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Dynamics of STO heteroepitaxial growth by pulsed laser deposition

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The heteroepitaxial growth dynamics of STO thin films on (100) $LaAlO_3$ substrate by pulsed laser deposition has been studied. The laser energy density was found to be an important factor to determine the growth mechanics. High laser energy density is benefit to two dimensional layer-by-layer growth. Island growth prevails at low substrate temperature. STO thin films deposited at low oxygen partial pressure showed pellicular square grains. High oxygen partial pressure resulted in spherical STO grains. Step-terrace on substrate surface acts as a preferential nucleation site for adatoms, which leads to step-flow growth. STO thin films with atomic flat surface has been prepared on step-terraced substrate.

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1. Introduction

STO thin films have recently become very attractive to microelectronics as a good candidate for application in high-density dynamic random access memory (DRAM) [1, 2]. In the past few years, high-density capacity memory has been rapidly shrinking in dimensions and expanding in capacities. Gbit DRAM memory requires large capacitor in a relatively small area. However, traditional SiO_2-based devices are causing many problems in the high-density device fabrication due to low dielectric constant. STO thin films are considered to be one of the best candidates because it exhibits not only high dielectric constant, but also weak voltage dependence of dielectric constant at room temperature [3, 4].

The rough morphology of surface and interface can alter the operational conditions of microelectronic devices. Random rough surfaces have been shown to drastically influence the image potential of charge situated in the vicinity of a plane interface between vacuum and dielectrics. Roughness effects could have a strong influence on an inversion layer at semiconductor/oxide interface, since it causes shifts of electronic energy levels and thus alters the device function. A number of experiments found that the surface/interface morphology has a great influence on electrical properties of dielectrics, especially the leakage current [5–7]. For examples, Li *et al.* found that with increasing surface roughness, the leakage currents of BST ($Ba_{1-x}Sr_xTiO_3$), SBT ($SrBi_2Ta_2O_9$) and PZT ($PbZr_{1-x}Ti_xO_3$) increase [8]. So the fabrication of DRAM requires STO thin films with atomic smooth surface.

It is well known that the microstructure and physical properties of thin films depend crucially on growth dynamics. The growth dynamics in turn are determined by growth parameters, such as substrate temperature, oxygen pressure, deposition rate, and substrate surface morphology. Understanding and controlling of the growth dynamics appear to be of exceeding importance.

STO thin films have been successfully synthesized by RF sputtering, metalorganic chemical vapor deposition and pulsed laser deposition (PLD) [9–11]. Among these processes, pulsed laser deposition is the most superior, for it possesses many advantages, such as low processing temperatures, near stoichiometric phase formation, deposition at high rates and ability to fabricate multi-layer structures. In this study pulsed laser deposition is adopted for synthesizing STO thin films on (100)$LaAlO_3$ (LAO) substrate. The effect of processing parameters (i.e., substrate temperature, ambient oxygen partial pressure, energy density of excimer laser, and substrate surface morphology) on surface morphology of STO thin films were studied.

2. Experimental

STO thin films were deposited on LAO substrates by PLD technique. KrF excimer laser radiation (Lamda Physik Compex 201), with a repetition rate of 5 Hz, was focused on a rotating target set in the chamber through a quartz window. The incident angle of laser beam to the target surface was fixed to be 45°. The output laser fluence was kept as 150 mJ per pulse which yielded a growth rate of 0.02 nm per pulse. The laser energy density was adjusted in a range between 1 and 2 J/cm^2 by changing the size of focused laser spot. STO single crystal was adopted for target to suppress droplet creation during PLD process. Substrates were placed

