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Growth of epitaxial γ-Al_2O_3(111) films using an oxidized Si(111) substrate

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High-quality epitaxial γ-Al_2O_3(111) films were grown on a Si(111) substrate covered with a chemically formed 2 nm SiO_2 layer using reactive ionized beam deposition. An epitaxial γ-Al_2O_3 layer was formed at above 800 °C, while the films showed polycrystalline below this temperature. Al_2O_3 films grown on an oxidized Si substrate showed a better crystalline quality, a more flat surface and a sharper interface than the films grown on a clean Si substrate. A thin SiO_2 layer acts as a barrier to prevent a direct reaction of incident Al with Si substrate, the thin layer is consumed during the Al_2O_3 growth to yield an abrupt Al_2O_3/Si interface. The role of the thin oxide layer on the film growth and the chemical reactions at the interface during the initial growth of Al_2O_3 were investigated.

Introduction

The growth of oxide films on semiconductors is of great importance to form high-quality thin insulating layers in metal–oxide–semiconductor devices and in silicon-on-insulator devices. As the scaling down of such devices continues, the currently used amorphous SiO_2 is expected to rapidly reach its physical limits as an insulating layer. To overcome this limitation, a variety of high dielectric materials such as ZrO_2, Ta_2O_5, TiO_2, and Al_2O_3 have been considered to replace SiO_2.[1,2] As for Al_2O_3, much additional effort has been devoted to obtain high quality thin Al_2O_3 layers for use in the magnetic tunneling junction for magnetic random access memory.[3,4] For these applications, a single crystalline Al_2O_3 film would be important, with the full benefit of its excellent electrical, chemical and thermal properties compared with those of any other oxides.

A single crystalline Al_2O_3 film on a silicon substrate was first reported by M. Ishida *et al.*,[5,6] which was grown by low-pressure chemical vapor deposition (LPCVD) using $Al(CH_3)_3$ at a substrate temperature of 1000 °C. Another growth technique, metal–organic molecular beam epitaxy (MOMBE) using aluminium alkoxide and dimethylethylamine–alane,[7,8] has made it possible to grow Al_2O_3 films at a lower substrate temperature. However, carbon contamination at the interface could not be avoided due to the organic by-product of the carrier gas. Although carbon contamination could be avoided by using physical vapor deposition (PVD) such as the magnetron sputtering technique using oxidized Al prelayer and mixed source MBE (Al–N_2O),[9,10] Al_2O_3 films grown on a clean Si substrate at high temperatures showed an obvious degradation in crystalline quality and the interface.

In this work, we present a new way to grow high-quality epitaxial γ-Al_2O_3 films (using an oxidized Si substrate). Using an Al solid source and O_2 gas, it was naturally possible to prepare carbon free Al_2O_3 films. By comparing these with the Al_2O_3 films grown on a clean Si substrate, the role of the oxidized Si substrate was made clear in yielding a higher crystallinity and flatness. Furthermore, the interface mixing of Al and Si at high substrate temperatures, known as spiking,[11] could be suppressed by using the oxidized Si substrate.

Experimental

The 3–5 nm Al_2O_3 films were prepared by ionized beam deposition (IBD). The UHV-IBD apparatus was evacuated to low pressure (10^{-10} Torr). The apparatus was equipped with *in situ* reflection high energy electron diffraction (RHEED). High purity Al (99.999%) was evaporated from a TiB_2-based ceramic crucible at 1500 °C, and then the Al vapor was ionized to be accelerated at 3 kV to the substrate. A detailed description of the Al ion source has been published elsewhere.[12] O_2 gas was introduced into the chamber with a partial pressure of 1.5×10^{-5} Torr during the growth. As a substrate, a vicinal *p*-Si(111) wafer with a 4° miscut angle was cleaned and then chemically oxidized through boiling processes in $NH_4OH : H_2O_2 : H_2O$ (1 : 1 : 5) and $H_2SO_4 : H_2O_2 : H_2O$ (1 : 1 : 5). It resulted in a uniform and flat SiO_2 layers of 2–3 nm thickness.[13] A clean Si(111)-7 × 7 surface was also used as a substrate for comparison. The crystalline quality of the Al_2O_3 films was estimated by RHEED and the surface roughness was measured by atomic force microscopy (AFM). The surface and interface state were investigated by photoemission spectroscopy (PES) using a synchrotron radiation beamline (8A1) at the Pohang Light Source (PLS).[14] High-resolution transmission electron microscopy (HRTEM) operating at 300 kV was also employed.

