Journal of Electronic Materials, Vol. 22, No. 2, 1993

Preparation and Characterization of Thin Films of MgO, Al_2O_3 and $MgAl_2O_4$ by Atomic Layer Deposition

RON HUANG

Department of Material Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4M1

ADRIAN H. KITAI

Department of Engineering Physics and Material Science and Engineering, McMaster Uiniversity, Hamilton, Ontario, Canada, L8S 4M1

MgO, Al_2O_3 and $MgAl_2O_4$ thin films were deposited on silicon substrates at various temperatures by the atomic layer deposition (ALD) method using bis(cyclopentadienyl)magnesium, triethylaluminum, and H_2O 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 Al_2O_3 and $MgAl_2O_4$ thin films were characterized as amorphous in structure. Applicability of ALD to complex oxides is discussed.

Key words: Atomic layer deposition, MgO, Al_2O_3, $MgAl_2O_4$, 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.[1–7] Aluminum oxide,[8–11] magnesium oxide,[12–16] and spinel ($MgAl_2O_4$)[17,18] have been actively studied metal oxides. Al_2O_3 thin films are used as insulator layers.[19] Spinel can be used as an insulator thin film, too,[18] and also is a potential laser material.[20] Magnesia (MgO) thin films have attracted attention in the last few years mainly as a buffer layer for the further deposition of high-T_c superconductors or ferroelectrics and as a wide band gap Group II-VI insulator for potential electronic applications.[15,21,22] These oxides have very low standard free energy and hence, high thermodynamic stability.

Atomic layer deposition (ALD)[23] 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.[24] Diverse equipment was developed to meet the requirement of ALD. Systems were operated from high vacuum to atmospheric pressure.[23] Al_2O_3 thin films have been studied extensively using $AlCl_3$ as a precursor.[25,26]

In this paper, an apparatus used for the deposition of MgO, Al_2O_3 and $MgAl_2O_4$ is described and the concept of self-control obtained through saturating surface reactions is discussed for the ALD of Al_2O_3 and $MgAl_2O_4$. Bis(cyclopentadienyl)magnesium (CP_2Mg), and H_2O are used for the deposition of MgO thin films on silicon substrates; triethylaluminum (TEAl) and H_2O are used for the deposition of Al_2O_3 thin films; CP_2Mg, TEAl and H_2O are used for the deposition of $MgAl_2O_4$ 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, Al_2O_3 and $MgAl_2O_4$ and to

---

(Received September 2, 1992; revised November 2, 1992)

