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Interfacial control of $LaAlO_3$ films deposited on Si (100) using a thin La–Al–Si–O silicate film as the barrier layer

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Abstract

Amorphous $LaAlO_3$ thin films have been deposited by laser molecular beam epitaxy system on Si substrate with an abrupt interface. The formation of the interface between $LaAlO_3$ and silicon was investigated in detail using high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. When several atomic-thick $LaAlO_3$ film was deposited at low temperature and subsequently annealed at high vacuum, a stable Si–La–Al–O silicate thin layer was formed. Using this very thin film as a buffer layer, $LaAlO_3$ films can be deposited with an atomically defined interface at the high temperature and oxygen pressure conditions. With good understanding of the formation mechanism for the interfacial structure, we can control the interface between high-k oxide and Si substrate via optimized deposition parameters and specific growth sequences.

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1. Introduction

The ability of the semiconductor industry to continuously scale down microelectronic devices to ever smaller dimensions is limited by the quantum mechanical effects: as the thickness of the conventional SiO_2 gate insulators is reduced to a few atomic layers, electrons can tunnel directly through the films. Thus, the decrease in device dimensions requires high-k oxides to replace SiO_2 as the gate dielectric in metal oxide semiconductor field-effect transistors [1]. Integration of a high-k oxide with silicon is one of the major challenges. An atomically defined interface between such oxides and silicon substrate without an interfacial SiO_x layer is required for desired performance. As a result, high-k oxides must meet various requirements for practical applications. Firstly, the high-k oxides must be chemically stable in contact with silicon and must have no interface states in the bandgap of silicon. Secondly, the diffusion coefficients of oxygen should be low. Thirdly, they must withstand high processing temperatures. However, it is very difficult to avoid the formation of an unwanted SiO_x layer between high-k oxide and Si substrate during either film deposition or post-annealing step. Recently, $LaAlO_3$ (LAO) has attracted much attention as one of the most promising candidate material to replace SiO_2 due to its known properties such as high dielectric constant (23–25) [2], wide energy bandgap (~5 eV), and excellent thermal stability (~2100 °C). Edge et al [3] and our group [4] have reported LAO films deposited on Si at a low substrate temperature (<400 °C) without substantial formation of interfacial SiO_2. However, it is difficult to avoid the formation of an unwanted SiO_x layer between LAO and Si substrate during the post-annealing [4], which is a particularly demanding step in the conventional metal oxide semiconductor production flow. Similarly, when amorphous LAO films directly deposited on silicon at high substrate temperature (>600 °C) and oxygen pressure (~0.1 Pa), it has been found that a thick interfacial Si–La–Al–O silicate layer between LAO film and Si substrate occurred [4]. Apparently, the quality of the interface between silicon and the oxides depends on the deposition conditions and specific growth sequences used in the experiments. Various

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methods and techniques have been used to control the interfacial characteristics between gate oxides and Si substrates. For example, a monolayer of strontium silicide has been deposited at the interface of $SrTiO_3$/Si grown by a molecular beam epitaxy [5]. In order to control the interfacial structure between gate oxides and Si substrates, in this paper, we report a two-step approach to deposit high-k oxide on silicon. The physical and chemical interactions between the film and substrate were investigated.

2. Experimental details

Amorphous LAO thin films were deposited on Si (100) by a computer-controlled laser molecular beam epitaxy system with a 1×10^{-8} Pa base pressure in the epitaxial chamber. The output of a Lambda Physik LEXTRA 200 excimer laser (308 nm, 20 ns, 2 Hz), which had an energy density of about 1.5 J/cm^2, was used as the deposition source by focusing it onto a single-crystal LAO target. After wet-chemical cleaning, the Si substrate was dipped into HF (~4%) solution for 30–40 s to remove the amorphous layer of native oxide from the silicon surface. Then, the Si substrate was immediately moved into the epitaxial chamber. The LAO/Si samples were prepared using the two-step approach. At the first step, a ~0.8 nm LAO layer was deposited at a background pressure of 4×10^{-5} Pa and a substrate temperature of 200 °C. Then the temperature of Si substrate was increased to 700 °C and kept for 5 min, to form an interfacial control layer (ICL). At the second step, the oxygen pressure of the chamber was increased to 0.2 Pa and the substrate temperature was held isothermally at 700 °C. A second LAO layer (SL) with a desired thickness was deposited at the high temperature and oxygen pressure. For comparison, two additional control samples have been prepared. For the first sample, the LAO film deposited on Si substrate only using the first step of the two-step approach, forming the ICL/Si sample. The second control LAO film was directly deposited on silicon at high temperature (700 °C) and oxygen pressure (0.2 Pa).

