Electron beam induced orientation selective epitaxial growth of CeO$_2$(100) layers on Si(100) substrates by dc reactive sputtering

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Abstract. From studies on the epitaxial growth of CeO$_2$ layers on Si(100) substrates using reactive dc magnetron sputtering, it has been found that the epitaxial CeO$_2$ layer with (100) or (110) orientation is selectively grown by controlling substrate bias and the growth rate. In order to develop this technology into two dimensional orientation selectivity, we attempt to grow CeO$_2$(100) by low energy electron irradiation, as an alternative way to substrate bias application. It proved that electron beams in two energy regions of 30 ∼ 40 and 80 ∼ 100 eV are effective on preferential growth of CeO$_2$(100) layers. Interfacial structures of CeO$_2$(100)/Si(100) are studied using cross-sectional transmission electron microscopy.

1. Introduction
Epitaxial growth of CeO$_2$ layers on Si substrates has been studied for the application to microelectronics, where CeO$_2$ layers on Si(100) substrates have strong tendency to grow with (110) orientation. [1–3] After the report on CeO$_2$(100) layer growth on Si(100) substrates with atomically cleaned reconstructed surfaces by molecular beam epitaxy, [4] it has been found that orientation selective epitaxy (OSE) of CeO$_2$(100) and CeO$_2$(110) layers on Si(100) substrates are capable by controlling substrate bias and the growth rate in reactive magnetron sputtering. [5,6] The epitaxial relation model of CeO$_2$(100) and CeO$_2$(110) on Si(100) has been proposed with CeSi$_2$(100) layer as intermediate layer [7] and it is reported that CeO$_2$(110) is usually preferred from thermodynamical considerations. [8] This preferential orientation selectivity is thought to be due to surface potential modification by substrate bias. This method has a lot of possibilities for applications to device fabrication processes and for OSE of many other materials. For future sophisticated applications, it is desired to develop a new technology for two dimensionally spatially varied OSE. This article describes a new technology to realize spatially varied OSE utilizing low energy electron beam irradiation, instead of substrate bias application. [9] Here we demonstrate the CeO$_2$(100) layer growth in a low energy electron beam irradiated area on Si(100) substrates and show its crystallinity analyzed by cross-sectional transmission electron microscopy (XTEM), which will give a way to two dimensional OSE growth.

2. Experimental
The p-type Si(100) wafers with resistivities of 15 ∼ 30 Ω·cm were chemically cleaned to make H-terminated surfaces by the following procedure: dipping in a hot aqueous solution of HCl and H$_2$O$_2$ and in diluted hydrofluoric acid, followed by rinsing in deionized water. CeO$_2$ layers were
grown by a dc magnetron sputtering system enhanced with an inductively coupled rf plasma (ULVAC MPS-2000-HC3). The applied power to a target and an induction coil were 120 and 50 W, respectively. Sputtering was performed under a total pressure of 0.13 Pa. We employed the two step growth procedure as reported before. [5,6] Briefly, at first, the metallic Ce layer was deposited using a metallic Ce target of 99.9% purity in the Ar gas flow rate of 7.0 sccm at room temperature. After heating the substrates, CeO$_2$ layers were deposited by reactive sputtering in an Ar and O$_2$ mixture environment, wherein gas flow rates of Ar and O$_2$ were 6.0 and 1.0 sccm, respectively. Substrate temperature at the second step was 800°C.

An electron gun (Biemtron, LEP-5) was equipped toward the sample surface in the angle of 33°. The distance between the electron gun and the sample surface was 50 mm, whose beam diameter was less than 3 mm. The electron source section and electron optics section of the electron gun were separated by serially located two orifices of 3.0 mm in diameter and the electron source section was differentially pumped by a 50 l/s turbomolecular pump. During reactive sputtering, low energy electron beams of 15 ~ 150 eV were irradiated, while the sample holder was grounded. The sample current was measured using a digital multimeter (Keithley 196). CeO$_2$ layer thickness data were obtained by ellipsometric measurements. The thickness and the growth rate of CeO$_2$ layers were 10 ~ 15 nm and approximately 0.08 nm/s, respectively.

Interfacial properties were characterized by XTEM observations (FEI TECNAI S-twin, 300 keV).

3. Results and Discussion

Figure 1 shows the sample current characteristics as a function of electron energy. The upward direction of the vertical axis is negative. Open and closed circles indicate the results measured in an ultra high vacuum (UHV) and in 0.13 Pa Ar, respectively. The sample current in UHV rapidly increases from 10 eV and reaches nearly constant above 30 eV, which is the fundamental characteristics of the electron gun. On the other hand, the sample current in the Ar ambient shows a quite different feature, which has a maximum at 35 eV and then decreases, reaching a zero-crossing point at 60 eV. Above 60 eV, it changes its sign and monotonically increases as a positive current. The zero-crossing at 60 eV is well explained by the ionization cross-section maximum of Ar atoms at ~ 60 eV, [10] where most electrons are consumed to ionize Ar atoms resulting in scarce electrons incident into the substrate surface. As the electron energy increases further, ionized Ar atoms also increase, resulting in a positive sample current due to Ar$^+$ ion increase.

