

Growth characteristics and surface roughening of vapor-deposited MgO thin films

Jong-Gul Yoon,* Hun Kyoo Oh, and Sung Jong Lee

Department of Physics, University of Suwon, Kyung-gi-do 445-743, Korea

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Highly (100)-oriented magnesium oxide (MgO) crystalline thin films were grown on Si, GaAs, and fused quartz substrates by an aerosol-assisted chemical vapor deposition using magnesium ethoxide as a source material. Structures of the substrates had little influence on the growth orientation of MgO films indicating that the growth orientation of the films is determined by the lowest surface energy of the crystal structure. Surface morphology of the films investigated by atomic force microscope as a function of the films thickness showed that the formation of three-dimensional islands dominates the initial stage of the film growth. Surface roughness exponent α was determined to be about 0.87 for all the MgO films grown on Si and GaAs. The result agrees approximately with the diffusion dominant model of kinetic roughening. Kinetic limitations play an important role in determining surface morphology of MgO/semiconductors that is qualitatively governed by near equilibrium growth mode of Volmer-Weber or Stranski-Krastanov. [S0163-1829(99)04728-1]

I. INTRODUCTION

Because of technical importance and fundamental interest, a great deal of effort has been devoted to understanding the mechanism of thin-film growth and the kinetic roughening of growing surfaces in various growth techniques. Thin crystalline films grow near equilibrium by one of three growth modes: Frank-van der Merwe (FM) for monolayer by monolayer growth,¹ Volmer-Weber (VW) for initial film nucleation by three-dimensional (3D) crystallite growth,² and Stranski-Krastanov (SK) for formation of an initial uniform layer followed by 3D crystallite growth.³ The growth modes depend on the relative magnitudes of the surface energies, γ_s, γ_f , of the substrate and the film, respectively, and of the interfacial energy γ_{in} . The FM mode obtains when $\gamma_f + \gamma_{in} \leq \gamma_s$ for all thickness. The increase of the strain energy with thickness leads to an increase of γ_{in} until the FM mode is not fulfilled any more at a given thickness and 3D crystals form (SK mode). If the FM mode condition is not fulfilled from the beginning, then 3D crystals form immediately on the substrate (VW mode). All of these models have been discussed in detail previously.⁴

In modern technological applications, demands are increasing for ever lower growth temperatures and higher growth rates of materials. However, in this situation of fast growth at low temperature, the growth is kinetically limited, i.e., nonequilibrium prevails and kinetic roughening has been found to occur in general. For kinetic roughening, scaling theory has been applied in most of the theoretical investigations to correlation functions of the growing surfaces under the assumption that rough surfaces exhibit self-affine characteristics.⁵⁻⁸ According to scaling theory, the height-height correlation function for the local surface profile $h(\mathbf{r}, t)$, $G(\mathbf{r}, t) \equiv \langle [h(\mathbf{r}, t) - h(0, t)]^2 \rangle$, can be expressed in the form⁶

$$G(\mathbf{r}, t) = 2w^2(t)g[r/\xi(t)], \quad (1)$$

where w is the width of the interface (the rms fluctuation about the mean height) and ξ is a correlation length parallel to the surface. If the surface is self-affine with a finite corre-

lation length, then $G(\mathbf{r}) \propto r^{2\alpha}$ for $r \ll \xi$ and $G(\mathbf{r}) = 2w^2$ for $r \gg \xi$. In the scaling regime, the interface width grows with time according to a power law $w(t) \sim t^\beta$. The parameter α ($0 < \alpha \leq 1$) is the roughness exponent and β is the growth exponent. The exponents α and β depend on specific growth models.

The scaling exponents characterize the local structure of rough surfaces making it possible to classify various surface-growth phenomena into discrete universality classes.^{7,8} Thus, these (scaling) exponents provide us with a convenient measure regarding growing surfaces and can be used for comparisons between experimental data and some theoretical model systems. However, the exponents may vary strongly with system parameters and with substrate temperature in experimental systems. Thus, although the scaling relation, Eq. (1), is usually applied to self-affine or self-similar surfaces grown under the conditions where kinetic limitation dominates, it is of interest to examine the behavior of the correlation functions for an arbitrary vapor deposited surface.