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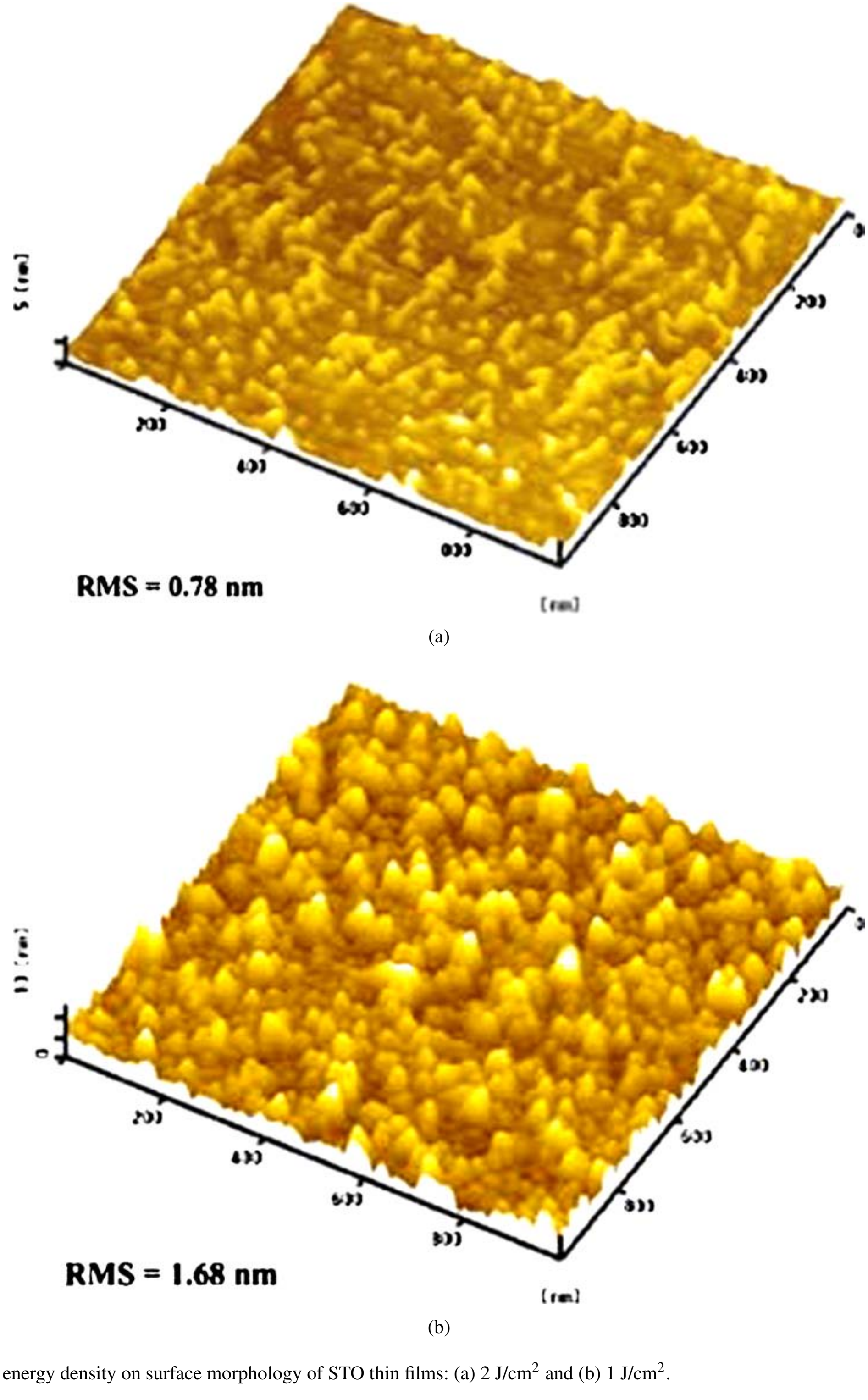
parallel to the target surface with a target-substrate distance of 50 mm. Pure oxygen was used as reactive agent during deposition, and was introduced into the chamber through a needle valve. The pressure during deposition was maintained in a range between 10 and 30 Pa. The substrate was heated by radiation from Pt resistive heater with a thermocouple embedded in the heater. The substrate temperature during deposition ranged from 680 to 740°C. After deposition the samples were cooled down quickly to freeze surface morphology of the as-grown films by introducing oxygen gas directly to the sample surface.

Atomic force microscopy (AFM) was employed to characterize the surface morphology of STO thin films. The crystal structure and epitaxy relationship between LAO substrate and STO thin films were characterized by X-ray diffraction. Film orientation and phases were obtained from the θ–2θ scans. The crystallinity of STO thin films was inferred from ω-scan (rocking curve around the (200) reflection). The epitaxy relationship between LAO substrate and STO thin films were characterized by ϕ-scan (diffraction from the (103) planes of LAO substrate and STO thin film) spectrum.

