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Infrared and high-energy electron diffraction analyses of electron-beam-evaporated MgO films

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Infrared spectroscopy and reflection high-energy electron diffraction have been used to analyze MgO films deposited at various deposition rates on "infrared" silicon wafers and hard glass substrates at various temperatures. Infrared spectra obtained for MgO films deposited at rates of 1350–1500 Å/min on substrates at room temperature and at 200°C showed that the amount of hydroxyl groups present was significantly less in the 200°C deposited films. The spectra also showed that the amount of hydroxyl groups present in films deposited at a very fast rate (~7800 Å/min) was much less than that in films deposited at a very slow rate (~160 Å/min) on substrates at 200°C. Some of the hydroxyl groups initially present in films deposited at ~160 Å/min and most of the hydroxyl groups in films deposited at ~1350 Å/min were removed by annealing the films in dry nitrogen at 500°C. The electron diffraction patterns obtained for MgO films (100–3000 Å) deposited at rates of 1350–1500 Å/min on substrates at a temperature in the range from room temperature to 200°C showed that the films initially nucleated in random orientation and as the film thickness was increased to and above 500 Å, a $\langle 111 \rangle$ preferred orientation developed at the surface independent of substrate temperature. These results suggest that adsorption of residual water on MgO does not influence the mode of film growth. The $\langle 111 \rangle$ preferred orientation developed in films deposited on substrates at 200°C dissolved, and some degree of the $\langle 100 \rangle$ preferred orientation developed upon annealing in dry nitrogen at 500°C. The preferred orientation remained, however, unchanged when these films were annealed in dry air. The orientation also remained unchanged when films deposited on substrates at room temperature were annealed in dry nitrogen at 500°C. These results suggest that the presence of hydroxyl ions and oxygen adsorption inhibit surface diffusion and, hence, the dissolution of the orientation during annealing.

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I. INTRODUCTION

The crystallographic orientations of MgO (NaCl structure) films evaporated onto amorphous and single-crystal film substrates have been the subject of several electron diffraction investigations.^{1–5} MgO films evaporated onto amorphous and single-crystal film substrates were found to possess a crystal orientation which varied with film thickness. On amorphous substrates,^{1–3} the films initially nucleated in random orientation, and as the film thickness was increased above ~500 Å a $\langle 111 \rangle$ preferred orientation developed at the surface. On $\langle 111 \rangle$ - and $\langle 100 \rangle$ -oriented silver-film substrates^{4,5} the initial orientation of the MgO films was found to depend on the orientation and temperature of the substrate. With increasing film thickness randomly oriented MgO was simultaneously formed at the surface, and in thick films the surface structure had a $\langle 111 \rangle$ preferred orientation independent of substrate orientation and temperature.

The interpretations of preferred orientations in evaporated films with a NaCl structure have been critically reviewed by Bauer.⁶ According to Bauer, the orientations may be either initial orientations or final-growth orientations. Initial orientations can be due to nucleation or growth depending on whether the interaction between the deposit and substrate is weak or strong. The driving force to form these initial orienta-

tions is the tendency of the deposited crystals to develop a minimum free-energy configuration. The final-growth orientations are quite different in nature, for here all crystals have the same (not necessarily minimum) free-energy configuration. The orientations are due to differences in the number of vapor ions or molecules condensing on differently oriented crystals. The $\langle 111 \rangle$ preferred orientation observed in thick MgO films has been interpreted as a final-growth orientation.¹

The surface free energy of a crystal and the condensation coefficient are influenced by adsorbed gases. The adsorbed residual gases can then influence the growth process and crystal orientation and, hence, also affect the physical properties of evaporated films. In the earlier investigations the effect of residual gases on the growth behavior of electron-beam-evaporated MgO films has not been investigated in detail. The present investigation was, therefore, undertaken to (1) determine the adsorbed residual gases as a function of the deposition parameters using infrared spectroscopy and (2) study the effect of composition and partial pressure of residual gases on crystal orientation as a function of film thickness and substrate temperature using reflection high-energy electron diffraction. The effects of annealing in a dry inert atmosphere (N_2) and dry air on adsorbed residual gases and crystal orientation have also been studied.

II. EXPERIMENTAL

MgO films were deposited with a 8-kW electron gun. A 99.95% pure single crystal of MgO was used as the source material. A residual gas pressure in the range from 1×10^{-7} to 4×10^{-6} Torr was obtained in the evaporation chamber prior to film evaporation. The residual pressure was shown by mass spectrometric analysis to consist mainly of water vapor but with traces of nitrogen and oxygen. The residual pressure generally reached 1×10^{-6} – 2×10^{-5} Torr during the evaporation. The pressure rise was mainly due to water vapor evolved from the source material. The evaporations were carried out without and with leaking oxygen into the vacuum system. A shutter was placed close to the substrate to shield the substrate from the source during the beginning and the end of an evaporation. The average thickness of the film and deposition rate were determined by a quartz crystal located close to the substrate. Calibration was carried out by measuring the film thickness using multiple-beam interferometry. The nominal deposition rates were about 1300–1500 Å/min; however, in special cases where the effect of the deposition rate was being determined, the very slow rates were about 130–160 Å/min and a very fast deposition rate was about 7800 Å/min. The thickness range investigated was from 100 to 3000 Å.

Infrared spectra of MgO films were taken by transmission through films deposited on "infrared" silicon wafers using a Perkin-Elmer 521 double-beam spectrophotometer. "Infrared" silicon wafers refer to wafers which meet the requirements necessary to obtain good infrared spectra by transmission through films deposited on the silicon wafers. These requirements have been discussed in early reports^{7,8} and discussed in detail in a recent review.⁹ Examinations were made of films deposited at various rates on substrates at a temperature in the range from room temperature to 200 °C.

