

DEPOSITION OF ZINC SELENIDE BY ATOMIC LAYER EPITAXY FOR MULTILAYER X-RAY OPTICS

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ABSTRACT

Thin film deposition techniques currently being used to produce multilayer x-ray optics (MXOs) have difficulty producing smooth, uniform multilayers with d-spacings less than about twelve angstroms. We are investigating atomic layer epitaxy (ALE) as an alternative to these techniques.

ALE is a chemical vapor deposition technique which deposits an atomic layer of material during each cycle of the deposition process. The thickness of a film deposited by ALE depends only on the number of cycles. Multilayers deposited by ALE should be smooth and uniform with precise d-spacings which makes ALE an excellent technique for producing multilayer x-ray optics.

We have designed and built an ALE system and we have used this system to deposit ZnSe using diethyl zinc and hydrogen selenide.

MULTILAYER X-RAY OPTICS

Multilayer x-ray optics (MXOs) are designed so that x rays which are diffracted from each interface of the multilayer constructively interfere to give a large total reflectivity. The maximum reflectivity is obtained when the interfaces between the layer pairs are abrupt and the layers are uniform and smooth with precise d-spacings, as depicted in Figure 1.

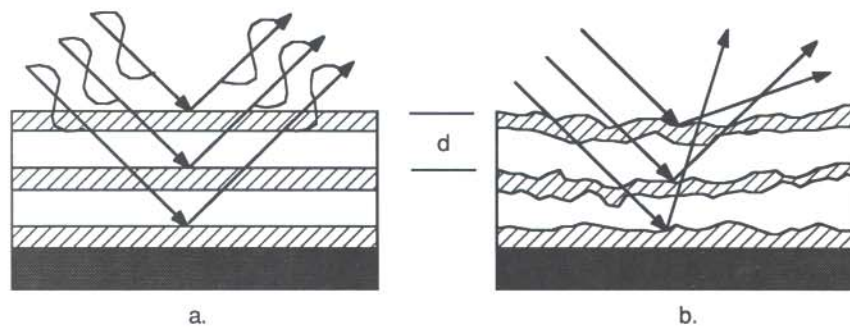


Figure 1. a. A good multilayer x-ray mirror which gives the maximum reflectivity. b. A poor multilayer x-ray mirror. Layers are rough and nonuniform so that the diffracted x rays do not constructively interfere.

ATOMIC LAYER EPITAXY

ALE was developed at the Lohja Corporation in Finland for producing large-area thin film electroluminescent displays [1]. It is currently being used to produce quantum well devices [2]. The ability of ALE to produce high quality thin films has prompted a great deal of research on ALE in the electronics industry. We are the first research group to apply ALE to the production of MXOs.

ALE is a thin film deposition technique which deposits an atomic layer of material during each cycle of the deposition process. The thickness of the deposited film depends only on the total number of cycles and is independent of other process parameters so that the thickness of a film deposited by ALE can be controlled to within one atomic layer [3-5].

ALE is possible due to the difference in bond energies of chemisorbed atoms and physisorbed atoms.

Chemisorption vs Physisorption

A chemisorbed atom shares electrons with atoms of the previous layer to form strong chemical bonds. A physisorbed atom is attracted to atoms of the previous layer by weak dipole-dipole interactions or Van der Waals forces. Covalent bonds are typically ten times stronger than Van der Waals forces, as depicted in Figure 3.

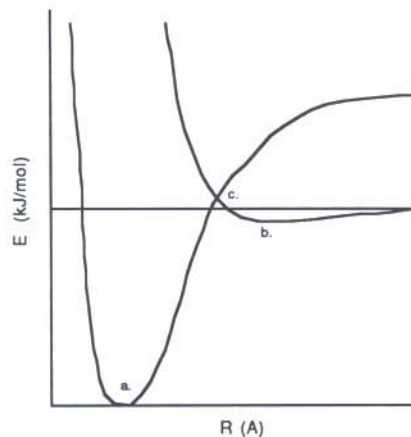


Figure 3. Interaction energy as a function of internuclear separation. a. Chemisorbed atoms form a strong chemical bond with atoms of the previous layer. b. Physisorbed atoms are only weakly bound to atoms of the previous layer c.. Energy barrier may or may not exist depending on the type of atoms being adsorbed.

