

Epitaxial growth of Al₂O₃ thin films on Si(100) using ionized beam deposition

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Al₂O₃ thin films were epitaxially grown on Si(001) substrates by using reactive ionized beam deposition. The substrate temperature dependence of crystallinity of Al₂O₃ films were investigated by *in situ* reflection high-energy electron diffraction. The epitaxial γ -Al₂O₃ 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 Al₂O₃ films with sharp interface were confirmed. The rms surface roughness of the epitaxially grown Al₂O₃ 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 (Al₂O₃) 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 SiO₂) and very low permeability of alkali ions, which prevents device properties from drifting and changes due to migration or diffusion of impurities.

Generally, epitaxial Al₂O₃ films on Si substrate have been grown by low-pressure chemical vapor deposition (LPCVD) and metalorganic molecular beam epitaxy (MOMBE) using Al(CH₃)₃ (tri-methyl aluminum: TMA) and N₂O 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 Al₂O₃ 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 Al₂O₃(100) films on Si(100) substrate and high-resolution transmission electron microscopy (HRTEM) images of epitaxial Al₂O₃ film, using an ionized Al beam in O₂ 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 TiB₂ 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-

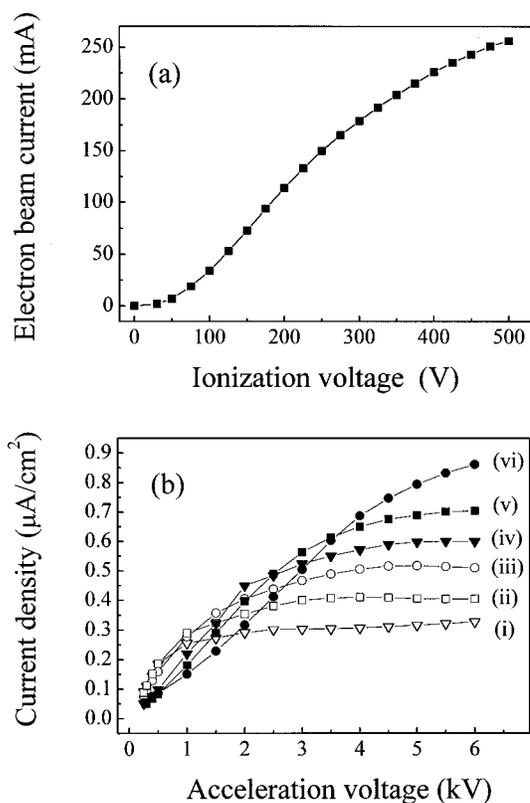


FIG. 1. Characteristics of Al ionized beam source. (a) The changes of electron beam current with varying ionization voltages. The electron beam current was detected at the grid. (b) Current density variations as a function of acceleration voltages at the ionization voltages of (i) 100 V, (ii) 150 V, (iii) 200 V, (iv) 250 V, (v) 300 V, and (vi) 400 V.

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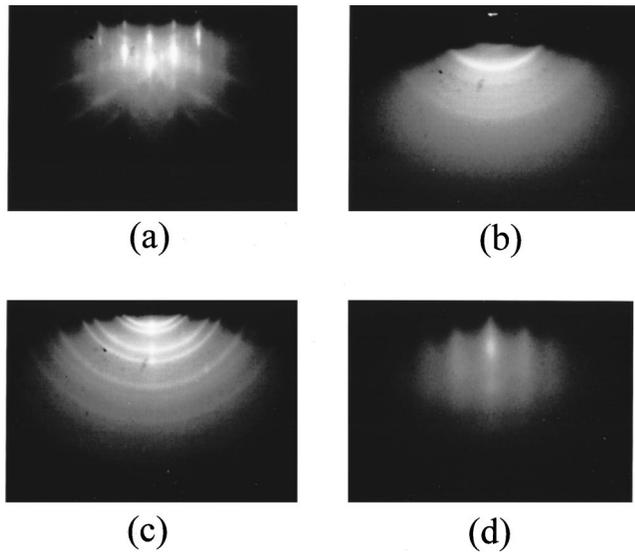


FIG. 2. RHEED patterns of (a) the Si(001)-2 \times 1 substrate before Al₂O₃ deposition, and the Al₂O₃ films grown at substrate temperatures of (b) 780 °C, (c) 820 °C, and (d) 850 °C. The incident electron beam is along the [110] azimuth.