Films which were annealed in a dry inert atmosphere (N_2) at various temperatures for 30 min were also examined. The films were usually close to 3000 Å; however, in some cases films as thick as 7000 Å were examined.

The crystal structure of MgO films (100–3000 Å) deposited on infrared silicon wafers and hard glass (high-silica glass) substrates was determined by grazing-incidence reflection high-energy electron diffraction. The substrates were outgassed at 200 °C for 1 h prior to film deposition. During deposition the substrates were held at a temperature in the range from room temperature to 200 °C. Examinations were also made of films annealed in a dry inert atmosphere (N_2) and dry air at various temperatures for 30 min.

III. RESULTS AND DISCUSSION

A. Adsorbed gases as shown by infrared spectroscopy

1. Effect of deposition rate

One of the most common impurities which can be picked up in relatively low-temperature deposited films is water which results in adsorbed water or at least in hydroxyl-containing films. The presence of hydroxyl groups can be determined by the use of infrared spectroscopy. This is shown in Fig. 1 by spectrum A which is the infrared spectrum of a 3000-Å MgO film deposited at a very slow rate (~ 160 Å/min) on a substrate at 200 °C. The $5 \times$ magnified spectrum shows a significant broad adsorption at 3600 cm^{-1} with a long tail off to lower frequency which is typical of hydrogen-bonded hydroxyl groups. The presence of practically no hydroxyl groups is indicated in spectrum C which is the spectrum obtained of a 4700-Å film deposited at a very fast rate (~ 7800 Å/min). Because of the fact that there are much less hydroxyl groups in the rapidly deposited film, we conclude that the hydroxyl groups which are present in

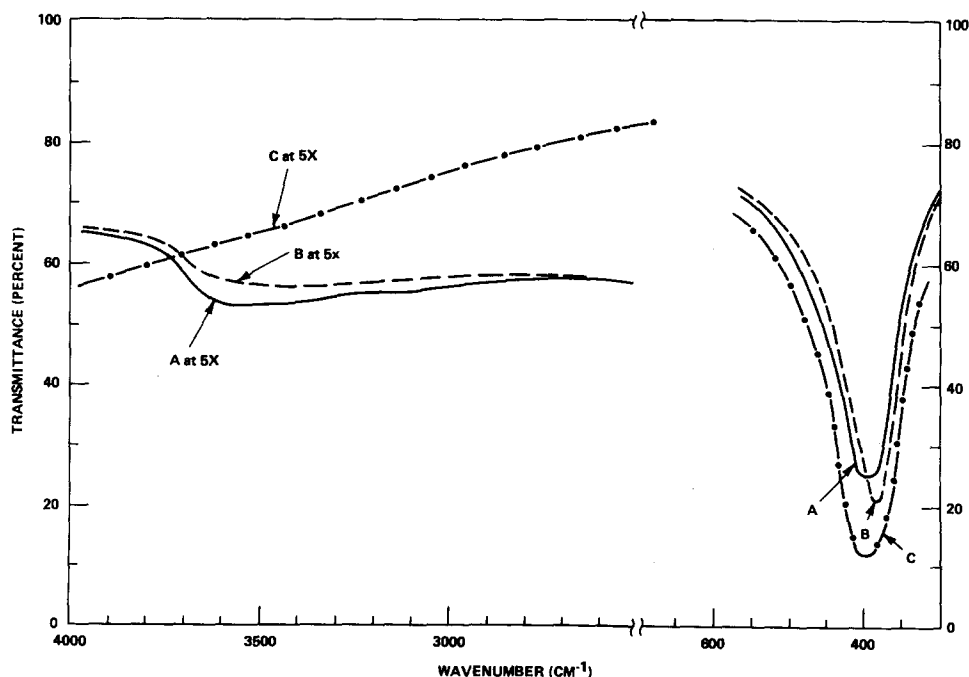


FIG. 1. Effect of the deposition rate on electron-gun-evaporated MgO film. Curves (A) very slow deposition rate (~ 160 Å/min) on 200 °C substrate; curves (B) after N_2 anneal at 500 °C for 30 min; curves (C) fast deposition rate (~ 7800 Å/min) on 200 °C substrate. SiO_2 references for $5 \times$: curves (A) and (B) 3413 Å; curve (C) 5412 Å.

