Formation of Interfacial Layers in $LaAlO_3$/Silicon during Film Deposition *

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We have studied the interfacial reactions between amorphous $LaAlO_3$ thin films and Si substrates, using high-resolution transmission electron microscopy and x-ray photoelectron spectroscopy. It has been shown that the interfacial layer between $LaAlO_3$ film and Si substrate is $SiLa_xAl_yO_z$. The depth distributions of La, Si and Al chemical states show that the ratio of La $4d_{3/2}$ to Al 2p of the interfacial layer remains unchanged with the depth compared to that of the $LaAlO_3$ film. Moreover, the Si content in the interfacial layer gradually decreases with increasing thickness of the interfacial layer. These results strongly suggest that the Al element is not deficient in the interfacial layer, as previously believed, and the formation of a $SiLa_xAl_yO_z$ interfacial layer is mainly due to the diffusion of Si from the substrate during the $LaAlO_3$ film deposition. With the understanding of the interfacial layer formation, ones can control the interface characteristics to ensure the desired performances of devices using high-k oxides as gate dielectrics.

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Among various potential candidates for the replacement of SiO_2 or SiO_xN_y as gate dielectrics to fabricate smaller and faster metal–oxide–semiconductor transistors,[1] lanthanum aluminate ($LaAlO_3$ or LAO) has been shown to be one of the most promising materials, due to its high dielectric permittivity, excellent thermal stability and low leakage current.[2−5] However, we have found that it is difficult to control the quality of the interfacial layer between LAO films and Si substrates. Namely, a low dielectric constant silicon-oxide layer is easily formed at the LAO/Si interface during deposition and postannealing processes, which makes the effect of the high-*k* oxide dielectric weaken. The interfacial characteristics of oxides/Si structures are significantly dependent on the deposition parameters, such as growth temperature, deposition rate, oxygen fractional pressure and specific growth sequences. Therefore, the optimized deposition conditions could be crucial to growing a high quality high-*k* gate oxide film on the Si substrate. Although some papers report that there is a clear interface in fabricated LAO/Si structures,[6,7] an interfacial layer may often be formed during fabrication of the structures. To fabricate LAO/Si structures with excellent interfacial characteristics, it is still necessary to understand the formation mechanism of the interfacial layers. Li *et al.*[4] has reported that the interfacial layer between LAO and Si is compositionally graded LaAlSiO silicate and Al element is deficient in the interfacial layer during the LAO films deposited at 650°C in O_2. In this Letter, the composition of the interfacial layer of LAO oxide deposited on Si is examined. The results clearly show that the formation of interfacial layers is attributed to the Si diffusion, and the ratio of La to Al of the interfacial layer is in agreement with that of the LAO film in the deposition process at temperatures of above 600°C.

The LAO films were deposited on an n-type (100) Si substrate of two-inch diameter by the laser molecular beam epitaxy (LMBE) technique. Prior to film depositions, Si wafers were cleaned with acetone, alcohol, and dilute HF solution to remove any native oxide layer, producing a hydrogen-terminated surface. The deposition of the LAO films was carried out at an oxygen pressure of 0.1 Pa and a substrate temperature of 700°C. The microstructure and thickness of the LAO films were characterized by a high-resolution transmission electron microscopy (HRTEM). The compositions of the LAO films and the interfacial layers were determined by x-ray photoelectron spectroscopy (XPS).

Figure 1 shows the HRTEM image of the LAO film deposited at 700°C on the Si substrate. The thickness of the amorphous LAO layer is about 6 nm. An interfacial layer with a thickness of about 3.1 nm can be observed in the sample. Additionally, a noticeable bright/dark contrast fluctuation is found in the amorphous interfacial layer. Since a significant amount of Si is present in the interfacial layer and the Si concentration gradually decreases in the direction from the substrate to the LAO layer, which has been confirmed by XPS measurements, the bright/dark fluctuation image of the interfacial layer can be attributed to the composition fluctuation of Si. Interfacial layers with similar characteristics were also observed in the

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LAO/Si samples deposited at 600°C.

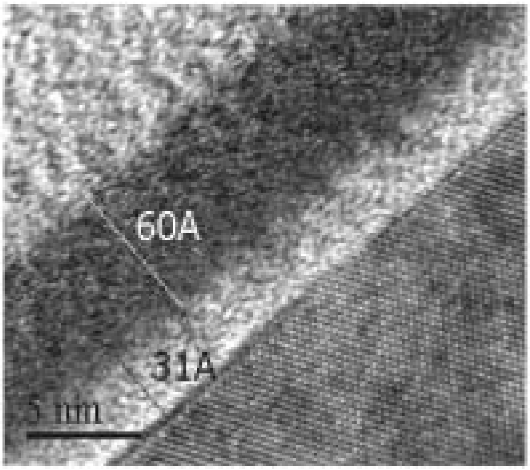

Fig. 1. Cross-sectional HRTEM image of the LAO film deposited at 700°C on a Si substrate.

