Preparation and Characterization of Thin Films of MgO, Al₂O₃ and MgAl₂O₄ by Atomic Layer Deposition

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MgO, Al₂O₃ and MgAl₂O₄ thin films were deposited on silicon substrates at various temperatures by the atomic layer deposition (ALD) method using bis(cyclopentadienyl)magnesium, triethylaluminum, and H₂O and were characterized systematically. High-quality polycrystalline MgO films were deposited for a substrate temperature above 500°C, and amorphous thin films were deposited around 400°C. The deposited Al₂O₃ and MgAl₂O₄ thin films were characterized as amorphous in structure. Applicability of ALD to complex oxides is discussed.

Key words: Atomic layer deposition, MgO, Al₂O₃, MgAl₂O₄, thin films

INTRODUCTION

In recent years, there has been considerable research on the deposition of metal oxide films on a variety of substrates because of the many applications of the oxide films in microelectronic, superconducting, and optoelectronic devices. Aluminum oxide, magnesium oxide, and spinel have been actively studied metal oxides. Al₂O₃ thin films are used as insulator layers. Spinel can be used as an insulator thin film, too, and also is a potential laser material. Magnesia thin films have attracted attention in the last few years mainly as a buffer layer for the further deposition of high-Tc superconductors or ferroelectrics and as a wide band gap Group II-VI insulator for potential electronic applications. These oxides have very low standard free energy and hence, high thermodynamic stability.

Atomic layer deposition (ALD) is a method for producing thin films and layers of single crystals one atomic layer at a time utilizing a self-control obtained through saturating surface reactions. It was originally developed to meet the needs of improved ZnS thin films and dielectric thin films for electroluminescent thin film display devices. It was successfully used for the deposition of Group III-V semiconductors. Diverse equipment was developed to meet the requirement of ALD. Systems were operated from high vacuum to atmospheric pressure. Al₂O₃ thin films have been studied extensively using AlCl₃ as a precursor.

In this paper, an apparatus used for the deposition of MgO, Al₂O₃, and MgAl₂O₄ is described and the concept of self-control obtained through saturating surface reactions is discussed for the ALD of Al₂O₃ and MgAl₂O₄. Bis(cyclopentadienyl)magnesium (CP₂Mg), and H₂O are used for the deposition of MgO thin films on silicon substrates; triethylaluminum (TEAl) and H₂O are used for the deposition of Al₂O₃ thin films; CP₂Mg, TEAl and H₂O are used for the deposition of MgAl₂O₄ thin films. The deposited films are analyzed by Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and x-ray diffraction.

EXPERIMENTAL

The basic mechanism of ALD is the growth of a saturated monolayer onto the surface, yielding a rate of growth that is proportional to the number of reaction cycles instead of the time of the growth and the intensity of the material flux. The reactants are introduced into the reaction chamber sequentially. The deposition system was designed here to carry out the deposition of MgO, Al₂O₃, and MgAl₂O₄ and to
adhere to this ALD concept. The reactant vapor sources are carried by nitrogen gas to the chamber sequentially. The apparatus, schematically illustrated in Fig. 1, was operated at atmospheric pressure. A 12-position valve (Valco Instruments), which is electrically actuated, is used to connect the reactant sources sequentially to the chamber, and it takes 0.33 sec to turn from one port to the next. A two-position valve (Valco Instruments), which is air-actuated, is used to interrupt the normal deposition process and to connect the doping reactant source to the chamber. The vapor pressures of CP$_2$Mg and TEAl are changed by changing the temperature of the compound cylinders, which can be independently controlled. The system is built in a box, whose temperature is higher than that of the compound cylinders to prevent compound condensation in the transportation tubing. The system is under the control of a computer.