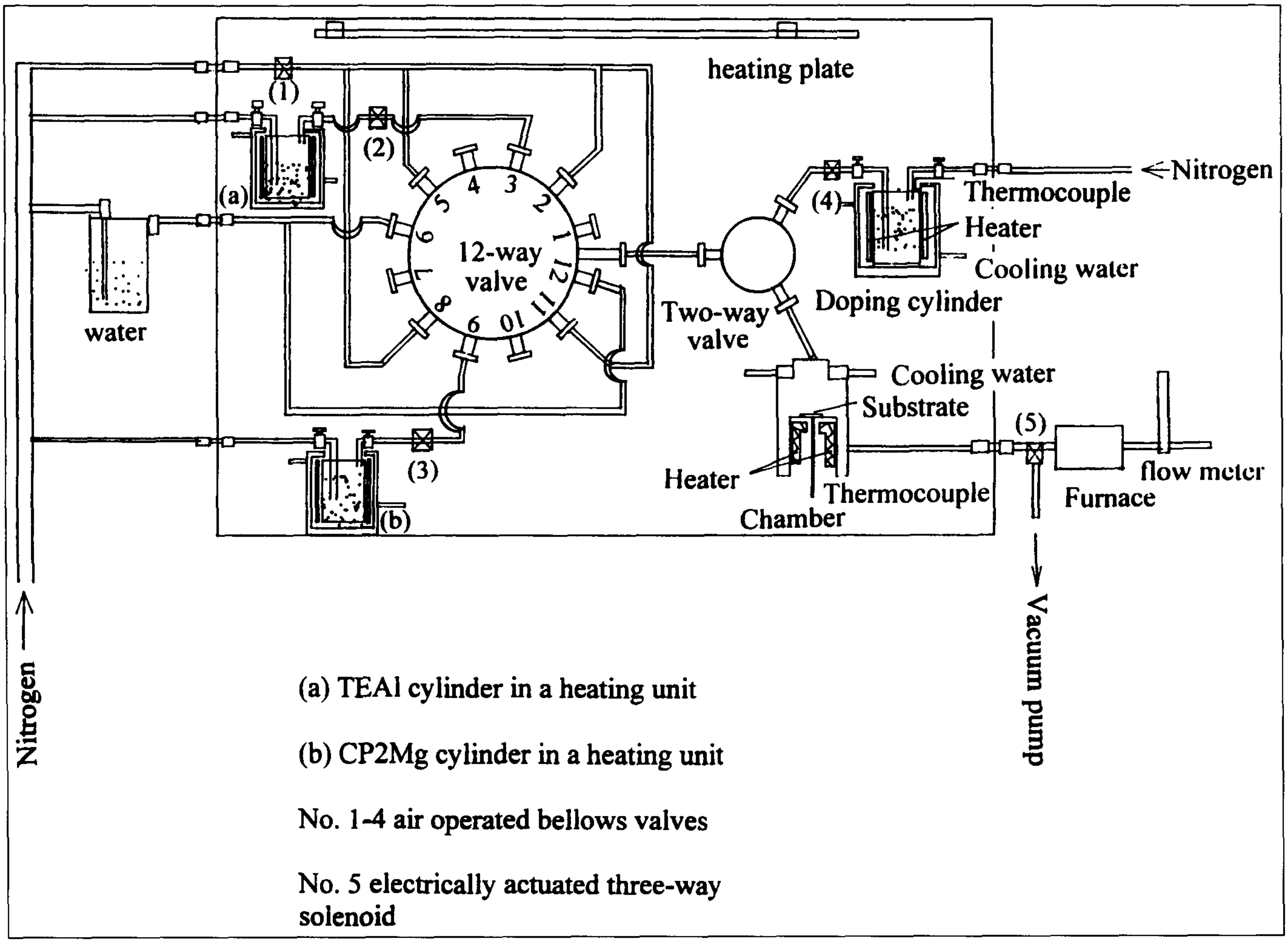

Fig. 1. Schematic diagram of the deposition system.

Table I. Typical Deposition Parameters for Growth of $MgAl_2O_4$

Temperature of CP_2Mg	64°C
Temperature of TEAl	61°C
Temperature of H_2O	rt
Temperature of box	100°C
Temperature of substrate	400°C to 1000°C
Flow rate of CP_2Mg	0.5 l/min
Flow rate of TEAl	0.5 l/min
Flow rate of H_2O	0.5 l/min
Flow rate of N_2	1 l/min
Flow time interval of CP_2Mg t_{Mg}	3 sec
Flow time interval of TEAl t_{Al}	3 sec
Flow time interval of H_2O t_O	3 sec
Purging time t_p	24 sec
Reaction time t_r	5 sec
Deposition cycles	100 to 1600
Substrate	(111)Si

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_2Mg 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_2O_3, the air operated bellows valve 3 was always closed. To finish a full cyclic deposition of Al_2O_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_{Al} 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_2O to the chamber; and 6) stopped at port 7 to allow the chemical reaction to finish.

For the deposition of MgO, the air operated bellow 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_{Mg} to admit enough CP_2Mg to the

