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Effect of silicon surface states on the properties of epitaxial Al_2O_3 films

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Abstract

Epitaxial γ-Al_2O_3 films were grown on a chemically oxidized Si(111) substrate by ionized beam deposition. The effects of an oxidized Si surface on the film properties were examined and compared with the results of the Al_2O_3 films grown on a clean Si surface. Al_2O_3 films grown on an oxidized Si surface showed higher crystalline quality, a flatter surface, and a more abrupt interface than those of the films grown on a clean Si substrate. Temperature dependence of Al_2O_3 films on the crystallinity and surface morphology was estimated by reflection high-energy electron diffraction and atomic force microscopy. Chemical composition and interface state of the films were evaluated by X-ray photoelectron spectroscopy and Rutherford backscattering spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Epitaxy; Aluminum oxide; Ionized beam deposition; Interfaces

1. Introduction

Aluminum oxide (Al_2O_3) has attracted great attention from many scientists and engineers, because of its properties such as high mechanical resistance, thermal and chemical stability, very low permeability of various photons, and low electrical conductivity maintained to high temperature. Recently, the capabilities of Al_2O_3 applications on microelectronic devices have been investigated. For example, because Al_2O_3 has a high dielectric constant and is an excellent insulator, it is thought to be a good candidate that substitutes for the SiO_2 gate oxide in metal–oxide–semiconductor field effect transistor (MOSFET) devices [1–3] and the insulating layer in a magnetic tunneling junction for a tunneling magnetoresistance (TMR) device [4,5]. In addition, if the epitaxial stacked structure of $Si/Al_2O_3/Si$ would be possible, the epitaxial Al_2O_3 thin films could be used as a buried oxide in a silicon-on-insulator (SOI) device, because it can effectively reduce the radiation damage of γ-rays [6,7]. For these applications, much effort has been made to obtain high quality thin Al_2O_3 layers.

Al_2O_3 films have been commonly produced by chemical vapor deposition (CVD) and metal-organic molecular beam epitaxy (MOMBE) using various kinds of aluminum sources such as $Al(CH_3)_3$ and $Al(BH_4)_3$ [8–11]. However, Al_2O_3 films grown by these techniques have carbon contamination at the interface due to the organic byproducts, and high substrate temperature or a post annealing process is required to obtain high crystalline quality. Recently, although an atomic-layer deposition (ALD) technique has also been employed to obtain Al_2O_3 films with accurately controlled film thickness and atomically flat surface, most films are amorphous due to the low processing temperature [12]. Therefore, it would be highly desirable to have the alumina thin film growth at a relatively low substrate temperature with no carbon contamination.

In this paper, Al_2O_3 films were grown on two types of substrates, one is clean Si(111) 7×7 surface and the other is a chemically oxidized-Si(111) surface. In our previous report, the oxidized Al prelayer was used for the prevention of Al–Si interdiffusion at high substrate temperatures, and the temperature dependence of interface states was investigated [13].

When the oxidized Al prelayer was used, we could not obtain epitaxial Al_2O_3 films, it was just polycrystalline. However, single crystalline Al_2O_3 films were

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obtained by using a chemically oxidized Si surface. The advantageous effects of an oxidized Si surface on the crystalline Al_2O_3 film growth are presented through the comparison with the results from the clean Si surface.

2. Experimental

High quality Al_2O_3 films with 5–50-nm thickness were prepared on a p-Si(111) substrate by a ultrahigh-vacuum ionized beam deposition (UHV-IBD) system, which is equipped with in situ reflection high-energy electron diffraction (RHEED). The system is composed of a load-lock chamber and a growth chamber. To improve the base pressure and prevent samples from contamination, a liquid nitrogen cold-trap is prepared inside the growth chamber. The base pressure of the growth chamber was low at 10^{-8} Pa.