Theory of ALE

To successfully deposit materials by ALE, the bond between the adatom and the previous layer must be stronger than the interaction between the molecules containing the adatom. For example, the bond between a selenide atom in the previous layer and the zinc atom in diethyl zinc is many times stronger than the weak interaction between molecules of diethyl zinc. The deposition temperature must also be selected so that the atoms which have been chemisorbed remain strongly bound to the surface while the atoms which have been physisorbed are evaporated, leaving only the single layer of chemisorbed atoms.

Deposition process

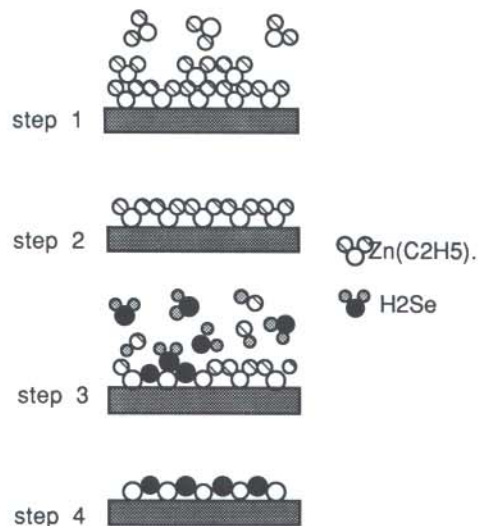


Figure 4. One cycle of the deposition process for depositing zinc selenide by ALE.

In the first step, diethyl zinc is introduced into the system. The diethyl zinc molecules react with the selenide atoms in the previous layer and are chemisorbed until a complete layer of zinc atoms is deposited. Once the chemisorbed layer has formed, diethyl zinc molecules can only be physisorbed.

During the second step, the gas flow is shut off and the system is evacuated so that any physisorbed diethyl zinc molecules will evaporate.

Hydrogen selenide is introduced into the system during the third step. The hydrogen selenide molecules react with the chemisorbed diethyl zinc molecules to form a single zinc selenide layer and ethane gas.

In the fourth and final step, the gas flow is again shut off and the system is evacuated so that unreacted hydrogen selenide and the ethane gas products are removed.

The cycle is repeated until the desired thickness of zinc selenide has been deposited. The layer growth in ALE is epitaxial which means that a complete atomic layer is deposited before the next atomic layer begins to grow, with the result that the structure of the deposited layer resembles that of the previous layer or substrate. To produce the required multilayers for use as MXOs, the reactant gases are switched and a different material deposited. Figure 5 depicts a ZnSe/CdS superlattice which could be used as a MXO.

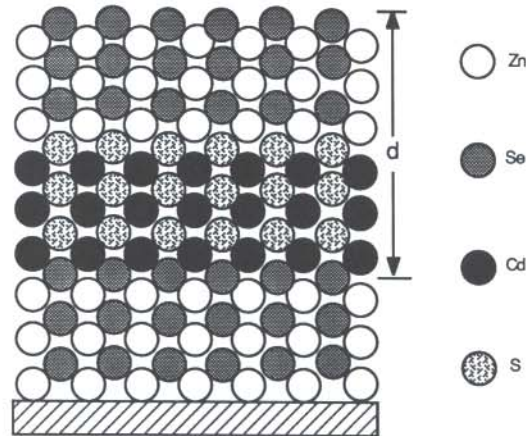


Figure 5. ZnSe/CdS superlattice which can be deposited by ALE and used as a MXO.

ZINC SELENIDE DEPOSITION

We recently completed construction of an ALE reactor. The system design has been described elsewhere [6]. We selected zinc selenide as the first material we would deposit by ALE, because other researchers have successfully deposited many of the II-VI and III-V semiconductor materials using metal-organic and hydride reactants[7] and we are interested in eventually producing a ZnSe/CdS superlattice for use as a MXO.