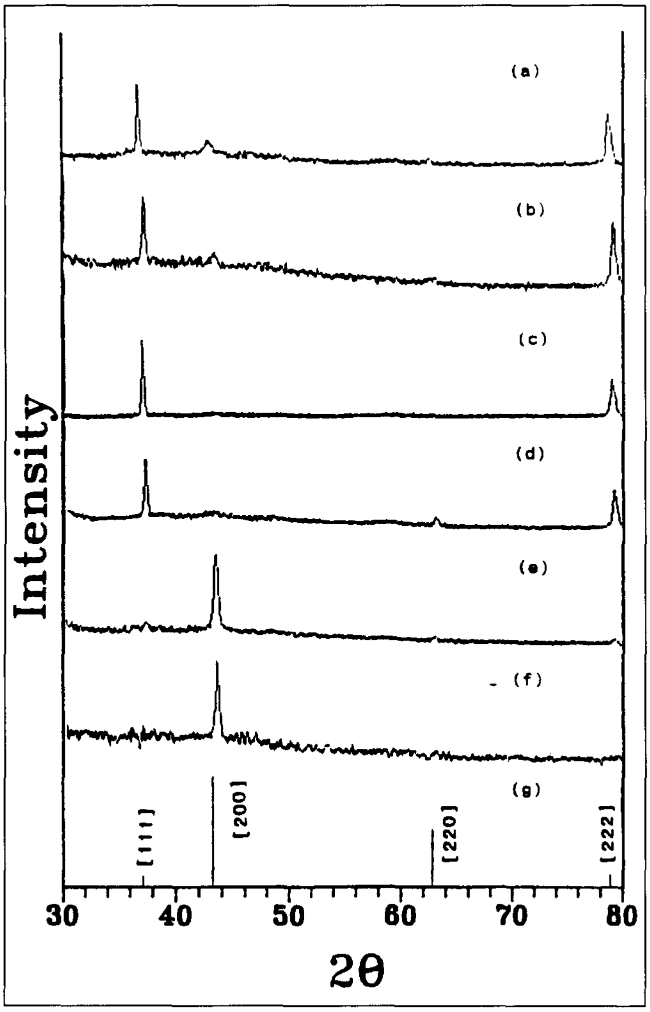

Fig. 2. X-ray diffraction of the MgO films deposited at a) 500°C; b) 560°C; c) 600°C; d) 700°C; e) 800°C; f) 900°C; and g) standard x-ray diffraction pattern.

chamber; 3) stopped at port 10 for t_r to allow the chemical reaction to happen; 4) stopped at port 11 for t_p to purge the chamber again; 5) stopped at port 12 for t_O to admit enough H_2O to the chamber; and 6) stopped at port 1 to allow the chemical reaction to finish.

For the deposition of $MgAl_2O_4$, the multiposition valve stopped at every port sequentially from port 1 as in the deposition of MgO or Al_2O_3. Before each deposition, the chamber was purged by N_2 and filled with N_2. The substrate was then heated to the desired temperature. The gas flow was monitored by a flow meter. Typical deposition parameters are listed in Table I.

The reactants that were used during deposition, CP_2Mg, and TEAl (Strem Chemicals), were received in all-welded stainless steel teflon coated cylinders. The vapor pressures of CP_2Mg and TEAl are 1 mm Hg at temperatures 60 and 64°C, respectively. Depositions were carried out on single crystal silicon wafers. The wafers were cleaned as described before.[27] The silicon had a thin native oxide on its surface due to exposure to air during mounting, and therefore no in-plane orientation of ALD films was expected.

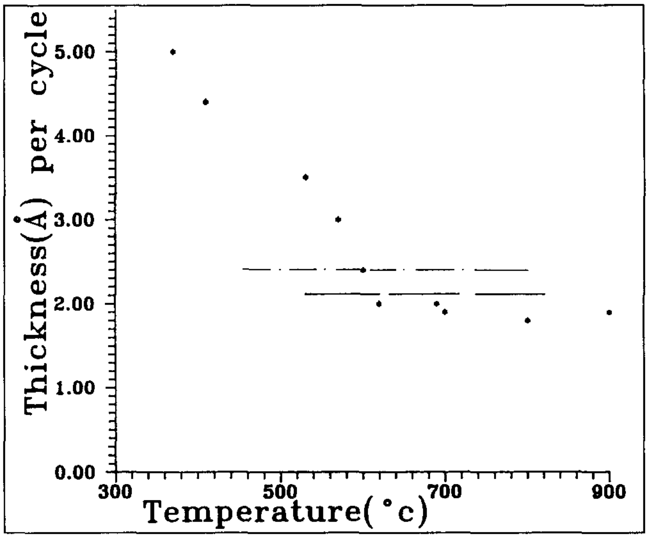

Fig. 3. The thickness/cycle of MgO films vs temperatures, the dot-and-dash line and the dashed line are theoretical thickness/cycle for [111] and [100] deposition direction, respectively.

