Multilayer x-ray optics produced by atomic layer epitaxy*

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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 relatively new thin film deposition technique which we believe can produce MXOs with very small d-spacings. ALE accomplishes this by depositing a single layer of atoms during each cycle of the deposition process. Multilayers deposited by ALE should have sharp interfaces and smooth, uniform layers with precise d-spacings.

1. INTRODUCTION

1.1 Multilayer x-ray optics

MXOs are designed so that the x rays which are reflected from each interface of the multilayer constructively interfere to give a large total reflectivity. This relationship is expressed in Bragg's equation, $nL = 2d \sin i$, where n is the refractive index, L is the x-ray wavelength, d is the thickness of the layer pair and i is the angle of incidence. To achieve a large total reflectivity, MXOs must have sharp interfaces between the layers and the layers must be uniform and smooth with precise d-spacings. This is depicted in Figure 1.

Layers deposited using current deposition techniques such a evaporation and sputtering begin as three-dimensional columns. These columns grow laterally into a solid film above a certain height. This height limits the d-spacing of multilayers produced by these techniques to about twelve angstroms which means that short wavelength x rays will not be reflected by these multilayers. Another problem is that the boundaries between these columns are uncontrolled and when they collide it may increase the roughness of the multilayers. These boundaries also provide a pathway for rapid interstitial diffusion which decreases the sharpness of the interface between layers. Rough multilayers with gradual interfaces have a smaller total x-ray reflectivity.

The problems with the deposition techniques currently being used to produce MXOs motivated us to search for a new deposition technique. We discovered ALE, a relatively new thin film deposition technique which is ideally suited to producing MXOs.

1.2 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 a single layer of atoms 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. This means that the thickness of a film deposited by ALE can be controlled to within one atomic layer[3-6].

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The layer growth in ALE is two-dimensional; a single layer is deposited before the next layer begins to grow. This means that the interfaces between the layers will be atomically abrupt and the layers will be smooth and uniform.

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

2. THE THEORY OF ALE

2.1 Chemisorption and physisorption

A chemisorbed atom shares electrons with atoms of the surface to form strong chemical bonds. A physisorbed atom is attracted to surface atoms by weak dipole-dipole interactions or Van der Waals forces. Covalent bonds are typically ten times stronger than Van der Waals forces. This is depicted in Figure 2.

The amount of chemisorption and physisorption which occurs on a surface is determined primarily by the temperature of the substrate. The temperature of the substrate must be selected so that the atoms which have been chemisorbed remain strongly bound to the surface while the atoms which have been physisorbed are removed. At the proper temperature, only a single layer of chemisorbed atoms will remain on the surface. If there is an energy barrier between the physisorbed state and the chemisorbed state, the temperature must be adjusted so that the depositing atoms have enough energy to overcome the barrier[1,3-6].

The chemisorption and physisorption of atoms on a surface also depend on the chemical state of the adsorbed atoms. The chemical state of the atoms determines the type of ALE being used to deposit the film. There are two types of ALE, ALE using molecular beam epitaxy (ALE/MBE) and ALE using chemical vapor deposition (ALE/CVD).

2.2 Molecular beam epitaxy vs. chemical vapor deposition

ALE/MBE evaporates atoms from the bulk material to deposit a layer. This type of ALE requires the bond between the evaporated atom and the previous layer to be stronger than the bond between two of the evaporated atoms[1,3-6]. For example, a zinc-sulfur bond in a zinc sulfide layer must be stronger than a zinc-zinc bond; otherwise the process is not self-limiting and more than a single layer of zinc will be deposited. The following test can be used to determine if a material can be deposited by ALE/MBE. The melting point of crystalline materials is an indication of the bond strength of the atoms, therefore if the melting point of the material to be deposited is greater than the melting points of the bulk materials being evaporated, then the material can most likely be deposited by ALE/MBE. Although this criterion can help in the selection of materials, it can not change the fundamental limits of this requirement.