For the deposition of Al$_2$O$_3$, the air operated bellows valve 3 was always closed. To finish a full cyclic deposition of Al$_2$O$_3$: 1) the multiposition valve stopped at port 2 for a time $t_p$ to purge the chamber; 2) then, stopped at port 3 for $t_{tA}$ time to admit enough TEAl to the chamber; 3) stopped at port 4 for $t_r$ to allow the chemical reaction to happen; 4) stopped at port 5 for $t_p$ to purge the chamber; 5) stopped at port 6 for $t_o$ to admit enough H$_2$O to the chamber; and 6) stopped at port 7 to allow the chemical reaction to finish.

For the deposition of MgO, the air operated bellows valve 2 was always closed. To finish a full cyclic deposition of MgO: 1) the multiposition valve stopped at port 8 for a $t_p$ time to purge the chamber; 2) then, stopped at port 9 for $t_{tM}$ time to admit enough CP$_2$Mg to the
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RESULTS AND DISCUSSION

The Deposition of MgO

Films were grown at several substrate temperatures in the range 370–900°C. The film deposited at 370°C was amorphous, giving no x-ray diffraction. The films deposited above 500°C were well-crystallized. Typical x-ray diffraction patterns are presented in Fig. 2. As described before, the growth orientation changes from [111] to [100] as the substrate temperature changes from 500 to 900°C. The change of the orientation of the silicon substrate surface from [111] to [100] resulted in no change to the growth orientation of MgO thin films.

The thickness per cycle of the films grown at different temperatures is presented in Fig. 3. Because the growth orientation changes with the substrate temperature, the theoretical thickness per cycle for one atomic layer by one atomic layer growth along orientation [111] and [100] are illustrated in Fig. 3 as the dot-and-dash line and the dashed line, respectively. At 600°C, the growth is very close to one atomic layer by one atomic layer deposition; below 600°C, the growth is faster than one atomic layer by one atomic layer deposition; above 600°C, the growth is slower than one atomic layer by one atomic layer growth.

Scanning electron microscope photomicrographs of the surfaces of the films deposited at 500 and 900°C are shown in Fig. 4. The surface morphology of the
Fig. 4. Scanning electron microscope photographs of the MgO films deposited at a) 500°C and b) 900°C.

Films show significant changes with temperature.\textsuperscript{28} Even though the deposition temperature was as high as 900°C and the silicon has a thermal expansion coefficient \(2.4 \times 10^{-6} \text{C}^{-1}\), much smaller than magnesium's \(12.4 \times 10^{-6} \text{C}^{-1}\), the deposited films, whose thicknesses range from 0.3 to 1 μm, were shiny and did not crack.

Figure 5 shows the first-derivative Auger spectrum of the films deposited using 1600 cycles at 500°C. Magnesium and oxygen Auger peaks are observed, while the signal level of carbon is comparable to or lower than the noise level. During AES depth profiling, 4 keV primary Ar\(^+\) ions were used to sputter away the surface. Detection was carried out using 5 keV primary electrons and an energy resolution of 0.5%. Auger depth profiles of films deposited at 500 and 800°C are shown in Fig. 6; magnesium, oxygen, and carbon remain constant with depth. The impurity carbon is very low and shows no significant difference between films deposited at different temperatures. Although the Y-axes of the AES profiles are labelled 0 to 200, 400, 600, 800, 1000, 1200, and 1400, the data for Mg and O cannot be directly assumed. It has been reported\textsuperscript{28} that the bombardment of oxides leads to the reduction of oxygen since more volatile oxygen is lost preferentially. However, the profiles do show that a constant magnesium to oxygen stoichiometry is being maintained throughout the deposition process, and the Mg/O ratio remains constant for the films deposited at different temperatures.
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The Deposition of Al₂O₃ and MgAl₂O₄

The films of Al₂O₃ and MgAl₂O₄ deposited on silicon gave no x-ray diffraction and are amorphous in structure. Below 600°C, the deposition of Al₂O₃ on silicon using TEAl and H₂O was unsuccessful. Above 750°C, the deposited films looked black and contained carbon. It is very possible that the radical of TEAl, which dissociated at high temperature, would further decompose releasing carbon.

