{S} \) dose are very similar. The DEZ mass increases following the first \( \text{H}_2\text{S} \) exposure after the ZnO ALD cycles are 47, 45, and 48 ng/cm² for the 1:1, 3:1, and 9:1 films, respectively.
Experiments can be performed to study the first H₂S exposure after numerous ZnO ALD cycles performed to establish ZnO steady-state growth conditions. The mass change after the first H₂S exposure following ZnO ALD is shown in the upper data set in Figure 3a. The results for ZnS ALD are shown for comparison in the lower data set. An enlargement of the subsequent DEZ exposure during ZnS ALD is shown in Figure 3b. The mass increase for this H₂S exposure is \( \Delta m_{H_2S} = 31 \text{ ng/cm}^2 \). This mass increase for the subsequent DEZ exposure is \( \Delta m_{DEZ} = 49 \text{ ng/cm}^2 \). In comparison, the mass increase for the H₂S exposure during ZnS ALD is only \( \Delta m_{H_2S} = 2 \text{ ng/cm}^2 \). The mass increase for the subsequent DEZ exposure during ZnS ALD is \( \Delta m_{DEZ} = 44 \text{ ng/cm}^2 \). The total mass change per cycle for ZnS ALD in Figure 3a is \( \Delta m = 46 \text{ ng/cm}^2 \). This mass change per cycle agrees with previous measurements.

The mass increase of \( \Delta m_{H_2S} = 31 \text{ ng/cm}^2 \) for the first H₂S exposure on the ZnO surface can be used to determine the amount of ZnS produced and the amount of ZnO lost by the H₂S exchange reaction. The mass change for the ZnOH* + H₂S → ZnSH* + H₂O or ZnO + H₂S → ZnS + H₂O exchange reactions is \( \Delta m = +16.067 \text{ amu} = 2.668 \times 10^{-23} \text{ g} \). This is the mass change for the conversion of each ZnO to ZnS. The number of ZnO to ZnS conversions can then be calculated by dividing the mass increase of \( \Delta m_{H_2S} = 31 \text{ ng/cm}^2 \) by the mass change for the conversion of each ZnO to ZnS. The number of ZnO to ZnS conversions is \( 31 \text{ ng/cm}^2 / 2.668 \times 10^{-23} \text{ g} = 1.16 \times 10^{15} \text{ conversions/cm}^2 \).

The mass per square centimeter of 1.16 \( \times 10^{15} \text{ ZnS units per cm}^2 \) is 1.88 \( \times 10^{-7} \text{ g/cm}^2 \). This mass per square centimeter divided by the ZnS density of 4.09 g/cm³ yields a ZnS thickness of 4.6 \( \times 10^{-8} \text{ cm} \) or 4.6 Å formed by the exchange reaction. Likewise, the mass per square centimeter of 1.16 \( \times 10^{15} \text{ ZnO units per cm}^2 \) is 1.57 \( \times 10^{-7} \text{ g/cm}^2 \). This mass per square centimeter divided by the ZnO density of 7 g/cm³ yields a ZnO thickness of 2.8 \( \times 10^{-8} \text{ cm} \) or 2.8 Å consumed by the exchange reaction. These calculations indicate that the mass increase of \( \Delta m_{H_2S} = 31 \text{ ng/cm}^2 \) for the H₂S exposure on the ZnO surface is consistent with losing a ZnO thickness of 2.8 Å and producing a ZnS thickness of 4.6 Å.

The ZnO ALD films are polycrystalline. The ZnO wurtzite structure has lattice constants of \( a = 3.25 \text{ Å} \) and \( c = 5.2 \text{ Å} \). The loss of 2.8 Å of the ZnO film is slightly less than the loss of one unit cell length. Similarly, the ZnS cubic structure has an edge cell length of 5.41 Å. The production of 4.6 Å of the ZnS film is slightly less than the gain of one unit cell length. The close correspondence of the ZnO thickness loss and ZnS thickness gain and their respective unit cell lengths indicates that the exchange reaction is confined to the top ZnO layer on the ZnO surface.

