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Observation of Si-oxide interlayer and Si nano-crystallites embedded in an amorphous SiO_x film

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Abstract

This study examined the rapid thermal annealing process of single crystal Si(0 0 1) substrates in oxygen ambient. A crystalline interlayer was observed between the amorphous silicon oxide (SiO_x) film and Si(0 0 1) substrate. The Si nano-crystallites embedded in the amorphous SiO_x film were studied by high-resolution transmission electron microscopy. The interface structure was affected by the annealing temperature. At 800 °C, no crystalline interlayer was observed, whereas a crystalline interlayer with the tridymite phase was observed when the sample was annealed at 1050 °C. A Si-oxide interlayer that contains oxygen interstitial atoms was formed when the Si(0 0 1) substrate was annealed at 1200 °C, wherein the thickness of the interlayer was limited to <2 nm. In addition, Si nano-crystallites were embedded in the amorphous SiO_x film with a size ranging from 1.5 nm to 5 nm. The size of the Si nano-crystallites might be limited by diffusion during phase separation and by oxidation of the host Si atoms.

Keywords: B. Interfaces; B. Nanocomposites; B. Electron microscopy; D. SiO_2

1. Introduction

The structural properties of silicon oxide, such as short-range order and transition interlayer between the silicon substrate and overgrown amorphous silicon oxide (SiO_x) film, have been long standing important issues both technologically and scientifically. In general, it is believed that the atomic stacking sequence is changed abruptly from the perfect crystal structure of Si to amorphous SiO_x. However, recent studies reported the observation of a crystalline transition interlayer. Ourmazd et al. [1,2] revealed an epitaxial transition interlayer <1 nm in thickness with a tridymite phase by transmission electron microscopy. On the other hand, synchrotron X-ray scattering studies also reported a crystalline interlayer but with a different crystal structure [3–5]. Fuoss et al. [5] analyzed the existence of a crystalline interlayer with the α-cristobalite phase at the amorphous SiO_x/Si interface. The crystalline transition interlayer was observed in a sample annealed below 1000 °C and its crystal structure changed by varying the annealing parameters, such as annealing temperature and ambient gas [6,7].

Recently, with the development of techniques for fabricating nanometer scale semiconductor materials, Si nano-particles embedded in an amorphous SiO_x matrix can be synthesized easily that resulted in controlling the size and distribution [8–10]. In contrast to the inefficient light emission from bulk Si or thin films due to the indirect bandgap, strong visible light emission from Si nano-structures and amorphous SiO_x thin films containing Si nano-particles has been reported. The quantum confinement effect is believed to be a source to enhance light emission. Therefore, it might be possible to adjust the emission spectra by controlling the size of the Si nano-particles. In order to synthesize Si nano-particles, several fabrication methods, such as direct deposition of Si nano-structures, ion implantation of Si to form a Si-rich oxide film, annealing of an amorphous SiO_x thin film, deposition of Si/SiO_x multilayer, have been reported [8,11–13]. Among them, high temperature annealing of a single crystal Si substrate has been investigated widely on account of the relatively simple process and the controllability of the particle size by changing the annealing temperature.

This paper reports an investigation of the structural properties of SiO_x thin films formed by the high temperature

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annealing of Si(0 0 1) substrates in oxygen ambient. High-resolution synchrotron X-ray scattering and transmission electron microscopy showed that the interface structure between the overgrown amorphous SiO_x film and Si(0 0 1) substrate was changed by varying the annealing temperature. The formation of Si nano-crystallites embedded in an amorphous SiO_x matrix was also observed.

2. Experimental procedures

The single-crystal Si(0 0 1) substrates were cleaned chemically in ultrasonic bath. To remove the native oxide from the surfaces, the substrates were etched in a dilute hydrofluoric acid solution and rinsed with deionized water. The samples were mounted in a specially designed chamber for annealing. High purity (99.9999%) oxygen gas was introduced into the chamber at a pressure of 300 mTorr during the entire annealing process. To form the oxide layer, the Si(0 0 1) substrates were oxidized by rapid thermal annealing at 800 °C, 1050 °C and 1200 °C, respectively. The samples were heated rapidly to the desired temperatures at a rate of 8 °C/s, and then cooled to room temperature in ambient gas.