The compositions of MgO films was examined by Auger electron spectroscopy (AES) and depth profiled. The surfaces of MgO films were examined by scanning electron microscopy (SEM). The crystallinity of the films was analyzed by x-ray diffraction with CuKα radiation. The thicknesses of the films were measured by a mechanical thickness profiler. The Al_2O_3 and $MgAl_2O_4$ thin films were subject to AES analysis, and the surfaces were examined by SEM.

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,[27] 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;[27] 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

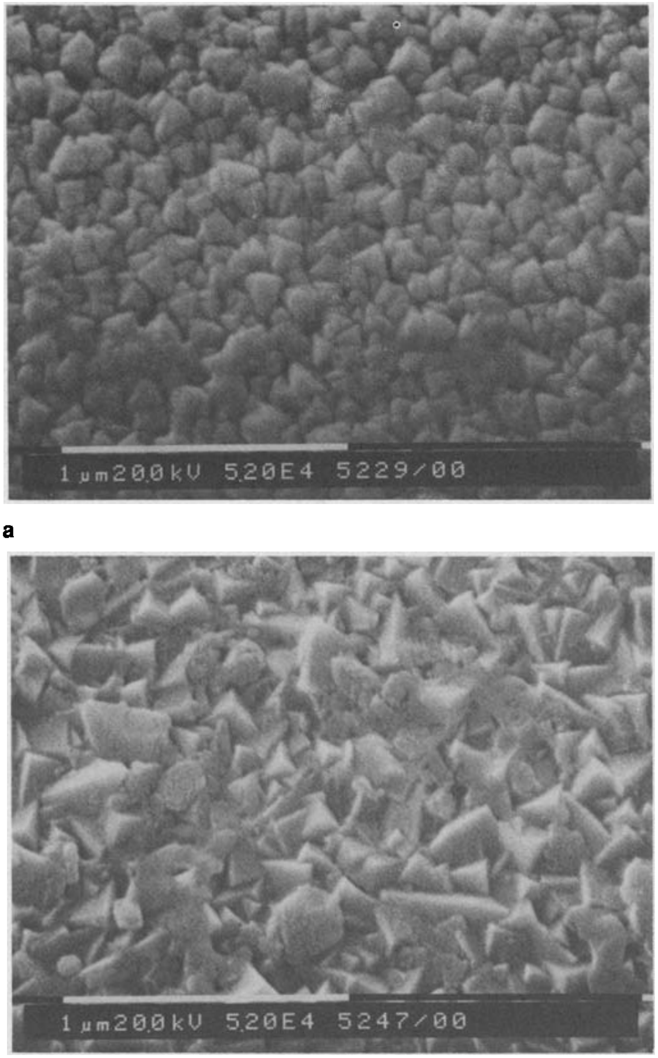

Fig. 4. Scanning electron microscope photographs of the MgO films deposited at a) 500°C and b) 900°C.

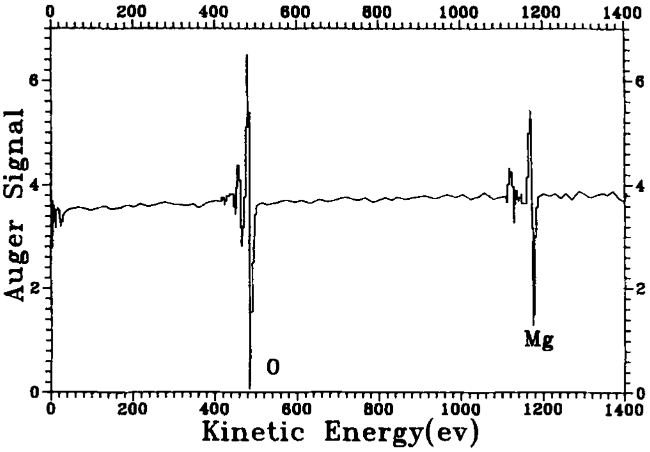

Fig. 5. First-derivative spectra taken from the film deposited 1600 cycles at 500°C.