An Al solid source (99.999% purity) was filled in the TiB_2 based ceramic crucible, which is a fairly inert material to molten Al [14]. The temperature of the crucible was kept at approximately 1460–1550°C during evaporation, as measured by an optical pyrometer. Al vapors were ionized by electron bombardment at the ionization region, located above the crucible, and then accelerated by the electric field. The ionized Al beam was deposited onto the substrate in an oxygen environment. The oxygen partial pressure during Al_2O_3 growth was 1.3×10^{-3} Pa. The details of the deposition conditions and the characteristics of the ion source were reported elsewhere [13,15].

The p-type Si(111) wafers with a resistivity of 1–3 Ω cm were used as a substrate. In this experiment, two kinds of substrate were prepared, one is a clean Si(111) 7×7 surface and the other is a chemically oxidized Si(111) surface. For the clean surface, the wafers were cleaned and dipped in a 5% dilute HF acid solution to remove a native oxide and then rinsed in deionized water. The substrate was dried by pure N_2 gas and loaded into the growth chamber. It was heated up to 1000°C to obtain a clean Si(111) 7×7 reconstructed surface, and checked by RHEED prior to deposition. To obtain the oxidized Si surface, the wafer 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 layer of 2–3 nm thickness on the Si surface [16].

The thickness of the grown films was measured by quartz crystal oscillator and calibrated by Rutherford backscattering spectroscopy (RBS). Atomic concentrations of Al_2O_3 films were measured by RBS and X-ray photoelectron spectroscopy (XPS). For RBS observations, the detector was positioned at 170° with the incident 2-MeV $^4He^{2+}$, and its nominal energy resolution was 21 keV. The stoichiometry of the films were evaluated by using the RUMP program to simulate the experimental spectra [17]. XPS data were obtained with a PHI 5700 ESCA spectrometer using monochromatized Al Kα ($h\nu=1486.6$ eV), with an energy resolution of 0.89 eV. The atomic composition of the films was estimated from the XPS peak areas using relative sensitivity factors obtained from single crystalline Al_2O_3 as a reference. An XPS depth-profiling technique was also employed to elucidate the interface state between the Al_2O_3 film and Si substrate. The crystalline quality of the Al_2O_3 films was estimated by in situ RHEED, permitting simultaneous observation of the film during

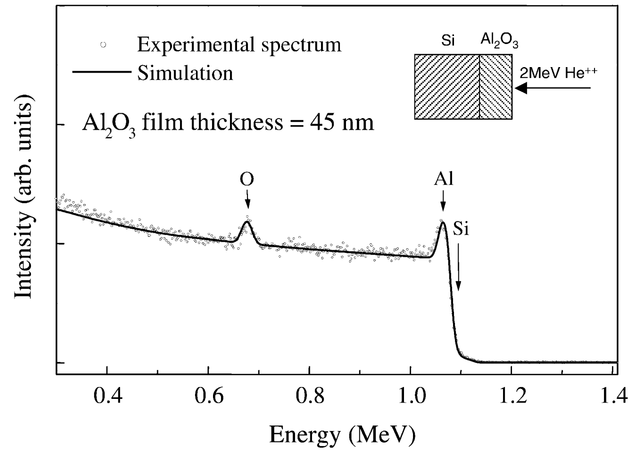

Fig. 1. RBS spectrum of Al_2O_3 thin films with 45-nm thickness.

