Design of an atomic layer deposition reactor for hydrogen sulfide compatibility

Neil P. Dasgupta,[1] James F. Mack,[1] Michael C. Langston,[1] Al Bousetta,[2] and Fritz B. Prinz[1,3]

[1]*Department of Mechanical Engineering, Stanford University, Stanford, California 94305, USA*
[2]*Swagelok Company, Santa Clara, California 95054, USA*
[3]*Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA*

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A customized atomic layer deposition (ALD) reactor was designed with components compatible with hydrogen sulfide (H_2S) chemistry. H_2S is used as a reactant for the ALD of metal sulfides. The use of H_2S in an ALD reactor requires special attention to safety issues due to its highly toxic, flammable, and corrosive nature. The reactor was designed with respect to materials compatibility of all wetted components with H_2S. A customized safety interlock system was developed to shut down the system in the event of toxic gas leakage, power outage, loss of building ventilation or compressed air pressure. ALD of lead sulfide (PbS) and zinc sulfide (ZnS) were demonstrated with no chemical contamination or detectable release of H_2S. © *2010 American Institute of Physics.* [doi:10.1063/1.3384349]

I. INTRODUCTION

Atomic layer deposition (ALD) is a process capable of depositing pinhole-free, conformal thin films on various substrates with atomic scale precision. ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible.[1] ALD is a variant to chemical vapor deposition (CVD), but its deposition mechanism is quite different. The precursors are kept separate throughout the deposition process and are introduced sequentially through a pulsing process to deposit at most one monolayer per cycle. Aspect ratios of up to (5000:1) have been demonstrated by ALD,[2] allowing for fabrication of novel structures which are very difficult to achieve by conventional thin-film deposition techniques such as CVD or sputtering. ALD is currently used for fabrication of high-*k* dielectric films in integrated circuit fabrication processes. Additionally, research in ALD applications has extended to a wide variety of emerging applications, including energy conversion,[3–5] biology,[6,7] and photonics.[8]

There is an increased interest in metal sulfide deposition using ALD processing. For example indium sulfide (In_2S_3) is being explored as a substitute for cadmium sulfide in CIGS-based solar cells to avoid toxic cadmium and obtain a more cost-effective and environmentally friendly photovoltaic technology.[9–11] Another example is the interest in ALD of Cu_xS for future applications in photovoltaics.[12,13] ZnS was the original material deposited by ALD using elemental sources in the 1970s for electroluminescence applications. Elemental sources were later replaced by H_2S as the sulfur source.[14–16] Additionally, PbS has been deposited by ALD,[17,18] which has been shown to have potential for use in quantum confinement structures.[19]

This paper focuses on the development of an ALD reactor for the deposition of metal sulfide thin films as a potential material for photovoltaic applications. For metal sulfide applications, the most common reactant used is hydrogen sulfide (H_2S). However, the use of H_2S in an ALD reactor requires special attention to safety issues due to its highly toxic, flammable, and corrosive nature. According to the material data safety sheet (MSDS), inhalation of H_2S gas results in damage to the respiratory tract and central nervous system, and may lead to death.[20] The Occupational Health and Safety Administration permissible exposure limit concentration is 20 ppm, and the concentration that is immediately dangerous to life and health according to the National Institute for Occupational Safety and Health is 100 ppm. While H_2S can be sensed by its characteristic odor of "rotten eggs" in the concentration range of ppb, the human sense of smell suffers from olfactory fatigue at higher concentrations.[21,22] Therefore, the odor of the gas is not an acceptable warning for humans of potential exposure.

Furthermore, H_2S is highly flammable. The autoignition temperature is 260 °C,[20] which is in the range of typical ALD substrate temperatures. Complicating the issue is the fact that H_2S reacts with water to form an acidic solution, which is highly corrosive. This poses the risk of a nominally sealed system becoming corroded and allowing H_2S to escape, exposing users to the toxic and flammable gas.