3. Results and discussion

In the XRD patterns of STO thin films in this study, there are only (100) diffraction lines. It shows that the films



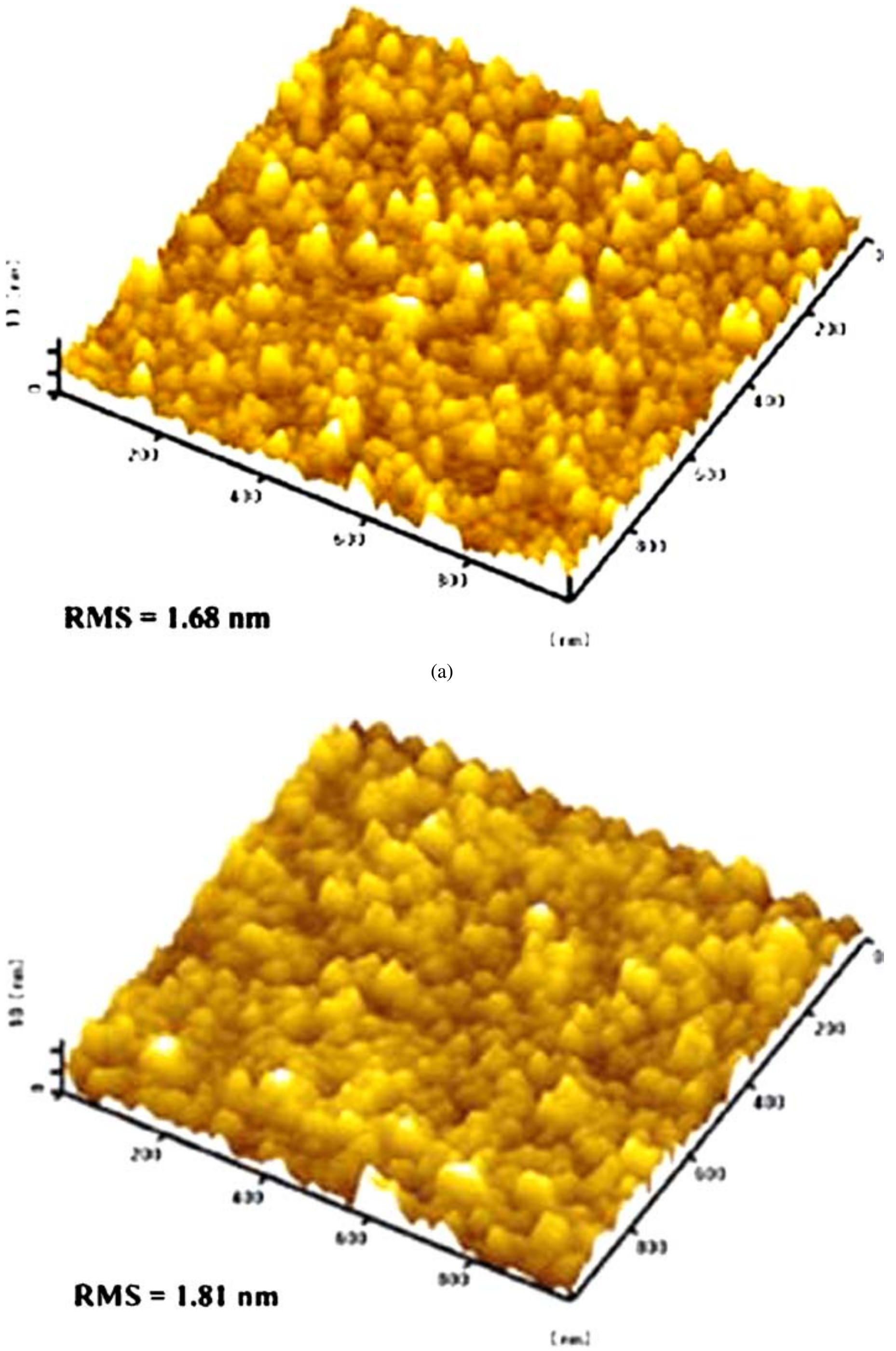
(a)

