

Orientation of MgO thin films on Si(001) prepared by pulsed laser deposition

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Abstract—Pulsed laser deposition method was employed to grow MgO thin films with preferred orientation on bare Si(100) and SiO₂/Si(100) substrates. The orientation of MgO thin films was systematically investigated by varying deposition parameters. XRD analysis showed that the preferred orientation of MgO thin films would change from (111) to (100) when laser fluence decreased and oxygen pressure increased to certain extent. But it was difficult to fabricate completely (100)-oriented MgO films. Substrate temperature seemed to have little influence on the orientation of MgO thin films at high laser fluence. SEM images of the MgO thin films on Si(100) deposited at 400°C and the laser fluence of 5J/cm² in the oxygen ambient of 200mTorr demonstrated that there was no presence of interfacial reactions or cracks and the film surface was very smooth. Such film is suitable as buffer layers for the growth of high-quality ferroelectric and superconducting overlayers.

Keywords—Pulsed laser deposition, thin films, MgO, orientation.

I. INTRODUCTION

IN recent years perovskite oxide thin films have been one of the most popular materials for their wide applications in microelectronic and optic-electronic devices such as non-volatile ferroelectric memories [1,2], piezoelectric micro-actuators and sensor [3-5], superconducting quantum interference devices (SQUID), optical waveguide, microwave devices [6-7] and so on. Among many types of perovskite thin films the lead zirconate titanate (PZT) and high temperature cuprate superconductor YBa₂Cu₃O_{7-δ} (YBCO) are being intensively examined due to their unique properties. Typically, submicron these films are deposited onto various oxide single crystal substrates, such as MgO [8], SrTiO₃ (STO) [9], LaAlO₃ (LAO) and yttria stabilized zirconia (YSZ) [10], over a wide range of deposition conditions because of their chemical natures and crystal structures. However, these substrates not only are expensive but are limited to diameters less than 5 cm, and especially have unacceptably large losses. Much research has been performed on the integration of high-quality superconducting and ferroelectric thin films into technically practical Si wafers because it is compatible with current Si integrated circuit (IC) processing, though it is difficult to

epitaxially grow perovskite thin films directly on Si single crystal substrates due to the interdiffusion and lattice mismatch between them.

An appropriate approach is the introduction of the buffer layers which are lattice-matched with both perovskite thin films and silicon, grow at relatively low temperatures, and act as diffusion barriers between them. MgO thin films have recently attracted much attention for their potential application as a chemically stable buffer layer for high temperature superconductor and ferroelectric thin films. In addition, MgO has a low dielectric constant for high T_c superconductor application and a low refractive index (1.735) useful for optical confinement in ferroelectric/MgO/semiconductor waveguide structures. Epitaxial or oriented MgO films are preferred for such applications since MgO films are suitable host lattice for a variety of other epitaxial materials and can be used as a template for growing oriented overlayers. MgO films with different orientations have been fabricated by various thin film growth techniques such as ion-beam-assisted deposition (IBAD), magnetron sputtering, metal organic chemical vapor deposition (MOCVD) and electron beam evaporation [11-13]. Pulsed laser deposition has also been successfully applied due to its flexible characteristics. For example, Fork et al. [14] reported the epitaxial growth of (100)-oriented MgO on Si (100) using Mg metal target. (111)-textured MgO grown on Si (100) substrates from magnesium oxide target was realized by Tiwari et al. [15]. For an applications standpoint, the MgO (100) plane has an advantage in preparing (001)-oriented tetragonal ferroelectric thin films, while the MgO (111) plane is beneficial for growing (111)-oriented rhombohedral ferroelectric thin films or (0001)-oriented hexagonal thin films. Therefore, it is of interest to pursue further investigation on texture development of MgO thin films on semiconductor substrates. In this paper, MgO thin films were deposited on bare Si (100) and SiO₂/Si(100) substrates by pulsed laser deposition method over various deposition conditions.

