Epitaxial growth of Al_2O_3 thin films on Si(100) using ionized beam deposition

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Al_2O_3 thin films were epitaxially grown on Si(001) substrates by using reactive ionized beam deposition. The substrate temperature dependence of crystallinity of Al_2O_3 films were investigated by in situ reflection high-energy electron diffraction. The epitaxial γ-Al_2O_3 stacked structure was formed at above 850 °C, and below this temperature the films were polycrystal. Film compositions and interface states were investigated by x-ray photoelectron spectroscopy and transmission electron microscopy measurements. From these results, stoichiometric Al_2O_3 films with sharp interface were confirmed. The rms surface roughness of the epitaxially grown Al_2O_3 film was 0.46 nm, and as the substrate temperatures increased, the crystalline quality and the surface flatness were improved.

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I. INTRODUCTION

High quality thin insulating layer growth on semiconductors is of great importance, which has potential applications as gate dielectric materials for complementary metal oxide semiconductors and silicon-on-insulator devices.1,2 For these purposes, the insulating layer needs to fit some required properties such as high dielectric constant, good crystalline quality, abrupt interface with substrate, and surface flatness of grown film. Aluminum oxide (Al_2O_3) is considered to be a candidate for these applications. An attractive feature of this material is its high dielectric constant (it is more than two times higher than SiO_2) and very low permeability of alkali ions, which prevents device properties from drifting and changes due to migration or diffusion of impurities.

Generally, epitaxial Al_2O_3 films on Si substrate have been grown by low-pressure chemical vapor deposition (LPCVD) and metalorganic molecular beam epitaxy (MOMBE) using Al(CH_3)_3 (tri-methyl aluminum: TMA) and N_2O gas sources.3–6 However, carbon contamination at the interface could not be avoided due to the organic by-product of TMA source dissociation. To date, epitaxial Al_2O_3 films on Si(100) without using a metalorganic source have not been reported. In this work, we present, for the first time, the successful growth of epitaxial Al_2O_3(100) films on Si(100) substrate and high-resolution transmission electron microscopy (HRTEM) images of epitaxial Al_2O_3 film, using an ionized Al beam in O_2 environments.

II. EXPERIMENT

The ionized beam deposition apparatus is equipped with in situ reflection high-energy electron diffraction (RHEED), and the chamber was evacuated to medium 10^{-10} Torr. For the generation of ionized Al beam, an aluminum solid source (99.999% purity) was filled in the TiB_2 based ceramic crucible. The temperature of the crucible was about 1460 °C during deposition, which was measured by an optical pyrometer. The evaporating aluminum vapors were ionized by electron bombardment at the ionization region located above the crucible, then the ionized beam was accelerated by an electric field. Figures 1(a) and 1(b) show the characteristics of ionized beam source. The change of electron beam current, captured at the grid, with varying ionization voltage was plot-
As the ionization voltage increased, the electron beam current continuously increased. Figure 1 shows the current density dependence on the acceleration voltage and ionization voltage, which was detected using a Faraday cup located at the position of substrate. As the acceleration voltage increased, the current density increased and then saturated at every ionization voltage. In addition, as the ionization voltages were increased, the saturation voltages of the current density plots were moved to higher voltages, so current density inversion was detected at a low acceleration voltage region in spite of high ionization voltages. It originated from the lens effect of the source.

During the Al2O3 film deposition, the ionization voltage was 400 V, and the acceleration voltage was fixed at 3 kV. It was optimum voltage to obtain Al2O3 films with high crystalline quality and surface flatness. As the acceleration voltage increased from 0 to 3 kV, the crystallinity of the films improved, on the other hand, surface roughness of the Al2O3 films increased at over 3 kV.

Oxygen gas with a purity of 99.995% was injected into the chamber for the reactive oxygen environments to a partial pressure of $1.5 \times 10^{-5}$ Torr. $p$-type Si(100) with a resistivity of 8–12 $\Omega \cdot \text{cm}$ were used as substrates. The Si substrates were pretreated by a conventional RCA method and heated up to 1000 °C to obtain a clean $2\times1$ reconstructed surface, which was confirmed by RHEED before deposition. The substrate temperature was varied in the range of 750–850 °C. The thicknesses of the grown films were measured by a quartz crystal oscillator. The crystalline quality and composed elements of the grown films were investigated by RHEED, TEM, and x-ray photoelectron spectroscopy (XPS). The XPS data were obtained with a Physical Electronics PHI 5700 ESCA spectrometer using a monochromatic Al $K\alpha$ ($h\nu = 1486.7$ eV) x-ray, with an energy resolution of 0.60 eV. The atomic compositions of the films were estimated from the XPS peak areas using relative sensitivity factors obtained from single crystalline Al2O3 as a reference.

