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Spatially varied orientation selective epitaxial growth of CeO_2(100) and (110) regions on Si(100) substrates by reactive magnetron sputtering utilizing electron beam irradiation

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ABSTRACT

Spatially varied epitaxial growth of CeO_2(100) and CeO_2(110) regions on Si(100) substrates is attained using electron beam induced orientation selective epitaxial (OSE) growth by reactive magnetron sputtering. The spatially controlled OSE grown samples are made on Si(100) substrates with various electric resistivity values. By X-ray diffraction measurements, we obtain the lateral orientation mapping within the epitaxial layer surfaces and reveal existence of the transition regions in between the above mentioned two orientation areas. The width of the transition regions is clarified to decrease proportionally with the logarithm of underlying Si substrate resistivity. A surface potential distribution model is proposed to explain the results.

1. Introduction

Epitaxial cerium dioxide (CeO_2) layers on silicon substrates are of great interest due to favorable properties as an electronic material, for example, high dielectric constant of 26, high chemical stability, transmission in visible and infrared regions and high efficient ultra-violet absorption. Epitaxial CeO_2 layers on Si(100) substrates usually grow with (110) orientation [1–4]. It was found that orientation selective epitaxy (OSE) of CeO_2(100) and CeO_2(110) layers on Si(100) substrates was capable by controlling substrate bias and the growth rate in reactive magnetron sputtering [5]. Parameters such as a growth rate, a growth temperature and surface potential distribution over a substrate have been pointed out to rule orientation selectivity. In the oxide layer growth on oxide substrates, the growth rate and the growth temperature are key parameters; for example MgO layers on Si(100) substrates [6], lead zirconate titanate (PZT) on Si substrates [7], CeO_2 on silica glass substrates [8], and $LiNbO_3$ layers on Al_2O_3 substrates [9]. When polar oxide materials grow on non-polar semiconductor substrates, surface potential of the substrates is a very important parameter, which is the case of this study, *i.e.* epitaxial CeO_2(100) and CeO_2(110) on Si(100) substrates.

The epitaxial relation model of CeO_2(100) and CeO_2(110) on Si(100) has been proposed with $CeSi_2$(100) layer as an intermediate layer [10] and it was reported that CeO_2(110) is usually preferred from thermodynamical considerations [11]. In our previous work, it was clarified that substrate bias of ± 15 V leaded to the CeO_2(100) layer growth, whereas CeO_2(110) layers grew on non-biased substrates [5]. The latter was explained by the preferential growth of non-polar CeO_2(110) layers on non-polar Si(100) substrates. This preferential orientation selectivity is thought to depend on surface potential modification by substrate bias. It is noted that OSE of CeO_2(100)/Si(100) is irrespective of surface potential bending directions (bias polarity), which gives us an idea of surface potential modification by irradiation of charged particles; electrons and/or ions. This method enables a technology of two dimensional controlled OSE, which will contribute to future sophisticated applications. In the field of large scale integration (LSI) devices, hybrid orientation technology (HOT) is strongly desired for higher speed logic LSI's using CMOS (complementary metal-oxide-silicon) devices; respective usage of (100) and (110) substrates for n- and p-channel MOS devices [12].

In the previous work, we have reported the results on the two dimensionally controlled growth of CeO_2(100) and (110) areas by scanning electron beam irradiation [13,14], where it has been clarified that a transition region containing both (100) and (110) components exists in between the two orientation areas [15]. The width of the transition region was found to be considerably large. From the viewpoint of applications to electronic device technology, the transition region width should be much more reduced. In order to get insight into this problem, we studied how the transition region width depends on the Si substrate resistivity. This article describes the experimental results and the details on the two dimensional control of CeO_2(100) and (110) areas within Si(100) substrate surfaces, which

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will lead to development in HOT. We analyzed precisely the Si substrate resistivity dependence of the width of the transition regions.

2. Experiments

In order to study the relation between the transition region width and Si substrate resistivity, Si(100) wafers with a wide range of resistivity from 0.1 to 2500 Ω cm were used. The Si(100) wafers were cut into 52×52 mm^2, which were chemically cleaned to make H-terminated surfaces by the following procedure: dipping in a hot aqueous solution of HCl and H_2O_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), whose base pressure of the growth chamber was below 2.0×10^{-7} Pa. In CeO_2 layer growth experiments, the applied dc power to the target and the induction coil were 120 and 50 W, respectively. We employed the two step growth procedure as reported before [5]. Briefly, at first, the metallic Ce layer deposition was carried out using a metallic Ce target of 99.9% purity and 75 mm diameter with the Ar gas flow rate of 7 sccm (sccm denotes cubic centimeter per minute at the standard temperature and pressure). The thickness of the layer was approximately 3.6 nm. After heating the substrates, CeO_2 layers were subsequently deposited by a reactive sputtering in an Ar and O_2 mixture environment, wherein gas flow rates of Ar and O_2 were 6.2 and 0.8 sccm, respectively. This oxygen flow rate was chosen after the optimization experiments reported before [14]. Substrate temperature at the second step was elevated to 800 °C, where a 2 kW halogen lamp heating system was used. During reactive sputtering, low energy electron beams of 90 eV were irradiated, while the sample holder was grounded. A low energy electron gun and an absorbed electron current image (AEI) observation system were equipped to the sputtering system. The electron beam diameter was approximately 3 mm and the distance between the electron gun head and the sample surface was 50 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. In order to protect W–Re filament from an oxidizing ambient during reactive sputtering by maintaining an ultra-high vacuum, the electron source section was differentially pumped by a 50 l/s turbomolecular pump. The electron source section was kept at 1.07×10^{-3} Pa, when the pressure of the sputtering chamber was 0.13 Pa after the sputtering gas introduction. The sample current was measured by a digital multimeter (Keithley 196). The electron beam was scanned in a rectangular area, whose position and size were determined using the AEI monitor. An oxygen radical source (ULVAC, DOS-1000HE) equipped toward the sample surface at an angle of 33°, was used to enhance oxidation reaction at the substrate surfaces, which was operated with 50 W rf power and oxygen gas inlet. The distance between the radical beam source and the sample surface was 150 mm. Oxygen radical beam application was utilized throughout this study, since it has been verified to enhance crystalline quality of OSE grown CeO_2(100) layers [16]. CeO_2 layer thickness data were obtained by ellipsometric measurements. The thickness and the growth rate of CeO_2 layers were 20–25 nm and approximately 0.2 nm/s, respectively. The samples were characterized by reflection high energy electron diffraction (RHEED, Eiko Engineering RHC-01) and $2\theta-\omega$ scan X-ray diffraction (XRD, Rigaku Ultima X) using a Cu Kα1 line.