Results and discussion

Using an oxidized Si(111) substrate, single crystalline epitaxial γ-Al_2O_3 films were successfully grown at substrate temperatures of between 800 °C and 850 °C, chosen from among the wide trial growth temperature range of 500–900 °C. Fig. 1(a) and (b) show the RHEED patterns and the corresponding theoretical diagrams of the Al_2O_3 layer grown on an oxidized Si(111) substrate at 850 °C, as observed from the <110> and <112> axes of the substrate, respectively. The clear streak patterns originate from the flat surface of the grown film and indicate the high crystalline quality of the epitaxial layer. From this, it can be seen that the γ-Al_2O_3 film has a hausmannite structure[15] with an orientational relationship of γ-Al_2O_3(111)‖Si(111), γ-Al_2O_3<110>‖Si<110> and γ-Al_2O_3<112>‖Si<112>. At a lower temperature of 800 °C, as shown in Fig. 1(c), spotty

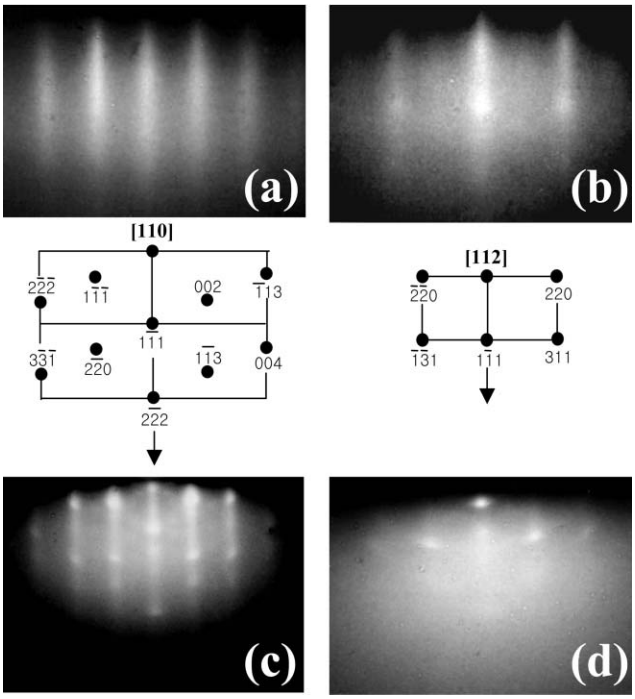

Fig. 1 RHEED patterns along the (a) <110> and (b) <112> azimuth of γ-Al_2O_3 films grown on an oxidized Si(111) substrate at a temperature of 850 °C. RHEED patterns observed along the <110> azimuth of the Al_2O_3 films (c) grown on an oxidized Si surface at 800 °C and (d) grown on a clean Si surface at 830 °C.

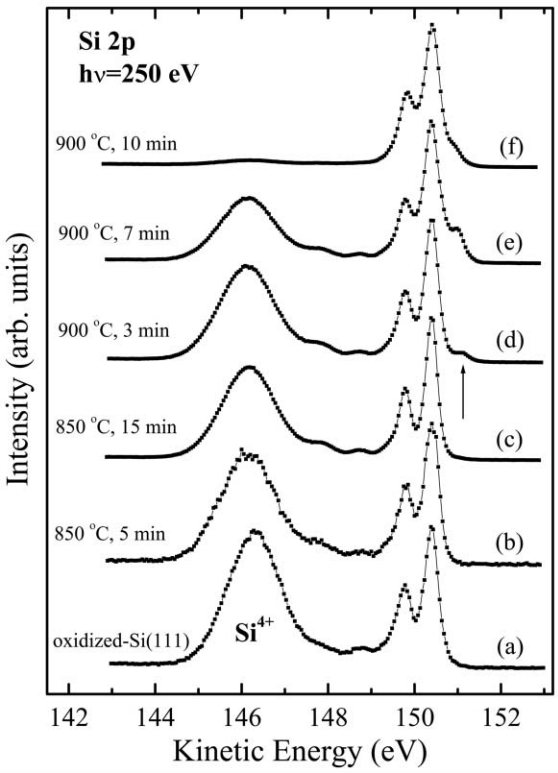

Fig. 2 Temperature and time dependence of the oxidized Si substrate.

patterns appeared including streaks, which indicated that small protrusions existed on the film surface. Below 750 °C, the streak patterns completely disappeared and ring and spot patterns were observed instead. The Al_2O_3 films were also grown on a clean Si(111)-7 × 7 substrate. Fig. 1(d) shows the RHEED pattern of such a film grown at 830 °C, which shows only spots and a faint ring. From the RHEED results, it is evident that: (i) the substrate temperature needed to grow an epitaxial γ-Al_2O_3 film is above 800 °C; and (ii) a chemically oxidized Si substrate is very effective for growing high quality epitaxial γ-Al_2O_3 films.