As many ALD reactors used in scientific research are custom-built rather than obtained commercially, and given the potential hazards involved in H_2S usage, it is especially crucial that comprehensive system design information is available. While depositing sulfides with ALD using H_2S as a precursor has been documented, to our knowledge there are no reports on the safe design of these systems.

In this article, we describe a carefully designed viscous-flow ALD reactor which is comprised of fully H_2S compatible components, contains a purging system for removing residual H_2S before venting, and contains an automatic safety interlock to be utilized in the event of a component or system failure. The reactor was used to successfully deposit PbS and ZnS thin films with correct stoichiometry and no chemical contamination.

II. ALD REACTOR DESIGN

Safety issues with H_2S are critical due to flammability and toxicity concerns. Flammability issues can be avoided by choosing a concentration of H_2S mixed with an inert gas such as nitrogen which is below the lower explosion limit (LEL) of 4.3%.[20] In this study, a gas mixture of 3.5% H_2S in nitrogen was used to avoid flammability but maintain sufficient reactivity with the substrate. At these concentrations, toxicity is a concern, so system design required detailed consideration of potential human exposure.

The main hazard of H_2S for human health is inhalation. Therefore, it was critical that all components in the vacuum system be leak-checked prior to installation and did not pose a risk for potential release of the gas. A major challenge for this arose from the corrosive nature of H_2S. H_2S reacts with many materials, including several metals and polymers causing corrosion. Additionally, when H_2S is mixed with water, an acidic solution is formed that causes further corrosion issues. Therefore, the materials of all components in the ALD system must be compatible with H_2S for appropriate system design.

Special care should be taken when selecting metal components for use with H_2S. Anhydrous H_2S is typically acceptable for use with a variety of materials at low temperatures, while at temperatures higher than 260 °C, corrosion of carbon steel becomes an issue due to sulfidation of the metal,[23] which is within the process window of several ALD reactions. At these temperatures, materials such as 300-series stainless steel or Inconel® should be used. Use of annealed and low-carbon stainless steel improves corrosion resistance from H_2S under these conditions.[23] In this study, the use of 316L stainless steel was maximized over lower grades of stainless steel typically used in vacuum systems due to its improved corrosion resistance and weldability.[24] Furthermore, if any moisture is present, sulfide stress cracking can occur, leading to failure of the metal.[23] Therefore, it is critical that the chamber remains leak-free to prevent moisture from the atmosphere from entering into the reactor.

Elastomer materials are used throughout ALD systems in O-rings, valve seat materials, and other seals in the pressure gauge, vacuum pump, and valves. Typically, Viton® (FKM) is used as an O-ring and seal material for flanges and components in ALD systems due to its relatively good corrosion resistance and temperature rating. However, H_2S is known to cause severe swelling in Viton and is not recommended for use. The approved elastomer and seat materials for use with H_2S include Teflon® derivatives (PFA, FEP), Kalrez® (FFKM), or Aflas® (TFE/P).[25] Therefore, careful evaluation of all wetted elastomers and plastic materials in the system was performed when designing the system. The critical components of the ALD system include the reaction chamber, vacuum pump, pressure gauge, tubing and hoses for gas transport, and a range of manual and pneumatic valves for control of gas flow in and out of the chamber.

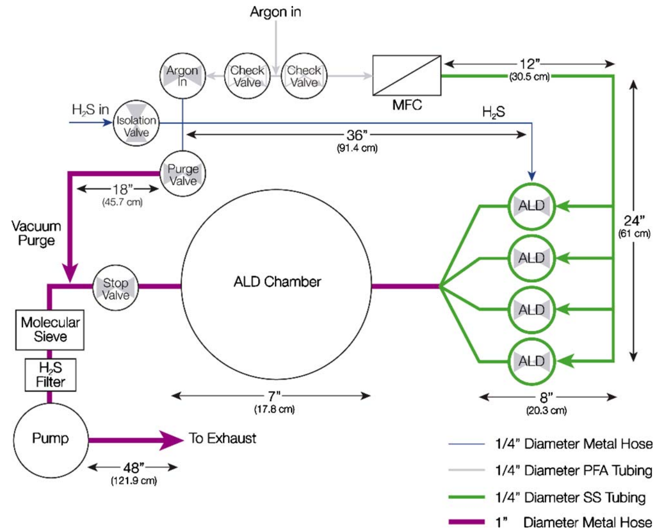

FIG. 1. (Color online) Schematic of ALD reactor. Swagelok ALD valves are used for precursor delivery.