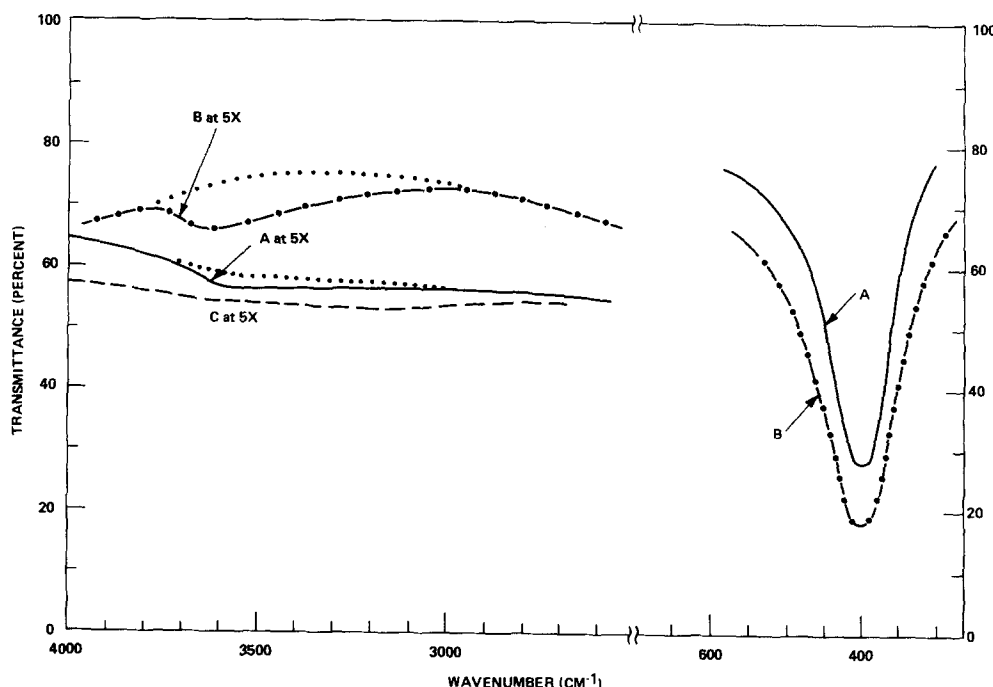


FIG. 2. Effect of substrate temperature on electron-gun-evaporated MgO film. Curves (A) 2760 Å, moderate deposition rate (~ 1350 Å/min) on 200°C substrate; curves (B) 4030 Å, moderate deposition rate (~ 1510 Å/min) on nonheated ($\sim 35^\circ\text{C}$) substrate; curve (C) background for 5 \times . Si wafer versus Si wafer.

the slowly deposited film is due to the pickup of residual water from the vacuum chamber during evaporation. Hydroxyl groups were observed in films deposited at 1300–1500 Å/min, but the amount was less than that observed in the very-slow-rate films.

2. Effect of substrate temperature

As with e-gun-evaporated SiO_2 films,¹⁰ the films deposited at lower substrate temperatures contain more hydroxyl groups than those deposited at higher substrate temperatures. In Fig. 2 we have compared the spectra of films formed at substrate temperatures of 200°C and room temperature. Spectrum A is that of a 2760-Å film deposited on a substrate at 200°C at a deposition rate of about 1350 Å/min. Spectrum B is that of a 4030-Å film deposited on a nonheated substrate at a deposition rate of about 1510 Å/min. Again the portions of the spectra at the higher frequency have been magnified five-fold. With magnified spectra for which the slit schedules are significantly greater than normal, one must be careful about instrumental peculiarities. Thus, spectrum C was taken for comparison or as a control. In this spectrum equivalent silicon wafers were placed in both the sample and reference beams. It is a spectrum which, if the instrument were perfect, would be flat. Comparison of spectrum A with that of spectrum C shows that there is a slight amount of hydroxyl groups present in the 200°C deposited film. On the other hand, the film deposited at room temperature shows a significant amount of hydroxyl groups present.

At higher frequencies both spectra have a very strong absorption at about 398 cm^{-1} , which is characteristic of all MgO films. However, close examination shows that the half-width (83 cm^{-1}) of spectrum A, the 200°C film, is less than the half-width (88 cm^{-1}) of spectrum B, the room-temperature-deposited film. The greater half-width is probably due to the greater porosity and high

degree of bond strain in the lower-temperature-deposited film just as with e-gun-evaporated SiO_2 films.¹⁰

3. Effect of annealing

Some effects of annealing are shown in Fig. 1. The film which had been deposited at a very slow rate was annealed in dry nitrogen at 500°C for 30 min, after which spectrum B was obtained. Because of the decrease in intensity of the 3600-cm^{-1} band, it is concluded that some of the hydroxyl groups were removed. In addition, the main absorption band at 393 cm^{-1} shifted to 386 cm^{-1} , and at the same time the half-width decreased from 86 to 73 cm^{-1} with a corresponding increase in the optical density. Similar effects of an absorbance increase and half-width decrease had been observed with e-gun-evaporated SiO_2 films on annealing.¹⁰ However, with low-temperature-deposited SiO_2 films, the main Si-O absorption band shifted to a higher frequency on annealing. Similar results on annealing, as shown in Fig. 1 for a MgO film deposited at a slow rate, were obtained with MgO films deposited at a moderate rate on heated substrates. In Fig. 3, spectrum A is the same as that in spectrum A of Fig. 2 and is that of a 2760-Å film deposited at a moderate rate (1350 Å/min) on a 200°C substrate. After annealing at 500°C for 30 min in nitrogen, spectrum B was obtained. In this case there were less hydroxyl groups in the initial spectrum A and most of the hydroxyl groups were removed (spectrum B) by the annealing treatment. In the low-frequency region the annealing again causes the main Mg-O band to shift to lower frequency, to increase in peak intensity, and to decrease in half-width.