We report that we have successfully deposited zinc selenide on a polished [111] silicon substrate using diethyl zinc and hydrogen selenide. The deposition temperature was 250 C. The diethyl zinc was introduced

into the deposition chamber by bubbling 200 ml/min of hydrogen through the liquid diethyl zinc. The hydrogen selenide was introduced directly into the deposition chamber at 200 ml/min. During each cycle the reactant gases were introduced for 2 seconds and the system was then evacuated for 8 seconds to a pressure of 3×10^{-4} torr before the next reactant gas was introduced. The total deposition consisted of 500 cycles.

We determined the thickness of the zinc selenide film to be approximately 360 Å using ellipsometry. The thickness of the zinc selenide film indicates that we deposited less than one layer of zinc selenide during each cycle. We believe that the explanation for this result is that we depleted the diethyl zinc supply before the 500 cycles were completed. We have modified the gas system so that we can now monitor the amount of diethyl zinc in the bubbler during the deposition.

X-ray Diffraction Results

We performed x-ray diffraction measurements on the film using the $\text{Cu K}\alpha$ line at 1.54 Å. The results are given in Figure 6 and clearly show that the film on the Si substrate is crystalline ZnSe.

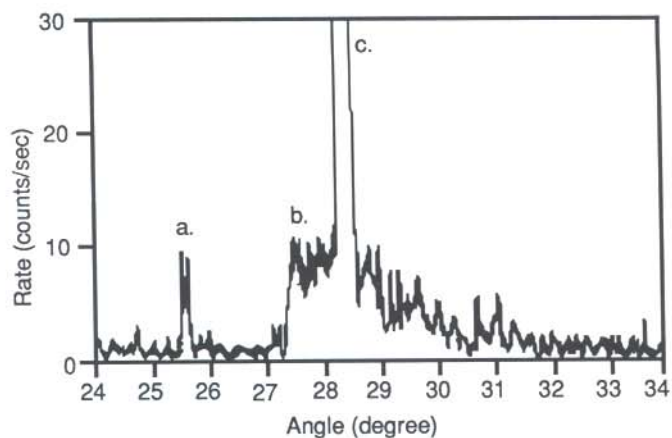


Figure 6. a. $\text{CuK}\beta$ from $\text{Si}[111]$. b. $\text{CuK}\alpha$ from $\text{ZnSe}[111]$. c. $\text{CuK}\alpha$ from $\text{Si}[111]$.

Electron Microscopy Results

To confirm the results of the x-ray diffraction measurements, we examined the film using a scanning electron microscope. The x-ray emission spectrum we obtained from the film and show in Figure 7 proves that the film is indeed ZnSe.

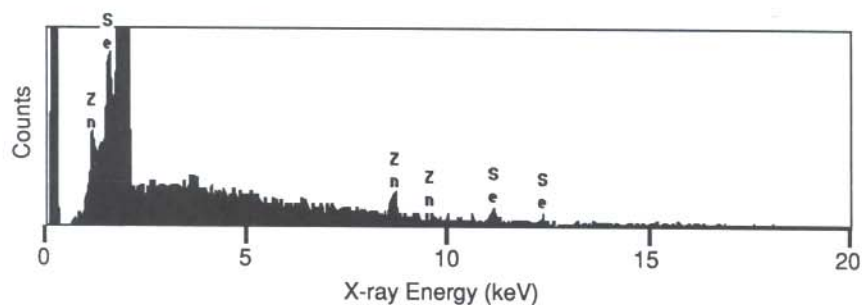


Figure 7 X-ray emission spectra of the film obtained using SEM. The largest peak is due to the Si substrate.

CONCLUSIONS

We have investigated the use of ALE as a new technique for producing MXOs. Our research suggests that ALE we be able to produce high quality MXOs with smooth, uniform layers and small d-spacings.

We have designed and built an ALE reactor and we have used this reactor to deposit crystalline zinc selenide. In the future, we will deposit a ZnSe/CdS superlattice for use as a MXO.

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