In this paper, we report structural and morphological investigations on MgO films, which were grown by an aerosol-assisted chemical vapor deposition (AACVD), using x-ray diffraction (XRD) and atomic force microscopy (AFM). MgO, which has NaCl structure, grows epitaxially on Si and GaAs at low temperatures below 400 °C. MgO films have been used as buffer layer in the growth of epitaxial oxides, such as high- T_C superconductors or ferroelectrics, on semiconductor substrates.⁹⁻¹¹ The use of buffer layer can optimize the physical properties of the active oxide films by controlling growth orientations and microstructures of the films. In this case, interface roughness is important. Physical properties of the active layers can be affected by the surface roughness of the buffer layer. It has been reported that the giant magnetoresistance effect in magnetic multilayer depends on the interface roughness.^{12,13} Reduction of roughness is desirable for a buffer layer as well as in the case of many quantum well structures. Although studies on the growth and structural properties of MgO films have been reported,^{9,14-17} little is known about the evolution of the interface and its effect on subsequent film growth process. Here, surface roughening is discussed for the system of

MgO/semiconductors that is qualitatively governed by near equilibrium growth mode of VW or SK. The measured value of α is consistent with growth model predictions incorporating surface diffusion.

II. EXPERIMENTAL PROCEDURE

MgO films were deposited by AACVD technique, which is based on the pyrolysis of an aerosol produced by ultrasonic nebulizer (sonicator frequency: 1.6 MHz). The liquid source to be misted was magnesium ethoxide $[\text{Mg}(\text{OC}_2\text{H}_5)_2]$ dissolved in 2-methoxyethanol. Si (100)/(111), GaAs (100), and fused quartz were used as substrates. Prior to deposition, surface oxides were removed from the Si and GaAs wafers. For Si, the oxide was removed using a dilute HF solution [1:5 (49%HF:H₂O)]. For GaAs, the substrates were etched in HCl:H₂O (1:10) solution, rinsed and dried. Also, the fused quartz substrates were degreased in acetone solution ultrasonically. The cleaned substrates were placed immediately on the heater inside the chamber, which was then evacuated and flushed with nitrogen gas. The aerosol which formed at the surface of the liquid was transported by a carrier gas (N₂) to the heated substrate on which the pyrolysis occurred. The substrates were preheated to temperatures of about 300–450 °C. The deposition chamber was maintained at atmospheric pressure. By adjusting the carrier gas-flow rate and the ultrasonic power level, the growth rate could be controlled to about 5 nm/min. The films were finally annealed at 500–800 °C for 1 h in a preheated furnace to enhance crystallinity of the films. High-temperature post-annealing can also cause diffusion of the constituent atoms to affect the surface morphology.

Microstructure of the films were investigated by XRD $\theta - 2\theta$ scan using X-ray diffractometer (Rigaku). *Ex situ* AFM measurements were carried out in air using a Park Scientific Instruments AutoProbe CP with a Si₃N₄ tip.

III. RESULTS AND DISCUSSION

The structure of vapor deposited MgO films was investigated by varying deposition and post-annealing temperatures. XRD patterns of as-deposited films showed weak and broad (200) peak indicating the formation of small crystalline grains. The XRD data taken from MgO films, which were deposited on Si (111) at several different temperatures and post-annealed at 750 °C for 1 h, are shown in Fig. 1(a). The XRD pattern reveals only the MgO (200) peak suggesting that highly (100)-oriented MgO films have been formed. The (200) peak intensity is observed to increase as the substrate temperature increases up to 430 °C. For the growth orientation of MgO films, it was found to be independent of the orientation of Si, i.e., the underlying lattice structure of the substrates. Highly (100)-oriented MgO films could also be obtained on Si (100) substrates. Variation of the post-annealing temperature up to 800 °C did not produce significant changes in the (200) peak intensity. Thus, the crystallinity of MgO films depends sensitively on the deposition temperature rather than the post-annealing temperature. The growth behaviors of MgO films on GaAs and fused quartz substrates were further investigated. All the films show highly (100)-textured structure regardless of the substrate