4. Effect of long-term exposure to room-temperature ambient

In Figs. 1–3 we did not show any of the region between 2600 and 600 cm^{-1} because there was no structure of any significance in any of the films. In Figs. 4(a) and

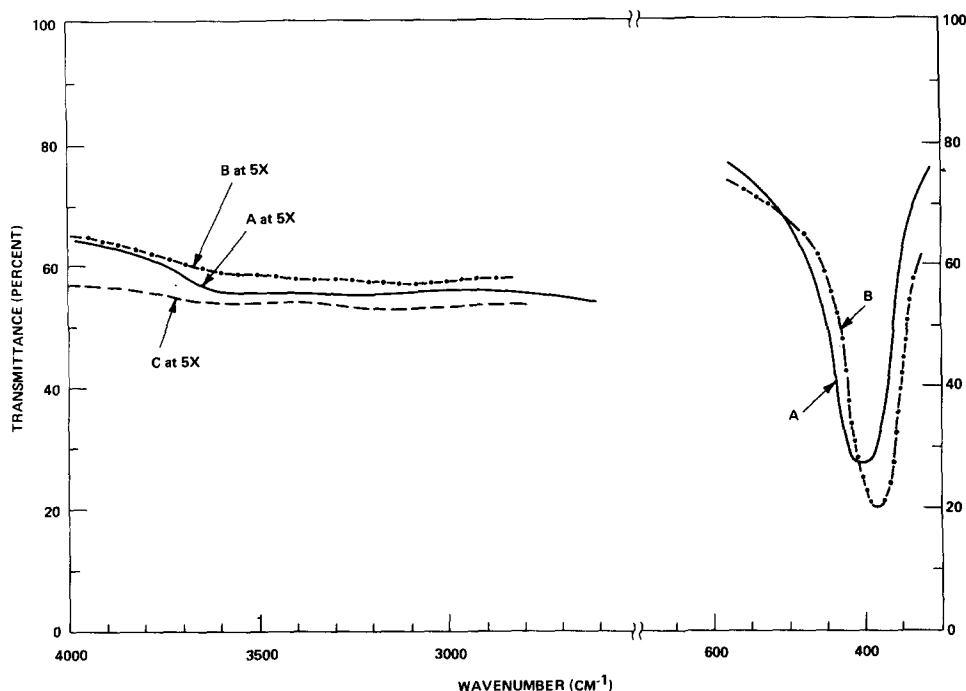


FIG. 3. Effect of annealing on electron-gun-evaporated MgO film. Curves (A) moderate deposition rate (~ 1350 Å/min) on 200°C substrate; curves (B) after N_2 anneal at 500°C for 30 min; curve (C) background for 5 \times . Si wafer versus Si wafer. SiO_2 references for 5 \times : Curve (A) 3620 Å; curve (B) 3413 Å.

4(b) we show the entire region from 4000 to 300 cm^{-1} for a thicker film (~ 7000 Å) of MgO deposited at a moderate rate (~ 800 Å/min) on a 200°C substrate (spectrum A). There are no absorption bands in the region between the hydroxyl bands at high frequency and the Mg-O band at low frequency in the initial spectrum (spectrum A), which was taken five days after deposition of the film. The wafer had been kept in a desiccator during that time. Spectrum A shows that there can be a greater amount of hydroxyl groups per unit thickness than in the spectra of other MgO films deposited at a moderate rate on substrates at 200°C . Presumably we did pick up some water even though the sample had been kept in a desiccator. In addition, we see the beginning of a sharper absorption at 3700 cm^{-1} which is characteristic¹¹ of $\text{Mg}(\text{OH})_2$. After this sample was exposed to the room ambient for one year, spectrum B was obtained. It shows no change in the MgO band at 400 cm^{-1} , however, it shows a considerable pickup of water leading to more intense bands at 3700 cm^{-1} due to the formation of more $\text{Mg}(\text{OH})_2$, at 3570 cm^{-1} due to more hydrogen-bond hydroxyl [other than $\text{Mg}(\text{OH})_2$ or water], and at 3450 cm^{-1} due to actual water in this somewhat porous film. In addition, we have broad bands at 1610, 1460, 1380 and 870 cm^{-1} . These bands are attributed to the deformation band in water and to C-O stretching absorption in bicarbonate and carbonate ions present in the films.^{11,12}

B. Crystal structure of MgO films as shown by electron diffraction

1. Effect of film thickness and substrate temperature

Figure 5 shows the diffraction patterns obtained, as a function of film thickness, for MgO deposited at 1300 – 1500 Å/min in a pressure of 1×10^{-6} Torr on substrates at room temperature. Initially, the films are

nucleated in random orientation [pattern (a)], and as the film thickness is increased to and above 500 Å the patterns show arcs [patterns (b)–(d)]. Figure 6 shows a schematic diagram of the positions of diffraction spots when the $\langle 111 \rangle$ axis of crystallites in MgO films is normal to the substrate surface. A comparison of patterns (b)–(d) of Fig. 5 with Fig. 6 shows that the surface structure of the MgO films has a $\langle 111 \rangle$ preferred orientation. The angular spread of the $\langle 111 \rangle$ axis from the mean is about $\pm 10^\circ$, as shown by the arc lengths in the diffraction patterns. The symmetry of the arcs with respect to the substrate normal is found to depend on the azimuth of incidence of the electron beam. This indicates that the $\langle 111 \rangle$ axis is tilted away from the substrate normal. The absence of any marked elongation of the diffraction arcs toward the shadow edge indicates that the surface region penetrated by the electron beam is atomically rough.

Films (100 – 3000 Å) deposited at 1300 – 1500 Å/min in a pressure of $(4\text{--}6) \times 10^{-6}$ Torr on substrates at 200°C followed the same behavior during growth, i.e., showing an initial random orientation followed by a $\langle 111 \rangle$ preferred orientation with an increasing film thickness to and above 500 Å. It has also been found^{1,3} that for MgO films deposited in a pressure of $\sim 2 \times 10^{-5}$ Torr on substrates at a temperature in the range from room temperature to 300°C , the initial orientation was random, followed by a $\langle 111 \rangle$ preferred orientation as the film thickness was increased to and above 500 Å.