A schematic of the ALD reactor designed in this study is shown in Fig. 1. Precursors are contained in bubblers or cylinders that are enclosed by a manual valve for transfer of reactive chemicals in air. This bubbler is connected to the inlet of a pneumatic ALD valve, which is rated for high temperatures (up to 392 °F/200 °C) and extended cycle life ($>50\times10^6$ cycles).[26] The precursors are transported through stainless steel tubing into the reaction chamber by an inert carrier gas, where a saturated precursor layer is deposited on the surface and excess chemicals are purged away into the vacuum pump. On the vacuum line, there is at least one additional valve to isolate the chamber from the vacuum pump. This valve can be used as a stop valve for an alternate mode of ALD referred to as "exposure mode." In this mode, the stop valve is closed before pulsing the precursors, effectively isolating the vacuum chamber. Then, the precursor is pulsed into the chamber, and allowed to remain several seconds to ensure saturation of the entire surface before opening the valve and purging the chamber. This technique is especially critical for complex topologies with high aspect ratios such as coating the inside of porous templates. Finally, the gases pass through various filtration media and into the mechanical vacuum pump as the exhaust.

III. SELECTION OF VACUUM COMPONENTS

Vacuum components were selected primarily for compatibility with the ALD process using H_2S, specifically with regard to material compatibility. Therefore, all wetted components of the reactor are either stainless steel or a compatible elastomer material. Swagelok VCR® metal gasket face seal fittings were used for 1/4 in. tubing, while ISO (International Organization for Standardization) flange fittings were used for 1 in. diameter tubing. The VCR fittings have no "virtual" leak zones or areas of entrapment and are used to reduce the risk of system contamination. In addition, the VCR fittings have precision manufactured gaskets for maximum seal performance. As mentioned previously, H_2S is a toxic gas and it is critical to have a leak-tight system to prevent potential release and human inhalation. Typically, VCR gaskets are plated with silver to aid in seal formation. However, H_2S is known to react with silver, forming silver sulfide (Ag_2S). Additionally, at high temperatures and in H_2S environments, the formation of silver whiskers can occur.[27] This could lead to a leak in the VCR sealing system, causing dangerous exposure of H_2S to the ambient environment, and atmospheric contaminants to enter into the ALD chamber. Therefore, Swagelok unplated stainless steel gaskets were used for all seals in this system.

O-rings were used to form the seal between the reaction chamber and its lid, as well as in the flanged bellows tubing used in the vacuum line. Kalrez® O-rings were used in high temperature zones due to their temperature rating of above 300 °C. For O-rings in the vacuum line and lower temperature zones, FEP-encapsulated Viton® O-rings were used to prevent exposure of the gas stream to the FKM material. No vacuum lubricant was used on any O-rings to avoid reaction of the lubricant with H_2S.

Precursors were stored in stainless steel cylinders, with welded VCR glands. Solid precursors were volatilized in these cylinders by heating to an appropriate temperature for sublimation. To deliver H_2S from the outlet of the pressure regulator on the gas cylinder to the ALD valve, Swagelok flexible 316L stainless steel hoses, with VCR end connections, were used to minimize transfer of torque and forces when changing connections downstream of the H_2S cylinder and to avoid loosening any connections on the regulator.