Similar experiments can also be performed to study the first H₂O exposure after a large number of ZnS ALD cycles performed to establish ZnS steady-state growth conditions. The mass change after the first H₂O exposure following ZnS ALD is shown in the lower data set in Figure 4a. The results for ZnO ALD are shown for comparison in the upper data set. An enlargement of the QCM results that highlight the first H₂O exposures following ZnS ALD is shown in Figure 4b. The mass loss for the first H₂O exposure is \( \Delta m_{H_2O} = -6 \text{ ng/cm}^2 \). The mass increase for the subsequent DEZ exposure is \( \Delta m_{DEZ} = 48 \text{ ng/cm}^2 \). In comparison, the mass loss for H₂O exposures during ZnO ALD in the steady-state growth region is \( \Delta m_{H_2O} = -2 \text{ ng/cm}^2 \). The mass increase for the steady-state DEZ exposure is \( \Delta m_{DEZ} = 113 \text{ ng/cm}^2 \). The total mass change per cycle for ZnO ALD in Figure 4a is \( \Delta m = 111 \text{ ng/cm}^2 \). This mass change per cycle agrees with previous measurements.

Approximately nine cycles are required for ZnO ALD to reach steady-state growth conditions following ZnS ALD. The \( \Delta m_{DEZ} \) mass gains for the DEZ exposures steadily increase during this nucleation period. The larger \( \Delta m_{DEZ} \) mass gains would be expected to lead to larger \( \Delta m_{H_2O} \) mass losses following H₂O exposures. However, the opposite trend is observed during the nucleation of ZnO ALD on ZnS. This behavior suggests that the larger mass loss of \( \Delta m_{H_2O} = -6 \text{ ng/cm}^2 \) for the first H₂O exposure after ZnS ALD is associated with the exchange reaction: ZnSH* + H₂O → ZnOH* + H₂S or ZnO + H₂O → ZnO + H₂S.

The exchange reactions affect the composition of the Zn(O,S) alloys grown using alternating ZnO ALD and ZnS ALD cycles. The composition of the Zn(O,S) alloys is much more sulfur-rich than would be predicted from a “rule of mixtures” prediction. This behavior indicates that the H₂S
The exchange reaction has a disproportionate effect on the Zn(O,S) alloy composition. XPS results for the Zn(O,S) film composition are shown in Figure 5. Results are shown for three different growth temperatures: 100 °C, 150 °C, and 225 °C. The %ZnS in the film is determined by the O 1s and S 2p XPS peaks. Figure 5 indicates that there is much more sulfur than expected from the fraction of ZnS ALD cycles. Similar sulfur-rich films were observed in the previous studies displayed in Figure 1a.

Figure 5 also shows that the %ZnS in the films increases rapidly over a narrow range of growth conditions. At 150 °C, the %ZnS varies with fraction of ZnS cycles from 21% ZnS at 8:1 to 73% at 3:1. In addition, Figure 5 indicates that higher growth temperatures increase the measured sulfur content. Zn(O,S) alloys grown at a 3:1 ratio of ZnO to ZnS cycles have %ZnS compositions of 65% at 100 °C, 75% at 150 °C, and 90% at 225 °C. This behavior suggests that there are more efficient H₂S exchange reactions at higher temperatures. At 150 °C, the Zn(O,S) films reach 95% ZnS at a 1:1 ratio of ZnO to ZnS cycles.

The size of the H₂S exposure also affects the %ZnS composition. The %ZnS in Zn(O,S) alloys grown at 150 °C using a 4:1 ratio of ZnO and ZnS ALD cycles versus H₂S exposure is displayed in Figure 6. The H₂S exposures were increased by varying the exposure pressure with the H₂S exposure time at 0.3 s. The %ZnS in the film increases with H₂S exposure until the %ZnS reaches a plateau at larger H₂S exposures. The %ZnS increases from 51% ZnS at 0.39 Torr·s to 66% ZnS at 0.57 Torr·s. A film of pure ZnS would be grown using a 0.3 Torr·s exposure. This trend for %ZnS versus H₂S exposure for the 4:1 films was also observed for the 3:1 and 2:1 Zn(O,S) films. This dependence of the %ZnS composition on the H₂S exposure suggests that the H₂S exposures undergo the exchange reaction with ZnO until most of the oxygen has been exchanged with sulfur on the surface of the Zn(O,S) alloy. At this point, larger H₂S exposures do not lead to higher %ZnS composition.

B. Codosing Method. Zn(O,S) films were also grown by combining the H₂O and H₂S exposures and codosing the two reactants using static exposures. These Zn(O,S) films were grown using DEZ and H₂O/H₂S mixtures at 100 °C. The H₂O/H₂S mixture was allowed to remain in contact with the surface for 30 s. Figure 7 shows that Zn(O,S) film growth is extremely linear using the codosing method for a mole fraction exposure.
of H$_2$S in the gas mixture of $X_{H_2S} = 0.23$. The growth rate was 1.5 Å/cycle and the %ZnS composition was 98.5%. This growth rate is significantly higher than the growth rate of 1.0 Å/cycle typical for ZnS ALD.\textsuperscript{34}

Figure 8 shows the relationship between the %ZnS in the Zn(O,S) alloy and the mole fraction of H$_2$S in the gas mixture. The %ZnS increases with increasing H$_2$S mole fraction in the combined H$_2$O/H$_2$S mixture. Note that the range of %ZnS is quite small and varies from only 91% to 99% in Figure 8. Although there is some scatter in the data, the scatter is only a few percent and probably results from the O 1s and S 2p XPS peak analysis.

