Structure Stability of $LaAlO_3$ Thin Films on Si Substrates *

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A series of amorphous and single-crystalline $LaAlO_3$ (LAO) thin films are fabricated by laser molecular-beam epitaxy technique on Si substrates under various conditions of deposition. The structure stability of the LAO films annealed in high temperature and various ambients is studied by x-ray diffraction as well as high-resolution transmission electron microscopy. The results show that the epitaxial LAO films have very good stability, and the structures of amorphous LAO thin films depend strongly on the conditions of deposition and post-annealing. The results reveal that the formation of LAO composition during the deposition is very important for the structure stability of LAO thin films.

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$LaAlO_3$ (LAO) is one of the perovskite oxide materials and is an insulator with a band gap of above 5 eV. LAO single crystal wafers have been widely used as the substrates for growing perovskite oxide thin films in superconducting and ferroelectric devices as well as in optical devices.[1−6] In recent years, LAO has been extensively studied as one of the most promising alternative gate dielectrics for future ultra large-scale integrated devices due to the advantages such as high dielectric constant of about 26, wide band gap, and keeping amorphous structure up to a high temperature of 850°C.[7−9] Previously, we reported heteroepitaxial growth of LAO films on Si substrates[10] and high quality amorphous LAO thin films grown on Si substrates without Si interfacial layer[11] as well as the characteristics of amorphous LAO thin films.[12−14] Unfortunately, there are two main problems for the LAO thin films grown on Si substrates. One is that a thin interfacial layer of an amorphous SiO_2 phase or metal silicides is often formed during the films growing or post-annealing. The other is that the structure of the films is not stable if they are directly deposited onto Si substrates under the lower temperature, because the films are a mixture of aluminium oxide or lanthanum oxide. Recently, compounds of La_2O_3, Al_2O_3 and LAO have drawn wide attention and been considered as another potential candidate for gate oxides.[9,15] However, the stability and repeatability of the structure and property are not good enough. From the point of view of practical application, it is very important to study the stability and repeatability of LAO thin films. We study the thermal stability of the amorphous LAO thin films on Si substrates by high-resolution transmission electron microscopy (HRTEM) and find that the characteristics of LAO thin films depend strongly on the conditions of the fabrication and subsequent annealing.[12] In this Letter, the structure stabilities of the amorphous and epitaxial growth LAO thin films on Si substrates are further studied by x-ray diffraction (XRD). The high-quality amorphous LAO thin films and single crystal LAO thin films on Si substrates have been fabricated. Our results indicate that the two-step method is one of the best methods to obtain high-quality LAO thin films, and the formation of LAO composition during deposition is very important for the structure stability of LAO thin films.

A series of amorphous LAO thin films and single crystal LAO thin films on Si substrates were fabricated by laser molecular-beam epitaxy (MBE) technique. Details of the laser MBE system were reported elsewhere.[16] As mentioned in our previous reports,[11] for the fabrication of LAO thin films, a focused pulsed XeCl excimer laser beam (about 20 ns, 2 Hz, about 1.5 J/cm^2) was irradiated onto a single crystal LAO target. Before depositing the LAO film, Si substrates were carefully cleaned with acetone, alcohol and deionized water, and then dipped into a 5% HF solution for 20–30 s to remove the native silicon oxide on the Si substrates and to form a hydrogen-terminated surface at the same time. Subsequently, the Si substrates were transferred into the epitaxial chamber immediately. Samples A, B, C and D of the amorphous LAO thin films and sample E of the single crystal LAO thin film used in this study were fabricated under different growth conditions.

For samples A and B, the amorphous LAO was continuously deposited when the Si substrate was heated to 400°C and 2×1 surface structure of Si was

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observed by *in situ* reflection high energy electron diffraction (RHEED). The difference between samples A and B is that the molecular oxygen pressure was 2×10^{-4} Pa for sample A and 1×10^{-1} Pa for sample B during the deposition process.