In order to evaluate the effect of oxygen on film crystal orientation, finite quantities of oxygen were leaked into the evaporation chamber and the oxygen pressure was maintained at a constant level prior to film evaporation. The patterns obtained for MgO films deposited at 1300 – 1500 Å/min on substrates at 200°C in oxygen

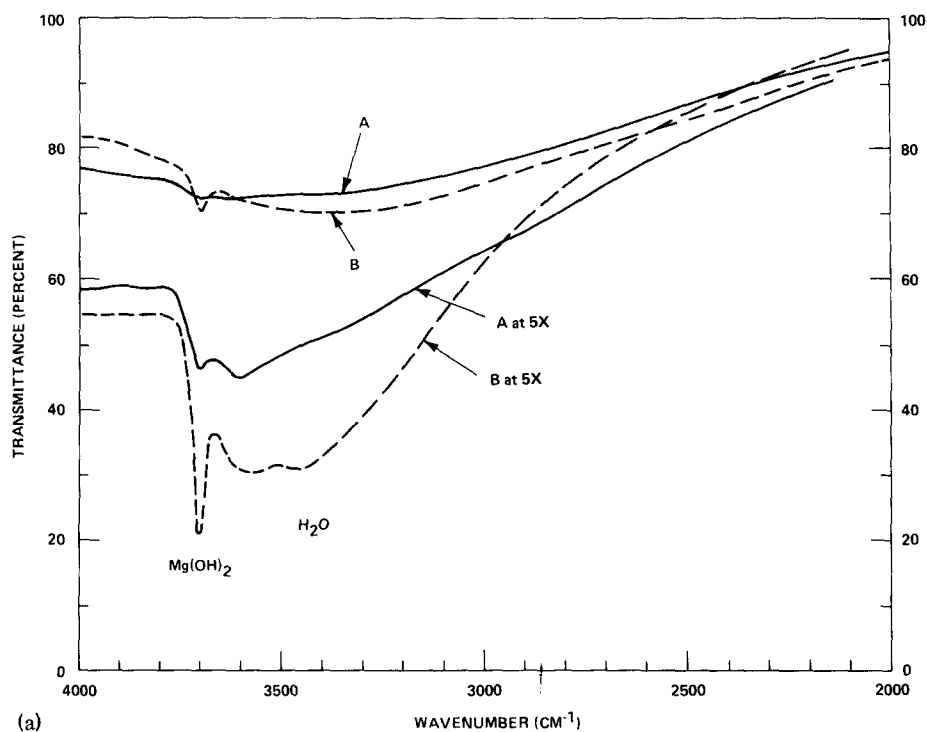
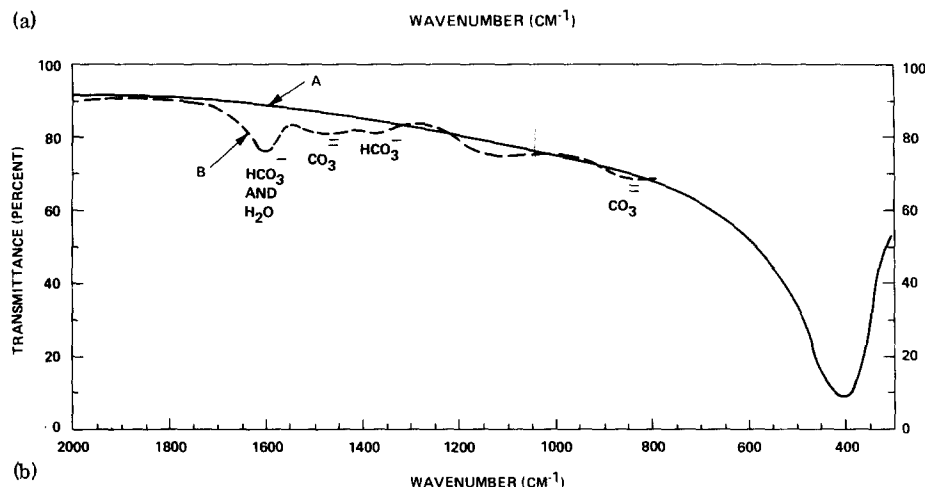


FIG. 4. Effect of long-term exposure to room ambient on electron-gun-evaporated MgO film. Curves (A) $\sim 7000 \text{ \AA}$ on 200°C substrate; curves (B) exposed to room ambient for one year. SiO_2 reference for $5\times$; Curve (A) 1035 \AA ; curve (B) 11098 \AA .



at 10^{-5} – 10^{-4} Torr showed that at and above 500 \AA the surface structure of the MgO films has the same $\langle 111 \rangle$ preferred orientation with a mean axis (the spread away from the mean being about $\pm 10^\circ$) tilted away from the substrate normal. Films thinner than 500 \AA showed a random orientation. Figure 7 shows the patterns obtained from a 2000-\AA -thick film deposited (a) in oxygen at $\sim 2 \times 10^{-5}$ Torr and (b) without introducing oxygen. These results thus show that the presence of oxygen at a pressure of 10^{-5} – 10^{-4} Torr does not influence the formation of the $\langle 111 \rangle$ preferred orientation.

The results of the present study show that in MgO deposited in a pressure of 1×10^{-6} to 2×10^{-5} Torr on amorphous substrates at a temperature in the range from room temperature to 200°C , there is initially randomly oriented growth up to a film thickness of about 500 \AA before $\langle 111 \rangle$ preferred orientation is developed in the further growth. Similar results for the film structure were also obtained in the case where "infrared" silicon wafers were used as substrates.