ALE/MBE requires a high substrate temperature because the evaporated atoms can form bonds like those in the bulk material. These bonds are generally stronger than the Van der Waals forces typical of physisorption. The high temperatures insure that these strongly physisorbed atoms can be removed.

ALE/CVD deposits a layer of atoms from a gas phase chemical species. This type of ALE also requires the bond between the atom and the previous layer to be stronger than the interactions between two molecules containing the atom. However with ALE/CVD, the molecule containing the atom of interest is a gas phase chemical species which means that the interactions between molecules is guaranteed to be weak[1,3-6]. For example, a bond between a surface sulfur atom and the zinc atom in diethyl zinc is many times stronger than the weak interaction between two molecules of diethyl zinc. The strength of the bond between the atom and the surface also depends upon the molecule which contains the atom. By carefully

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selecting the chemical species which contains the atom of interest, almost any type of atom can be deposited. This makes ALE/CVD more versatile than ALE/MBE.

ALE/CVD can be performed at lower substrate temperatures than ALE/MBE. This is because the interaction between two gas phase molecules is generally weaker than the interaction between two evaporated atoms. For example, it requires less energy to break a bond between two diethyl zinc molecules than to break a bond between two zinc atoms.

We determined that ALE/CVD is the best method for producing MXOs since it has greater versatility and requires lower substrate temperature.

3. THIN FILM DEPOSITION BY ALE/CVD

3.1 The deposition process

Figure 3 depicts the overall ALE/CVD process for depositing zinc selenide. There are four steps in the process. A cycle consists of two steps and deposits a single layer of atoms.

In the first step, the gas containing the zinc atoms is introduced into the system. The molecules of the gas collide with the surface and if the energy of a molecule is small enough it is physisorbed onto the surface. The physisorbed molecule then migrates along the surface until it comes to a binding site where it is chemisorbed. This process continues until all the binding sites on the surface are occupied by chemisorbed molecules. Molecules which collide with the surface after it is completely covered by chemisorbed molecules can only be physisorbed. The time required for the surface to be completely covered by a layer of chemisorbed molecules is a function of the number of collisions, the energy of the chemisorbed and physisorbed states and the activation energy. Kinetics predicts the rates of chemisorption to be rapid which means a rapid cycling rate should be achievable.

In the second step, the gas flow is shut off and any physisorbed molecules are removed. The physisorbed molecules are removed by evacuating the system and allowing them to evaporate. The time required to pump out the system determines the overall cycling rate and is an important part of the reactor design. At this point in the process, a single layer of zinc has been deposited on the surface.

In the third step, a gas containing the selenide atom is introduced into the system. The selenide molecules react with the zinc molecules which are chemisorbed on the surface to form a zinc selenide layer.

In the fourth and final step, the gas flow is again shut off and any unreacted physisorbed molecules and any gas reaction products are removed. These four steps are repeated until the desired thickness of zinc selenide is obtained. The reactant gases can then be switched and a different material deposited.

There are many different materials which can be deposited by ALE/CVD and for each material there are several possible reactants[1,3-6]. The selection of the chemical reactants to be used for the ALE/CVD process is very important.

3.2 Reactant Selection

We based the selection of reactants for the ALE/CVD process on several criteria. First, the reactants should be volatile. This criteria insures that the interaction between the molecules of each species is weak and it also simplifies the transport of the reactant gases to the deposition chamber. Second, the reactants must react to give the desired products at low temperatures. This can be determined by

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calculating the Gibb's free energy of the desired reaction. To simplify the calculations, the Gibb's free energy of the gas phase reaction can be used as an approximation to the surface reaction since surfaces often catalyze reactions. If the Gibb's free energy is negative, the reaction most likely will occur. Using these criteria we have determined that metal-organic (MO) compounds have the best properties for depositing films by ALE/CVD[3-6]. There is one additional advantage to using metal-organic reactants. It has been shown that with some materials irradiating the surface with laser radiation while the metal-organic reactant is being introduced into the system allows the selective deposition of the material on the irradiated area of the surface[7]. This means that patterning is possible during the ALE/MOCVD deposition process.