II. EXPERIMENTAL PROCEDURE

Pulsed laser ablation deposition was used to fabricate MgO films on Si (100) and SiO₂/Si(100) substrates as

shown schematically in Fig.1. The PLD chamber comprises a multi-target station for mounting six targets with a facility to rotate and position any target of interest in line of the laser beam. The substrate holder assembly comprises a resistive heater and a thermocouple for measuring substrate temperature. Pulsed KrF excimer laser beam ($\lambda = 248\text{nm}$, pulse width = 25ns, repetition rate = 1-50 Hz) is incident on the target at an angle close to 45° with a spot size around $1\text{mm} \times 4\text{mm}$. The distance between the target and substrate was kept around 30-60mm. The chamber is evacuated by a combination of a mechanical pump and turbomolecular pump to a base pressure less than 2×10^{-5} Torr. The Si and SiO₂/Si substrates were cleaned in organic solvent baths in an ultrasonic container. Then bare Si substrates were dipped in 40% HF solution for 2 minutes to remove surface native oxide prior to loading into the chamber. The MgO target was fabricated by pressing MgO powder of 99.9% purity into a $\phi 27\text{mm} \times 4\text{mm}$ disk and sintering at 1450°C for 2 hrs. The laser ablation was carried out at a laser fluence of 3-7 J/cm² and a repetition rate of 10Hz. The films were deposited in the substrate temperature range of 350-600°C, whereas the oxygen partial pressures varied in range 0.1-200 mTorr. In order to avoid oxidization of Si surface, the oxygen gas was introduced into the deposition chamber after the MgO films were pre-deposited for about 60 seconds. The total deposition time was about 1 hr because MgO is hard to ablate.

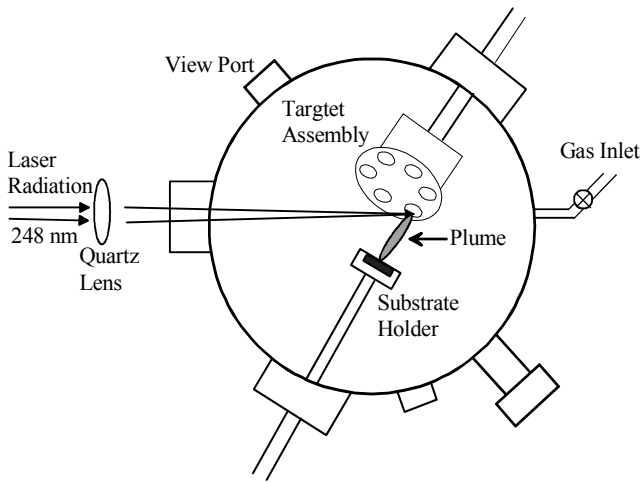


Figure 1. Schematic illustration of a pulsed laser deposition system.

An X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu K_α radiation was used to investigate the crystallographic structure of the thin film samples. The microstructure and surface morphology of the thin films were examined with a scanning electron microscopy (SEM, JEOL JSM-5600LV). The film thickness was also measured from cross-sectional SEM image.

III. RESULTS AND DISCUSSION

The effect of deposition parameters on orientation of MgO thin films has been investigated in this study. The key factors in PLD technique influencing orientation of thin films are the oxygen pressure, the substrate temperature and laser energy density. When a parameter was varied, the other parameters were maintained so that effect of each parameter could be separately identified. During the deposition of MgO films, a bright green plume was observed in a direction normal to the target, showing that the laser fluences of 3-7 J/cm² are above the ablation threshold of MgO target. Fig.2 shows XRD spectra for the MgO thin films on Si (100) at the substrate temperature of 450°C and laser fluence of 7J/cm² with the different oxygen pressures ranging from 0.1mTorr to 200mTorr. It can be seen that only (111) reflections of MgO thin films were obtained at O₂ pressure of 0.1mTorr, 20mTorr and 100mTorr. The mixed (111) and (100) orientation was observed at O₂ pressure of 200mTorr, which showed high oxygen partial pressure was possibly more favorable to growth of (100) oriented MgO thin films, while low oxygen pressure was correct choice for achievement of preferred (111) orientation. This result is in agreement with that reported by Witanachchi et al. [16], who found that MgO buffer layers grown at 400°C in 0.1 to 0.5 mTorr oxygen using an ArF laser (193nm) had preferred (111) orientation. As is known, MgO has a NaCl type crystal structure with face-centered-cubic Mg and O sublattices. The (100) planes are the cleavage planes of MgO, they are charge neutral, naturally occurring orientation, and have a low surface energy. It is suggested that the kinetic energy of particles in the plume composed of the ablated species could be changed by controlling the oxygen pressure, which allows the energy of the incident particles to be adjusted such that the (111) preferred orientation is favored over the (100) orientation at low oxygen pressures.