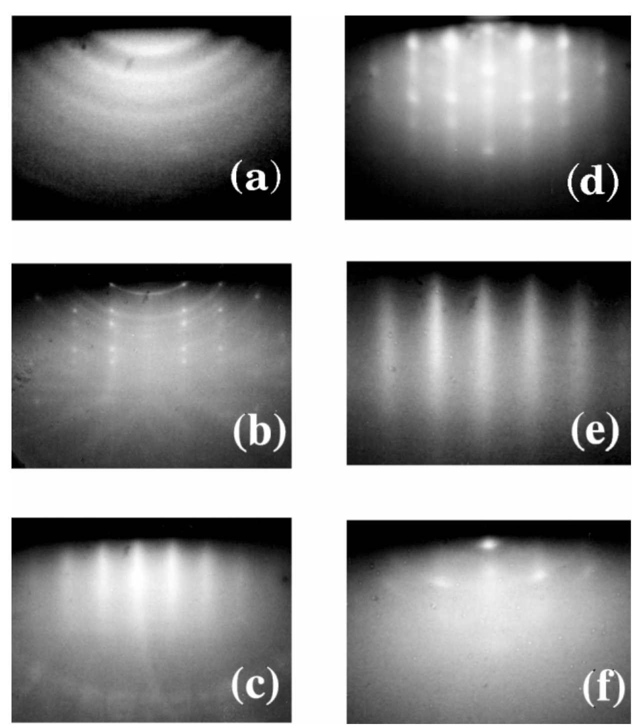

Fig. 2. RHEED patterns of the Al_2O_3 layers grown on an oxidized Si(111) substrate at temperatures of (a) 500 (b) 700 (c) 750 (d) 800 and (e) 850°C. For comparison, the RHEED pattern of Al_2O_3 film grown on clean Si surface is shown in (f). They were observed along the [110] azimuth of the Si substrate.

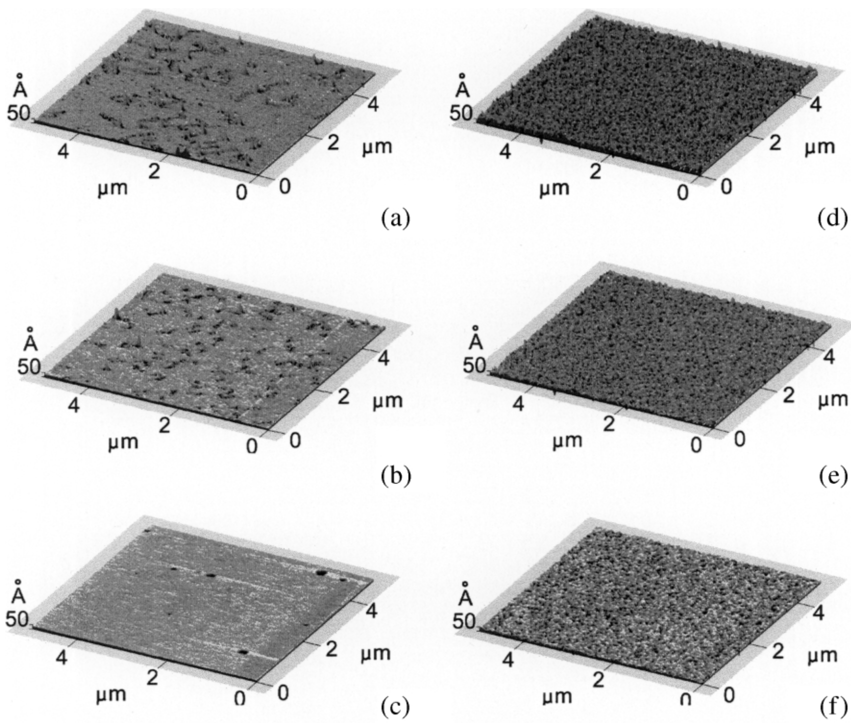

Fig. 3. AFM images of the Al_2O_3 layers (a–c) grown on an oxidized Si(111) substrate (series I), and (d–f) grown on a clean Si(111) substrate (series II). The growth temperatures of (a–f) are 750, 800, 830, 830, 850 and 870°C, respectively.

the growth. The RHEED instrument was operated at the acceleration voltage of 20 kV. The surface morphology was measured by atomic force microscopy (AFM, PSI Co.), under ambient conditions.

3. Results and discussion

The stoichiometry of Al_2O_3 films was investigated by RBS and XPS. Fig. 1 shows the RBS spectrum of the Al_2O_3/Si system and the solid line was obtained from the calculation of the RUMP code. The ratio of the oxygen concentration to the aluminum concentration (C_O/C_{Al}) is estimated to be 1.5, so the Al_2O_3 films are stoichiometric. To confirm this RBS result, XPS was also employed and the single crystalline alumina (sapphire) was used as a reference material. The ratio of signal intensities of Al 2p and O 1s peaks appeared similar to that of sapphire and the values of C_O/C_{Al} were 1.5 ± 0.2 for all samples.