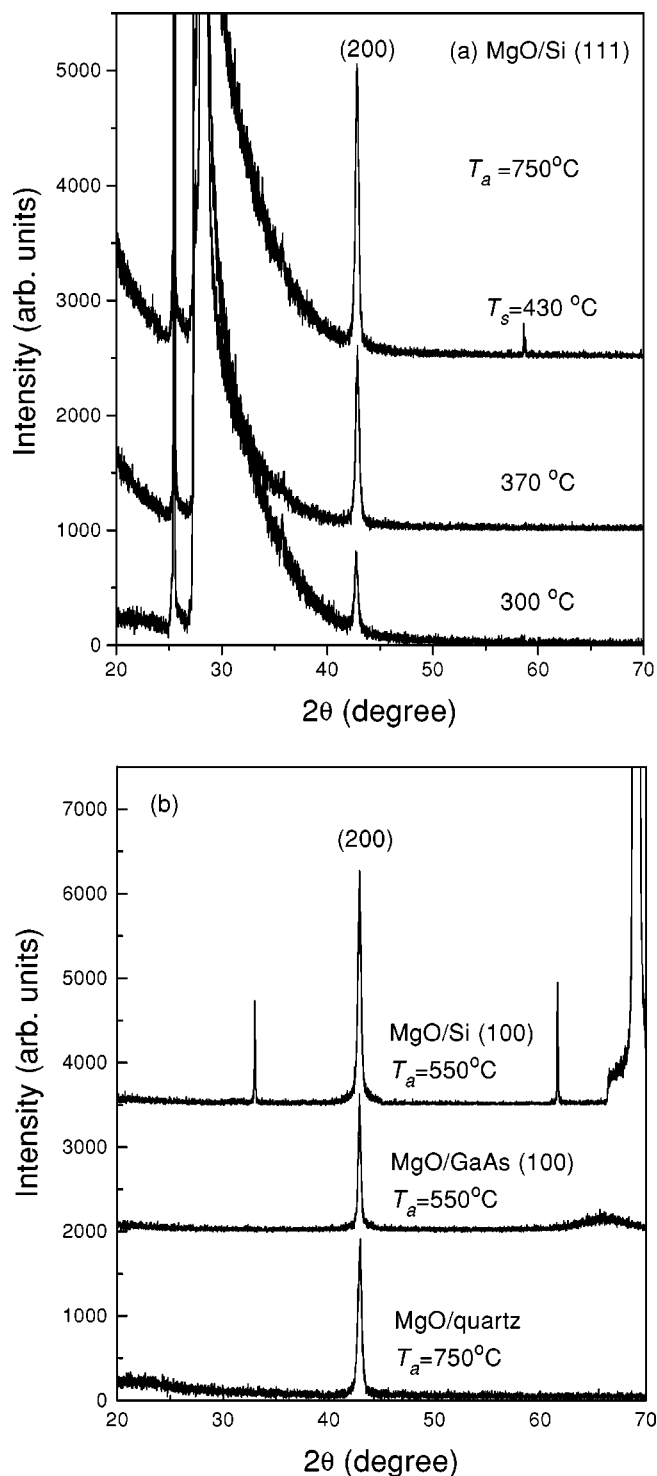


FIG. 1. XRD pattern of AACVD MgO thin films on (a) Si (111), (b) Si (100), GaAs (100), and fused quartz substrates. The MgO films grown on Si (111) were deposited at different substrate temperatures (T_s) and post-annealed at $T_a = 550^\circ\text{C}$ for 1 h. Other films were deposited at 400 °C and post-annealed at different T_a for 1 h.

materials, as shown in Fig. 1(b). These results suggest that the texturing of vapor deposited MgO films is a nucleation-controlled process. Recent study on in-plane textured (100) MgO films, which were deposited on amorphous Si₃N₄ substrates by ion beam assisted deposition, also showed that the texturing process for MgO is a nucleation process.¹⁸