Because the growth temperature for an epitaxial alumina film was over 800 °C, the silicon oxide layer might be removed through a thermal decomposition process before Al_2O_3 deposition. It has been known that the thermal decomposition temperature of a thin SiO_2 layer depends on the oxide thickness and type.[16,17] Therefore, the surface state of the oxidized Si(111) substrate was investigated just before Al_2O_3 deposition. Fig. 2 shows the high resolution Si 2p photoemission spectra of an oxidized Si substrate and also shows the thermal behavior of a 2 nm thick silicon oxide layer. As the temperature increased up to 850 °C, the Si^{4+} peak (SiO_2) shows a little decrement, but no further decrease occurred up to 15 min heating, as shown in Fig. 2(b) and (c). Thermal decomposition of the SiO_2 network began at the elevated temperature of 900 °C. As heating continued the total amount of Si^{4+} peak decreased abruptly and the surface peak (indicated by the arrow) caused by the clean Si(111) surface appeared and increased. From this result, it was determined that the the oxide layer was thermally stable up to 850 °C, therefore, the thin oxide layer is maintained just before Al_2O_3 deposition even at high temperature.

Fig. 3(a) and (b) show the Si 2p spectra, taken at a photon energy of 250 eV, before and after the Al_2O_3 growth. In Fig. 3(a), the oxidized Si substrate shows the distinctive Si 2p components for the suboxides (Si^{1+}–Si^{3+}) and for SiO_2 (Si^{4+})[18,19] as well as the clear spin–orbit doublet of Si $2p_{1/2}$ and Si $2p_{3/2}$ from the bulk Si (component B). After the Al_2O_3 (3 nm) growth, the Si^{4+} peak completely disappears due to an SiO_2 consuming process. The Al atoms at the initial growth stage may react with SiO_2 to create a thin Al_2O_3 at the interface. This reaction is speculated to promote a strong adhesion between Al and SiO_2. A similar reaction between Al and SiO_2 to form Al_2O_3 and Si can be found in nature, when metal aluminium penetrates the silicate ceramic at 700–900 °C.[20] In considering the difference of the heat of formation (ΔH_f between Al_2O_3 (-1676 kJ kmol^{-1}) and SiO_2 (-908 kJ.kmol^{-1}),[21] the formation of Al_2O_3 is naturally more favorable and dominant than the formation of SiO_2. Surely, the SiO_2 consuming process has a dependence upon the thickness and the density of the SiO_2 layer. Although the oxide thickness was not mentioned, H. Iizuka *et al.*[7] reported that Al_2O_3 layers grown on a thermally oxidized silicon surface were polycrystalline. In our own experiments, for comparison, the Al_2O_3 layers were also grown on an O_2 bubbled SiO_2 layer of 8 nm thickness, which also showed polycrystalline. Thus, it is likely that a critical thickness of the SiO_2 layer is needed for the Al_2O_3 layer to grow epitaxially. We suggest the optimum thickness of SiO_2 to be around 2–3 nm from our results.

The broadened bulk Si peak and the suboxides might be due to intermediate Al–O–Si bondings, which is an inevitable bonding state at the γ-Al_2O_3/Si interface. The exact interface bonding configuration is not clear at present. However, the existence of Al–O–Si bonding is corroborated by the Al 2p spectrum shown in Fig. 3(c), which exhibits a main Al^{3+} peak and a small lower binding peak (component A). That the small component A is energetically located between the oxidized Al^{3+} peak and the metallic Al^0 peak, which has a 2.5–3.0 eV lower binding energy than that of the Al^{3+},[22,23] means, therefore, that it can be attributed to the intermediate Al–O–Si bondings at the interface.

An HRTEM image of a 3.5 nm thick γ-Al_2O_3 (111) film grown on an oxidized Si(111) substrate at 830 °C is presented in Fig. 4. Clear atomic fringes are observed for the first time for an artificially grown γ-Al_2O_3 film. The interface is shown to be incoherent; the γ-Al_2O_3 film maintains its registry right up to the interface and few rigid constraints are observed. Although the Al_2O_3 film was grown on an oxidized Si substrate, no