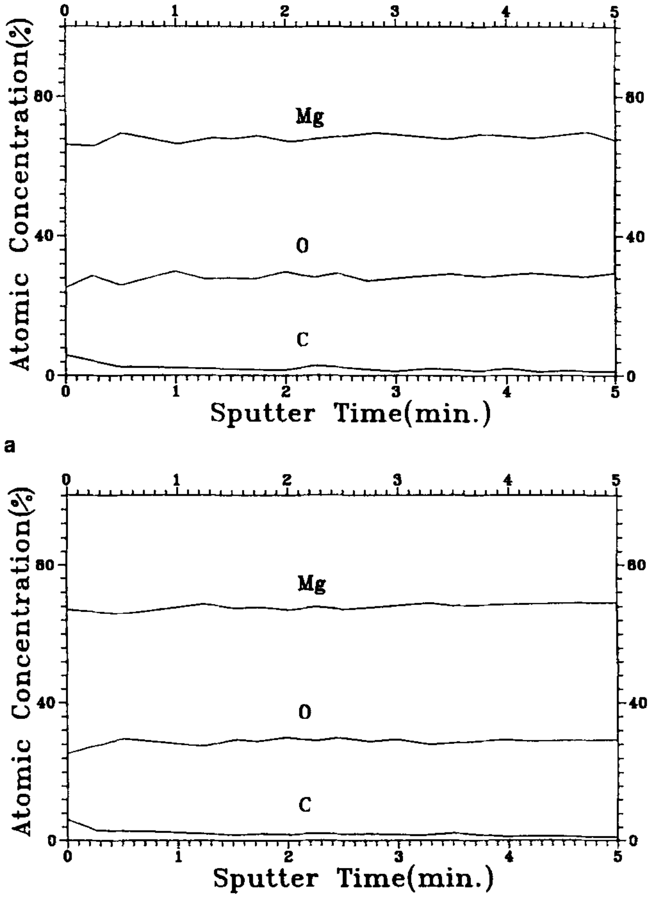

Fig. 6. Auger electron spectroscopy sputter profiles of the MgO films deposited 1600 cycles at 500 and 800°C.

films shows significant changes with temperature.[28] Even though the deposition temperature was as high as 900°C and the silicon has a thermal expansion coefficient (2.4×10^{-6}°C^{-1}), much smaller than magnesia's (12.4×10^{-6}°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 "atomic concentration %" quantitative concentration data for Mg and O cannot be directly assumed. It has been reported[29] 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.

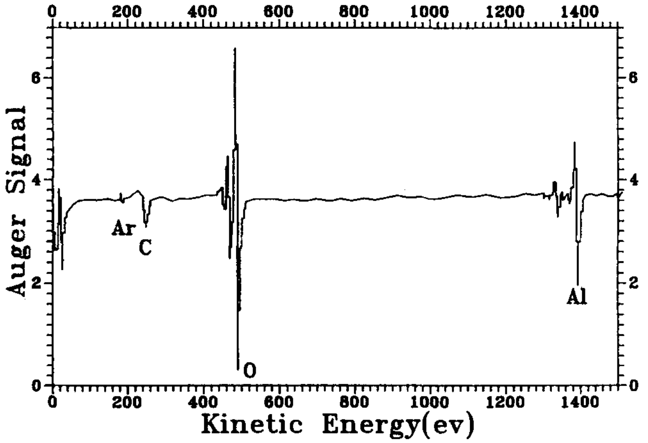

Fig. 7. First-derivative spectra taken from the Al_2O_3 film deposited 200 cycles at 700°C.

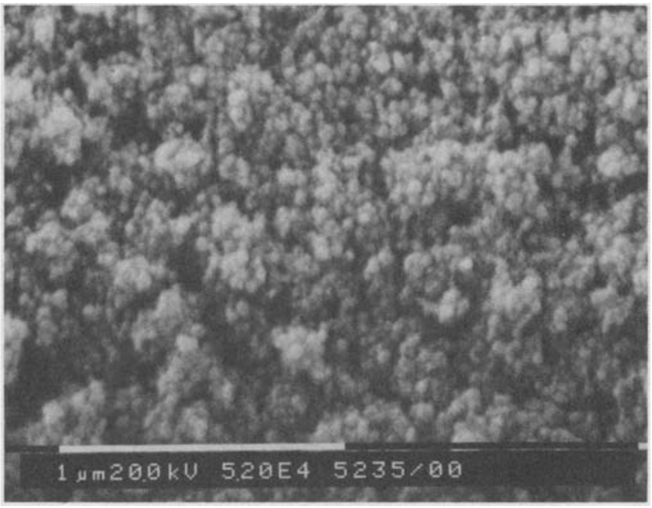

Fig. 8. Scanning electron microscope photographs of the Al_2O_3 film deposited 200 cycles at 700°C.