The multilayers required for x-ray optics will be deposited as a superlattice composed of two alternating materials. We have selected zinc selenide and cadmium sulfide as the materials for our first multilayers. We will deposit the zinc selenide from diethyl zinc and hydrogen selenide and the cadmium sulfide from dimethyl cadmium and hydrogen sulfide.

4. The Superlattice

4.1 Lattice parameters

ALE/CVD has been used to deposit amorphous and crystalline thin films. We will deposit a crystalline superlattice to produce MXOs because we believe that crystalline multilayers will give us better x-ray reflectivity. Figure 4 depicts a zinc selenide/cadmium sulfide superlattice. The number of layers of each material is variable as long as the II-VI structure is maintained. A high quality crystalline superlattice can be obtained by carefully matching the lattice parameters of the two materials to be deposited. The lattice parameters of the substrate should also match the lattice parameters of the deposited materials. We selected zinc selenide and cadmium sulfide because their lattice parameters closely match. We also selected a germanium substrate for the same reason. It is important to note that matching the lattice parameters may not be critical to the process since superlattices have been deposited from materials with a large lattice mismatch.

4.2 Diffusion

During the deposition of multilayers, the atoms of each layer diffuse across the interface into the adjacent layers. The higher the substrate temperature the greater the amount of diffusion. Diffusion degrades the sharpness of the interface which decreases the x-ray reflectivity of the multilayers. To prevent diffusion, the temperature of the substrate must be as low as possible during deposition. Thin films have been deposited by ALE/CVD at 250 C to 650 C depending on the reactants being used. As was explained previously, we selected metal-oraganic compounds because they can deposit thin films at the lowest temperatures.

We performed a simple calculation to determine the degree of diffusion which will occur between layers. The model we used assumes there is only interstitial diffusion of a one bulk material into another and that the diffusion coefficient is independent of concentration. The results are given in Figure 5 for zinc selenide and cadmium sulfide and show that the diffusion at 350 C for one hour will be less than one atomic layer. We conclude that the interfaces between multilayers deposited by ALE/MOCVD will be very sharp.

5. REACTOR DESIGN

5.1 Gas system

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Figure 6 shows a block diagram of the ALE/MOCVD reactor we have designed and built. The reactants we selected are flammable and toxic and special procedures were required for their safe use. The entire system was constructed of stainless steel. We used VCR connectors because they are reliable and leak-free. The valves are all high purity diaphragm or bellows valves. The metal-organic compounds are liquids at room temperature and require a bubbler system. Hydrogen gas is bubbled through the metal-organic liquid and carriers the vapors into the deposition chamber. The gas flows are monitored and controlled by mass flow controllers and a computer. The automatic valves are also computer controlled to allow the rapid switching of the reactant gasses.

5.2 Deposition chamber

The deposition chamber is a 2.5 inch stainless steel cross with high vacuum knife-edge flanges sealed with copper gaskets. The substrate holder is a 2 inch diameter copper block which can be heated resistively to 1000 C. The temperature of the substrate is monitored and controlled by a thermocouple and a computer. The deposition chamber also contains a window port directly above the substrate to allow photo-assisted deposition for patterning the multilayers. We have also connected a 0-200 amu residual gas analyzer to the system. The residual gas analyzer is an important part of the system. It will allow us to perform adsorption and desorption experiments and it will help us to determine the mechanisms involved in the ALE/MOCVD process.

