Enhanced strain relaxation induced by epitaxial layer growth mode of MgO thin films

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Abstract

Growth of MgO films on silicon substrate was conducted by KrF excimer pulsed-laser ablation system. Two kinds of growth mode were revealed in situ by reflection high energy electron diffraction. It was found that the layer growth mode of MgO thin films could remarkably reduce the misfit strain originated from the different lattice constant and thermal expansion coefficient between MgO films and Si. An enhanced strain relaxation was discovered for MgO films, which were grown with the layer growth mode, in the film thickness range of 40–100 nm. The value of critical thickness for the formation of misfit dislocation agrees well with the calculated one. This exceptional phenomenon should be ascribed to the layer growth mode of epitaxial MgO films.

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1. Introduction

Strain relaxation in oxide thin films has attracted much attention because they play a pronounced role in influencing their crystalline quality and subsequent performances, which is especially important for buffer/barrier-layer applications [1–3]. Strain can originate from thermal expansion mismatch and/or lattice mismatch between thin film and substrate, and as well as defects (e.g., oxygen vacancies, etc.) in thin films. Detailed investigations of strain relaxation in oxide thin films are of both scientific and technological significance. Growth of MgO film on silicon substrate, which provides a possible template for epitaxial or textured growth of perovskite oxides, is of great valuable both in terms of integration with silicon and in ridding of the need for expensive MgO single crystals as substrates. In addition, the low dielectric constant and low dielectric loss of MgO make it a good host for microwave devices based on high-\(T_c\) superconductors [4]. MgO can be grown on Si(100) with parallel epitaxy interpreted by domain-matching (4-on-3 cube-on-cube mode) [5,6], which dramatically reduces the lattice mismatch from 22.5 to 4.1%. However, the thermal expansion coefficient of MgO (\(\kappa = 12.6 \times 10^{-6}/K\)) is about three times greater than that of Si (\(\kappa = 3.8 \times 10^{-6}/K\)). Therefore, the evolution of MgO thin films’ strain during in situ growth and subsequent cooling to room temperature (RT) is a complex process, and a clear understanding of the nature of MgO thin films’ strain-relaxation is vital for preparations of high-crystalline-quality MgO thin films.

In the course of our investigation of integrating MgO with silicon substrate, we have found that the growth modes and orientations (in-plane and out-of-plane) of MgO thin films could be changed by using an ultrathin TiN seed layer at the initial growth stage. In the present paper, two types of MgO film with different growth mode and orientation were prepared on Si(100) by the pulsed-laser deposition (PLD)
technique and a study of strain relaxation of the MgO films as a function of thickness was conducted. It was found that the strain in the epitaxial MgO films grown with the layer mode (denoted as films-A) could relax remarkably at a thickness range of 40–100 nm. Peng et al. [7] have reported the strain relaxation of SrTiO3 (STO) thin films, in which they found that the strain relaxed sufficiently when the STO thin film reached a thickness of 250 nm. Comparing with this result, the strain relaxation in the MgO films grown with the layer mode is intensified. This enhanced strain relaxation is apparently different from that of MgO films grown with non-layer mode, especially, different from the MgO films with random in-plane crystallographic orientations (denoted as films-B).

2. Experimental

All the samples were prepared by a Lambda Physik KrF ($\lambda = 248$ nm) excimer laser system (COMPex201). Si(100) wafers were thoroughly cleaned to remove the surface native oxide layer before loading into the chamber. The focused laser fluence was set at 7 J/cm$^2$ and the target-substrate distance was optimized to 70 mm. The targets were mounted to a holder which would rotate to bring over the desired target for laser irradiation. Considering that TiN can be grown epitaxially on Si via domain matching epitaxy [8–10] and has the same crystal structure with MgO, we employed an ultrathin TiN seed layer (1 nm-thick) to promote the nucleation of MgO crystallites. A sintered TiN (density $>95$%) and an MgO (density $>90$%) target were ablated at a pulsed repetition rate of 3 and 5 Hz, respectively. Prior to the ablation of TiN, the stainless-steel vacuum chamber was evacuated with a turbomolecular pump to the order of 10$^{-5}$ Pa. After the 1 nm-thick TiN seed layer was grown (for films-A), in situ deposition of MgO films was carried out in an oxygen ambient of 10$^{-2}$ Pa; while, for films-B, directly ablating the MgO target was performed in the same oxygen partial pressure after the base pressure reached the order of 10$^{-5}$ Pa. A thickness series of MgO films, i.e. 10, 40, 100, 150, 250 and 400 nm, were employed for investigating the correlation of MgO films’ strain relaxation with the films thickness. The overall growth process of films was monitored in-situ by reflection high energy electron diffraction (RHEED) at an electron acceleration voltage of 20 kV, while film crystallinity and out-of-plane orientations were characterized by X-ray diffraction (XRD) (D/MAX-2550V Cu Ka Diffractometer).