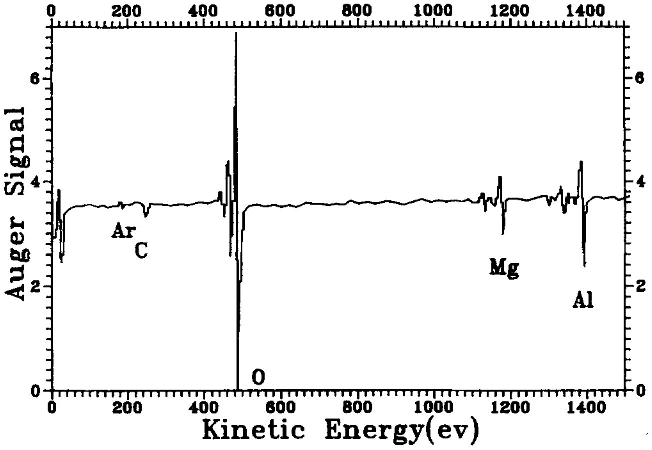

Fig. 9. First-derivative spectra taken from the $MgAl_2O_4$ film deposited 200 cycles at 640°C.

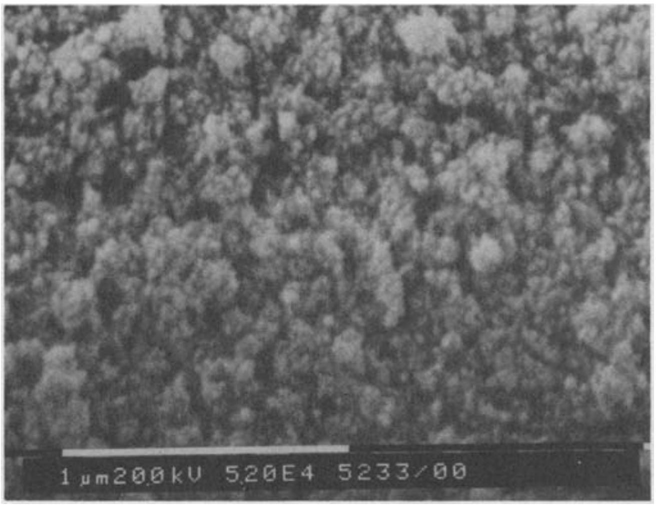

Fig. 10. Scanning electron microscope photographs of the $MgAl_2O_4$ film deposited 200 cycles at 640°C.

The Deposition of Al_2O_3 and $MgAl_2O_4$

The films of Al_2O_3 and $MgAl_2O_4$ deposited on silicon gave no x-ray diffraction and are amorphous in structure. Below 600°C, the deposition of Al_2O_3 on silicon using TEAl and H_2O 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 Al_2O_3 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 Al_2O_3. This is discussed below. Surface examination by SEM is illustrated in Fig. 8. The grain structure was not observed, as expected for amorphous Al_2O_3.

For the deposition of $MgAl_2O_4$, the chemical compounds were introduced into the chamber in the sequence CP_2Mg-H_2O-TEAl-H_2O. 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 Al_2O_3 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 Al_2O_3 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 Al_2O_3 and $MgAl_2O_4$ films were noncrystallized. This is very possibly due to the complex crystal structure of Al_2O_3 and $MgAl_2O_4$. If the deposition of Al_2O_3 is on the (0001) plane of Al_2O_3, 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 Al_2O_3, whereas there is no reason for this stoichiometry to be obtained through saturating surface reactions. For $MgAl_2O_4$, the crystal structure is even more complex. Oxygens form a close-packed plane in $MgAl_2O_4$, 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 Al_2O_3 and $MgAl_2O_4$ 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 $MgAl_2O_4$ films were amorphous as deposited and were crystallized by high-temperature annealing.[17] 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, Al_2O_3, and $MgAl_2O_4$ has been designed and constructed. Thin films of MgO, Al_2O_3, and $MgAl_2O_4$ have been deposited at various temperatures. MgO deposited above 500°C was polycrystalline; MgO deposited around 400°C was amorphous. The deposited Al_2O_3 and $MgAl_2O_4$ 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. Al_2O_3 and $MgAl_2O_4$, 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