5.3 Vacuum system

The vacuum system consists of a turbomolecular pump with a two-stage rotary vane roughing pump. The base pressure of the system is 10^{-8} torr and the entire system was helium leak checked to 10^{-10} torr. The low pressure is not required for the ALE/MOCVD process but is necessary for the adsorption and desorption experiments we will perform using this system. As we explained previously, the key to achieving rapid cycling rates is to have rapid gas exchange. This means that a vacuum system with a large throughput is desirable. A necessary precaution is that the exhaust of the vacuum system must be connected to a chemical fume hood to prevent any unreacted materials from entering the laboratory.

6.0 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 determined that ALE/MOCVD was the best technique for depositing the required multilayers, because metal-organic compounds are volatile and can be deposited at relatively low temperatures and they also allow the possibility of doing photo-assisted deposition for producing patterned structures.

The first MXO we produce by ALE/MOCVD will be a zinc selenide cadmium sulfide superlattice. We selected these materials for several reasons. First, their crystal lattices match and second, the required reactants are readily available.

Finally, we have designed and built an ALE/MOCVD reactor and within the next few months we will produce and test the first MXOs produced by ALE.

7.0 ACKNOWLEDGEMENTS

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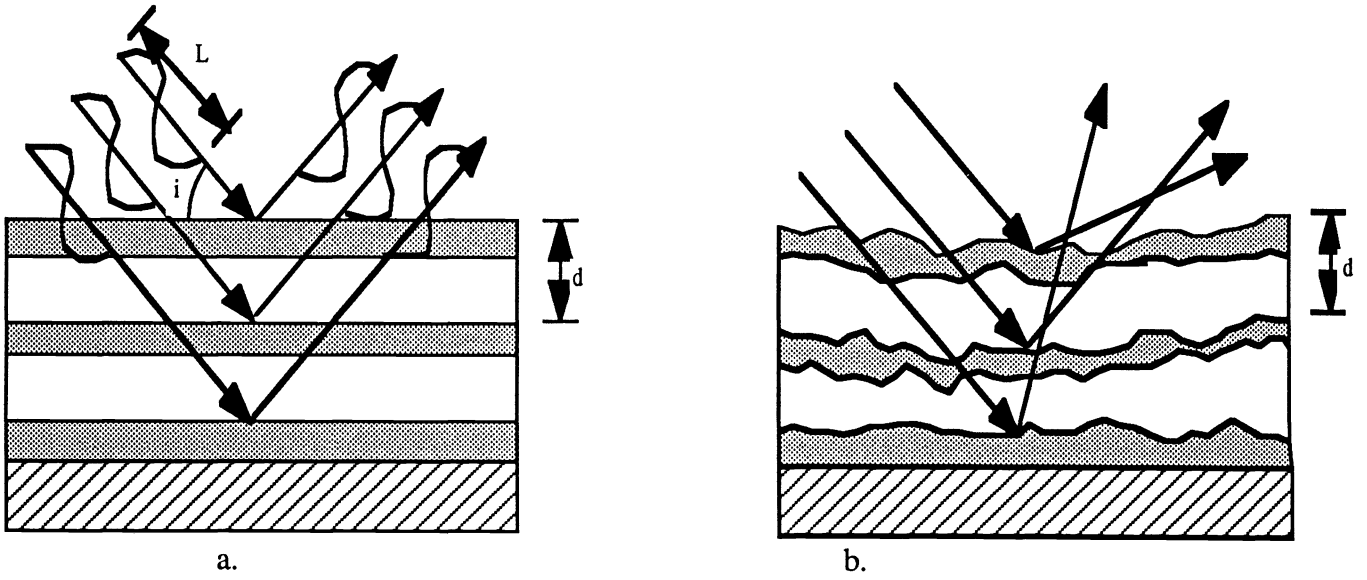


Figure 1. a. A good x-ray reflector. X rays reflected at each interface constructively interfere to give a large total reflectivity. b. A poor x-ray reflector. Layers are rough and nonuniform so x rays reflected at each interface do not constructively interfere.