Initial nucleation orientations developed in films on a substrate are determined by the minimum of the surface free energy, including the interface between the films and the substrate, if a constant bulk free energy for a unit volume can be assumed.¹³ If the surface free energy of the film σ_f is higher than that of the substrate σ_s (here, the high surface energy predominates over the interfacial energy), the interfacial interaction is weak. A $\langle 100 \rangle$ orientation would then be preferred in ionic crystals with a NaCl structure since this orientation best minimizes the surface and interfacial energies, provided that the deposited ions or molecules possess sufficient mobility to form the $\langle 100 \rangle$ configuration. On the other hand, if $\sigma_f < \sigma_s$ (here, a low interfacial energy predominates over the surface energy), the interfacial interaction is strong, and due to the random arrangement of the substrate ions no preferred orientation would be expected. In the MgO–high-silica glass system, $\sigma_{\text{MgO}} > \sigma_{\text{glass}}$.^{14,15} Therefore, a $\langle 100 \rangle$ preferred orientation would be expected to develop during the initial stages of growth. In the present experiments,

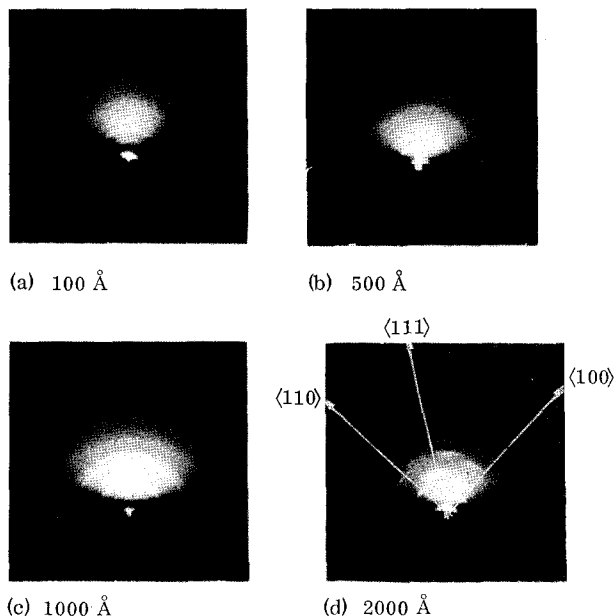


FIG. 5. Reflection electron diffraction patterns from MgO films deposited at rates of 1300–1500 Å/min on hard-glass substrates at room temperature.

however, the deposit initially nucleated in random orientation. This may be attributed to the reduced mobility of the deposited ions or molecules, possibly as a result of a strong interfacial interaction between the deposit and substrate. A reduced ion or molecule mobility would lead to a higher nucleation rate, and due to the random arrangement of the substrate ions, no preferred orientation is initially developed. The fact that the deposited crystals nucleate in random orientation indicates that the interfacial free energy between the deposit and substrate is independent of the crystal orientation. These results thus show that not only the surface free energy but also the interfacial interaction between the deposit and substrate contributes to the determination of the initial crystal orientation.

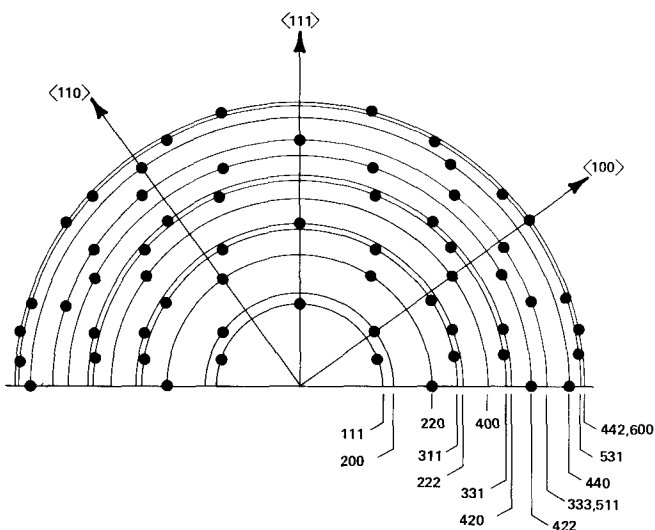


FIG. 6. Schematic representation of the diffraction pattern from a $\langle 111 \rangle$ preferred orientation.

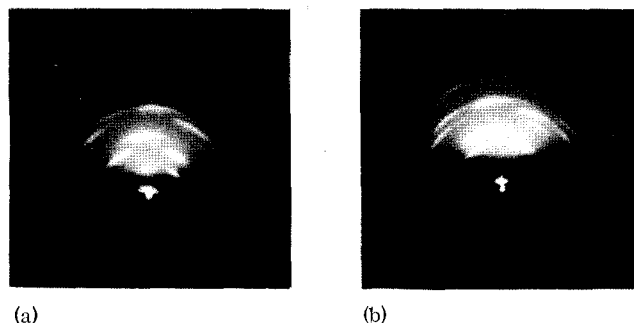


FIG. 7. Reflection electron diffraction patterns from a 2000-Å-thick MgO film deposited at rates of 1300–1500 Å/min on hard glass substrates at 200 °C (a) in oxygen at $\sim 2 \times 10^{-5}$ Torr and (b) without introducing oxygen.