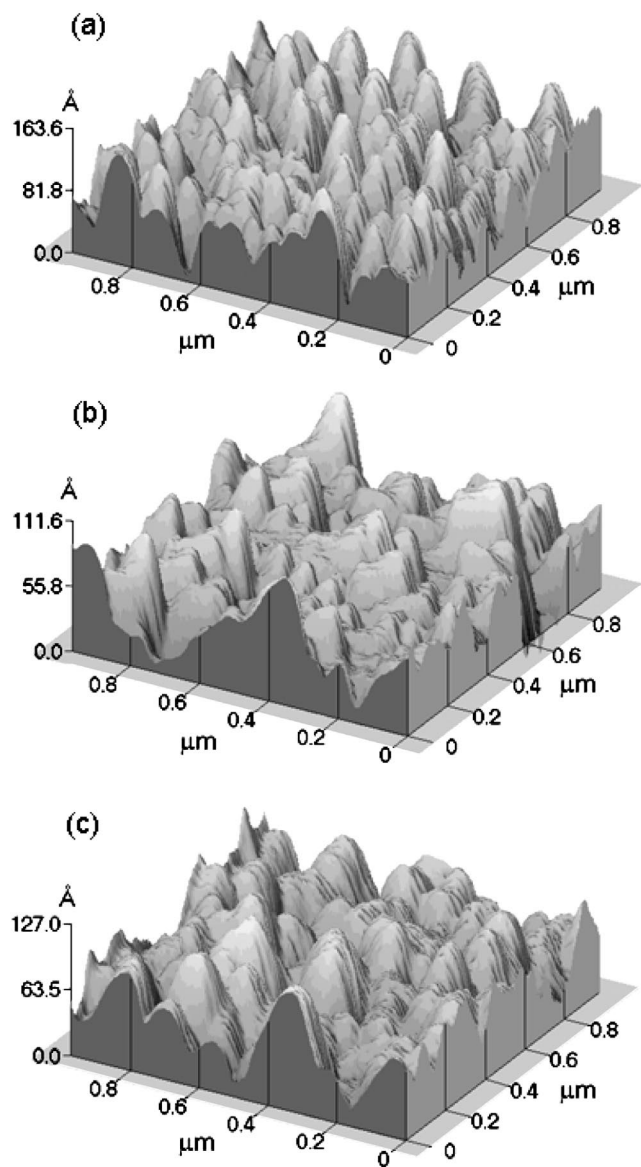


FIG. 2. AFM surface images of MgO films with different thickness of (a) 50, (b) 125, and (c) 390 nm. For a 50-nm thickness film, the surface morphology is rougher than the other samples.

The (100) growth orientation is thought to be determined by the lowest surface energy of MgO. For strongly ionic oxides, it has been suggested that fast diffusion on the neutral cleavage plane can make epitaxial growth possible at temperatures as low as $\sim 0.1T_m$, with T_m the melting temperature.¹⁹ The same conditions recur for MgO,¹⁴ which is also strongly ionic with low-energy (100) cleavage planes, and it can be grown epitaxially at temperatures down to 140 K ($T_m/20$). In the initial nucleation process, minimization of surface-free energy drives the atomic reordering of crystal surface resulting in energetically favorable (100) MgO orientation by diffusion. Post-annealing may also cause the atomic reordering that results in crystalline grain growth.

AFM images of 256×256 data points were obtained with scanning areas ranging from 0.5×0.5 up to $3 \times 3 \mu\text{m}^2$. Figures 2(a)–2(c) show surface images of MgO films, which were deposited on Si (100) at 400°C and post-annealed at 550°C for 1 h, of different thicknesses. MgO film morphol-