(b)

Figure 1 Effect of laser energy density on surface morphology of STO thin films: (a) 2 J/cm^2 and (b) 1 J/cm^2.

are purely *a*-axis oriented. No grains with other orientation and no impurity phases were detected. Typical full width at half maximum (FWHM) values of the rocking curves ranged from 0.6° to 0.8°. It shows that the out-of-plane orientation of the films is good. The Φ scan spectrums of the films showed that the orientation of the STO films is identical with LAO substrate. The crystallographic orientation relationship between LAO substrate and STO films in *a*-*b* plane is [100] STO//[100] LAO. The STO thin films are heteroepitaxial grown. Because substrate temperature is the primary factor to affect crystallinity of thin films, and the substrate temperature was selected to be optimal for STO epitaxial growth on LAO substrate in this study, so the energy density, oxygen partial pressure and substrate surface morphology have a weak impact on crystallinity of epitaxial STO films. There is little difference between the XRD patterns of STO films.

The effect of laser energy density on surface morphology of STO thin films is shown in Fig. 1. The STO thin films shown in Fig. 1a and b were prepared with laser energy density of 2 and 1 J/cm^2 respectively. The root mean square (RMS) values of surface roughness for STO thin films shown in Fig. 1a and b were 0.78 and 1.68 nm which equal to about 2 and 4 STO unit cells respectively. From the surface morphology shown in Fig. 1, It can be concluded that the laser energy density is an important factor to determine the growth



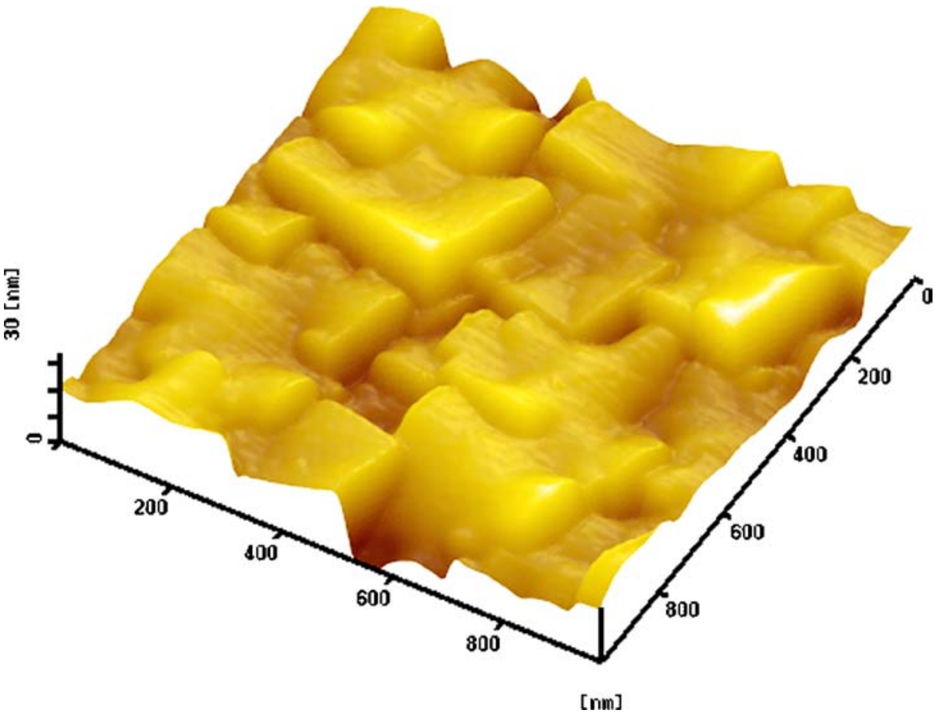
(a)

(b)