Samples for high-resolution transmission electron microscopy (HRTEM) were prepared by standard cross-section techniques with argon ion milling as the final step. The microstructure and thickness of the LAO films were measured using a 200 kV transmission electron microscope (JEOL JEM 2010F) equipped with a field-emission gun, an annular dark-field detector, and a postcolumn imaging filter (Gatan GIF200). The compositions of the LAO film and interfacial layer were examined in an ESCALAB 220i-XL high-sensitivity X-ray photoelectron spectroscopy (XPS) system with monochromatic Al K_α radiation manufactured by VG Scientific. We have used standard analysis techniques and applied them to the XPS data for each of the core levels (Si 2*s*, Si 2*p*, La 4*d*, O 1*s*). Before examining the individual areas of the XPS spectrum, the methods used to obtain information from the raw data are described here. A Shirley background subtraction was performed on all the raw data [6]. After this, peaks were fit with a mixture of Gaussian (80%) and Lorentzian (20%) line shapes to deconvolve multiple peaks that are close together in binding energy.

3. Results and discussion

Cross-sectional HRTEM images recorded along <011> Si of the two samples, directly deposited on Si substrate at high temperature and oxygen pressure and deposited via the two-step approach, are shown in Fig. 1(a) and (b), respectively. The interfacial structures of the two samples are distinguished different from each other. An interfacial layer is observed in the sample directly deposited on Si substrate. The thicknesses of the interfacial layer and LAO film are 3.1 and 6 nm, respectively. Our previous study indicated that the interfacial layer was a mixture of $SiLa_xAl_yO_z$ [4]. In contrast, the sample fabricated via the two-step approach has no distinct interfacial layer.

To understand the mechanism of controlling over the interfacial structure, we examined the structural and chemical properties of the ICL/Si sample. A thin LAO layer was deposited

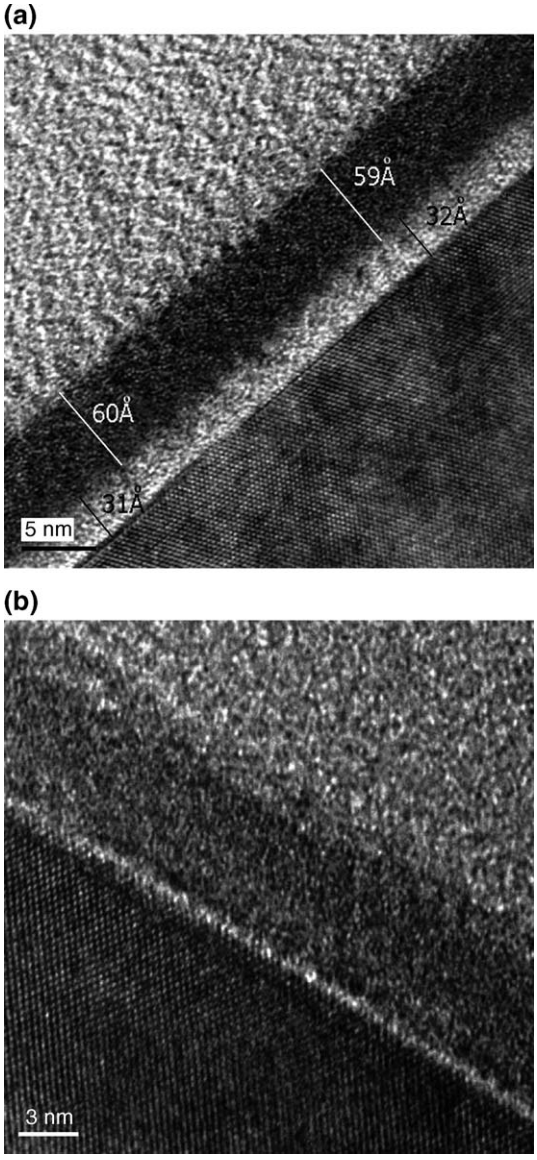

Fig. 1. HRTEM images of the $LaAlO_3$ layers: (a) directly deposited on Si substrate at the oxygen pressure of 0.2 Pa and substrate temperature of 700 °C; (b) deposited via the two-step approach.

on Si at 200 °C, 4×10^{-5} Pa and subsequently high vacuum annealed during the temperature rising from 200 to 700 °C. Fig. 2 shows the HRTEM image recorded along <011> Si of this ICL/Si sample. There are no visible changes compared to the interfacial structure of the sample prepared by two-step approach (Fig. 1(b)), implying a sharp interface maintained before and after the deposition of the second LAO layer. This result indicates that the ICL is very stable at high temperatures (~700 °C) in the oxygen rich environment up to 0.2 Pa. It suggests that the ICL suppressed the formation of an interfacial layer during the deposition of the second LAO layer. Specially, the two samples (Figs. 1(b) and 2) show a slight contrast effect along the direction of the film thickness; a thin white band existing at the film/Si surface. This may be due to the high concentration of Si at the surface of Si substrate [7,8].