Due to the pulsed nature of ALD deposition, valve selection was critical in the design of the ALD chamber. All valves were selected for H_2S compatibility, temperature rating, and cycle life. Swagelok manual bellows sealed valves were selected for use between the precursor cylinder and pneumatic valve in order to transfer precursor cylinders safely between the chamber and the nitrogen glove box used for refilling precursor. These valves are rated to operate at temperatures up to 315 °C (599 °F) with 316 and 321 stainless steel wetted components. These manual valves remain open during ALD operation. Next, the precursors pass through pneumatic ALD valves, which are actuated during every cycle in a sequential manner. These valves are perhaps the most critical for ALD reactor design due to the high temperature, cycle life, flow rate, and chemical compatibility requirements.

As shown in Fig. 2, several features are designed into the Swagelok ALD valve for high-performance operation. The pneumatic actuator assembly has a flow setting mechanism to provide a high and consistent flow to ± 3%. The single diaphragm with a bonnet package are optimized for extended cycle life ($>50\times10^6$ cycles) and a high-purity PFA seat is used for high-temperature performance and chemical compatibility. Ultrahigh-purity 316L VIM-VAR (VIM VAR denotes Vacuum Induction Melted/Vacuum Arc Remelted) and a high-purity 316L VIM stainless steel material are used for the valve body and VCR end connections, respectively. Therefore, all wetted components of the valve are suitable for H_2S use. For high temperature operation (>200 °C/392 °F), a thermal isolation coupling housing and stem are designed to significantly reduce the actuator

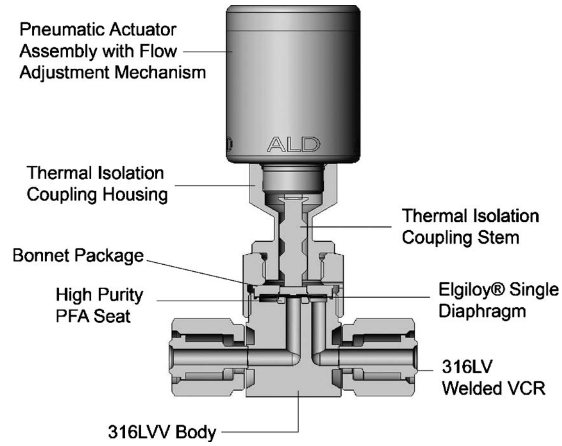

FIG. 2. Swagelok® ALD valve wetted and nonwetted materials of construction.

temperature and minimize cold and hot spots in the fluid path. The use of the thermal isolator has the additional benefit of reducing the power required to maintain temperature when the valve body is actively heated.

The use of an all-metal sealed pneumatic diaphragm valve has several advantages over alternate valves which may be used for precursor delivery. The all-metal seal to atmosphere eliminates exposure of the gas to the elastomer or soft seals used in other valves, which are often made of H_2S incompatible materials such as Viton®. Furthermore, the Swagelok ALD valve is constructed of 316L VIM VAR stainless steel and electropolished leaving a chromium enriched oxide layer. This material provides excellent corrosion resistance compared to lower grade stainless steels such as 304. Finally, the use of a PFA seat provides compatibility with H_2S, ensuring leak-free performance compared to noncompatible seat materials.

The precursors are then transported into the reaction chamber with the assistance of an argon carrier gas, which is provided at a flow rate of 10 SCCM (SCCM denotes standard cubic centimeter per minute at STP). A sufficient quantity of precursor is introduced during each pulse to ensure saturation of the entire surface. In order to increase exposure time for high-aspect ratio structures, a pneumatic valve is placed at the outlet port of the reaction chamber. This valve is normally open during ALD operation, but can be closed to allow longer exposure times of the substrate to the precursor vapor, allowing diffusion into nanoscale features. For this valve, a high C_v valve was required to maintain sufficient conductance of gases to the vacuum pump. Additionally, since a constant flow of argon is provided at the inlet of the chamber, a high conductance of the exhaust system to the vacuum pump is important in order to maintain a sufficiently low base pressure of the chamber during deposition. If the base pressure becomes higher than the vapor pressure of the ALD precursors, effective transport of the precursor molecules from the cylinder to the chamber becomes difficult. For this process a Swagelok ALD valve with a C_v of 0.6 was used, while maintaining the same temperature, material compatibility, and life cycle requirements.