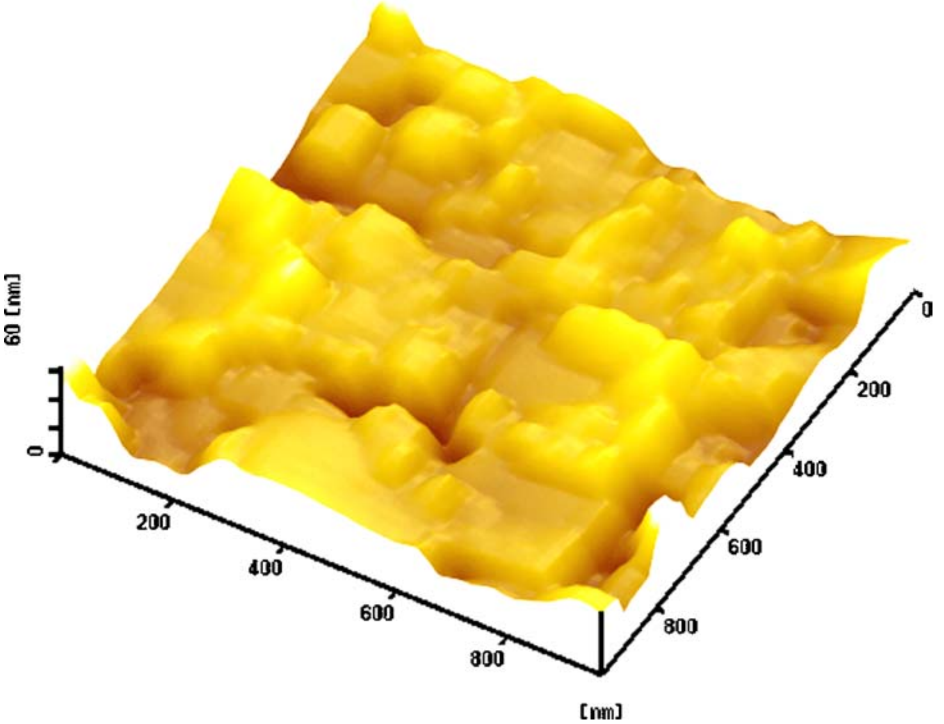
Figure 2 Effect of substrate temperature on surface morphology of STO thin films: (a) 740°C and (b) 680°C.

mechanics. High energy density is benefit to two dimensional layer-by-layer growth.

The experimental evidence observed in this study is different from that reported by Song [12]. Song reported that the amplitude of RHEED oscillation decreased with increasing of laser energy density, which implied that low energy density is benefit to layer-by-layer growth. It should be noticed that the energy density was adjusted by changing the total output laser fluence in Song's experiment. With high output laser fluence the influx of adatoms was large. The deposition rate was high. Therefore the density of nuclei was large. So the growth mechanism was dominated by the nucleation process, and island growth was favorable. In this study, the energy density was adjusted by changing the size of focused laser spot. The total output laser fluence was kept unchanged which yielded a constant deposition rate. With high laser energy density the adatoms arrived at the substrate surface with high kinetic energy, and the mean free distance of diffusion for adatoms is