The development of a preferred orientation in thick MgO films indicates that, with increasing film thickness, the deposited ions or molecules attain sufficient mobility to form faces of dense ionic packing on the surface of the growing crystals. If the $\langle 111 \rangle$ orientation is due to a higher growth rate of the $\{111\}$ faces as a result of a high mobility of the condensed ions or molecules, the orientation axis would be expected to be normal to the substrate surface independent of the angle of incidence of the vapor beam. Furthermore, if the tilted $\langle 111 \rangle$ orientation originates from the preferential growth of those crystals out of the random initial deposit in azimuths such that the $\{100\}$ faces are close to the vapor beam,¹⁶ the orientation would be expected to be $\langle 100 \rangle$ at normal vapor incidence. This is not, however, what has been observed experimentally. The fact that the orientation axis tilts away from the substrate normal suggests that the orientation is influenced by the supply of vapor ions or molecules which favors the $\langle 111 \rangle$ orientation. The tilted $\langle 111 \rangle$ orientation may then be interpreted as a final-growth orientation, originating from differences in the number of ions or molecules condensing on differently oriented crystals as suggested by Bauer.⁶ The results also show that the development of the $\langle 111 \rangle$ orientation after an initial randomly oriented growth up to about 500 Å is independent of the substrate temperature, thus indicating that adsorption of the residual water on MgO does not influence the mode of film growth.

2. Effect of annealing

The effect of annealing on the $\langle 111 \rangle$ preferred orientation is shown in Figs. 8–10. Figure 8 is typical of the patterns obtained from 3000-Å-thick films deposited in a pressure of $(1-3) \times 10^{-6}$ Torr on silicon wafers [pattern (a)] and hard-glass substrates [pattern (b)] at 200 °C and then annealed in dry nitrogen [pattern (c)] and in dry air [pattern (d)] at 500 °C for 30 min. Pattern (c) shows that the $\langle 111 \rangle$ preferred orientation developed during deposition dissolves upon annealing and some degree of $\langle 100 \rangle$ preferred orientation develops. The pattern also shows significant grain growth as detected by the sharpening of the diffraction rings. Pattern (d) shows, on the other hand, that the $\langle 111 \rangle$ preferred orientation remains unchanged upon annealing in dry air. Figure 9 shows the patterns obtained from films depos-

ited on substrates at room temperature and then annealed in dry nitrogen at 500 °C for 30 min. These patterns show that the $\langle 111 \rangle$ preferred orientation developed during deposition remains unchanged upon annealing. Similar results were also obtained³ for 2000-Å-thick films deposited in 1×10^{-5} Torr on substrates at room temperature and then annealed *in situ* at 400–500 °C for 1 h. Films deposited in oxygen at $\sim 2 \times 10^{-5}$ Torr on substrates at 200 °C were also annealed at 500 °C for 30 min in dry nitrogen. Figure 10 is typical of the results obtained from these films. These results show that, in this case, annealing does not affect the preferred orientation developed during deposition.

The observations that the preferred orientation developed in films deposited on substrates at room temperature remains unchanged upon annealing in dry nitrogen suggest that the presence of hydroxyl ions inhibits surface diffusion and, hence, the dissolution of the preferred orientation. This is confirmed by the result that the $\langle 111 \rangle$ preferred orientation dissolves and some degree of the $\langle 100 \rangle$ preferred orientation develops when films deposited on substrates at 200 °C are annealed in dry nitrogen. In this case, a significantly lesser amount of hydroxyl ions is initially present in these films, and, in addition, most of the hydroxyl ions are removed during annealing (Fig. 3). Furthermore, the results that the preferred orientation developed in a film deposited on substrates at 200 °C remains unchanged upon annealing in dry air suggest that oxygen adsorption also prevents the dissolution of the preferred orientation. These results also show that the $\langle 111 \rangle$ preferred orientation developed during deposition is not always energetically stable but changes to a more stable configuration with the aid of surface diffusion during annealing.

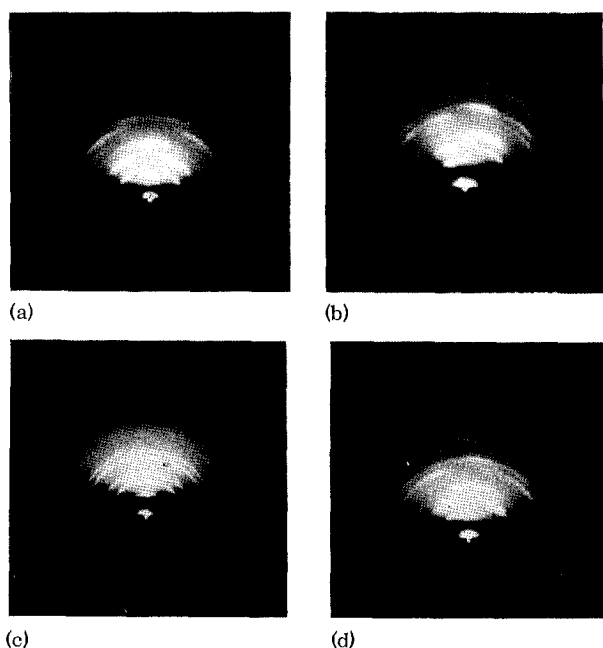


FIG. 8. Reflection electron diffraction patterns from 3000-Å-thick MgO film deposited on (a) silicon wafers and (b) hard-glass substrates at 200 °C and then (c) annealed in dry nitrogen and (d) in dry air at 500 °C for 30 min.