For samples C and D, a two-step method was used in the fabrication of amorphous LAO films. The difference from the previous report[11] is that about 8 Å (nearly 2 unit cells) LAO film was initially deposited onto the surface of Si substrate at room temperature when the base pressure of epitaxial chamber was pumped to 5×10^{-6} Pa to prevent the formation of amorphous SiO_2 layer. Then the LAO was continuously deposited when the Si substrate was raised to 630°C. An active gas source was introduced into the chamber and a pressure of 3×10^{-2} Pa was kept during the deposition. The difference between samples C and D is that an atomic oxygen source was used for sample C to form an LAO thin film and an active nitrogen source was used for sample D to form an N_2-doped LAO thin film. In order to control the thickness of amorphous LAO films, we grew epitaxially LAO films on $SrTiO_3$ substrates in advance. From the RHEED intensity oscillations, we can know that how many laser pulses correspond to one unit cell of LAO (3.789 Å). Thus, the thickness of the amorphous LAO films can be determined by controlling the number of laser pulses, and the thicknesses for samples A, B, C, and D all were 8 nm.

For sample E of the single crystal LAO thin film, firstly the Sr (nearly 2 unit cells) was deposited onto the Si substrate surface at room temperature to prevent the formation of amorphous SiO_2 layer. Then the Si substrate was raised to 630°C under about 2×10^{-4} Pa O_2. An *in situ* RHEED system and a charge coupled device (CCD) camera were used to monitor the growth process of the LAO thin films. When the RHEED streak pattern of the SrO appeared, the LAO was continuously deposited, meanwhile an atomic oxygen source was introduced into the chamber and a pressure of 3×10^{-2} Pa was kept during the deposition. The thickness of the epitaxial LAO film was 50 nm.

The structure stability of the amorphous and single crystal LAO thin films post-annealed in a quartz tube under various ambients was studied with XRD.

Figures 1 and 2 show the XRD patterns of samples A and B annealed at 1050°C for 20 min and under various ambients: (a) as-deposited, i.e. no annealing, (b) Ar, (c) O_2 and (d) N_2, respectively. The as-deposited films show the amorphous structure. There are three regular peaks appearing in the patterns of Figs. 1(b), 1(c), 1(d) and 2(d). The three regular peaks correspond to the (310), (311) and (800) peak of Al_2O_3, respectively, which means that there are some Al_2O_3 crystallized in the films by the thermal annealing. By comparing the XRD patterns in Figs. 1 and 2, it can be concluded that LAO films deposited in higher O_2 ambient (1×10^{-1} Pa) have better stability than the ones deposited in lower O_2 ambient (2×10^{-4} Pa), and films annealed in O_2 have the stability better than that annealed in N_2 or Ar. The results are in agreement with Rutherford backscattering spectrometry[13] because the LAO films nearly do not have oxygen deficit when the oxygen pressure of deposition is above 10^{-1} Pa.

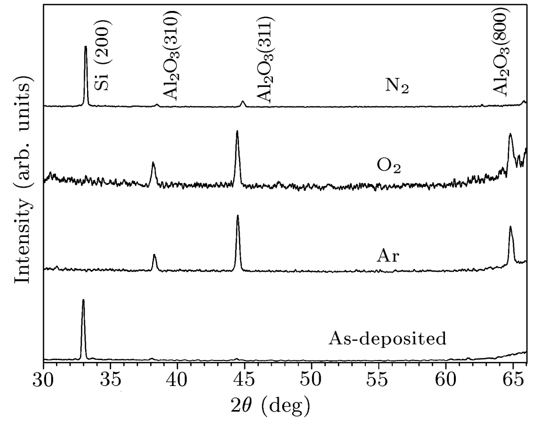

Fig. 1. XRD patterns of as-deposited sample A and post-annealed at 1050°C for 20 min under various ambients: Ar, O_2, and N_2.