Fig. 2a–e show the RHEED patterns of the Al_2O_3 films grown on an oxidized Si surface at temperatures of 500, 700, 750, 800 and 850°C, respectively. The incident direction of the electron beam was along the [110] azimuth of Si(111) substrate. As shown in Fig. 2a the ring patterns indicate the Al_2O_3 film is polycrystalline and it is obtained at a relatively low temperature. Polycrystalline Al_2O_3 generally appears at temperatures over 600°C. When the temperature increases to 700°C, the ring patterns are cleared and the dim streaks begin to appear as shown in Fig. 2b. Above 750°C, the streaks are sharpened with increasing substrate temperature and the spot patterns appear and are brightened up to 800°C (Fig. 2c,d). The streak patterns are due to a smooth surface and indicate that the grown film is an epitaxial-layer, and the spot pattern means that there exists small protrusions on the film surface. The single crystalline Al_2O_3 films with atomic-scale flatness were obtained at 850°C as shown in Fig. 2e, the RHEED pattern is streaked due to a very smooth surface and high crystalline quality. The structure of the grown film was that of γ-Al_2O_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 [18]. The orientation relationship between epitaxial γ-Al_2O_3 film and the Si substrate was found to be γ-Al_2O_3(111)//Si(111) with γ-$Al_2O_3[\bar{1}10]$//Si$[\bar{1}10]$ and γ-$Al_2O_3[11\bar{2}]$//Si$[11\bar{2}]$ having a lattice mismatch of 2.4%. For comparison, Fig. 2f shows the pattern of Al_2O_3 film grown on a clean Si surface at 830°C, which shows poorer crystalline quality than that of the Al_2O_3 films grown on an oxidized Si surface. As a result, the epitaxial γ-Al_2O_3 films were successfully grown on an oxidized Si(111) surface and showed better crystalline quality, and the temperature for the epitaxial γ-Al_2O_3 growth was over 800°C.

In order to investigate the surface morphology of the

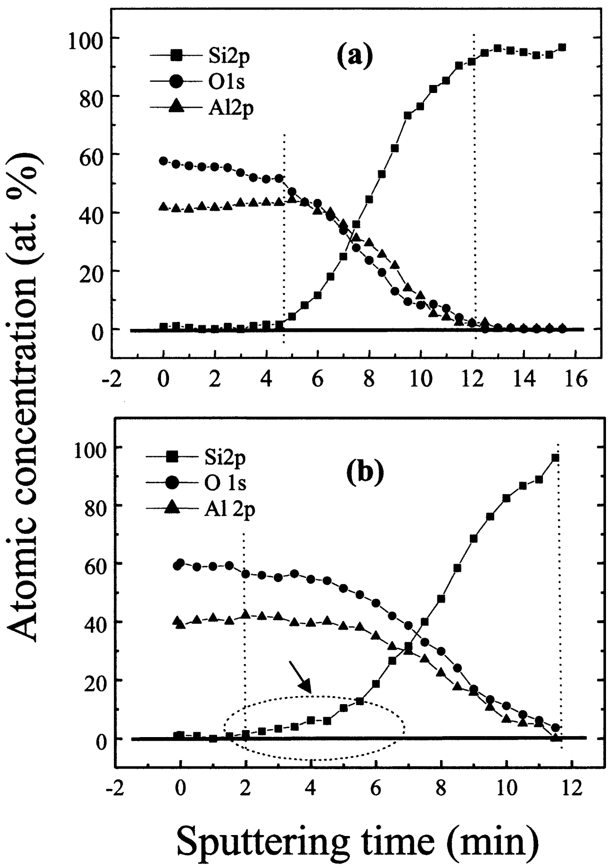

Fig. 4. XPS depth profiling spectra obtained from the Al_2O_3 films grown at 700°C: (a) Al_2O_3/oxidized-Si (b) Al2O3/clean Si.