### III. RESULTS AND DISCUSSION

Figure 2(a) shows a RHEED pattern of the Si(100)-2×1 reconstructed surface before Al2O3 deposition. Sharp streaks and Kikuchi lines indicate that the Si substrate is clean and flat. Figures 2(b), 2(c), and 2(d) show the substrate temperature dependence of the Al2O3 films grown at 780, 820, and 850 °C, respectively. The thicknesses of these films were 4–5 nm. The Al2O3 films deposited below 750 °C show an amorphous phase. As the substrate temperature increased, the crystalline quality was improved. As shown in Figs. 2(b) and 2(c), the ring patterns, which mean the Al2O3 films were polycrystal, were clearly changed and a streaky pattern started to appear. Epitaxial Al2O3 films were obtained at the substrate temperature of 850 °C, the RHEED pattern was streaked due to a smooth surface as shown in Fig. 2(d). The
structure of the grown film is that of $\gamma$-$\text{Al}_2\text{O}_3$, which is the structure of hausmannite, a tetragonal distortion of the spinel arrangement with $a_0 = 0.795$ nm and $c_0 = 0.779$ nm, and this result coincides with the earlier report. The orientation relationship between epitaxial $\text{Al}_2\text{O}_3$ film and the Si substrate was found to be $\langle 100 \rangle$, $\text{Al}_2\text{O}_3$/(100) Si with [110] $\text{Al}_2\text{O}_3$/[110] Si. The growth of epitaxial $\text{Al}_2\text{O}_3$ films on (100) Si substrate by LPCVD and MOMBE techniques using a metalorganic source has been reported by Ishida et al., however successful growth using Al solid source in an oxygen atmosphere has not yet been reported. The growth temperature of epitaxial $\text{Al}_2\text{O}_3$ film was 850 °C, which was lower than that using LPCVD (above 1000 °C).

To investigate the chemical bonding states at the interface, XPS measurement was carried out. Figure 3 shows the survey spectrum of $\text{Al}_2\text{O}_3$/Si, and the insets are $2p$ and $2p$ peaks, respectively. From the survey spectrum which was obtained after Ar$^+$ ion gun sputtering for 0.3 min to eliminate the surface contamination, there are no elements except Al, Si, and O. The atomic concentrations of the $\text{Al}_2\text{O}_3$ films were evaluated from the sensitivity factors obtained from single crystalline $\text{Al}_2\text{O}_3$ (Sapphire), and the ratios of Al to O were 0.66–0.68 in all samples, therefore, the films were stoichiometric. In addition, compared with the $\text{Al}_2\text{O}_3$ films grown by CVD, carbon contamination (284.5 eV) was not detected in the XPS resolution limit. As shown in Fig 3(a), the $2p$ peak appearing at 99.3 eV from the substrate shows only Si–Si bonding. It was a very noteworthy result and appeared for all samples. The Si substrate is easily oxidized at high temperature in an O$_2$ atmosphere. Although $\text{Al}_2\text{O}_3$ deposition was carried out above 750 °C in oxygen atmosphere, an interface SiO$_2$ (103.3 eV) was not formed. Therefore, the $\text{Al}_2\text{O}_3$ growth process can be considered to be the competitive process between SiO$_2$ and $\text{Al}_2\text{O}_3$ nucleation in the initial growth stage. It might be caused by the difference of heat of formation values ($\Delta H_f$) between $\text{Al}_2\text{O}_3$ (−1676 kJ/kmol) and SiO$_2$ (−908 kJ/kmol). $\text{Al}_2\text{O}_3$ formation would be more effective and dominant than SiO$_2$ formation, so there is no SiO$_2$ layer at the interface. Similar results had been obtained at an epitaxial Y$_2$O$_3$/Si system, which was reported in our previous work. In addition, the binding energy of Al$2p$, as can be seen in Fig. 3(b), corresponds to that of a single-crystal $\text{Al}_2\text{O}_3$ (75.7 eV) peak, which means that the Al atoms in the grown $\text{Al}_2\text{O}_3$ film were totally oxidized. Therefore, looking at Fig. 3 as a whole, it can be concluded that the sharp interface between $\text{Al}_2\text{O}_3$ film and the substrate was formed without any mixed layer or carbon contamination.

Figure 4 show the cross-sectional HRTEM image of the epitaxially grown $\gamma$-$\text{Al}_2\text{O}_3$ film on Si(100) substrate. The substrate temperature was 870 °C. The $\text{Al}_2\text{O}_3$ film shows surface-parallel fringes, as shown in the TEM image of a single crystalline sapphire, which indicate that the film is not a highly fiber textured structure but a single crystalline. The interface is abrupt to the resolution limit of the instrument and is incoherent, which means that there is no continuity of crystalline planes and lines across the interface. These results agree well with the result of XPS measurements.

Substrate temperature dependence of the surface morphology of $\text{Al}_2\text{O}_3$ films was investigated using atomic force microscopy (AFM). Figures 5(a)–5(c) show the AFM images of $\text{Al}_2\text{O}_3$ films deposited at a temperature of 780, 820, and 850 °C, respectively. As shown in Figs. 5(a) and 5(b), ring patterns from RHEED images, and small circle-shaped grains are observed. However, in the case of epitaxially grown $\text{Al}_2\text{O}_3$ film [Fig. 5(c)], the grains are not observed. As the substrate temperature increased, the film surfaces were more flattened. The rms surface roughnesses of Figs. 5(a)–5(c) were 2.72, 0.95, and 0.46 nm, respectively.

IV. CONCLUSION

Epitaxial $\gamma$-$\text{Al}_2\text{O}_3$ films were grown on Si(100) substrates using ionized beam deposition for the first time. The epitaxial temperature was 850 °C, which was lower than that of CVD technique using a TMA source and was similar to that of the MOMBE process. However, carbon contamination at the interface and in the films was avoided by using this growth technique. $\text{Al}_2\text{O}_3$ films were stoichiometric and formed a sharp interface with the Si substrate. As the growth temperature increased, crystalline quality and surface morphology of $\text{Al}_2\text{O}_3$ films were improved.

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