In situ monitoring of chamber pressure is very important during ALD deposition to monitor the pressure as a function of time during deposition. Typically, a series of pressure peaks is observed in a pressure-time plot, indicating a consistent delivery of precursors during every ALD half-cycle. Additionally, a rise in base pressure could be indicative of a leak in the system, which could produce a hazardous situation when using H_2S. An Edwards capacitance manometer was selected for the pressure gauge due to its high sensitivity and material compatibility. All wetted materials in the pressure gauge are either 316 stainless steel, Inconel® or Monel® alloy.

Before precursors reach the vacuum pump, it is desirable to remove hazardous gases from the exhaust stream. In the case of H_2S, the system was designed to minimize even trace quantities of H_2S from being passed into the building exhaust. Therefore, a vacuum-compatible H_2S filtration material was utilized to adsorb H_2S from the exhaust stream before reaching the vacuum pump. The media selected was SulfaTreat Select Ultra®, a mixed metal oxide from M-I LLC of Houston, TX. SulfaTreat Select Ultra is a high-capacity, fast-reacting absorbent with enhanced macroporosity for improved activity. It is specifically formulated for the removal of hydrogen sulfide and light mercaptans from gaseous streams. H_2S scrubbing is achieved by reaction with mixed metal oxides forming stable metal sulfides. The use of a dry, vacuum-compatible filtration media allowed for the placement of the filter upstream of the vacuum pump to minimize exposure of the pump to H_2S, which could cause corrosion of the internal pump components. Additionally, a molecular sieve was placed between the vacuum pump and the chamber to prevent pump oil from backstreaming into the chamber, and to adsorb precursor molecules before they reach the pump.

The vacuum pump selected was an Alcatel® 2021 C1 series rotary vane pump, which is designed for compatibility with corrosive chemicals. The pump is filled with Fomblin® 25/6 grade oil to avoid reaction with H_2S and other precursors. Finally, the exhaust from the pump is connected directly to the building fume hood exhaust system to avoid release of trace quantities of gas which escape into the exhaust stream.

IV. PURGING GAS DELIVERY

Due to the fact that H_2S has deleterious health effects at ppm levels, special care should be taken to ensure that the user is not exposed to trace amounts of the gas when opening the reactor to load and unload samples. Before venting the chamber to atmospheric pressure, a series of purging steps are performed to reduce the residual quantity of H_2S remaining after deposition. If this is not performed, then users can be exposed to the toxic effects of H_2S. Argon gas is used as a purge gas, which is introduced into the chamber through a customized manifold. A schematic of this manifold can be seen in the top left of Fig. 1. Argon is passed through a Swagelok check valve with Aflas® seals, and which is connected to a Swagelok manual diaphragm valve. This valve is kept closed during deposition, and opened during purging cycles to introduce argon. The valve is connected by a VCR cross to two other manual diaphragm valves and a stainless steel braided hose. The hose connects to the ALD valve associated with H_2S. The other two valves are used to isolate the hose from the chamber (vacuum purge valve) and to isolate the H_2S regulator from the chamber (H_2S isolation valve) when venting.

During purging, argon is introduced into the hose with the vacuum purge valve closed until a gauge pressure of −10 in Hg. is reached in the hose. This pressure is subsequently evacuated by opening the vacuum purge valve, which is repeated five times. This process is used to thoroughly flush the hose, which was filled with H_2S for several hours during deposition. Next, the pump isolation valve is closed and Argon is introduced into the entire chamber until a gauge pressure of −10 in Hg. is reached, and a set of five pump-purge cycles is performed to flush the entire chamber. This procedure ensures that H_2S levels in the chamber are sufficiently low when opening the chamber to atmosphere so that no respiratory equipment is required by the user.