3. Results and discussion

The deposition of MgO films was monitored in-situ by RHEED system, in which the incidence azimuth of the electron beam was along $\langle011\rangle$ of the Si(100) substrate. The typical RHEED patterns for films-A and films-B are shown in Fig. 1(a) and (b), respectively. It is obvious that the pattern for films-A exhibits sharp streaks, indicating layer-growth mode and the formation of extremely smooth surface; while, the one for films-B shows some vague diffraction rings, indicating random in-plane crystallographic orientation and poor crystallinity. The presence of streaks in Fig. 1(a) also evidences that the in-plane alignments of films-A and Si(100) substrate follows the relationship: MgO $\langle011\rangle$/Si$\langle011\rangle$. The out-of-plane orientations of both films were examined by XRD, which are...
shown in Fig. 2(a) and (b), respectively, with the $\theta - 2\theta$ scans in the 2$\theta$ angle-degree range of 32–44°. Besides the peak from the Si substrate, there is only a single MgO(200) diffraction peak in both patterns. However, the MgO(200) peak for films-A (shown in Fig. 2(a)) is much more intensified than that for films-B (shown in Fig. 2(b)), indicating a great improvement of MgO films’ crystallinity induced by the layer growth mode. From the aspect of the values of the full width at half-maximum (FWHM) (seen in Fig. 3), the FWHM’s value of films-A is smaller than that of films-B, also showing the good crystallinity of films-A.

The RT out-of-plane lattice constants of the MgO films, which are intimately correlated with the strain in the films, were also characterized by X-ray diffraction (XRD). In Fig. 2(a), the MgO(200) diffraction peak shifts from high-angle region to low-angle one when the film thickness increases, indicating a change of the lattice constant with the film thickness. More noticeable one is that a greatly apparent shift in 2$\theta$ angle occurs in the thickness range of 40–100 nm, which suggesting an enhanced strain relaxation. Whereas, in Fig. 2(b), no such obviously enhanced strain relaxation was presented within the entire thickness range of 10–400 nm. The strain in MgO thin film calculated from the out-of-plane lattice constant, which is expressed as $K = (a_{\text{bulk}} - a_{\text{film}})/a_{\text{bulk}}$, is plotted in Fig. 4 as a function of the MgO film thickness. For films-A, the value of $K$ decreases drastically in the thickness range of 40–100 nm; while, at large thickness ($\gtrsim 250$ nm), the out-of-plane lattice constant is about the same as the bulk value, with the $K$ value close to 0.1. In contrast, $K$ value of films-B decreases slowly and gradually within the entire thickness range. Even at a film thickness of 250 nm, the value of $K$ still approximates to 0.45, indicating its poor strain relaxation.

The strain relaxation can be intimately associated with the generation and motion/pinning of misfit dislocations. For films-A, an enhanced strain relaxation occurs at a thickness range of 40–100 nm. This suggests that a critical thickness of MgO film is reached where the complete strain

![Fig. 2. XRD patterns and out-of-plane orientations of films-A (a) and films-B (b).](image)

![Fig. 3. Values of FWHM versus films thickness.](image)

![Fig. 4. Strain in MgO thin films as a function of films thickness.](image)
relaxation can occur. Taking into consideration of the simple Matthews–Blakeslee mode, one can use the equation,

$$H_c = \frac{b(1 - \nu \cos^2 \alpha)}{2\pi f(1 + \nu \cos \lambda)} \left( \ln \frac{H_c}{b} + 1 \right)$$

[11], for roughly estimating the critical thickness. Giving $\nu = 1/3$, $b = 0.4$ nm, $\cos \alpha = 1/2$, $\cos \lambda = 1/2$, $\chi_0 = 1.4$ and $f = 0.018$, the theoretical value for films-A is about 35 nm, which is agreed reasonably with the experimental value. It is convinced that via the layer growth mode, MgO films (films-A) can be grown on Si(100) with perfect 4-on-3 cube-on-cube coincidence-site-lattice mode, resulting in excellent crystallinity, which have been evidenced by the RHEED and XRD analysis in Figs. 1 and 2. Considering the epitaxial growth of films-A, one can suppose that it is energetically favorable for misfit dislocations in films-A to motion (e.g., climb and glide) due to a decrease in pinning centers and sites. Therefore, when the critical thickness is reached, the pronounced strain relaxation can occur. However, for films-B, because of poor crystalline quality and random in-plane orientation, it is believed that pinning effects of misfit dislocations must play a decisive role in determining the film strain. More and more dislocations will be generated to relieve the misfit strain when the film thickness increases. But due to the pinning effects originated from defects in films-B, the motion of misfit dislocation are effectively suppressed. Before the strain sufficiently relaxes, further increase in the thickness of films-B only increases the volume fraction of the film having misfit dislocations. This indicates that the gradual strain relaxation process of films-B is accompanied by the generation of enormous misfit dislocations.

Discrepancy of lattice constants in thin films than in bulk materials has been widely reported [12–14]. This has often been attributed to oxygen vacancies in films because the lattice constant increases with oxygen deficiency [12,13] and the volume of a vacancy in ionic solids is in general larger than the atomic volume of the missing ion [15]. However, since both films-A and films-B were deposited on Si substrates under the same oxygen partial pressure in our cases, the oxygen vacancies should have similar effects on the change of lattice constant. Therefore, the remarkable change of lattice constant occurred in films-A should not be entirely ascribed to oxygen vacancies in films. Our result and discussion suggest that the layer growth mode can effectively relax the strain in MgO films, and in return, resulting in the high crystalline quality of MgO films.

4. Conclusion

We have investigated the strain relaxation in two kinds of MgO thin films, which were grown with different growth modes by means of pulsed-laser deposition (PLD). A critical thickness range, where complete strain relaxation occurs, is revealed for the MgO thin films grown with the layer growth mode. The enhance strain relaxation can be considered to be induced by the layer growth mode of MgO films. Our results suggest that this layer growth mode may provide a valuable technique for effectively reducing the misfit strain in the MgO thin films.

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References