High-resolution synchrotron X-ray diffraction (XRD) experiments were carried out at the 5C2 GIST beamline of the Pohang Light Source in Pohang, Korea. Incident X-rays with an energy of 9 keV were selected by a double crystal Si(1 1 1) monochromator. To achieve the high-resolution setup, two pairs of slits were used in front of the samples. The typical XRD profile (θ–2θ scan) was measured along the surface normal direction. In addition, specular X-ray reflectivity was measured to examine the interfacial and surface structure. The details of the atomic structure in the overgrown SiO_x film were determined using high-resolution cross-sectional transmission electron microscopy (TEM) (Jeol 2010). The microscope was operated at an acceleration voltage of 200 kV. Typical imaging resolution was approximately 2 Å. To prepare the TEM sample, the standard mechanical polishing procedure was used to thin the section below 5 μm using the diamond lapping films with particle sizes of 3, 1, 0.5, and 0.1 μm in sequence. Ion beam polishing was then performed with liquid nitrogen cooling to minimize the damage.

3. Results and discussion

The interface structure between the overgrown SiO_x films and host Si substrates were examined as a function of the annealing temperature. Fig. 1(a) shows a cross-sectional TEM image taken from a sample oxidized at 800 °C for 5 min. Lattice images of the atomic stacking sequence along the surface normal are the (0 0 1) planes of a single crystal Si substrate. In addition, no lattice and short range ordered phase were observed in the SiO_x film indicating that the SiO_x film was amorphous. As expected, the typical abrupt interface between the SiO_x film and Si substrate was observed. The interface was quite flat and smooth without defects. It is likely that the order of the atomic position had changed abruptly from the perfectly ordered Si substrate to the completely disordered amorphous SiO_x film.

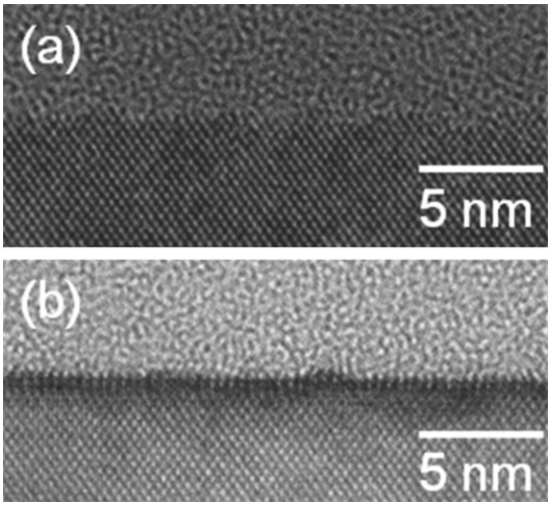

Fig. 1. Cross-section TEM images of the samples annealed at (a) 850 °C and (b) 1050 °C.

When the oxidation temperature was increased to 1050 °C, the interface structure changed drastically, as shown in Fig. 1(b). Amorphous SiO_x film with a thickness of 430 Å was formed. In contrast to the sample annealed at 800 °C [Fig. 1(a)], a thin crystalline interlayer on top of the Si substrate was observed. The periodicity of the lattice through the interface was modified. The atomic structure of such a small crystal was difficult to determine completely because only two or three atomic layers were distinguishable in the TEM image. The thickness of the crystalline interlayer was estimated to be <1 nm. To clarify the atomic structure of such thin crystalline interlayer, the atomic arrangement in both the surface normal [0 0 1] direction and in-plane [1 1 0] direction was reconstructed and compared with a possible model. From this result, it might be concluded that the crystalline interlayer was similar to the previously reported result [1,2]. In this case, the authors claimed the formation of a crystalline SiO_x interlayer with a tridymite phase based on TEM observations and simulation results. A tridymite phase is a bulk structure of SiO_x with a monoclinic lattice and lattice constants of 18.49 Å, 4.991 Å and 25.832 Å and an angle of $\beta = 117.75°$ [14]. Since the darkness of the interlayer represents the relative electron density of the materials, it was assumed that the crystalline interlayer would be slightly dense compared to the Si substrate.