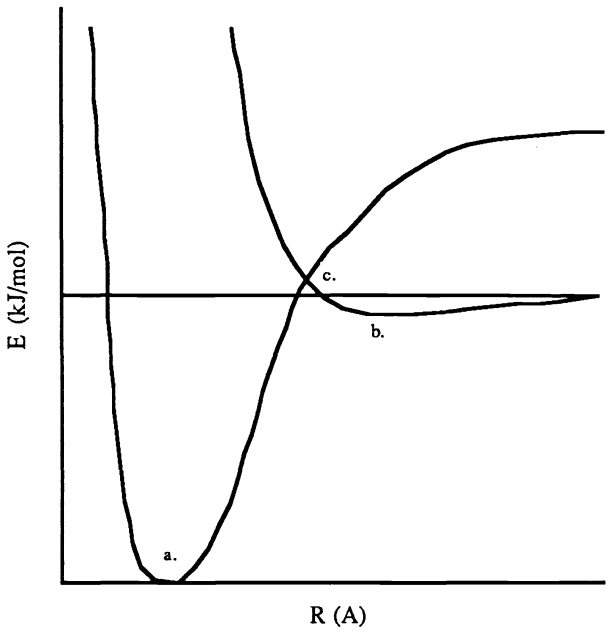


Figure 2. Interaction energy as a function of nuclear separation. a. Chemisorption. b. Physisorption. c.. Energy barrier.

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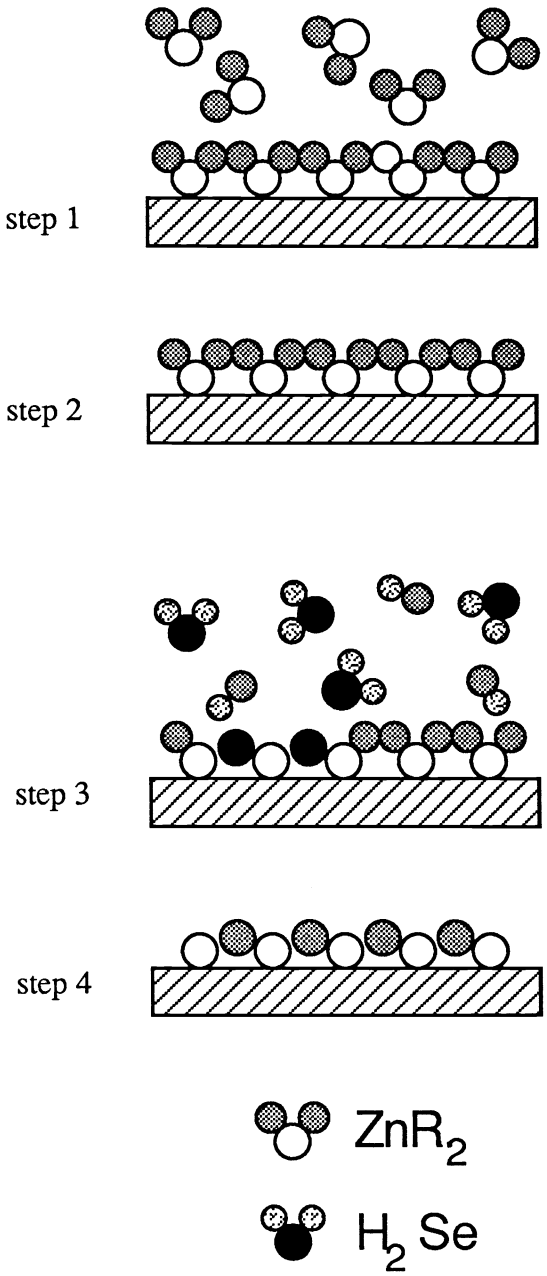


Figure 3. The ALE/CVD Deposition Process.