1. D.K. Fork, D.B. Fenner, G.A.N. Connell, Julia M. Phillips and T.H. Geballe, *Appl. Phys. Lett.* 57, 1137 (1990).
2. M. Mikami, Y. Hokari, E. Egami, H. Tsuya and M. Kanamori, *Ext. Abst. 15th Conf. on Solid State Devices and Mater.*, Tokyo, 31 (1983).
3. H. Fukumoto, T. Imura and Y. Osaka, *Appl. Phys. Lett.* 55, 360 (1989).
4. T. Inoue, Y. Yamamoto, S. Koyama, S. Suzuki and Y. Ueda, *Appl. Phys. Lett.* 56, 1332 (1990).
5. D.K. Fork, D.B. Fenner and T.H. Geballe, *J. Appl. Phys.* 68, 4316 (1990).
6. M. Ishida, K. Sawada, S. Yamagushi, T. Nakamura and T. Suzaki, *Appl. Phys. Lett.* 55, 556 (1989).
7. W.J. DeSisto and R.L Henry, *J. Cryst. Growth* 109, 314 (1991).
8. J.A. Aboaf, *J. Electrochem. Soc.* 114, 948 (1967).
9. J. Saraie, J. Kwon and Y. Yodogawa, *J. Electrochem. Soc.* 132, 890 (1985).
10. J. Saraie, K. Ono and S. Takeuchi, *J. Electrochem. Soc.* 136, 3139 (1989).
11. T.H. Hua and M. Armgarth, *J. Electron. Mater.* 16, 27 (1987).
12. M.O. Aboelfotoh, *J. Vac. Sci. Technol.* 12, 67 (1975).
13. H.Z. Durusoy, *J. Mat. Sci. Lett.* 10, 1023 (1991).
14. B.S. Kwak, E.P. Boyd, K. Zhang, and A. Erbil, *Appl. Phys. Lett.* 54, 2542 (1989).
15. T. Saburo, N. Hidenori and H. Kenjiro, *Jpn. J. Appl. Phys.* 29, 1059 (1990).
16. M. Toshiro and S. Jun, *Jpn. J. Appl. Phys.* 29, L810 (1990).
17. N. Dalacu, A.H. Kitai, B.W. Sanders and R. Huang, *Thin Solid Films* 209, 207 (1992).
18. M. Ihara, Y. Arimoto, M. Jifuku, T. Kodama, H. Yamawak and T. Yamaoka, *J. Electrochem. Soc.* 129, 2569 (1982).
19. T. Suntola and M.J. Antson, U.S. Patent No. 4,058,430 (1977).
20. R. Clausen, K. Petermann, *IEEE J. Quantum Electron* 24, 1114 (1988).
21. D.K. Fork, F.A. Ponce, J.C. Tramontana and T.H. Geballe, *Appl. Phys. Lett.* 58, 2295 (1991).
22. W. Hsu and R. Raj, *Appl. Phys. Lett.* 60, 3105 (1992).
23. T. Suntola, *Mat. Sci. Report* 4, 261 (1989).
24. M. Ozeki, *Mat. Sci. Report* 8, 97 (1992).
25. G. Oya, M. Yoshida and Y. Sawada, *Appl. Phys. Lett.* 51, 1143 (1987).
26. G. Oya and Y. Sawada, *J. Cryst. Growth* 99, 572 (1990).
27. R. Huang and A Kitai, *Appl. Phys. Lett.* 61,1450 (1992).
28. R. Huang and A. Kitai, to be published.
29. R. Kelly, *Surf. Sci.* 100, 85 (1980).