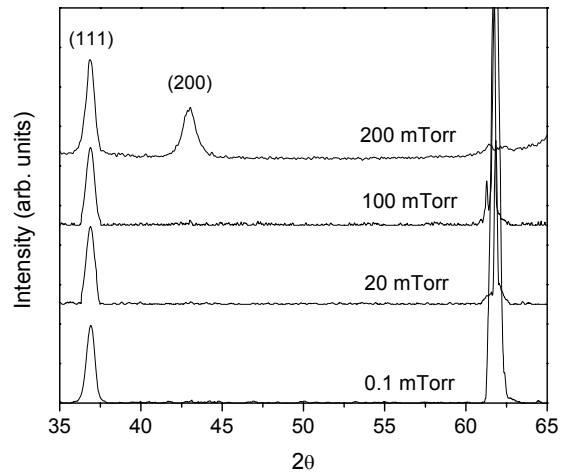


Fig.2. XRD spectra for the MgO thin films on Si (100) at the substrate temperature of 450°C and laser fluence of 7J/cm²

with the different oxygen pressures. (The peak at 62° is the Si(400) Cu K_{β} diffraction peak)

It is of interest to examine the orientation of MgO thin films on SiO₂/Si substrates since amorphous SiO₂ insulator layers are often used in IC fabrication. Therefore we also deposited MgO films on SiO₂/Si substrates for comparison under the conditions similar to growth of MgO thin films on bare silicon substrates. XRD spectra for MgO/SiO₂/Si structure grown under the different oxygen pressures are shown in Fig.3. It is evident that the relatively high oxygen pressure facilitated the growth of (100)-textured MgO layer though (220) peak of the MgO thin film on SiO₂/Si could be also remarkably observed at the oxygen pressure of 200mTorr.

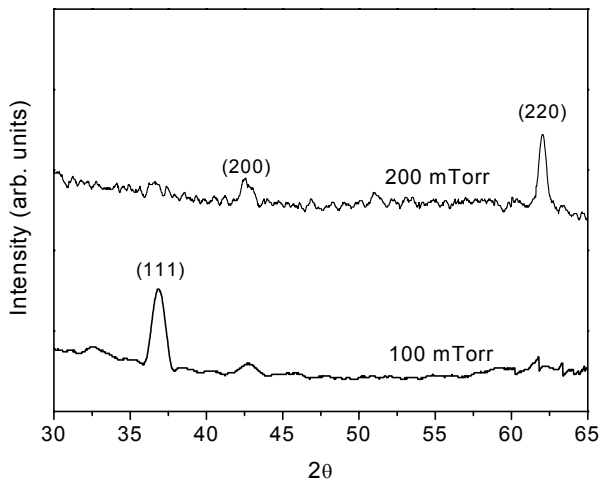


Fig.3. XRD spectra for MgO/SiO₂/Si structures grown at the substrate temperature of 450°C and laser fluence of 7J/cm² with the different oxygen pressures.

Fig.4 shows XRD spectra for the MgO thin films on Si (100) at various substrate temperatures with the oxygen pressure of 200mTorr and the laser fluence of 7J/cm². The mixed (100) and (111) orientation for all three MgO thin films deposited at substrate temperatures of 400°C, 450°C and 500°C were observed. It seemed that substrate temperature did not significantly affect the orientation of MgO thin films grown at O₂ pressure of 200mTorr and laser fluence of 7J/cm². This was possibly caused by high laser fluence, 7J/cm², used in this work, which made the particles in the ablated species high energetic so that increasing substrate temperature had little effect on the movement of particles on the growing surface and hence the orientation of MgO thin film. But 450°C is likely optimal substrate temperature for the growth of (100)-oriented MgO films. The similar results were available for the MgO thin films on SiO₂/Si substrates fabricated under the same deposition conditions as those on bare Si substrates.