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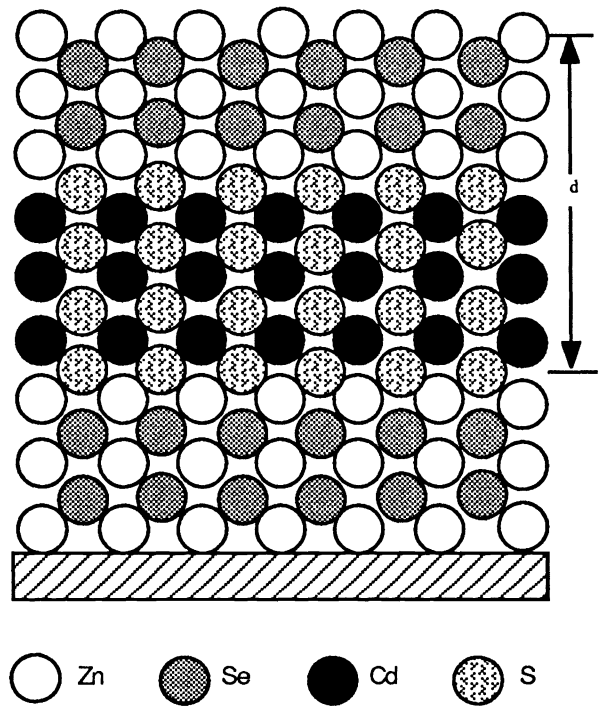


Figure 4. Zinc selenide/ cadmium sulfide superlattice.

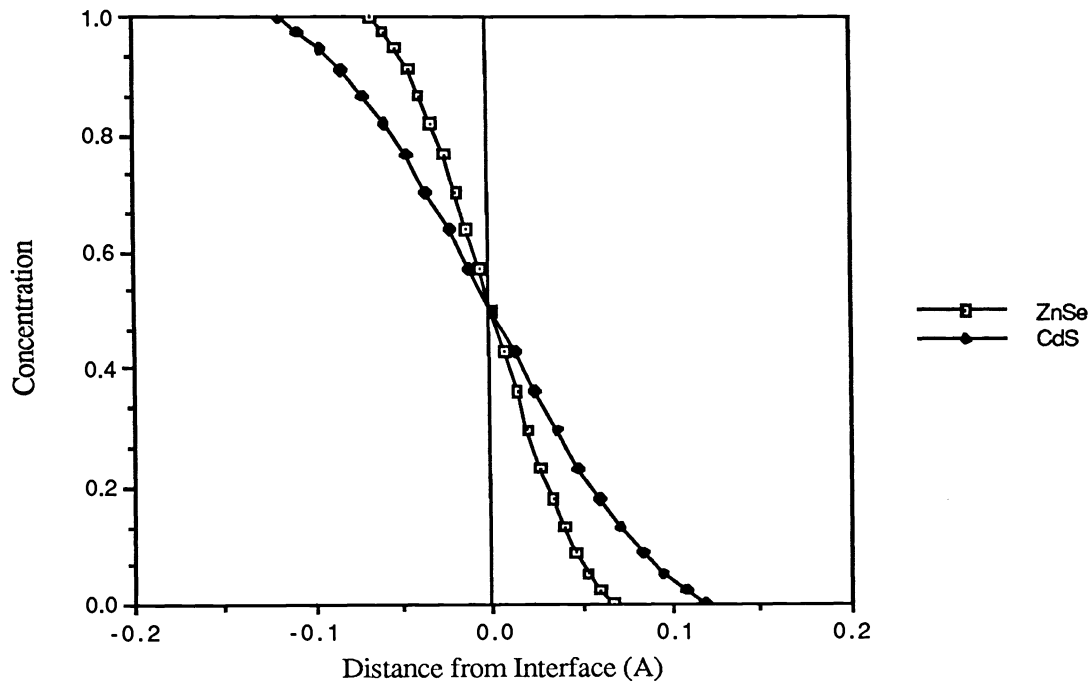


Figure 5. Diffusion of ZnSe and CdS into a bulk material.