Figure 7 is the first-derivative Auger spectrum from the Al₂O₃ film, which was deposited at 700°C for 200 cycles using the conditions indicated in Table I, after 1 min argon presputtering to clean the surface. Aluminum and oxygen Auger peaks are observed along with the impurity carbon. Small argon Auger peaks are due to Ar⁺ used to presputter the sample. Absolute stoichiometry is not obtainable from these results, and we do not expect that of Al₂O₃. This is discussed below. Surface examination by SEM is illustrated in Fig. 8. The grain structure was not observed, as expected for amorphous Al₂O₃.

For the deposition of MgAl₂O₄, the chemical compounds were introduced into the chamber in the sequence CP₃Mg-H₂O-TEAl-H₂O. Figure 9 shows the first-derivative Auger spectrum from the film deposited at 640°C for 200 cycles. Magnesium, aluminum, and oxygen Auger spectra are observed with the impurities carbon and argon. As with the Al₂O₃ films, argon peaks are due to Ar⁺ used to presputter the sample. Figure 10 is the SEM observation of the film. The films deposited at different temperatures showed no obvious difference from the film deposited at 640°C by SEM examination and Auger analysis. As with Al₂O₃ thin film deposition, above 750°C the films looked black and contained much carbon.

Unlike the atomic layer deposition of MgO, which can be deposited along the [111] direction by one atomic layer by one atomic layer stacking at 600°C, the deposited Al₂O₃ and MgAl₂O₄ films were non-crystallized. This is very possibly due to the complex crystal structure of Al₂O₃ and MgAl₂O₄. If the deposition of Al₂O₃ is on the (0001) plane of Al₂O₃, oxygen forms a close-packed plane, and just two-thirds of the octahedral sites on the plane should be occupied by aluminum to form stoichiometric Al₂O₃, whereas there...
is no reason for this stoichiometry to be obtained through saturating surface reactions. For MgAl₂O₄, the crystal structure is even more complex. Oxygenes form a close-packed plane in MgAl₂O₄, on which only half the octahedral sites are occupied by aluminum and one quarter of the tetrahedral sites are occupied by magnesium. Furthermore, the octahedral and tetrahedral sites are indistinguishable on the plane before another layer of oxygen covers the surface. This would explain why stoichiometry is hard to achieve in ALD of Al₂O₃ and MgAl₂O₄ and the deposited films are amorphous in structure. To achieve chemical stoichiometry, a deliberately designed deposition cycle might be attempted in which a certain metal atom is admitted on only every second or third growth cycle, in order to allow saturating surface reactions of the metal atoms to result in only partial filling of oxygen interstitial sites. A high temperature anneal would then be necessary to achieve the desired crystalline phase.

It is reported that low temperature e-beam evaporated MgAl₂O₄ films were amorphous as deposited and were crystallized by high-temperature annealing. High temperature deposition in ALD resulted in further decomposition of the dissociated radicals and deposited films contained too much carbon. It is conceivable that some other precursor for the aluminum source could be used at high temperatures in order to eliminate the need for the post deposition anneal, but another problem remains: by its very nature, a saturating surface reaction only exists within a restricted temperature range, and without it, ALD does not take place.

CONCLUSION

A system to carry out the atomic layer deposition of MgO, Al₂O₃, and MgAl₂O₄ has been designed and constructed. Thin films of MgO, Al₂O₃, and MgAl₂O₄ have been deposited at various temperatures. MgO deposited above 500°C was polycrystalline; MgO deposited around 400°C was amorphous. The deposited Al₂O₃ and MgAl₂O₄ films were amorphous in structure. Because a simple atomic stacking sequence exists in MgO, it was especially suitable to be deposited by self-control obtained through saturating surface reactions in ALD. The deposited films showed that the growth orientation changed from [111] to [100], and the surface had a cubic-like to plate-like morphology, when the deposition temperature changed from 500 to 900°C. Al₂O₃ and MgAl₂O₄, which lack a simple atomic stacking sequence like MgO in crystal structure, suffer additional complexities in atomic layer deposition: the deposition cannot be realized by self-control obtained through saturating surface reactions.

REFERENCES