The codosing was performed by introducing H$_2$O and H$_2$S gases into the reactor at the same time. To explore the effect of reactant timing, a 2 s delay was intentionally added between the introduction of either H$_2$O or H$_2$S into the reactor. This delay allowed the initial reaction to take place exclusively with either H$_2$O or H$_2$S prior to the introduction of the second precursor. Delaying the input of H$_2$O by 2 s after the input of H$_2$S produced Zn(O,S) films with a %ZnS composition that was <1% greater than the %ZnS composition resulting from delaying the H$_2$S by 2 s after the input of H$_2$O. The comparable compositions of the two films suggest that they both reach a similar state regardless of their initial state.

Films grown using the codosing (CD) method do not have the control needed to tune the %ZnS composition over a narrow range of high sulfur composition. Controlling the %ZnS composition between 90 and 99% is extremely difficult because the H$_2$S exchange reaction increases the %ZnS composition. In addition, films at high %ZnS composition are problematic for the alternating cycle method. These films were grown at 100, 150, and 225 °C using the alternating cycle (AC) method and at 100 °C using the codosing (CD) method. The measured band gaps for ZnO of 3.23 eV and ZnS of 3.63 eV agree with previous measurements for ALD films.\textsuperscript{18} These band gaps are close to the bulk crystalline band gaps of ZnO at 3.3 eV and ZnS at 3.54 eV. The growth temperature does not greatly affect the magnitude of the band gap. Although there is some scatter, the band gaps for Zn(O,S) films grown at the different temperatures are in general agreement.

The Zn(O,S) films grown at 150 °C span the widest range of %ZnS composition. The band gaps of these Zn(O,S) films grown at 150 °C follow a roughly parabolic shape. This distinct “bowing” is consistent with the bowing observed for other Zn(O,S) films deposited by other methods.\textsuperscript{3,41} The minimum band gap occurs at 2.77 eV in the region of 20–80%ZnS where the change in %ZnS does not greatly affect the band gap. This broad band gap minimum is different than most of the previous measurements displayed in Figure 1b for the band gap of Zn(O,S) alloys grown by ALD.\textsuperscript{2,32} Films with band gaps between 3.23 eV (ZnO) and 3.63 eV (ZnS) could not be produced from the alternating cycle method. These large band gaps could be obtained only for films grown using the codosing method. The alternating cycle method does not have the control needed to tune the %ZnS composition over a narrow range of high sulfur composition. Contrasting the %ZnS composition between 90 and 99% is extremely difficult because the H$_2$S exchange reaction increases the %ZnS composition. In addition, films at high %ZnS composition are problematic for the alternating cycle method.
At low ZnO:ZnS ratios of <1:10, the films are more likely to be heterogeneous and should be viewed as nanolaminates instead of homogeneous films. The band gaps of the Zn(O,S) films as a function of %ZnS grown using the codosing method are shown in Figure 10. The band gap is moderately linear as a function of %ZnS. There is scattering of the band gap values that may be related to the uncertainty in the %ZnS composition. This uncertainty in the %ZnS composition is attributed to the difficulty obtaining accurate oxygen-to-sulfur ratios from the O 1s and S 2s XPS signals when the O 1s signals are low.

Figure 11 shows the band gaps of the Zn(O,S) films grown using the codosing method as a function of H₂S in the H₂O/H₂S mixture. In contrast to the scattering in Figure 10 between the band gap and %ZnS values caused by uncertainty in the %ZnS composition, the band gaps in Figure 11 are linear with the mole fraction of H₂S in the dosing mixture. The mole fraction of H₂S in the dosing mixture is controlling the %ZnS composition much more accurately than can be determined from the XPS analysis. This control of the %ZnS composition yields excellent control of the band gap.

C. Modeling the Exchange Reactions Yielding Film Composition. The H₂S exchange reaction plays a dominant role in determining the composition of the Zn(O,S) alloys. To obtain more understanding of this H₂S exchange reaction, a model was developed to characterize the H₂S exchange reactions during codosing experiments. The model assumes that the Zn(O,S) film composition reaches a steady-state value when exposed to the H₂S and H₂O gas mixture.