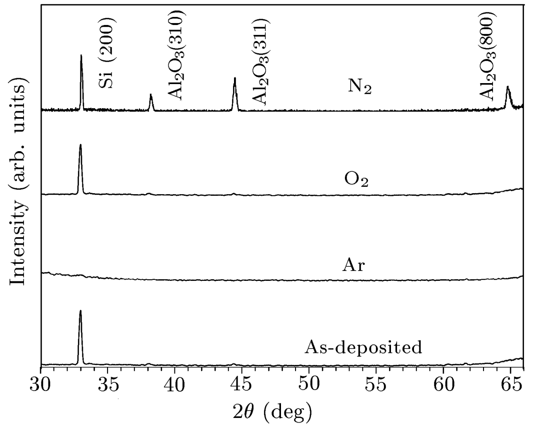

Fig. 2. XRD patterns of as-deposited sample B, and post-annealed at 1050°C for 20 min under various ambient: Ar, O_2, and N_2.

Figure 3 shows the XRD patterns of sample C under the same annealing temperature and time as samples A and B (1050°C, 20 min) and with the various ambients of annealing: (a) O_2 and (b) N_2, respectively. In Fig. 3, except for Si (400) diffraction peak, there is no diffraction peak from impurity phases or randomly oriented grains, which implies that the sample C remains amorphous after annealing at 1050°C for 20 min. Thus sample *C* has much better stability than that of samples *A* and *B*.

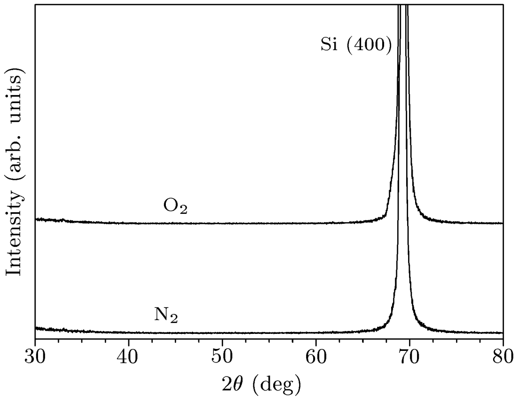

Fig. 3. XRD patterns of sample *C* annealed at 1050°C for 20 min under various ambients: N_2 and O_2.

For sample *D*, under the same annealing temperature and ambients with sample *C*, the XRD patterns shows the same results with sample *C*. Figure 4 shows the cross-sectional HRTEM image of N_2-doped LAO thin film (sample *D*) after deposited poly-silicon and annealed at 900°C for 60 s. The result is in agreement with our previous report on amorphous LAO thin films on Si substrates in Ref. [11]. Almost no interface layer and no interdiffusion can be observed in the HRTEM image, which is consistent with the previous report.[17] The thickness of the thin film measured from the HRTEM image is in good agreement with the thickness obtained by fabrication control. From the results of Figs. 3 and 4, we can conclude that LAO and N_2-doped LAO films deposited with the two-step method at higher temperature (630°C) under an active oxygen or nitrogen have the best structure stability.

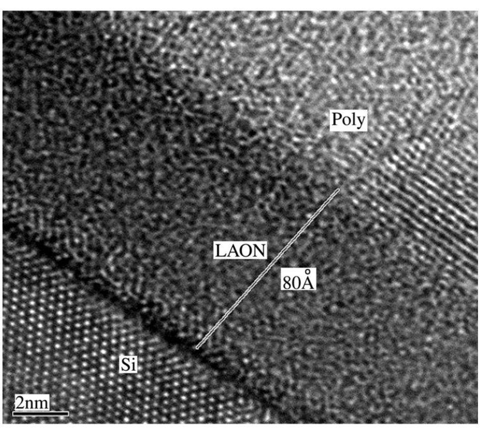

Fig. 4. Cross-sectional HRTEM image of sample D of N_2-doped LAO thin film after deposited poly-silicon and annealed at 900°C for 60 s.

Figures 5 and 6 show the XRD patterns of sample E of epitaxial LAO films on Si substrates annealed at 1050°C under various ambients: N_2 (Fig. 5) and O_2 (Fig. 6), and in the different annealing times: (a) 2 min, (b) 5 min, and (c) 60 min, respectively. According to the XRD patterns shown in Figs. 5 and 6, the epitaxial LAO films on Si substrates have the excellent structure stability even if annealed at 1050°C for 60 min. From the XRD patterns, it is noteworthy from the LAO (300) peak that the crystallinity of the epitaxial LAO films becomes better with the increasing annealing time.