3. Results and discussion

Orientation selectivity for the CeO_2(100) layer growth is thought to correlate with surface potential modification for facilitating adsorption of nuclei with a polar CeO_2(100) surface. In the previous work, we have reported that electron beams with acceleration energies around 35 and 90 eV lead to the CeO_2(100) layer growth, which is thought to give surface potential modification effect similar to ±15 V bias application [13]. Crystalline quality evaluation by XRD proved that 90 eV electron beams are superior to 35 eV. 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 [17]. The ion current component is thought to correlate with higher crystalline quality of the CeO_2(100) layers grown with 90 eV electron beam irradiation than that with 35 eV electrons, *i.e.* the epitaxial growth facilitation effect by the positive ions of mainly Ar^+ with very low kinetic energy [14].

We carried out two dimensionally patterned OSE growth experiments using 90 eV electron beams scanned in the 5×5 mm^2 region of the substrates. The upper part of Fig. 1 shows a plan view illustration of the two dimensionally controlled OSE sample. The electron beam scanned during the second step growth process in the area indicated by the cross-hatched bar located in $x=-15\sim-20$ mm in the upper part of Fig. 1. Simultaneous irradiation of oxygen radical beams was applied as mentioned in Section 2. It is expected that CeO_2(110) grows in the

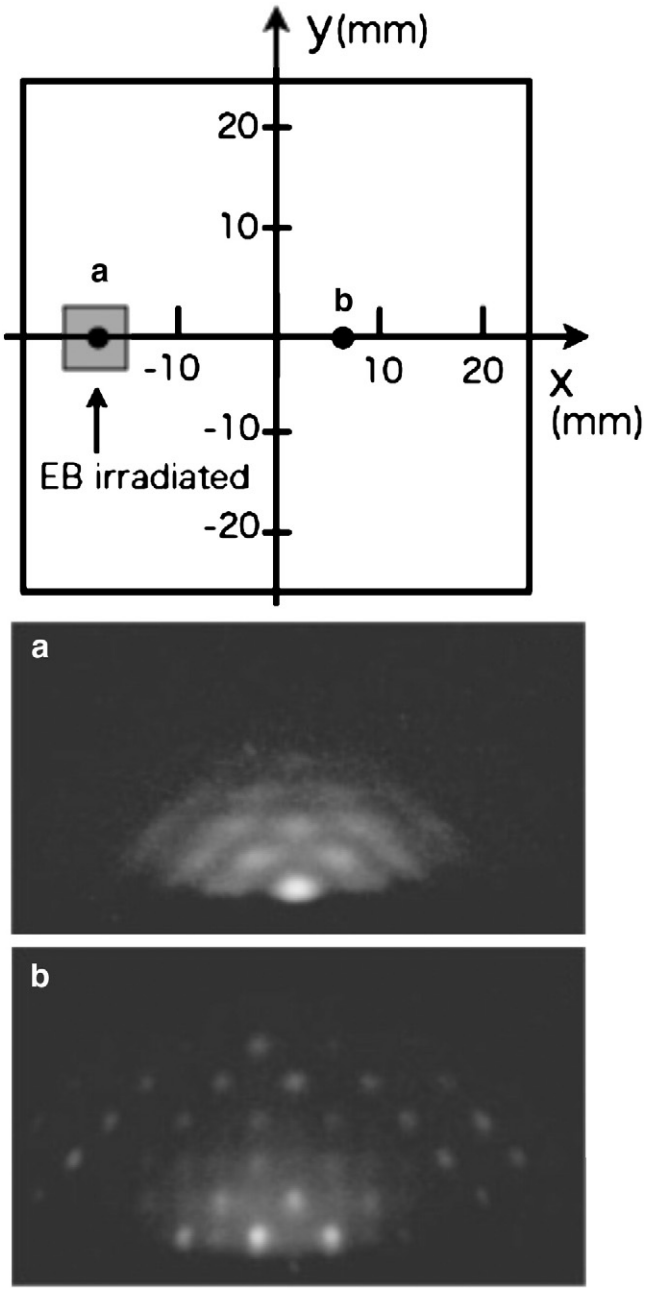

Fig. 1. An illustration in the upper part shows two dimensionally controlled OSE grown sample. Electron beams are irradiated in the 5×5 mm^2 square region. RHEED patterns denoted by (a) and (b) in the lower part are taken at the respective positions of (a) and (b) in the upper illustration.