The film composition is assumed to result from kinetic processes that define the rate of change of the Θ_S and Θ_O surface coverages. k_{H₂S} is the rate constant for the exchange of the surface oxygen with sulfur by H₂S (eq 1). k_{H₂O} is the rate constant for the exchange of surface sulfur with oxygen by H₂O (eq 3). Θ_S and Θ_O are the fractional surface coverages of sulfur and oxygen, respectively, where Θ_S + Θ_O = 1. A schematic illustrating the H₂S and H₂O exchange reactions on a Zn(O,S) film is shown in Figure 12.

The kinetic processes governing the rates of change of the Θ_S and Θ_O coverages are as follows:

\[ \frac{d\theta_S}{dt} = k_{H₂S}P_{H₂S}\theta_O - k_{H₂O}P_{H₂O}\theta_S = -\frac{d\theta_O}{dt} \]  

(5)

\[ \theta_S = \theta_{S,i} + \frac{d\theta_S}{dt} \]  

(6)

\[ \theta_O = 1 - \theta_S \]  

(7)

P_{H₂S} and P_{H₂O} are the initial pressures of H₂S and H₂O in the reactor at the start of each codose exposure. The initial pressures are assumed to remain constant throughout the reaction.

To calculate a final sulfur coverage, Θ_{S,f}, the initial sulfur coverage is assumed to be Θ_{S,i} = 0. The rate equations are then iterated until there is convergence on a constant Θ_S value. To determine k_{H₂O}, the k_{H₂S} is fixed and the k_{H₂O} value is varied until the Θ_{S,f} value matches the measured %ZnS value determined by the XPS analysis. A constant, Q, can then be determined by the ratio of k_{H₂S} and k_{H₂O}.

\[ Q = \frac{k_{H₂S}}{k_{H₂O}} \]  

(8)
Experiments and modeling were conducted for H₂S mole fractions in the H₂S and H₂O gas mixture ranging from X₁H₂S = 0.07 to X₁H₂S = 0.39. These H₂S mole fractions were obtained using a wide range of partial pressures for H₂S and H₂O. Table 1 also lists the %ZnS composition for the Zn(O,S) films grown using these H₂S mole fractions determined by XPS analysis. There is some correlation between the H₂S mole fractions and the %ZnS compositions. In addition, Table 1 reports the values of Q for different Zn(O,S) films grown using the codosing method. The values of Q vary from 71 to 231.

The equilibrium constant corresponding to \( \Delta G^0 = -17.5 \) kcal for the bulk reaction \( \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \) given by eq 2 at 100 °C is \( K = 1.8 \times 10^{30} \). This equilibrium constant is orders of magnitude larger than \( Q = 71-231 \) determined by the kinetic model. This disparity can be attributed to the differences between the surface and bulk reactions. The Q value represents the ratio of rate constants for the surface reactions given by eqs 1 and 3. These surface exchange reactions are primarily between H₂S and hydroxyl groups and H₂O and thiol groups, as shown in Figure 12. These reactions take place in the top layer of the surface. The QCM measurements indicated that the H₂S exchange reaction with the ZnO surface leads to the loss of ZnO from the top 2.8 Å of the initial ZnO film and the production of ZnS in the top 4.6 Å of the final film. The surface reactions result in exchange over distances slightly less than the unit cell lengths for ZnO and ZnS.

The equilibrium constant, \( K \), represents the ratio of the rates of the bulk reactions given by eqs 2 and 4. The equilibrium constant does not account for kinetic barriers that may exist for the surface reactions. The surface exchange reactions may have reaction cross sections that are not correlated with the bulk thermodynamics. The surface reactions are also performed with initial mole fractions of H₂S and H₂O that are far from equilibrium. Because of the limited conversion for the exchange reactions restricted to the top layer of the surface, there may be no possibility to establish equilibrium conditions.

The Q values do not appear to correlate with any of the parameters in Table 1. The range of Q values from 71 to 231 is partially attributed to the uncertainty of the %ZnS composition values from XPS analysis. %ZnS compositions that are higher than the real %ZnS composition would lead to \( k_{H_2S} \) and Q values that are lower than the real Q values. %ZnS compositions that are lower than the real %ZnS composition would lead to \( k_{H_2S} \) and Q values that are lower than the real Q values.

The Q values indicate that the \( k_{H_2S} \) rate constant is 71–231 times higher than the \( k_{H_2O} \) rate constant. This larger \( k_{H_2S} \) rate constant is expected from the favorable thermochrometry of the H₂S exchange reaction. The codosing experiments provide a means to determine the relative exchange rate constants. These relative rate constants would be difficult to measure by other experimental means. Molecular beam surface scattering experiments could provide an alternative method.