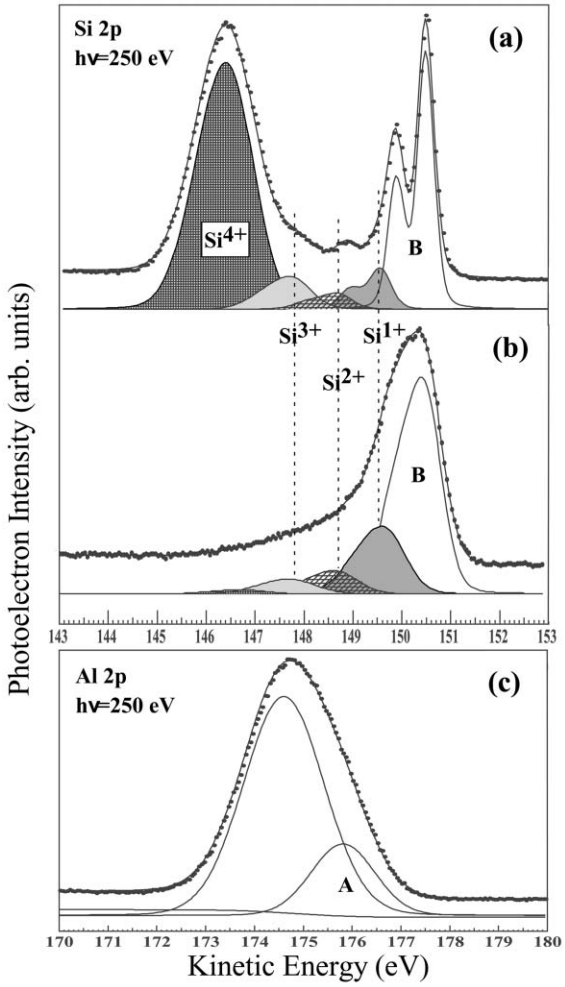

Fig. 3 Si 2p photoelectron spectra for the oxidized Si substrate (a) before and (b) after Al_2O_3 film growth. Each suboxide component is indicated by different shading. Decomposition of Al 2p spectrum is depicted in (c).

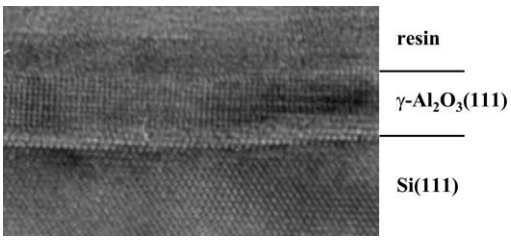

Fig. 4 HRTEM image of epitaxial $Al_2O_3(111)$ film grown on an oxidized Si(111) substrate at 830 °C.

interface SiO_2 layer is observed, confirming an interesting SiO_2 consuming process during the growth.

Fig. 5 shows the root mean square (rms) surface roughness, measured by AFM, of the Al_2O_3 films grown on both kinds of substrates. The surfaces are flattened with increasing substrate temperature, suggesting the improvement of the crystalline quality of the films. The Al_2O_3 films grown on the oxidized Si substrate are smoother overall than the films grown on a clean Si substrate. The rms surface roughness values of epitaxially grown Al_2O_3 films in the optimal temperature of 830 °C are measured as low as 0.4 nm. This atomically flat surface is very desirable for growing epitaxial multi-stacked structures and device fabrications, and this result is comparable with the amorphous Al_2O_3 films grown by atomic layer deposition technique developed for atomic-level thickness control and excellent uniformity.[24–26]

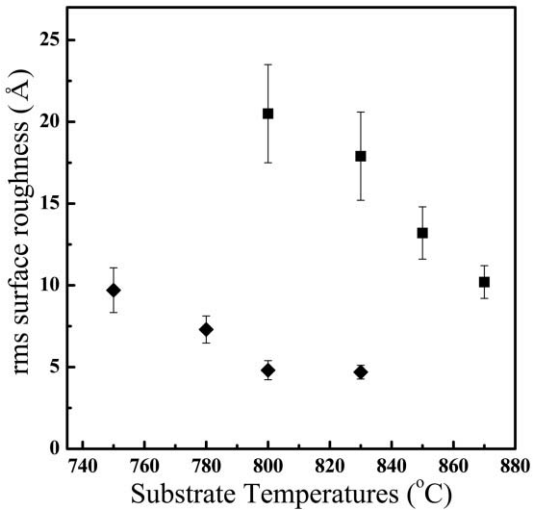

Fig. 5 Temperature dependence of the rms surface roughness of Al_2O_3 films grown on an oxidized Si surface (◆) and a clean Si surface (■).

Conclusions

Epitaxial γ-Al_2O_3(111) films were grown on an Si(111) substrate with a thin SiO_2 layer using reactive ionized beam deposition. The thin chemically formed SiO_2 layer plays an important role in forming the single crystalline γ-Al_2O_3 layers. Through an SiO_2 consuming process, the thin oxide layer prevents the direct reaction of Al and Si substrate to yield an abrupt interface. Therefore, the resulting Al_2O_3 films showed improved film and interface properties compared with the films grown on a clean Si(111) substrate.

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