Figures 2 and 3 show an RHEED pattern and a $\theta$-2$\theta$ XRD scan taken from the CeO$_2$(100) sample grown with 90 eV electron beam irradiation, respectively. The RHEED result showed a CeO$_2$(100) pattern of (110) azimuth, which consisted of considerably large spots indicating not so good crystallinity. We can see a large (200) and small (111) XRD peaks in Figure 3. The appearance of the (111) peak indicated that the layer was not purely CeO$_2$(100) single crystalline, wherein the (111) component was estimated to be 5.2% from integrated intensities of the peaks and structure factor data. Full width at half maximum values of the (111) and (200) peaks are 0.923 and 0.605°, respectively.

Since it is commonly recognized that CeO$_2$(100) layers do not grow on non-biased Si(100) substrates except for the growth on
reconstructed surfaces, [4] it is apparent that electron irradiation does have the effect on the CeO$_2$(100) growth. The similar quality CeO$_2$(100) layers were obtained for electron energies in the range from 80 to 100 eV.

In addition, electron energy of 30 ~ 40 eV proved to have the same effect, which was confirmed by RHEED and XRD measurements. As a result, it is clarified that there are two optimum electron energy regions of 30 ~ 40 and 80 ~ 100 eV for the CeO$_2$(100) growth. The orientation preferential growth is thought to be due not to joule heating but to surface potential modification, since electron beam power is estimated to be at most 1.6 mW/cm$^2$, which corresponds substrate temperature rise of ~1°C. On the contrary, it is clarified that electron beams with energies around 60 eV and above 100 eV have little effect on the CeO$_2$(100) growth, resulting in XRD spectra having a main (111) peak and very small (200) and (220) peaks. These are explained as follows: Since the beam current of 60 eV electrons are nearly zero, electron irradiation effects scarcely occur. Electrons above 100 eV may have too much energy to give surface effects. At present, a complete explanation of optimum energy for the CeO$_2$(100) growth has not yet given.

We think that electrons of 30 ~ 40 eV are primarily effective in modifying surface potential. The reason why 90 eV electrons are effective is due that 90 eV electrons should reduce their kinetic energy down to ~30 eV, since they lose energy by ~ 60 eV to ionize Ar atoms. [10] It is not surprising that different sign currents have the same effect, though the sample currents at two optimum electron energies have opposite signs, since the OSE effect is irrespective of the band bending direction. [5, 6]

In order to understand the OSE growth mechanism, it is important to clarify how is the potential modulation at the substrate surface. We think that band bending due to irradiated electrons leads to orientation selection of CeO$_2$(100). [6] Different from OSE by substrate bias application, electron beam induced OSE has potential ability of realizing two dimensionally patterned OSE, where spatial distribution should be an important parameter to be studied. The spread of the potential modulated region outside the electron beam irradiated area must be influenced by migration of electrons, which should correlate with the conductivity of the silicon substrate. We carried out subsidiary experiments of growing CeO$_2$ layers on Si(100) substrates with different resistivities under the same growth condition. The CeO$_2$ layers grown on low resistivity substrates of 1.0 ~ 2.0 Ω·cm had (100) orientation and showed similar results to those shown in Figures 2 and 3, whereas CeO$_2$ layer grown on lower resistivity substrates of 0.1 ~ 0.2 Ω·cm had no longer (100) orientation. It is supposed that surface mobility determines the spreading of OSE region and roughly speaking, substrate resistivity above 2 Ω·cm is needed for OSE.

For crystallinity analysis especially on interfacial structures, XTEM observations were carried out on CeO$_2$(100)/Si(100) samples grown with 90 eV electron beam irradiation and under
Figure 4. XTEM image of CeO$_2$(100) layer on Si(100) grown with 90 eV electron irradiation.

Figure 5. XTEM image of CeO$_2$(100) layer on Si(100) grown under substrate bias of 15 V.

substrate bias of +15 V (for comparison) in Figures 4 and 5, respectively. Although the latter has no interfacial amorphous layer as a result of perfect interface control, [11] the former has $\sim 2.7$ nm thick amorphous suboxide layer, which indicates that electron beam irradiation enhanced interfacial oxidation during the growth process. [12] In order to improve the interfacial properties, it is needed to optimize the growth conditions, including the oxygen flow decrease.

4. SUMMARY
It was found that spatially varied OSE growth of CeO$_2$(100)/Si(100) was capable by irradiation of $\sim 35$ and $\sim 90$ eV electron beams in reactive magnetron sputtering. Resistivity of Si substrates above $\sim 2$ $\Omega$·cm proved to be necessary in realizing electron beam induced OSE. XTEM observations indicated electron enhanced oxidation, resulting in amorphous interfacial layers. In order to improve this problem, optimization of the oxygen flow rate, plasma power and the intensity of electron beams will be needed, including a combination of electron beam irradiation and substrate bias. Extensive studies on patterned electron beam irradiation experiments will lead to a new technology for finely patterned OSE growth and give a way to future advanced device technologies, such as a- and c-axes oriented high temperature superconducting layers and respective usage of semiconductor wells with optimum orientations for maximum carrier mobilities in corresponding n- and p-channel transistors.

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