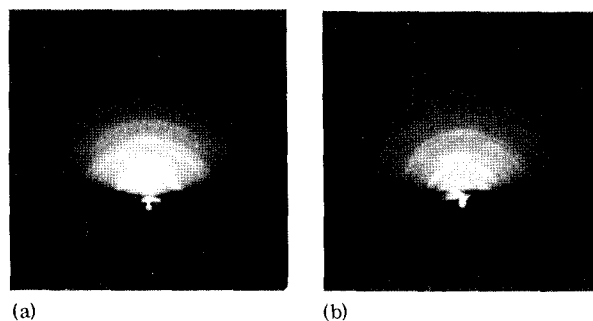


FIG. 9. Reflection electron diffraction patterns from 3000-Å-thick MgO films deposited on hard glass substrates at (a) room temperature and (b) then annealed in dry nitrogen at 500 °C for 30 min.

IV. CONCLUSIONS

Infrared spectroscopy and reflection high-energy electron diffraction have been used to analyze MgO films deposited at various deposition rates on “infrared” silicon wafers and high-silica glass substrates at various temperatures. Infrared spectra obtained for MgO films deposited at rates of 1350–1500 Å/min on substrates at room temperature and at 200 °C show that the amount of hydroxyl groups present is significantly less in the 200 °C deposited films. The spectra also show that the amount of hydroxyl groups present in films deposited at a very fast rate (~ 7800 Å/min) is much less than that in films deposited at a very slow rate (~ 160 Å/min) on substrates at 200 °C. Some of the hydroxyl groups initially present in films deposited at ~ 160 Å/min and most of the hydroxyl groups in films deposited at a moderate rate (~ 1350 Å/min) on substrates at 200 °C are removed by annealing the films in nitrogen at 500 °C for 30 min. The electron diffraction patterns obtained for MgO films (100–3000 Å) deposited at rates of 1350–1500 Å/min on substrates at various temperatures show that the films initially nucleate in random orientation, and as the film thickness is increased to and above 500 Å, a $\langle 111 \rangle$ preferred orientation develops. The development of a $\langle 111 \rangle$ preferred orientation after an initial randomly oriented growth up to about 500 Å, independent of substrate temperature, suggests that adsorption of residual water on MgO does not influence the mode of film growth. The $\langle 111 \rangle$ preferred orientation developed in films deposited on substrates at 200 °C

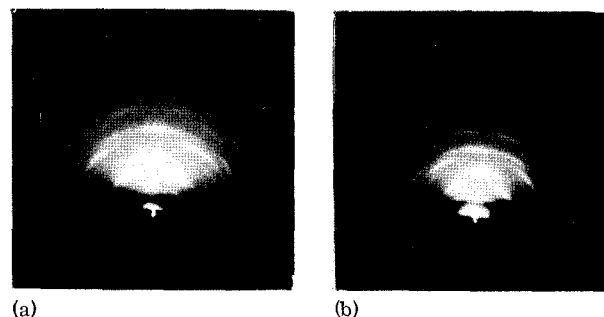


FIG. 10. Reflection electron diffraction patterns from 3000-Å-thick MgO films deposited in oxygen at $\sim 2 \times 10^{-5}$ Torr on hard-glass substrates at (a) 200 °C and then (b) annealed in dry nitrogen at 500 °C for 30 min.

dissolves, and some degree of the $\langle 100 \rangle$ preferred orientation develops upon annealing in dry nitrogen at 500 °C. The preferred orientation remains, however, unchanged when these films are annealed in dry air. The orientation also remains unchanged when films deposited on substrates at room temperature are annealed in dry nitrogen at 500 °C. These results suggest that the presence of hydroxyl ions and oxygen adsorption inhibit surface diffusion and, hence, the dissolution of the orientation during annealing.

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¹M.O. Aboelfotoh, J. Vac. Sci. Technol. **10**, 621 (1973).

²M.O. Aboelfotoh, Bull. Am. Phys. Soc. **18**, 495 (1973).

³M.O. Aboelfotoh, Appl. Phys. Lett. **24**, 347 (1974).

⁴M.O. Aboelfotoh, J. Vac. Sci. Technol. **12**, 67 (1975).

⁵M.O. Aboelfotoh, Proceedings of 3rd International Conference on Thin Films, Budapest, Hungary, 1975 (unpublished); Thin Solid Films **33**, 373 (1976).

⁶E. Bauer, in *Single Crystal Films*, edited by M.H. Francombe and H. Sato (Pergamon, London, 1964), p. 43.

⁷W.A. Pliskin and H.S. Lehman, J. Electrochem. Soc. **112**, 1013 (1965).

⁸W.A. Pliskin, in *Measurement Techniques for Thin Films*, edited by B. Schwartz and N. Schwartz (The Electrochemical Society, New York, 1967).

⁹W.A. Pliskin, in *Semiconductor Silicon* edited by H.R. Huff and R.R. Burgess (The Electrochemical Society, New York, 1973).

¹⁰W.A. Pliskin and P.P. Castrucci, Electrochem. Technol. **6**, 85 (1968); J. Electrochem. Soc. **112**, 148C (1965).

¹¹R.A. Nyquist and R.O. Kagel, *Infrared Spectra of Inorganic Compounds* (Academic, New York, 1971).

¹²T.J. Bellamy, *The Infra-red Spectra of Complex Molecules* (Wiley, New York, 1954).

¹³H. Sato, Annu. Rev. Mater. Sci. **2**, 217 (1972).

¹⁴G. Jura and C.W. Garland, J. Am. Chem. Soc. **74**, 6033 (1952).

¹⁵C.A. Neugebauer, in *Handbook of Thin Film Technology*, edited by L.I. Maissel and R. Glang (McGraw-Hill, New York, 1970), Chap. 8.

¹⁶D.M. Evans and H. Wilman, Acta Crystallogr. **5**, 731 (1952).