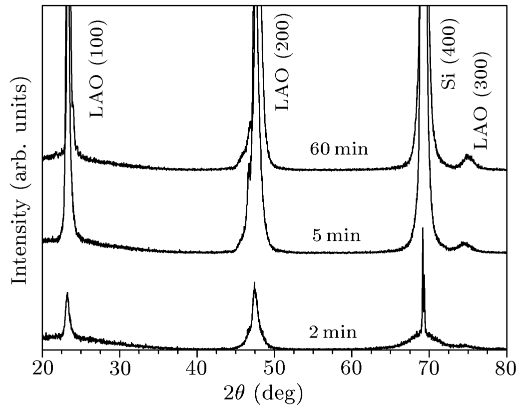

Fig. 5. XRD patterns of sample E of epitaxial LAO film on Si substrates annealed at 1050°C in N_2 ambient for the different annealing times: 2 min, 5 min, and 60 min.

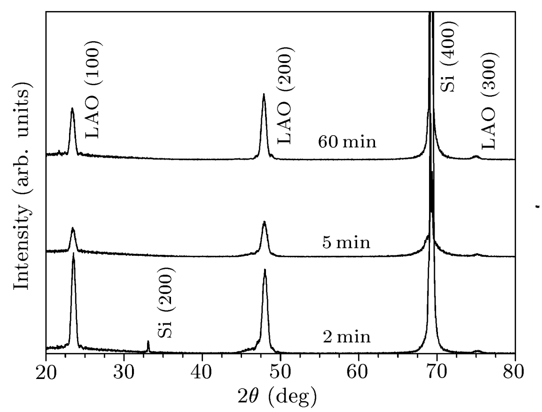

Fig. 6. XRD patterns of sample E of epitaxial LAO film on Si substrates annealed at 1050°C in O_2 ambient for the different annealing times: (a) 2 min, (b) 5 min, and (c) 60 min.

The analysis of all XRD patterns and HRTEM image presented here as well as our previous studies[10−14] show that LAO composition is very stable. The two-step method is one of the best methods to obtain the high-quality LAO thin films grown on Si substrates. The formation of LAO composition during the deposition is very important for the structure stability. The most reasonable explanation may be that the films deposited in lower temperature are easier to form some different compounds during the deposition and post-annealing, such as La_2O_3, Al_2O_3, LAO and so on, because the films deposited in the lower temperature are a mixture of aluminium oxide and lanthanum oxide. In other words, the films deposited in lower temperature are not pure LAO composition. The films deposited with the two-step method at higher temperature (630°C) under an active oxygen or nitrogen have the best structure stability because the films can form the LAO composition during the deposition. Maybe there are three reasons to explain the formation of Si interfacial layer when LAO films were deposited directly on Si wafers at a lower or higher temperature. Firstly, the Si interfacial layer has been formed before the LAO film deposition when the film was deposited directly on Si wafer at the higher temperature. Secondly, the combination reaction between Si and some compounds of aluminium oxide or lanthanum oxide is easier than that between Si and LAO. Lastly, the oxygen can pass through the film into Si interface and react with Si during the deposition and post-annealing because the film of a mixture of aluminium oxide and lanthanum oxide is not so compact. However, the high-quality LAO thin films of single crystal and amorphous on Si substrates can be fabricated by the two-step method, and the films have very good structure stability.

In summary, a series of amorphous and single-crystalline $LaAlO_3$ (LAO) thin films on Si substrates have been fabricated by laser molecular-beam epitaxy technique in various conditions of deposition. The structure stability of the films was systematically studied by XRD as well as HRTEM. The results show that the epitaxial LAO films have excellent stability and the quality of the amorphous films is strongly correlated to the deposition conditions. The LAO and N_2-doped LAO films deposited with a two-step method at higher temperature (630°C) under an active oxygen or nitrogen have the best structure stability, which makes them become one of the most promising high dielectric constant materials for future ultra large scale integrated devices. Furthermore, the epitaxial LAO films on Si substrates are promising for the applications in superconducting, ferroelectric and optical devices.

The RHTEM analysis was carried out at Digital DNA Laboratories, Semiconductive Production Sector, Motorola Inc.

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