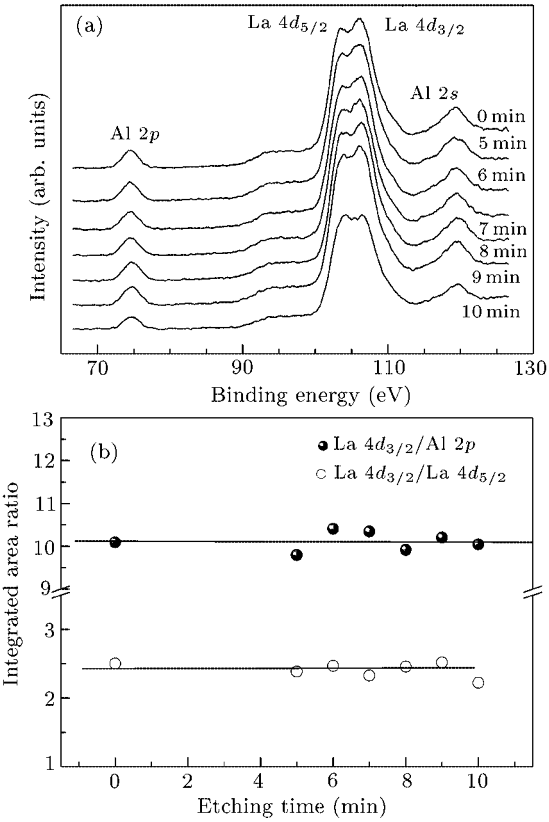

Fig. 2. XPS depth profiles of the La $4d$ and Al $2p$ levels of the LAO/Si structure (a) and the integrated intensity ratios as a function of the etching time (b).

To study the composition variation of the LAO amorphous film and the interfacial layer, the depth profiles of La, Al and Si were examined using XPS. The LAO/Si samples were etched by an argon ion beam (Ar^+). Figure 2(a) shows the XPS depth profiles of the La $4d$, Al $2p$ and Al $2s$ levels after etching for different times. The relative intensities of Al $2p$ and La $4d$ peaks have no obvious change with increasing etching time for the samples etched for 9 min or less. However, after etching for 10 min, intensity of the La $4d_{5/2}$ peak shows a slight increase compared to that of the La $4d_{3/2}$ peak, indicating that the amorphous LAO layer was almost completely removed and the interfacial layer started to appear. This observation will be discussed in the following. The XPS integrated intensity ratios of La $4d_{3/2}$ to Al $2p$ (La $4d_{3/2}$/Al $2p$) and La $4d_{3/2}$ to La $4d_{5/2}$ (La $4d_{3/2}$/La $4d_{5/2}$) as a function of the etching time are illustrated in Fig. 2(b). The ratios are almost constant with increasing etching time, suggesting that the LAO film has a spatially uniform composition distribution.

After removing the amorphous LAO layer, the interfacial layer could easily be studied. Figure 3(a) shows the angle-resolved XPS spectra of the La $4d$, Al $2p$ and Si $2p$ levels of the interfacial layer measured at various escape angles. The XPS intensity ratios of La $4d_{3/2}$/Al $2p$ and La $4d_{3/2}$/La $4d_{5/2}$ as a function of the escape angle are shown in Fig. 3(b). The results can be summarized as follows. Firstly, compared with the spectra of the LAO film, the Si $2p$ peak associated with the Si substrate coexists with the La $4d$ and Al $2p$ peaks, and the relative intensity of the Si $2p$ peak increases gradually with the increasing escape angle, confirming that the information is from the interfacial layer. Secondly, the relative intensities of the La $4d$ and Al $2p$ peaks decrease as the escape angle increases. However, the ratio of La $4d_{3/2}$/Al $2p$ in the interfacial layer is in qualitative agreement with that in the LAO film. The results suggest that the La and Al contents in the interfacial layer decrease with the increasing depth, but the La-to-Al ratio in the interfacial layer does not change in comparison with that in the LAO film, indicating that the Al element is not deficient. Thirdly, the intensity of the La $4d_{5/2}$ peak increases compared to that of the La $4d_{3/2}$ peak with the increasing escape angle. In particular, the intensity of the La $4d_{5/2}$ peak is higher than that of the La $4d_{3/2}$ peak for the 40° profile. It is well known that, in the XPS spectra, the Si $2p$ peaks with a binding energy of 103.2 eV are associated with the Si–O bond of SiO_2, and the ones with a binding energy of 101–102 eV are corresponding to silicates. Because the Si $2p$ peaks are very close to the La $4d_{5/2}$ peaks (102.5 eV),[8] it is reasonably suggested that the La $4d_{5/2}$ peaks in the XPS spectra have been overlapped by the Si $2p$ peaks. Therefore, the increase of intensity of the La $4d_{5/2}$ peaks is attributed to the increase of the Si content. In other words, Si atoms diffused into the LAO film during the deposition process, forming an interfacial layer of $SiLa_xAl_yO_z$. The fact that the ratio of La $4d_{3/2}$/La $4d_{5/2}$ in the interfacial layer decreases with the increasing escape angle indicates that the Si content gradually decreases with the increasing thickness of the interfacial layer.