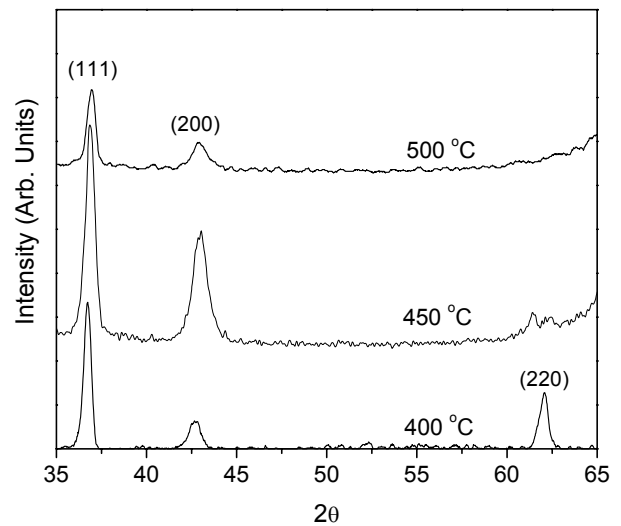


Fig.4. XRD spectra for the MgO thin films on Si (100) at various substrate temperatures with the oxygen pressure of 200mTorr and the laser fluence of 7J/cm².

Laser fluence is another important parameter in pulsed laser deposition technique. XRD spectra of the MgO thin films on Si (100) fabricated at the laser fluence of 3J/cm², 5J/cm² and 7J/cm² are illustrated in Fig.5. For all three films, the oxygen pressure of 200mTorr and the substrate temperature of 400°C were used. It was obvious that (100)-textured MgO thin films can be easily obtained over the spectrum of low laser fluences. The observed relationship between the MgO orientation and the laser fluence may be discussed in terms of the migration of molecules and atoms on a growing surface. At a low laser fluence, which means a low deposition rate, sufficient migration occurs to form the (100) plane of MgO, which is energetically stable. On the other hand, at a high laser fluence, insufficient migration tends to form the energetically unstable (111) plane of MgO, which has lower atomic density than the (100) plane. Unfortunately, it is difficult to grow completely (100)-oriented MgO thin films on Si (100) under such deposition condition because of the existence of MgO (220) reflection. Comparing the above results with those illustrated in Fig.6, which was the case deposited on SiO₂/Si substrates with the same deposition parameters as those of the counterparts in Fig.5, one can find that the MgO thin films deposited on SiO₂/Si substrates have seemingly more strong (220) diffraction peak than the films on bare Si substrates. Therefore it was suggested that the occurrence of (220) peak for the MgO thin films on Si (100) could be attributed to the presence of amorphous SiO₂ layers, which were possibly formed by the oxidization of Si surfaces at the used substrate temperature before deposition of MgO thin films.

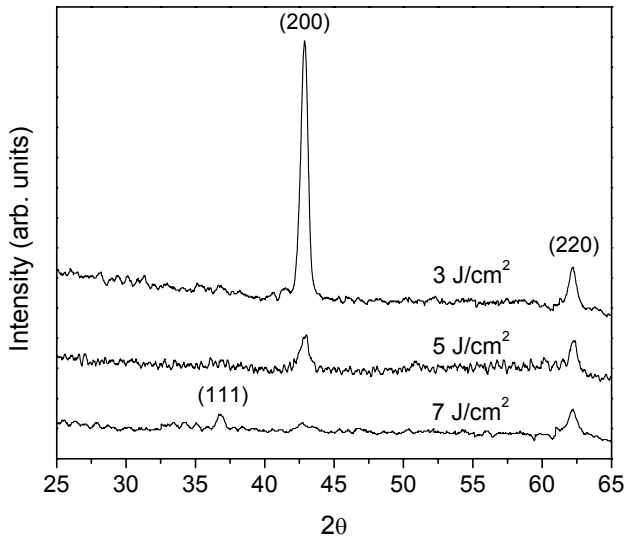


Fig.5. XRD spectra of the MgO thin films on Si (100) fabricated at the different laser fluences with the substrate temperature of 400°C and O₂ pressure of 200mTorr.