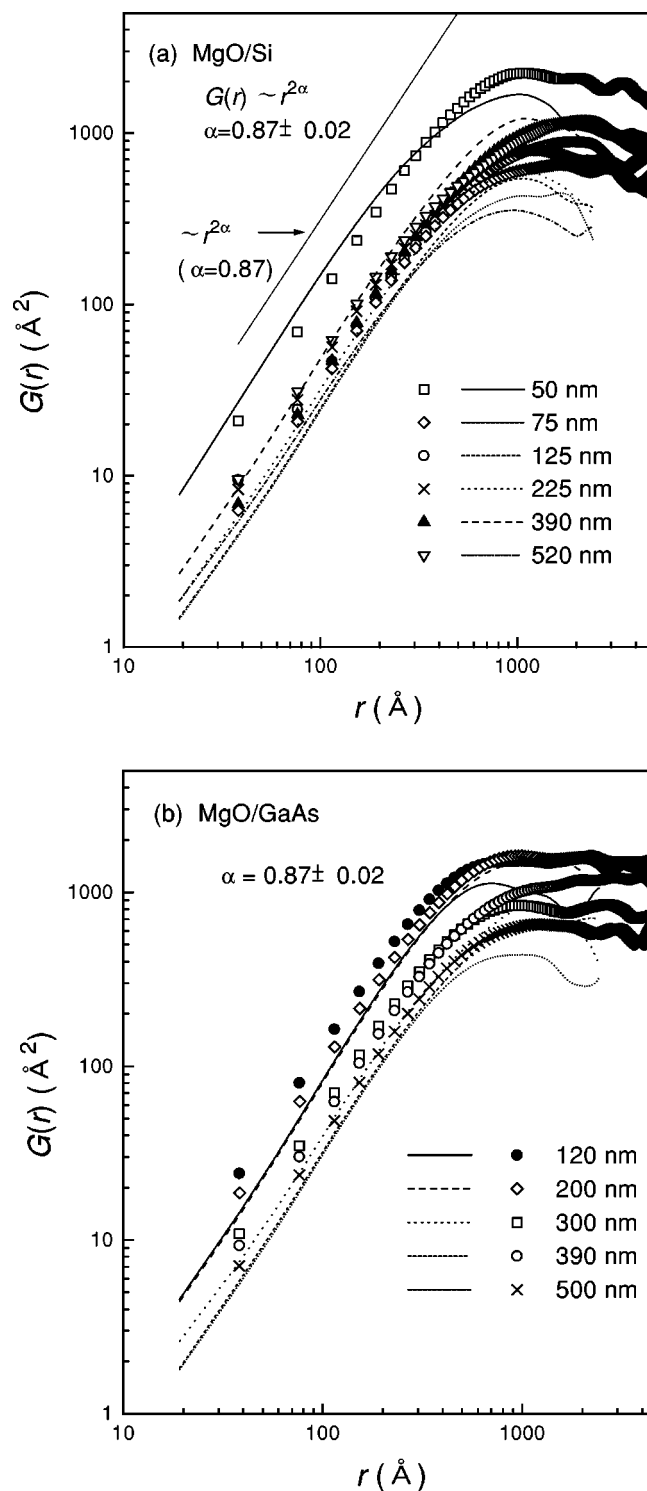


FIG. 3. Log-log plot of the height-height correlation as a function of lateral distance of observation for MgO films grown on (a) Si (100) and (b) GaAs (100) substrates. Lines and symbols are the experimental data obtained from the surface morphology with scanning areas of 0.5×0.5 and $1 \times 1 \mu\text{m}^2$, respectively.

ogy shows a continuous distribution of mounds. Surface diffusion, which was argued to play an important role in (100)-textured film growth, may be responsible for the observed morphology. Also, the morphology is very similar to the results of the computer simulations by Amar and Family for a growth model in which the full diffusion of adatoms along

the surface was taken into account.²⁰ The rms surface roughness of the films were less than 40 Å.

In addition, a qualitative analysis of the images in Figs. 2(a)–2(c) reveals that the 3D islands nucleate fairly uniformly and then grow as expected for SK or VM growth mode. For a 50-nm thickness film, the surface appears to be rougher than those of thicker films because of island formation, as can be seen in Fig. 2(a). As the islands coalesce, further deposition smoothens the surface, and the roughness decreases with increase of thickness. This behavior is in contradiction to the predictions of scaling theory.

In order to examine quantitatively the characteristics of the MgO/Si film morphology and the detailed growth processes, we plot in Fig. 3(a) the height-height correlation functions, $G(r, t)$, as a function of separation r for different film thickness (which is proportional to the deposition time t). AFM data were analyzed after applying a subtraction procedure for the instrument plane. The average was taken over pairs of points which were separated horizontally by distance r along x and y coordinate axes. The log-log plot of $G(r, t)$ exhibits a linear region for small r indicating that $G(r, t)$ follows a power law in this region. The slope of the plot is about the same for all thickness of the films giving $\alpha = 0.87 \pm 0.02$. The α value is in agreement with the range of values (0.7–0.9) reported for other experimental systems.^{21–25} They are consistent with the α values derived from growth models incorporating surface diffusion. For the growth processes driven by surface diffusion, where the desorption is negligible, the growth equation can be written as²⁶