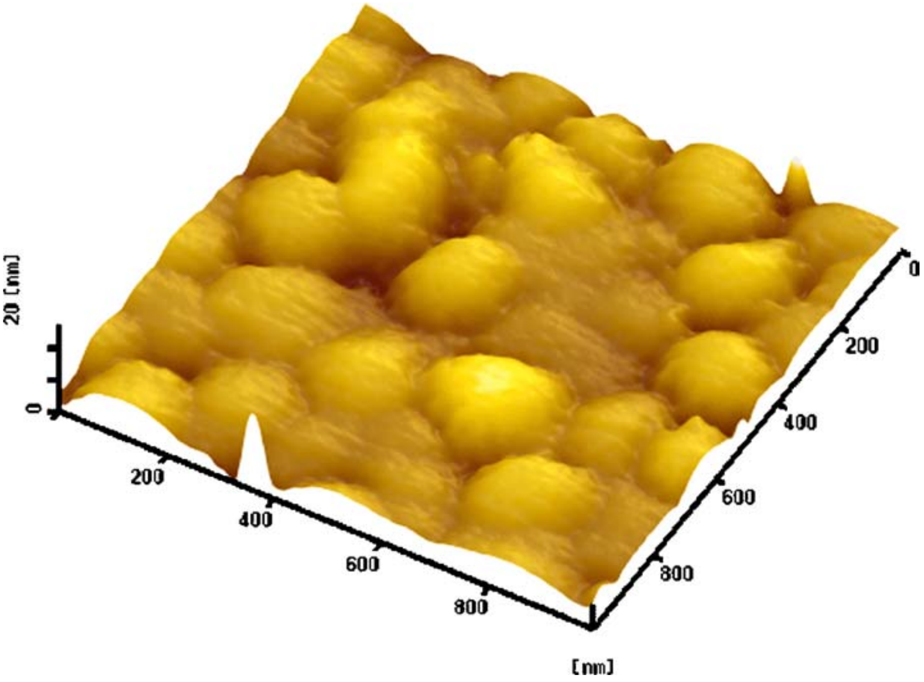


(a)



(b)

Figure 3 Effect of oxygen pressure on surface morphology of STO thin films: (a) 10 Pa, (b) 20 Pa, and (c) 30 Pa. (*Continued*)



(c)

Figure 3 (*Continued*)

large. So STO thin film growth was determined by the growth process. High energy density was found to be benefit to layer-by-layer growth.

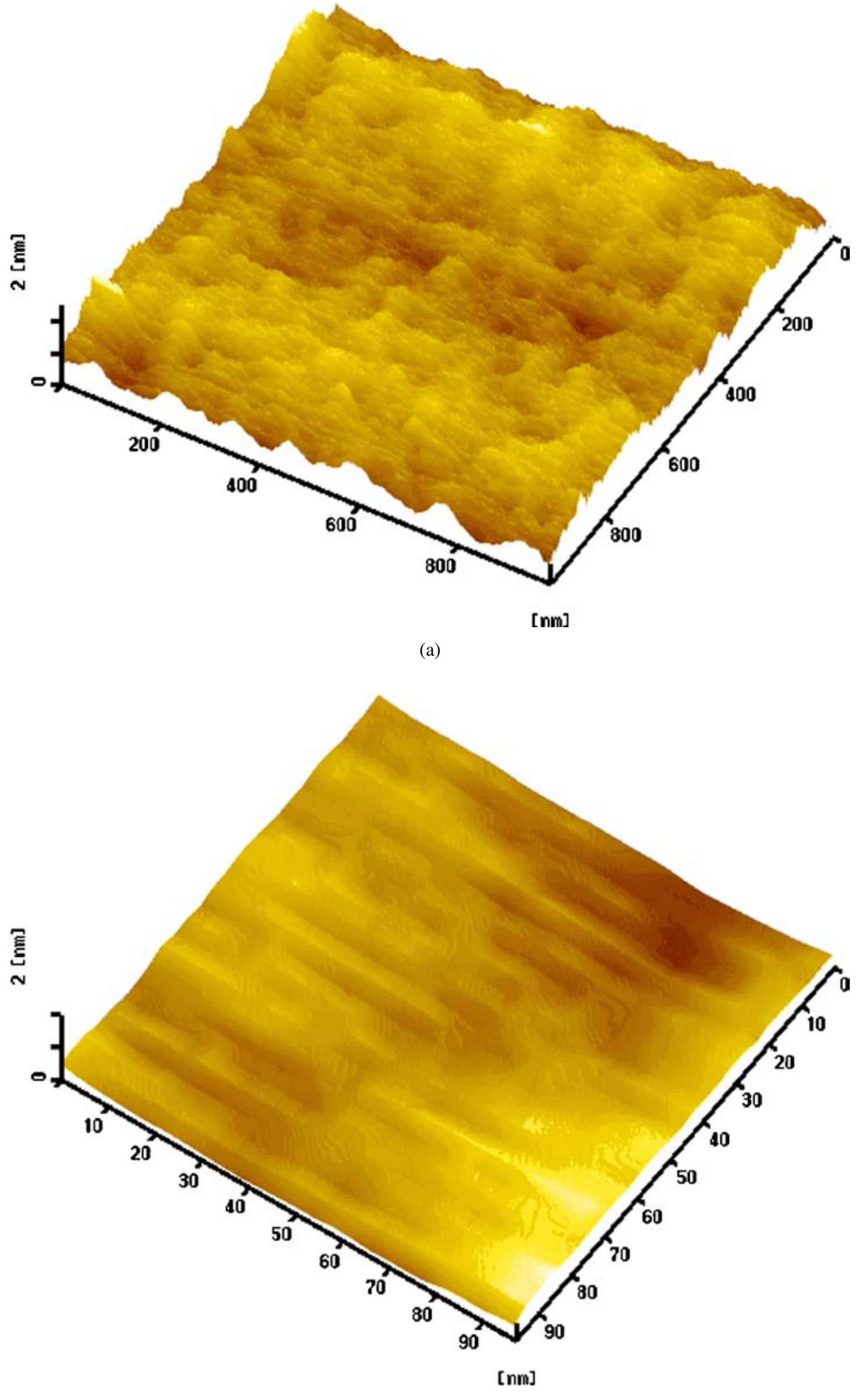
The effect of substrate temperature on STO thin film surface morphology is shown in Fig. 2. The STO thin films shown in Fig. 2a and b were deposited at 740 and 680°C respectively. The RMS values of surface roughness were 1.68 and 1.81 nm respectively. Although no significant differences about surface roughness were observed, the density of nuclei between the two films were different. The nuclei density for STO films deposited at high temperature is lower than that deposited at low temperature. Except laser energy density, the diffusion coefficient of adatoms is affected by substrate temperature. High temperature, which results in large diffusion coefficient, large mean free diffusion distance of adatoms, and low nuclei density, is benefit to layer-by-layer growth of STO thin films. Island growth prevails at low substrate temperature.