D. Exchange in Other Surface Reactions. The exchange of sulfur and oxygen by the ZnOH* + H₂S → ZnSH* + H₂O surface reaction is one example of many other surface exchange reactions. These reactions are driven, in part, by the favorable thermochrometry of the exchange process. These exchange reactions can convert the surface layer to a more thermodynamically favorable reaction product. These surface reactions may be prevalent during a wide range of surface reactions.

Surface exchange reactions can also explain observations during Al₂O₃ ALD or HfO₂ ALD on various compound semiconductors surfaces. During the exchange reactions, the TMA or hafnium precursors replace the initial surface oxide on the semiconductor surface with Al₂O₃ or HfO₂, respectively. These reactions have been defined as “self-cleaning” reactions because they remove the initial surface oxide that is detrimental to electrical performance of the dielectric film on the semiconductor substrate. These exchange reactions are proposed during Al₂O₃ ALD on the initial surface oxides of GaAs, InP, and InSb. Similar exchange reactions are believed to occur during HfO₂ ALD on the initial surface oxides of GaAs and InGaAs.

Other surface exchange reactions have been reported where the metal in the initial metal oxide is exchanged to produce another metal oxide. One prominent example is the reaction of TMA with ZnO according to 3ZnO + 2Al(CH₃)₃ → Al₂O₃ + 3Zn(CH₃)₂. This exchange reaction has been observed during the growth of ZnO/Al₂O₃ nanolaminates. Additional surface exchange reactions occur where the metal in an initial metal sulfide is exchanged to produce another metal sulfide. Examples of these exchange reactions include DEZ reacting with In₂S₃ or Cu₂S to produce ZnS.

Most of the surface exchange reactions have been observed during thin-film growth by ALD. Surface exchange can also occur during surface etching processes. For example, TMA exchange reactions can convert ZnO to Al₂O₃ during thermal ZnO atomic layer etching (ALE). This exchange reaction mechanism is referred to as “conversion-etch”. TMA exchange reactions can also convert SiO₂ to Al₂O₃ and aluminosilicates during the thermal SiO₂ ALE reaction mechanism. The conversion of SiO₂ to Al₂O₃ may also occur during Al₂O₃ ALD on SiO₂ surfaces. Atomic layer processing by ALD and ALE is expected to yield many more examples of surface exchange mechanisms.

V. CONCLUSIONS

Zn(O,S) thin films were grown using atomic layer deposition (ALD) techniques to produce tunable band gaps. Alternating cycles of ZnO ALD and ZnS ALD were initially used to deposit the Zn(O,S) films. The composition of the Zn(O,S) alloys deposited using the alternating cycle method was not easy to control. The problem is an efficient surface exchange reaction.
between ZnO and gaseous H₂S given by ZnOH* + H₂S → ZnSH* + H₂O. This exchange reaction produces much higher sulfur content in the Zn(O,S) films than expected based on the ratio of ZnO ALD and ZnS ALD cycles. The effect of the exchange reaction on the composition of Zn(O,S) films grown using alternating cycles was examined by varying the reaction conditions. These experiments revealed that the sulfur content was higher in Zn(O,S) films grown at higher temperatures and with longer H₂S exposures.

An alternative method of growing the Zn(O,S) thin films was then explored that uses codosing of H₂O and H₂S at 100 °C. This codosing method produced different compositions of the Zn(O,S) film by varying the mole fraction of the dosing mixture. The codosing method controlled the Zn(O,S) alloy composition much more accurately than the alternating cycle method. The band gaps for Zn(O,S) thin films were measured using the alternating cycle or codosing method. The band gaps could be produced with the most control by the mole fraction of H₂S in the H₂O/H₂S codosing mixture.

The relative magnitudes of the exchange reaction rate (k₁) for ZnOH* + H₂S → ZnSH* + H₂O and the competing exchange reaction rate (k₂) for ZnSH* + H₂O → ZnOH* + H₂S were also determined using the codosing method. A model was used to determine the ratio of the exchange reaction rates, Q = k₁/k₂, based on the composition of the Zn(O,S) films grown using the codosing method with different H₂O and H₂S partial pressures. The ratio of the exchange reaction rates was determined to be Q = 71–231. This ratio is consistent with a much higher exchange reaction for H₂S with ZnOH* than for H₂O with ZnSH*. Surface exchange reactions are possible because of favorable thermochemistry and may be fairly ubiquitous during atomic layer processing.

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Notes

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