$$\frac{\partial h}{\partial t} = -\kappa \nabla^4 h + \lambda \nabla^2 (\nabla h)^2 + \eta(\mathbf{r}, t), \quad (2)$$

where κ and λ are constants, and η is white noise in the flux of arriving species responsible for surface roughening. The exponent α for this nonlinear equation is solved to be $\alpha = \frac{2}{3}$ for the growth on a two-dimensional substrate.²⁶ However, if one neglects the second term ($\lambda = 0$) in the equation, i.e., for the linear equation, the exponent is known to be $\alpha = 1$.²⁷ Hence linear diffusion process appears to dominate roughness development of AACVD MgO films grown at 400 °C and post-annealed at 550 °C.

At sufficiently large r , each plot in Fig. 3(a) exhibits a saturation. The value of lateral position at the crossover point is equal to ξ , which is a measure of the average mound size. The saturation value depends on the interface width w with $G(r, t) \propto w^2$. For self-affine surfaces, w is also predicted to grow as a power law, $w \sim t^\beta$. However, our results do not show such variation as the film thickness increases. After the fast increase of the interface width of films in the very early stage (island formation) of growth, the interface width decreases and then exhibits a mild oscillatory behavior as the film thickness increases. That is, the growth of interface width does not seem to follow a power law in this system. This probably is due to the growth characteristics of vapor deposited MgO films on Si. During the initial stage of nucleation, the surface can roughen more rapidly than in the case of homoepitaxy because of island formation. In the later stage of growth, the anisotropic surface energy of MgO may cause additional diffusion to reduce the area of energetically unfavorable facets exposed. Moreover, post-annealing pro-

cess performed on the system can further reduce the surface roughness of the thicker films by local diffusion. Thus, the growth of interface width would not follow a simple power law. These features may be characteristics of films grown in near equilibrium conditions and annealed at higher temperatures. The most important observation, nevertheless, is that the rough surface is still correlated in the region $r < \xi$ with $\alpha = 0.87 \pm 0.02$ for all the samples. Earlier work on CuCl films deposited on CaF₂ from a molecular beam has shown similar growth behaviors.²¹

The same features, as shown in Fig. 3(b), were observed for the MgO films grown on GaAs (100) under the same deposition conditions. The roughness exponent α was determined to be 0.87 ± 0.02 from the slope of $G(r, t)$ in log-log plots. Although the measured value of exponent α is close to the prediction of the Schwoebel barrier model ($\alpha = 1$),²⁸ the observed morphology differs from that in the Schwoebel barrier model where large-scale uniformly sized pyramids with stationary slope will be formed. Moreover, the MgO films showed polycrystalline structures with preferred orientation. However, the fact that α is essentially constant for MgO films on Si and GaAs demonstrates that the fundamental mechanisms involved in the film growth are the same for all the samples. The results show that kinetic limitation, i.e., local surface diffusion of the deposited species, are important for the vapor deposited MgO films on semiconductors even though the growth mechanism seems to fall into the category of thermodynamic model of the VW or SK growth mode. Kinetic roughening generated during deposition is thought to be retained considerably even after the post-annealing process.

IV. CONCLUSIONS

Highly (100)-oriented MgO films were grown on Si, GaAs, and quartz substrates by the AACVD technique using magnesium ethoxide as a source material. Surface diffusion in the initial nucleation stage of growth was argued to determine the growth orientation of the films. Investigation of the surface morphology of the films indicates that the growth mechanism may be either VW or SK mode of thermodynamic model. A quantitative analysis of the surface morphology gave the roughness exponent value $\alpha = 0.87$ for MgO films grown on Si and GaAs. The value of α is consistent with growth model predictions incorporating surface diffusion. The growth of interface width did not follow a power law probably due to near equilibrium growth conditions and the post-annealing. It is noteworthy that the local structure of the surfaces is still correlated at all stages of growth in spite of high-temperature equilibrium growth condition and post-annealing. Kinetic limitations are important even for the system of MgO/semiconductors that is qualitatively governed by near equilibrium growth modes.

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- *Electronic address: jgyoon@mail.suwon.ac.kr
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