ted as shown in Fig. 1(a). As the ionization voltage increased, the electron beam current continuously increased. Figure 1(b) 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

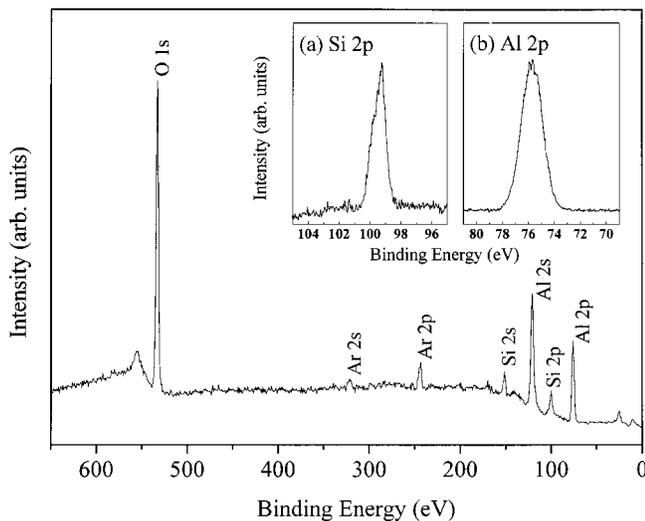


FIG. 3. XPS survey spectrum of the epitaxial Al₂O₃ film grown at 850 °C. Insets (a) and (b) are the spectra of the Si 2p peak and Al 2p peak, respectively.

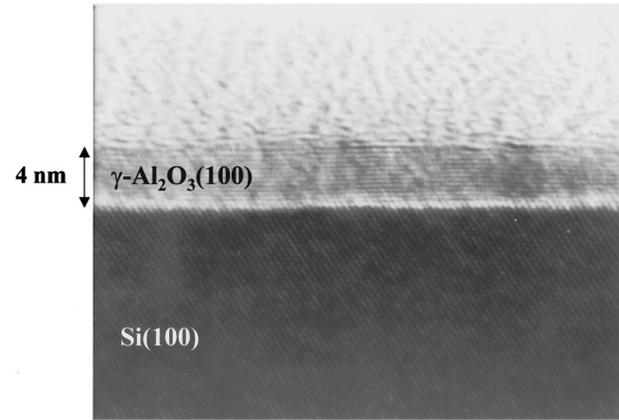


FIG. 4. HRTEM image of Al₂O₃ film on a Si (100) substrate.

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 1.5×10^{-5} Torr. *p*-type Si(100) with a resistivity of 8–12 Ω 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 \times 1 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* α ($h\nu = 1486.7$ 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 \times 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

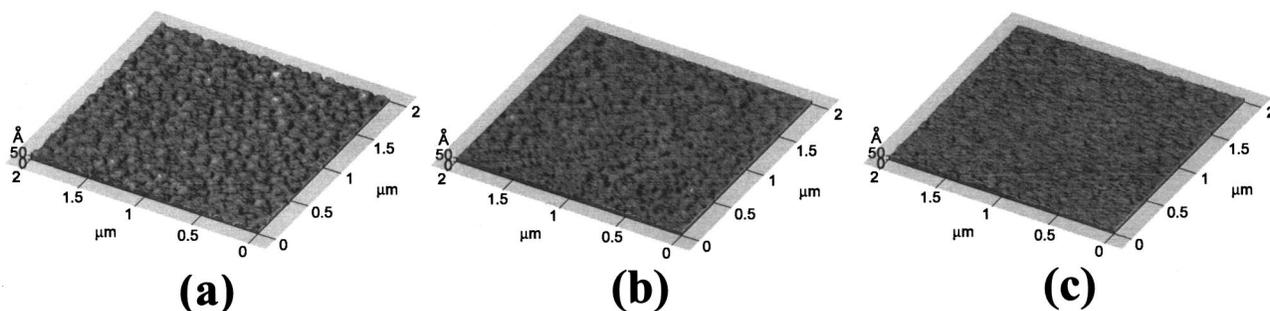


FIG. 5. AFM images of the Al₂O₃ films deposited at substrate temperatures of: (a) 780 °C, (b) 820 °C, and (c) 850 °C.

