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Surface Science 600 (2006) 2523–2527

SURFACE SCIENCE

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Formation of 10–30 nm SiO_2/Si structure with a uniform thickness at ∼120 °C by nitric acid oxidation method

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Received 7 December 2005; accepted for publication 13 April 2006
Available online 11 May 2006

Abstract

Silicon dioxide (SiO_2) layers with a thickness more than 10 nm can be formed at ∼120 °C by direct Si oxidation with nitric acid (HNO_3). Si is initially immersed in 40 wt.% HNO_3 at the boiling temperature of 108 °C, which forms a ∼1 nm SiO_2 layer, and the immersion is continued after reaching the azeotropic point (i.e., 68 wt.% HNO_3 at 121 °C), resulting in an increase in the SiO_2 thickness. The nitric acid oxidation rates are the same for (1 1 1) and (1 0 0) orientations, and n-type and p-type Si wafers. The oxidation rate is constant at least up to 15 nm SiO_2 thickness (i.e., 1.5 nm/h for single crystalline Si and 3.4 nm/h for polycrystalline Si (poly-Si)), indicating that the interfacial reaction is the rate-determining step. SiO_2 layers with a uniform thickness are formed even on a rough surface of poly-Si thin film.

Keywords: Scanning transmission electron microscopy; X-ray photoelectron spectroscopy; Oxidation; Silicon; Silicon oxides; Polycrystalline thin films; Insulating films; Semiconductor–insulator interfaces

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1. Introduction

Si/silicon dioxide (SiO_2) structure attracts much interest not only from academic viewpoint but also for technological application to semiconductor devices such as large scale integration (LSI) and thin film transistors (TFT). In the case of TFT using poly-crystalline Si (poly-Si) thin films, the formation of relatively thick gate SiO_2 layers (i.e., ∼50 nm) is required. This is because (i) the conventional method (i.e., plasma-enhanced chemical vapor deposition (PECVD) using tetraethylorthosilicate (TEOS)) [1–7] cannot form uniform SiO_2 layers on rough poly-Si surfaces which result from laser annealing of amorphous Si films to crystallize [8], and (ii) the deposition method cannot form high quality dense SiO_2 layers. Thick gate SiO_2 layers increase a threshold voltage, resulting in an increase in the power consumption. Moreover, the deposition methods result in poor interfacial characteristics (e.g., high interface state density) because of incomplete interfacial bond formation, incomplete cleaning of poly-Si surfaces before deposition, etc [1–3]. The SiO_2 layers fabricated from TEOS include water, hydroxyl species, and carbon species, which increase the leakage current density [1,2]. The leakage current density also increases with a decrease in the deposition temperature [3]. To improve the electrical characteristics of the SiO_2 layers formed from TEOS, low pressure deposition [1], low deposition rate [4], NH_3 plasma treatment [5], N_2O plasma treatment [1], multi-layers fabrication [6,7], etc., have been employed.

Several methods have been investigated to form SiO_2 layers at low temperatures, e.g., plasma oxidation [9,10],

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0039-6028/$ - see front matter
doi:10.1016/j.susc.2006.04.015

metal-promoted oxidation [11,12], and ozone oxidation [13]. However, the low temperature formation of thick SiO_2 layers with good electrical characteristics has not been successful.

We have recently developed a nitric acid oxidation of Si (NAOS) method to form SiO_2 layers at ~120 °C [14–18]. The NAOS method is a direct Si oxidation method in which oxygen atoms formed by decomposition of nitric acid (HNO_3) react with Si. Consequently, the SiO_2/Si interface is clean, leading to good interfacial characteristics. Ultrathin (i.e., ~1.3 nm) SiO_2 layers formed with 68 wt.% HNO_3 (i.e., azeotropic mixture with water) have a much lower leakage current density than those for thermally grown SiO_2 layers, and possess a high atomic density of 2.34×10^{22} atoms/cm^3 (i.e., ~3% higher than that of thick thermal SiO_2 layers), preventing further growth of the SiO_2 layers [14–16]. We have recently found that a two-step NAOS method (i.e., immersion in ~40 wt.% HNO_3 followed by the immersion in 68 wt.% HNO_3), on the other hand, can form thicker SiO_2 layers [18].

In the present study, the two-step NAOS method has been applied to form SiO_2 layers with thickness more than 10 nm on single crystalline Si and poly-Si. The oxidation rate is found not to depend on the Si surface orientations and the conduction types, and uniform thickness SiO_2 layers can be formed even by oxidation of poly-Si thin films with a rough surface.