V. SAFETY INTERLOCK

There are several potential hazards that could lead to a dangerous situation when using H_2S in an ALD chamber. For example, several solenoid and pneumatic valves are used throughout the system, some of which are normally open until energized, and others which are normally closed. In the case of an electrical or compressed air outage in the laboratory, the system should be designed to relax into the safest possible state to avoid leakage of any toxic gases into the room. Additionally, in case a leak develops in the system, H_2S levels could build up in the ambient environment. For this purpose, the ALD station is placed under a ventilation hood in an enclosure, and H_2S levels are monitored by a toxic gas monitor (Sierra Monitor Corp.). The use of a gas monitor to detect dangerous levels of the gas and activate the interlock is critical due to the potential for olfactory fatigue at dangerous concentrations of H_2S. In order to ensure that the system returns to the "shutoff" state in which the potential for gas leakage is minimized, an interlock system was designed.

A schematic of the interlock is given in Fig. 3. To ensure that the no-energized state of each valve is in the safest configuration, normally closed valves were used for the pneumatic ALD valves, while a normally open valve is used for the stop valve to ensure that the vacuum pump continually pumps the system in case of a loss of compressed air from the building. Additionally, a normally closed pneumatic valve is inserted between the H_2S cylinder and regulator to act as a shutoff valve in case of H_2S leakage from the chamber. All of these valves receive their compressed air from a manifold, which is supplied air from the building through a three-way valve.

The interlock is based on the three-way valve between the compressed air supply and the manifold. In the energized state, this valve supplies air to the manifold and the system operates normally. When the interlock is activated, power is cut to this valve, which relieves pressure to the manifold, causing all valves to fall into their safety condition. The in-

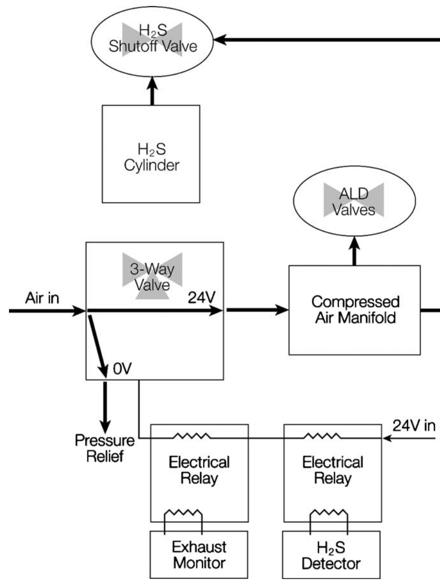

FIG. 3. Interlock schematic. All valves are normally closed, relay pass current until the control circuit is energized.

terlock is therefore designed for multiple routes of failure. If the building electricity or compressed air supply goes out, pressure will not be supplied to the gas manifold, causing the system to go into safety mode. Additionally, two solid-state relays are used which are associated with the H_2S gas detector, and the exhaust monitor associated with the fume hood enclosure. If either of these detectors is set off, the relay will cause power to be cut off to the three-way valve, relieving pressure to the manifold. In this way, the interlock prevents against a loss of building power, compressed air supply, exhaust flow, and detection of dangerous levels of H_2S. The interlock is connected to a status indicator light, which will inform the user if the interlock was activated since the previous time that the user visited the chamber.

VI. EXPERIMENTAL VERIFICATION

After completion of the reactor assembly, ALD experiments were performed to verify the feasibility of the system. The first material deposited was lead sulfide (PbS) due to its favorable properties to study quantum confinement effects in low-dimensional structures. The precise thickness control of ALD suggests its applicability toward precise fabrication of ultrathin structures that could be used as quantum confinements such as quantum wells. The precursors used in this study were Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)lead(II) [$Pb(tmhd)_2$] (Strem Chemicals, Inc.) and 3.5% H_2S in N_2. This H_2S gas mixture was used because 3.5% is below the LEL of H_2S, resulting in a nonflammable gas mixture. This allowed the installation of the gas cylinder in close proximity to the ALD chamber, instead of in a flammable gas cabinet. The lead precursor was sublimated at a temperature of 140 °C, while the substrate temperature was maintained at 160 °C. Further details of this process can be found in Ref. 19.