Fig. 3 shows the XPS peaks of Si 2*s*, La 4*d*, and O 1*s* for the ICL sample formed by the first step of two-step approach. The binding energies of the core level were calibrated by setting the adventitious C 1*s* peak at 284.6 eV. Si 2*s* spectrum consists of a sharp and strong peak and a small shoulder developed at high binding energy side of the peak (Fig. 3(a)), which can be fitted by two peaks. The low-binding-energy component at 149.5 eV is attributed to bulk Si 2*p* peak of the substrate. The high-binding-energy component at 152.2 eV is attributed to the silicate. Fig. 3(b) shows two XPS spectra of La 4*d* portion of LAO. One was taken for the ICL sample (bottom) and compared to a spectrum taken for a clean $LaAlO_3$ bulk sample (top). In this figure, some differences can also be identified. As the thickness of the LAO film is comparable to the inelastic mean free path of the escaping photoelectrons emitted from the silicon substrate, a clear Si 2*p* peak can be identified at a binding energy of about 99.3 eV in the bottom spectrum. In the XPS spectra, the intensity of La $4d_{3/2}$ peak for pure LAO is higher than that of La $4d_{5/2}$ peak (the top spectrum). However, the intensity of La $4d_{5/2}$ peak for ICL is equal to that of La $4d_{3/2}$ peak, which indicated that the Si atoms are incorporated into the LAO film, owing to the position of Si 2*p* peaks for oxidation state are very close to that of La $4d_{5/2}$ peak of LAO [9]. It is well known that different positions of O 1*s* peaks in XPS spectrum correspond to different oxygen bonds. The peak positions of O 1*s* portion for SiO_2, La_2O_3, and Al_2O_3 are approximately at 533, 528.5, and 531.6 eV, respectively [9]. In our case, only a symmetric peak at 530.8 eV is measured to fall between SiO_2 and metal oxide. No signal from SiO_2 is observed. These results suggest that the chemical composition of the ICL is a silicate of Si–La–Al–O oxide instead of a pure LAO oxide. Furthermore, no SiO_2 layer was formed at the interface.

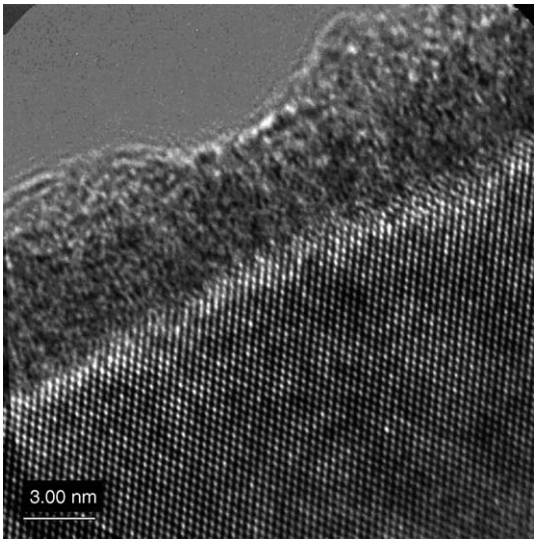

Fig. 2. HRTEM image of ICL formed by the first step of the two-step approach.