A Si-oxide interlayer was observed at the sample annealed at 1200 °C for 10 min as shown in Fig. 2. The thickness of the amorphous SiO_x film was approximately 700 nm. A black region near the interface was clearly seen. The atomic stacking sequence along the surface normal direction and the in-plane direction might be the same as the host Si(0 0 1) substrate. The thickness of the interlayer was estimated to be approximately 2 nm.

The specular X-ray reflectivity was measured to examine the surface and interface structures quantitatively, as shown in Fig. 3. The X-ray reflectivity curve showed the continuous decay of intensities measured with increasing incident angles

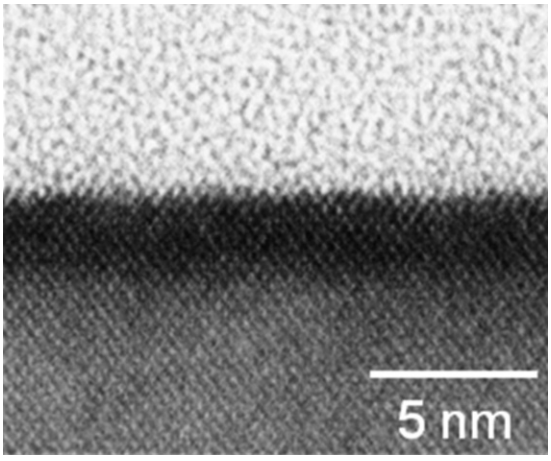

Fig. 2. Cross-section TEM image of the sample annealed at 1200 °C. The dark interlayer can be seen at the interface.

and broad modulation, which is the interference pattern. For a typical thin film, the X-ray reflectivity can be represented simply by the interference between the X-rays reflected from the film surface and from the film/substrate interface. In Fig. 3, the broad modulation around $Q_z = 0.2–0.6$ Å^{-1} was detected, even though it is unclear due to the dominant continuous decrease in reflectivity. To elucidate such modulation, the reflectivity curve was manipulated by a factor of Q^4 and plotted in the inset in Fig. 3. The interference fringes originated from the interlayer. The thickness of interlayer was estimated to be approximately 2 nm by using the equation, $t = (2\pi/\Delta Q)$, where ΔQ is the period of interference fringes, which is similar to that obtained from TEM. The density of interlayer was also obtained from the critical angle where incident X-rays are totally reflected, *i.e.* a total external reflection phenomenon, which is about 2.46 g/cm^3 slightly larger than that of Si (2.33 g/cm^3).

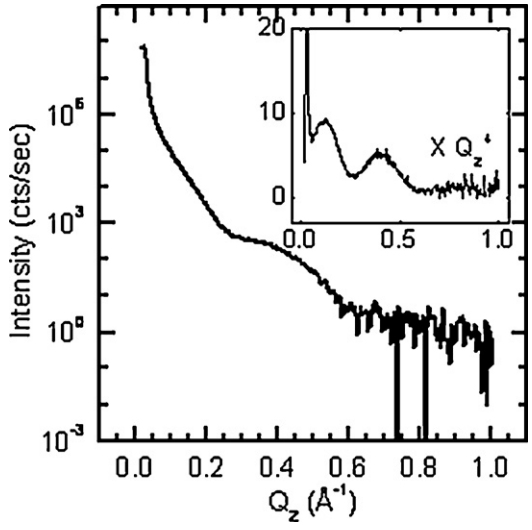

Fig. 3. X-ray specular reflectivity profile revealed the existence of an interlayer. The inset shows the magnified profile by a factor of Q^4 to elucidate the interference patterns.