structure of the grown film is that of γ -Al₂O₃, 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,⁷ and this result coincides with the earlier report.⁶ The orientation relationship between epitaxial Al₂O₃ film and the Si substrate was found to be (100) Al₂O₃//(100) Si with $[1\bar{1}0]$ Al₂O₃// $[1\bar{1}0]$ Si. The growth of epitaxial Al₂O₃ films on (100) Si substrate by LPCVD and MOMBE techniques using a metalorganic source has been reported by Ishida *et al.*,^{3,6} however successful growth using Al solid source in an oxygen atmosphere has not yet been reported. The growth temperature of epitaxial Al₂O₃ 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 Al₂O₃/Si, and the insets [Fig. 3(a) and 3(b)] are Al 2*p* and Si 2*p* 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 Al₂O₃ films were evaluated from the sensitivity factors obtained from single crystalline Al₂O₃ (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 Al₂O₃ films grown by CVD, carbon contamination (284.5 eV) was not detected in the XPS resolution limit. As shown in Fig 3(a), the Si 2*p* 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 O₂ atmosphere. Although Al₂O₃ deposition was carried out above 750 °C in oxygen atmosphere, an interface SiO₂ (103.3 eV) was not formed. Therefore, the Al₂O₃ growth process can be considered to be the competitive process between SiO₂ and Al₂O₃ nucleation in the initial growth stage. It might be caused by the difference of heat of formation values (ΔH_f) between Al₂O₃ (–1676 kJ/kmol) and SiO₂ (–908 kJ/kmol).⁸ Al₂O₃ formation would be more effective and dominant than SiO₂ formation, so there is no SiO₂ layer at the interface. Similar results had been obtained at an epitaxial Y₂O₃/Si system, which was reported in our previous work.⁹ In addition, the binding energy of Al 2*p*, as can be seen in Fig. 3(b), corresponds to that of a single-crystal Al₂O₃ (75.7 eV) peak, which means that the Al atoms in the grown Al₂O₃ film were

totally oxidized.^{10,11} Therefore, looking at Fig. 3 as a whole, it can be concluded that the sharp interface between Al₂O₃ 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 γ -Al₂O₃ film on Si(100) substrate. The substrate temperature was 870 °C. The Al₂O₃ film shows surface-parallel fringes, as shown in the TEM image of a single crystalline sapphire,¹² 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 Al₂O₃ films was investigated using atomic force microscopy (AFM). Figures 5(a)–5(c) show the AFM images of Al₂O₃ 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 Al₂O₃ 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 γ -Al₂O₃ 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. Al₂O₃ films were stoichiometric and formed a sharp interface with the Si substrate. As the growth temperature increased, crystalline quality and surface morphology of Al₂O₃ films were improved.

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- ¹R. Ludeke, M. T. Cuberes, and E. Cartier, *Appl. Phys. Lett.* **76**, 2886 (2000).
- ²E. P. Gusev, M. Copel, E. Cartier, I. J. R. Baumvol, C. Krug, and M. A. Gribelyuk, *Appl. Phys. Lett.* **76**, 176 (2000).
- ³M. Ishida, I. Katakabe, T. Nakamura, and N. Ohtake, *Appl. Phys. Lett.* **52**, 1326 (1988).
- ⁴K. Hayama, T. Togun, and M. Ishida, *J. Cryst. Growth* **179**, 433 (1997).
- ⁵H. Lizuka, K. Yokoo, and S. Ono, *Appl. Phys. Lett.* **61**, 2978 (1992).
- ⁶K. Sawada, M. Ishida, T. Nakamura, and N. Ohtake, *Appl. Phys. Lett.* **52**, 1672 (1988).
- ⁷R. W. Wychoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1965), Vol. 3, p. 84.
- ⁸G. V. Samsonov, *The Oxide Handbook*, 2nd ed. (IFI/Plenum, New York, 1982), p. 22.
- ⁹M.-H. Cho, D.-H. Ko, K. Jeong, S. W. Whangbo, C. N. Whang, S. C. Choi, and S. J. Cho, *J. Appl. Phys.* **85**, 2909 (1999).
- ¹⁰G. Faraci, S. La Rosa, A. R. Pennisi, Y. Hwu, and G. Margaritondo, *Phys. Rev. B* **47**, 4052 (1993).
- ¹¹R. Z. Bachrach, S. B. M. Hagstrom, and S. A. Flodstrom, *Phys. Rev. B* **19**, 2837 (1979).
- ¹²F. A. Ponce, *Appl. Phys. Lett.* **41**, 371 (1982).