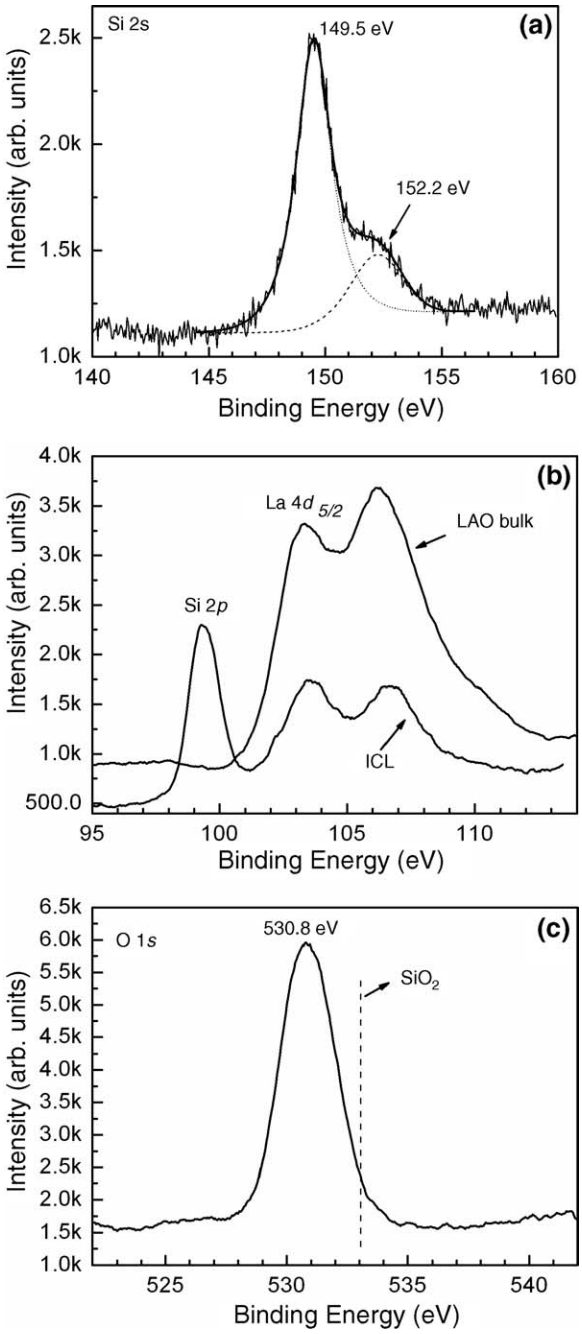

Fig. 3. XPS spectra for (a) Si 2*s* core level of the ICL on Si substrate, (b) La 4*d* core level of the ICL on Si substrate (bottom) and a clean bulk LAO (top), (c) O 1*s* core level of the ICL on Si substrate. The ICL sample was formed by the first step of the two-step approach.

We suggest that the interfacial Si–La–Al–O silicate layer between LAO film and Si can be formed by two mechanisms: (i) oxidation of the silicon surface during the oxide deposition and (ii) a reaction between silicon and LAO oxide. When LAO films are directly deposited on Si at high oxygen pressure, the silicate layer mainly resulted from the oxidation of the silicon surface [10]. The ICL was deposited at low temperature and annealed at high vacuum and temperature conditions subsequently. Then, the ICL of Si–La–Al–O silicate is mainly owing to the second mechanism [11]. It is reported that Al_2O_3 reacts easily with silicon to form SiAlO silicate [12]. In other words, in our two-step approach, we formed a very thin silicate layer (ICL) in the first step by using the reaction between Si and LAO oxide. Specially, this ICL exhibits a property desirable for the deposition of oxide on Si. Compared to the interfacial structure of LAO films directly deposited on Si at the temperature of 700 °C and oxygen pressure of 0.2 Pa, the ICL film is able to prevent the increase of interfacial layers because it is a good diffusion barrier to oxygen and Si. The two-step approach developed in the present letter is similar to the approach for the growth of single-crystal oxide on Si used by Liang et al. [13]. Comparing the two approaches, we have found that the process of vacuum annealing plays an essential role to form the stable ICL. In Liang's report, the Sr/Si (001) reconstructions were unstable with regard to oxidation and the subsequent growth of SrO films. Their results showed the presence of SiO_2 interfacial layer after oxidation and/or SrO growth. However, oxidation of the Sr/Si (001) surface at low temperatures and subsequent annealing of this oxidized surface in UHV at high temperature led to the formation of a stable silicate layer on the Si surface.

Though the formation of such an ICL prevents the increase of the interfacial layer between LAO film and Si substrate, the ICL has a lower dielectric constant. If the ICL is thicker than about several nanometers, the effective dielectric constant of the insulator layer (LAO/ICL) in a MOS structure could be significantly reduced [14]. According to Liang's report [13], a stable silicate could be formed by depositing 0.5 monolayers of Sr followed by oxidation and annealing. Therefore, in order to preserve the benefit of high-k dielectric, experiments are being accomplished, especially concerning the optimum thickness of ICL.

4. Conclusions

In summary, a two-step approach has been used to deposit amorphous LAO on Si substrate, almost without the formation of an interfacial layer, via a laser molecular beam epitaxy. The very thin ICL deposited at low temperature and subsequently high vacuum annealed at high temperature is a silicate of La–Al–Si–O, which exhibits a desirable barrier to prevent the diffusion of Si and O, thus suppressing the formation of an interfacial layer.

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