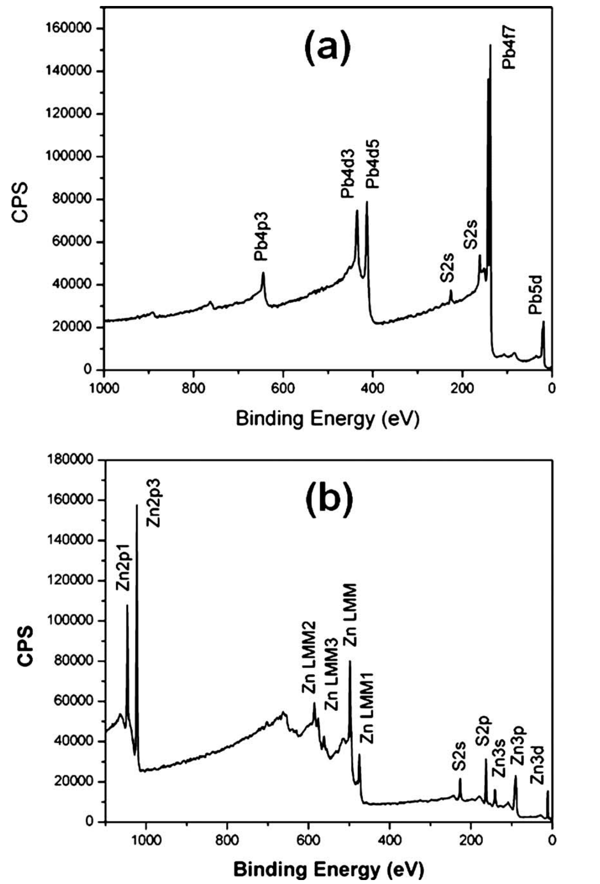

FIG. 4. XPS spectra for ALD deposited (a) PbS (b) ZnS. Figure 4(a) was adapted with permission from Ref. 19. Copyright 2009 American Chemical Society.

The resulting film composition was analyzed by x-ray photoelectron spectroscopy (XPS), and the results are shown in Fig. 4(a). The spectrum was taken after standard etching for 1 min by an Ar ion gun to remove surface contamination which adsorbed from exposure to air during transport from the ALD chamber to the XPS chamber. As indicated in the XPS spectrum, lead sulfide was successfully deposited with no carbon or oxygen contamination within the bulk of the film. This indicates that no organic or oxidizing contaminants were present in the chamber during deposition. Therefore, the sealing of the system was successful, and no contaminants from degradation of polymer materials were present.

Subsequently, ALD of zinc sulfide (ZnS) was performed, to study another material chemistry. The precursors used were diethylzinc (Aldrich) and the same H_2S gas mixture. The XPS spectrum of a ZnS film deposited on Si (100) substrates is shown in Fig. 4(b). Again, no oxygen or carbon contamination was observed in the deposited film. This demonstrated that the nonflammable mix of 3.5% H_2S in N_2 was sufficient to react with a variety of organic ligand groups used as ALD precursors. Additionally, the system design with respect to H_2S compatibility was successful, with no detectable amounts of H_2S leaking from the chamber. Furthermore, the absence of oxygen in the films indicated that all sealing was sufficiently resistant to corrosion to prevent incorporation of water from the surroundings, even after exposure to greater than 100,000 ALD process cycles.

VII. SUMMARY

An ALD reactor was designed for compatibility with H_2S gas for deposition of metal sulfides. A low-concentration gas mixture of H_2S was used to avoid flammability. All vacuum components were selected with consideration of materials compatibility with H_2S to avoid corrosion. A safety interlock system was constructed to shut down the system in case of a variety of environmental hazards. The system was successfully used for deposition of PbS and ZnS films, with no chemical contamination or detectable release of H_2S to the reactor environment.

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