Al_2O_3 films, AFM measurements were conducted. Fig. 3a–c shows the surface topographies of Al_2O_3 films grown on an oxidized Si(111) surface (series I), and Fig. 3d–f shows that of the films grown on a clean Si surface (series II). The growth temperatures of Fig. 3a–f are 750, 800, 830, 830, 850 and 870°C, respectively. Surface morphologies of the Al_2O_3 films grown on an oxidized Si surface are flat and smooth, compared to those of the films grown on a clean Si surface. As the growth temperature increases, surface roughness of series I and II is improved, but the changes of the grain size are not detected. In the case of series I, the flat area on the surface is enlarged with increasing growth temperature, so that a very smooth surface is obtained at 830°C, its root-mean-square (rms) surface roughness is 0.42 nm and this value is comparable with the results ($\pm$0.3 nm) of the films grown by ALD process [12]. These results show good agreement with the RHEED data.

The interface states of Al_2O_3/Si were also investigated by XPS depth profiling. Fig. 4a,b displays XPS depth profiles of the Al_2O_3 films grown on oxidized Si and clean Si at substrate temperature of 700°C. The chemical compositions (C_O/C_{Al}) of the two samples were 1.49 and 1.52, i.e. the Al_2O_3 is stoichiometric. In this report, we will use the term 'interface region' as the region where the concentration of Si 2p changes from an appearance point, to maximum values in our depth profile. The interface region is denoted as the region between two dotted lines in each depth profile. Regardless of the substrate conditions, the decreasing rate of C_O is higher than that of C_{Al} at the interface region, which is due to the sputtering-yield difference of oxygen and aluminum atoms. After the Al_2O_3 growth on an oxidized Si surface at high temperature, we could not observe that the SiO_2 layer still exists or not as shown in Fig. 4a. The result of high resolution transmission electron microscopy revealed that the SiO_2 layer was consumed during Al_2O_3 growth so that the abrupt interface of Al_2O_3–Si was formed [19]. When the Al atoms are deposited on the thin SiO_2 layer, Al reacts with SiO_2 to create Al_2O_3 at the interface. Simultaneously, it promotes strong adhesion between Al and SiO_2 [20]. Therefore, Al diffused through the resultant, Al_2O_3 layer continuously and the SiO_2 layer is eventually consumed.

In the case of Al_2O_3 growth on a clean Si surface, the Si surface is easily oxidized at high temperature in an O_2 atmosphere. However, although Al_2O_3 growth was carried out above 700°C in an oxygen atmosphere, an interface SiO_2 was not formed as presented in our previous report [15]. Al_2O_3 formation would be more favored than SiO_2 formation at all initial growth stages, because of a much larger negative heat of formation for Al_2O_3 compared to SiO_2 [22]. A much wider interface region is observed for the Al_2O_3 film growth on a clean Si surface, and the outdiffusion of the Si atoms into the Al_2O_3 film is also observed (this region is indicated by the arrow) as shown in Fig. 4b. In other words, the junction spiking has occurred. It is known that direct aluminum–silicon contact exhibits various poor contact characteristics, one of them is a junction spiking phenomenon occurring from the high solubility of silicon in aluminum at high temperature (e.g. approx. 0.5% at 400°C) [21]. Considering the growth temperature of 700°C, it is a sufficiently high temperature to generate the outdiffusion of Si. On the other hand, the interface of Al_2O_3/oxidized Si shows a sharp interface and no outdiffusion of Si atoms. This result implies that the existence of a thin SiO_2 layer of oxidized Si surface plays an important role in improving the sharpness of the interface. The thin SiO_2 layer prevents the direct interactions of Al–Si during Al_2O_3 growth and promotes the crystalline quality and surface flatness of Al_2O_3 films.