2. Experiments

Phosphorus-doped n-type or boron-doped p-type Si wafers having (1 1 1) or (1 0 0) orientation were used for the substrates. Intrinsic poly-Si films with ~50 nm thickness deposited on glass by means of the PECVD method were also employed for the substrates. After cleaning these Si specimens using the RCA method, the specimens were immersed in 40 wt.% HNO_3 aqueous solutions at the boiling temperature of 108 °C. The boil of the HNO_3 solutions increased the concentration to 68 wt.% (i.e., azeotropic mixture with water) [15], and after reaching the azeotropic point, immersion in the azeotropic mixture was continued for various periods. The metal impurity concentration in the HNO_3 solutions employed in the present study was less than 1 ppb. The resistivity of water used was 18.2 MΩ cm.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Scientific Escalab 220i-XL spectrometer with a monochromatic Al Kα radiation source. Photoelectrons were collected in the surface-normal direction. Ellipsometry measurements were performed using a Sopra GES-5 ellipsometer. Transmission electron micrographs (TEM) were observed using a JEOR JEM-3000F apparatus.

3. Results and discussion

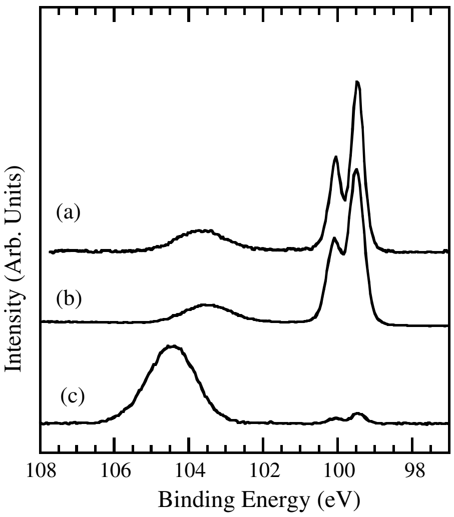

Fig. 1. XPS spectra in the Si 2p region for the SiO_2/Si(1 0 0) structure formed by the NAOS method. Si wafers were immersed (a) in 68 wt.% HNO_3 at 121 °C for 15 h, and in 40 wt.% HNO_3 at 108 °C and the immersion was continued for the following periods after reaching the azeotropic point: (b) 0 h; (c) 15 h.

Fig. 1 shows XPS spectra in the Si 2p region for the SiO_2/Si(1 0 0) structure formed by the NAOS method. Doublet peaks were due to Si $2p_{3/2}$ and $2p_{1/2}$ levels of the Si substrate and a broad peak in the higher binding energy region was due to the SiO_2 layers. The thickness of the SiO_2 layers was determined from the intensity ratio between the SiO_2 peak and the substrate peaks [19], using 3.2 nm as the mean free path of photoelectrons in SiO_2. Using this mean free path value, XPS measurements give nearly the identical SiO_2 thickness to that estimated from ellipsometry measurements when the SiO_2 thickness is larger than ~4 nm. By the immersion of Si in 68 wt.% HNO_3 (i.e., azeotropic mixture of HNO_3 with water) at its boiling temperature of 121 °C, an ultrathin SiO_2 layer of ~1.4 nm thickness was formed during 10 min immersion [14,15] but its thickness did not increase even when the immersion was kept for 15 h (spectrum a). When Si was immersed in 40 wt.% HNO_3 at the boiling temperature of 108 °C and the boiling was kept for 15 h after reaching the azeotropic point, on the other hand, the SiO_2 thickness increased to 14.4 nm (spectrum c). In this case, it took ~1 h to reach the azeotropic point from 40 wt.% HNO_3, and at this point, a 1.1 nm SiO_2 layer was formed (spectrum b). The energy difference between the SiO_2 peak and the substrate Si $2p_{3/2}$ peak was 3.9 eV for the 1.1 nm SiO_2 layer, and it increased with the SiO_2 thickness. This higher energy shift is attributable to an increase in the magnitude of charging, resulting in an increase in the potential drop across the SiO_2 layer [20,21].

XPS measurements show that the SiO_2 layers formed by the two-step NAOS method are almost stoichiometric, i.e., Si:O $= 1:2 \pm 0.05$. In spite of the stoichiometric SiO_2 layers, diffusion of the oxidizing species (most probably oxygen atoms) proceeds smoothly due to the small size, as explained below.

Fig. 2 shows the thickness of the SiO_2 layers formed on the Si(1 0 0) substrates (plot a) and poly-Si thin films (plot