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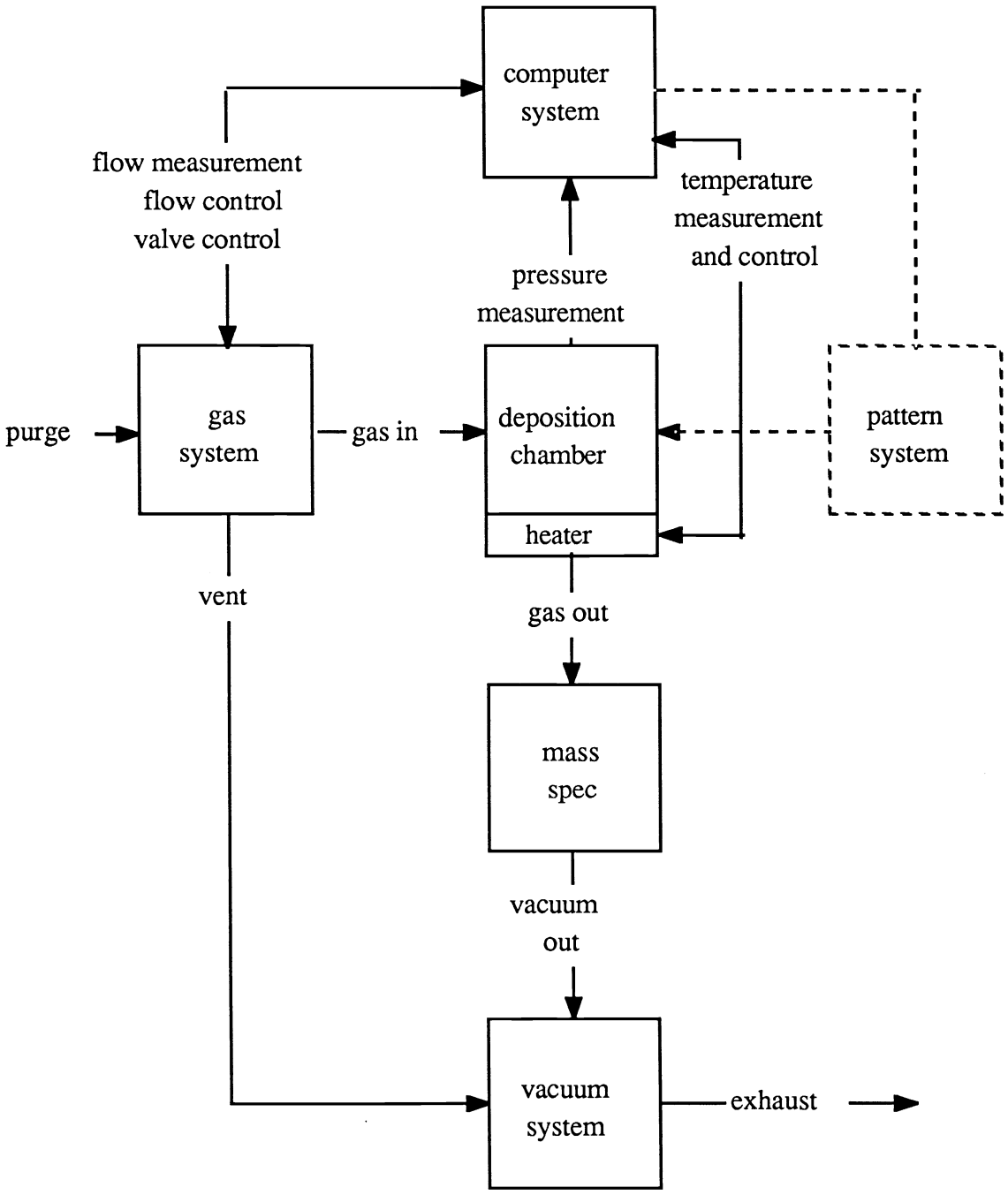


Figure 6. ALE/MOCVD reactor block diagram

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