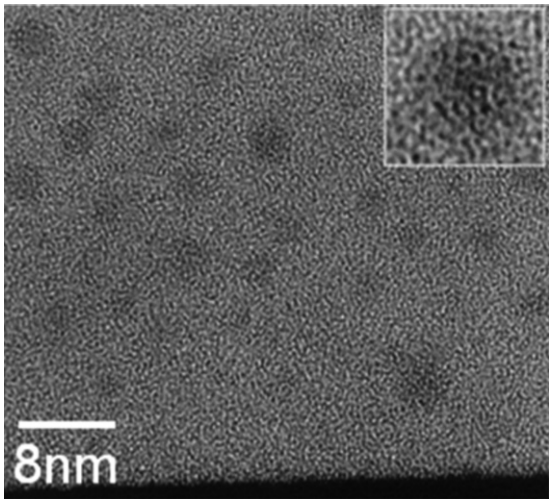

Fig. 4. TEM image shows the Si nano-crystallites. The inset shows a magnified view of the nano-crystallite to present the crystalline structure.

The formation of high density interlayer can be explained by the diffusion of the limited amount of oxygen atoms into host Si substrate. Such interlayer seems to be Si-oxide rather than SiO_x. Oxygen atoms were placed at the interstitial sites similar to reported theoretical model [15,16] depending on annealing temperatures. This resulted in the same crystal structure and lattice parameter with single crystal Si.

In addition to the Si-oxide interlayer observed in the sample annealed at 1200 °C, Si nano-crystallites embedded in amorphous SiO_x film were also observed, as shown in Fig. 4. The magnified view shown in the inset of the figure highlights the Si nano-crystallites. The lattice in the Si nano-crystallites can be clearly seen. The Si nano-crystallites were distributed and oriented randomly with no preferred orientations in the amorphous SiO_x film. High-resolution TEM revealed the Si nano-particles to be 1–5 nm in size. As a result, Fig. 5 shows the number of Si nano-crystallites as a function of the particle size. The best fit to the simple Gaussian profile indicated that 2.5 nm in diameter was dominant in this case, and

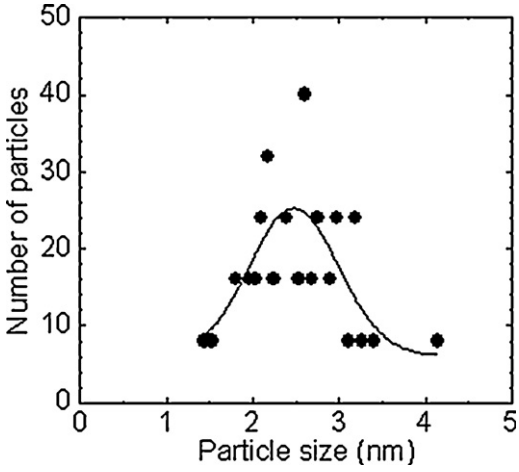

Fig. 5. The number density of Si nano-crystallites as a function of the size. The best fit to the Gaussian profile was displayed by the line.

might be dependent on the annealing parameters. The thermally annealed amorphous SiO_x film at high temperatures was typically Si-rich silicon oxide rather than silicon dioxide [9]. Upon high temperature annealing, the silicon atoms were separated from the amorphous SiO_x matrix to form Si nano-crystallites. Because no Si nano-crystallites were observed in the sample annealed at 1050 °C, the phase separation of Si might be a kinetic constraint process rather than equilibrium process, indicating that there is an activation energy barrier to nucleate Si nano-crystallites in SiO_x matrix [17].

4. Conclusions

This study examined the oxidation of single crystal Si(0 0 1) substrates at high temperatures as well as the formation of Si nano-crystallites. The structure of the interlayer was dependent on the annealing temperatures. Si nano-crystallites embedded in the amorphous SiO_x matrix were also observed. Photoluminescence spectroscopy measurement will be needed to characterize the optical properties that are indispensible to determine the band edge emission from Si nano-crystallites.

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