4. Conclusions

Single crystalline γ-Al_2O_3 (111) films were grown on Si(111) substrate using a thin SiO_2 layer by ionized beam deposition. The chemically formed thin SiO_2 layer plays an important role in forming the high-quality γ-Al_2O_3 layers. Al_2O_3 films grown on an oxidized Si surface showed higher crystalline quality, a flatter surface and a sharper interface than those films grown on a clean Si surface. The chemical reactions at the interface and the initial growth mechanism of Al_2O_3 on the oxidized Si surface are so complicated that further research is required. The stoichiometry of the Al_2O_3 films was found to be nearly identical to that of sapphire. The temperature for the epitaxial γ-Al_2O_3 layer was over 800°C, and the crystalline quality was improved with increasing growth temperatures up to 850°C. Rms surface roughness of the film grown at optimum conditions is less than 0.5 nm and this atomically flat surface is very desirable for the growth of epitaxial multi-stacked structures, silicon-on-insulator and other devices.

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References

[1] A. Chin, C.C. Liao, C.H. Lu, W.J. Chen, C. Tsai, Proceedings on 1999 Symposium on VLSI Technology, Japan Society of Applied Physics, 1999, p. 135.
[2] E.P. Gusev, M. Copel, E. Cartier, I.J.R. Baumvol, C. Krug, M.A. Gribelyuk, Appl. Phys. Lett. 76 (2000) 176.
[3] R. Ludeke, M.T. Cuberes, E. Cartier, Appl. Phys. Lett. 76 (2000) 2886.
[4] J.S. Moodera, L.R. Kinder, J. Nowak, P. LeClair, R. Meservey, Appl. Phys. Lett. 69 (1996) 708.
[5] T. Miyazaki, S. Kumagai, T. Yaoi, J. Appl. Phys. 81 (1997) 3753.
[6] J.B. Kuo, K-W. Su, CMOS VLSI Engineering Silicon-on-Insulator (SOI), Kluwer Academic Publishers, Boston, 1998, p. 1.
[7] K.H. Zaininger, A.S. Waxman, IEEE Trans. Electron Devices, ED-16, 1969, p. 333.
[8] M. Ishida, I. Katakabe, T. Nakamura, N. Ohtake, Appl. Phys. Lett. 52 (1988) 1326.
[9] W. Koh, S.J. Ku, Y. Kim, Thin Solid Films 304 (1997) 222.
[10] H. Iizuka, K. Yokoo, S. Ono, Appl. Phys. Lett. 61 (1992) 2978.
[11] J.A. Jr. Glass, S.S. Kher, J.T. Spencer, Chem. Mater. 4 (1992) 530.
[12] A.W. Ott, K.C. McCarley, J.W. Klaus, J.D. Way, S.M. George, Appl. Surf. Sci. 107 (1996) 128.
[13] S.W. Whangbo, Y.K. Choi, H.K. Jang, Y.D. Chung, I.W. Lyo, C.N. Whang, Thin Solid Films 388 (2001) 290.
[14] Y. Torii, H. Yamada, Proc. Int' Ion Engineering Congress (1983) 363.
[15] S.W. Whangbo, Y.K. Choi, K.B. Chung, H.K. Jang, C.N. Whang, J. Vac. Sci. Technol. A 19 (2001) 410.
[16] W. Kern, D.A. Puotinen, RCA Rev. 31 (1970) 187.
[17] L.D. Doolittle, Nucl. Instrum. Methods Phys. Rev. B 15 (1987) 227.
[18] R.W. Wychoff, Crystal Structures, 2nd ed., Interscience, New York, 1965, p. 84.
[19] S.W. Whangbo, Y.K. Choi, K.B. Chung, H.K. Jang, C.N. Whang, Material Research Society Symposium Proceedings (2000) (in press).
[20] S. Wolf, Silicon Processing for the VLSI Era, 2, Lattice Press, California, 1990, p. 111.
[21] S. Wolf, Silicon Processing for the VLSI Era, 2, Lattice Press, California, 1986, p. 333.
[22] G.V. Samsonov, The Oxide Handbook, 2nd ed., IFI/Plenum Press, New York, 1982, p. 22.