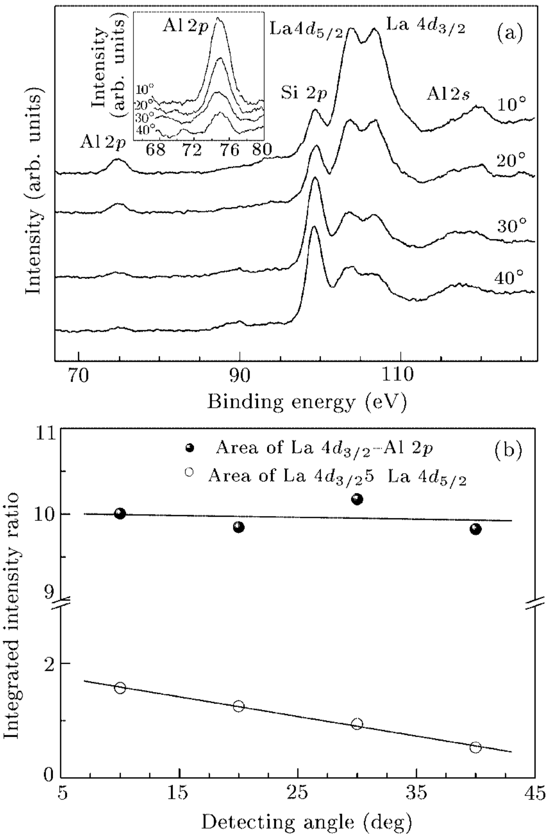

Fig. 3. Angle-resolved XPS profiles of the Si 2*p*, La 4*d* and Al 2*p* levels of the interfacial layer in the LAO/Si structure (a) and the integrated intensity ratios as a function of the escape angle (b).

Previous studies indicated that Si could also be incorporated into high-*k* oxides, such as tantalum oxide and HfO_2,[9,10] where Si diffusion was found to be an important contribution to the formation of interfacial layers. Kageshima *et al.*[11] reported that the emission of Si atoms through the interface plays a critical role in the process of Si oxidation if the thickness of oxide is less than 10 nm. They found that when the oxide layer is very thin, Si atoms can easily diffuse through the oxide to the surface, and emit as SiO molecules or grow as an oxide layer there. However, when the oxide layer is thick, Si atoms mostly diffuse into the oxide layer and are trapped there through the oxidation. In the present study, according to the HRTEM and XPS results, we suggest that the formation of the interfacial layer in the LAO/Si structure is similar to the thermal oxidization process of Si. During the initial stage of the LAO film deposition, the Si surface was fast oxidized by oxygen species. Due to the large volume expansion during the oxidation, the accumulation of strain at the interface between Si substrate and oxide layer should be released effectively by the emission of Si atoms. Therefore, the Si atoms are incorporated into the LAO film, forming a Si-rich $SiLa_xAl_yO_z$ film. With the deposition going on, it would be much more difficult for Si atoms to diffuse through the Si-rich oxide layer. This leads to a decrease in the Si content with the increasing thickness of the interfacial layer. To limit the diffusion of Si atoms during the LAO film deposition, we used a two-step approach to deposit the LAO film. A 0.8-nm LAO layer was firstly deposited at an oxygen pressure of 4×10^{-5} Pa and a substrate temperature of 200°C. Then, the substrate temperature was raised to 600–700°C. Meanwhile, the oxygen pressure was increased to 0.2 Pa. A second layer of LAO with a desired thickness was deposited. It is shown that the diffusion of Si atoms was greatly suppressed and the interfacial layer nearly disappeared.[6]

In summary, we have investigated the compositions of the interfacial layers in LAO/Si structures, using HRTEM and XPS. It has been found that Al element is not deficient in the interfacial layer between the LAO film and Si substrate, which is in direct contradiction to the model proposed previously. Moreover, the Si content in the interfacial layer gradually decreases with the increasing thickness. Obviously, this fact shows that the interfacial layer is formed mainly due to the diffusion of Si atoms from the substrate. Therefore, the ability of controlling the diffusion of Si atoms during deposition and postannealing to reduce or eliminate the interfacial layers is of great significance for the fabrication of high-*k* oxide gate dielectric structures. According to this model, we apply a two-step approach to control the diffusion of Si during LAO film deposition.

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