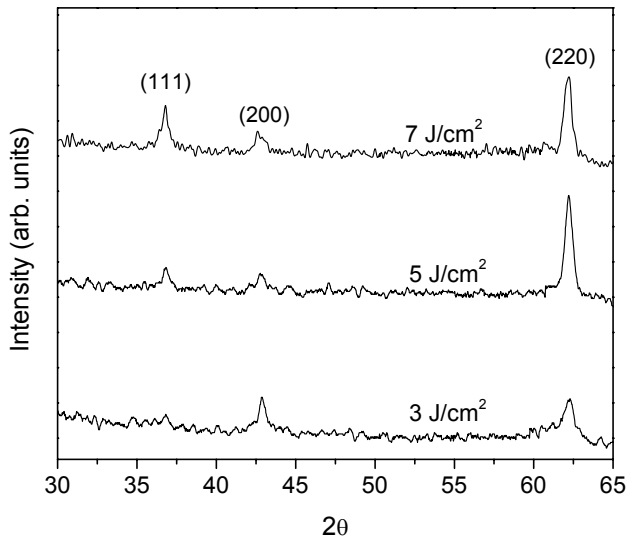


Fig.6. XRD spectra of the MgO thin films on SiO₂/Si(100) fabricated at the different laser fluences with the substrate temperature of 400°C and O₂ pressure of 200mTorr.

Figure 7 shows the fracture section and surface morphology images observed by SEM for the MgO thin film on Si(100) deposited at 400°C and 5J/cm² in oxygen ambient of 200mTorr. The MgO thin film of about 260nm thickness was obtained. The corresponding deposition rate was 0.014nm/pulse (1.4Å/s). There was no evidence of cracks or interfacial reactions and the MgO thin film looks dense with smooth surface although very few particulates and pinholes can be occasionally seen. Similar results were also obtained for the MgO/SiO₂/Si(100) structure. The MgO films with this quality should be suitable as buffer layers for the subsequent growth of overlayers.

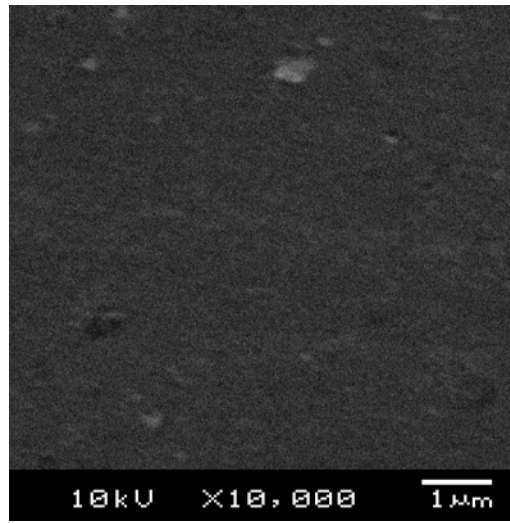
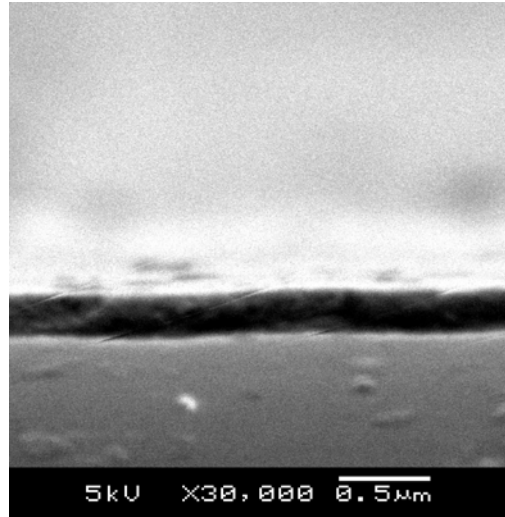


Fig.7. SEM images for (a) the fracture section and (b) the surface morphology of the MgO films deposited on Si(100) at 400°C and 5J/cm² in oxygen ambient of 200mTorr.

IV. SUMMARY

MgO thin films with smooth surfaces were grown on both Si (100) and SiO₂/Si(100) substrates by pulsed laser deposition under various deposition conditions. The orientation of MgO thin films on bare Si and SiO₂/Si changed from (111) to (100) with an increase in oxygen pressure or a decrease in laser fluence. These results indicate that the possibility of controlling the orientation of MgO thin films on semiconductor substrates by changing the deposition parameters. This orientation control is promising for application in the integration of ferroelectric and superconducting devices with semiconductor devices. However, completely (100)-oriented MgO films have not been obtained in the present investigation. PZT thin films have also been deposited on MgO/Si(100) with hope of obtaining (001)-oriented PZT films. Unfortunately, all PZT films deposited at 600°C and in 200mTorr O₂ showed the existence of pyrochlore phase. Further effort will be made to

grow high quality (100)-oriented MgO and subsequently deposit YBCO or LSCO as bottom electrodes and PZT films as active layer for microelectronic applications.

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