The diffusion coefficient of adatoms is correlated with oxygen pressure. In general, low oxygen pressure results in high diffusion coefficient of adatoms and low density of nuclei. The effect of oxygen pressure on STO thin film surface morphology is shown in Fig. 3. The STO thin films shown in Fig. 3a, b, and c were deposited at oxygen pressure of 10, 20, and 30 Pa respectively. Different characters of surface morphology were observed. The STO thin films deposited at low oxygen pressure showed pellicular square grains which resulted in large diffusion distance of adatoms and low nuclei density as shown in Fig. 3a. As the oxygen pressure increase, because of inceased nuclei density, small spherical grains appeared as shown in Fig. 3b. The STO thin films grown at high oxygen pressure were characterized by spherical grains as shown in Fig. 3c.

Besides the growth parameters, the growth mechanism of STO films depends on substrate surface morphology. It has been frequently shown that there is little reproducibility in properties of thin films because of different substrate morphology. The controlling of substrate surface morphology is very important for ensuring run-to-run reproducibility. One approach to control the substrate surface morphology is to employ surface treatments, such as annealing of substrate at high temperature. Some evidence has been shown that annealing of STO single crystal substrate in oxygen can produce a periodic step-terraced substrate surface. The surface morphology of untreated LAOsubstrate is very flat and featureless. In contrast to the polished substrate, a periodic step-terraced substrate, which resulted from annealing of LAO substrate at 1000°C in flowing oxygen for 2 h, was observed. The morphology of STO thin films grown on step-terraced substrate is shown in Fig. 4. STO thin films deposited on step-terraced substrate is very smooth. The RMS value of surface roughness over 1 μm × 1 μm scan area is 0.3 nm, which is less than one STO unit cell. STO thin films with atomic flat surface has been prepared on step-terraced LAO substrate by PLD. A clear step-terrace morphology is observed in a 10 times magnification image as shown in Fig. 4b. The periodic steps act as preferential nucleation sites for adatoms, which leads to a step-flow growth of STO thin films. However, on untreated commercially polished LAO substrate with no step-terraced surface, the STO thin films nucleates as numerous islands and grows by adding materials to the circumference of these growing islands, which is known as island growth.

4. Summary

Besides the growth parameters, such as laser energy density, substrate temperature and oxygen pressure, the substrate surface morphology influences the heteroepitaxial growth dynamics of STO thin film. High laser



(a)

(b)

Figure 4 Surface morphology of STO films grown on step-terraced substrate: (a) 1 μm × 1 μm and (b) 0.1 μm × 0.1 μm.

energy density is benefit to two dimensional layer-by-layer growth. Island growth prevails at low substrate temperature. High oxygen pressure resulted in spherical STO grains. STO thin films with atomic flat surface has been prepared on step-terraced LAO substrate.

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