

Praseodymium silicate formed by postdeposition high-temperature annealing

Akira Sakai,^{a)} Shinsuke Sakashita, Mitsuo Sakashita, and Yukio Yasuda
*Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

Shigeaki Zaima
*Center for Cooperative Research in Advanced Science and Technology, Nagoya University, Furo-cho,
Chikusa-ku, Nagoya 464-8603, Japan*

Seiichi Miyazaki
*Department of Electrical Engineering, Graduate School of Advanced Science of Matter,
Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan*

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Praseodymium silicate (Pr silicate) has been synthesized by molecular-beam deposition of Pr_2O_3 layers on Si(111) substrates and subsequent high-temperature postdeposition annealing at 1000 °C. This thermal treatment drastically changes the film texture from the crystalline Pr_2O_3 epitaxially grown on Si, into Pr silicate with completely amorphized structures, resulting from intermixing of Si from the substrate. It was found that the electrical characteristics of Pr silicate were critically dependent on the quality of the as-deposited Pr_2O_3 films. A typical dielectric constant and a leakage current density of Pr silicate grown under an optimal condition were, respectively, 19.7 and 3×10^{-9} A cm^{-2} at +1 V relative to the flatband voltage for an equivalent oxide thickness of 1.9 nm. Using x-ray photoelectron spectroscopy, a valence-band offset at the Pr-silicate/Si(111) interface of 2.75 eV and a band gap of 6.50 eV were obtained. The large band gap and the highly symmetric band alignment account for the observed low leakage current density. © 2004 American Institute of Physics. [DOI: 10.1063/1.1828584]

Investigation of high- k dielectric materials has recently been accelerated by continual miniaturization of Si metal-oxide-semiconductor (MOS) devices. This is because the scaling to a diminished size of device structures requires a corresponding reduction of SiO_2 gate dielectric film thickness, leading to an increase in tunneling leakage current and degraded dielectric reliability. Considerable efforts have already been made with various materials, exhibiting a dielectric constant greater than that of SiO_2 , to replace the SiO_2 gate dielectric.¹ The stability of high- k films in contact with Si must be taken into account when developing and exploiting high- k gate dielectric materials, compatible with the MOS device manufacturing.²⁻⁴

It has been generally reported that thermal instability results in the growth of parasitic interfacial layers with a dielectric constant lower than that of high- k materials, such as SiO_2 and silicates,^{5,6} with a noticeable decrease in the effective capacitance being eventually observed. Furthermore, the homogeneity of crystallographic and chemical characteristics in high- k films is a critical factor in determining the applicability of the film to the MOS device, since defects, such as grain boundaries in polycrystalline texture, and compositional inhomogeneities may often act as sites at which local degradation of electrical properties occurs.⁷ Therefore, the preparation of thermally robust high- k films with homogeneous structural and chemical characteristics is an urgent issue to be addressed in meeting the stringent requirements for the next generation of MOS device technology. In this work, we focus on praseodymium silicate (Pr silicate), which meets requirements for both a high dielectric

constant and high thermal stability. This paper addresses an approach to the formation of Pr silicate by deposition of a Pr_2O_3 layer on a Si substrate and high-temperature postdeposition annealing.

Deposition experiments were conducted in a molecular-beam epitaxy system with a base pressure of 1×10^{-10} Torr. The substrates used were n -type Si(111) wafers with a resistivity of 2–3 Ω cm. Prior to deposition, a substrate was treated in an HF solution to produce a hydrogen-passivated surface. A sintered powder ceramic, 99.9% Pr_6O_{11} , was used for electron-beam evaporation. Initially, a 1-nm-thick Pr-oxide layer was deposited at a temperature between 300 and 700 °C in vacuum in order to suppress unintentional formation of SiO_2 -based interfacial layers. The pressure during the deposition was in the low range of 10^{-8} Torr. Subsequently, a second Pr-oxide layer with a thickness ranging from 6 to 9 nm, was deposited on the initial layer, either in vacuum or in O_2 with a partial pressure of 5×10^{-7} Torr. Some films were subjected to postdeposition annealing (PDA) using a rapid thermal annealing system at a temperature of 1000 °C for 15 sec in a N_2 environment. Structural analysis was performed on each sample using *in situ* reflection high-energy electron diffraction (RHEED) and transmission electron microscopy (TEM). For electrical properties, current-voltage (I - V) and capacitance-voltage (C - V) characteristic measurements were performed by using MOS capacitors made from both as-deposited films and the films after PDA, with a Pt counterelectrode having an area of 3.83×10^{-4} cm^2 on the surface and an Al sheet on the back of the Si substrate. X-ray photoelectron spectroscopy (XPS) was also used to measure the chemical composition of the films and the energy-band profile of Pr-silicate/Si systems.

^{a)}Electronic mail: sakai@alice.xtal.nagoya-u.ac.jp

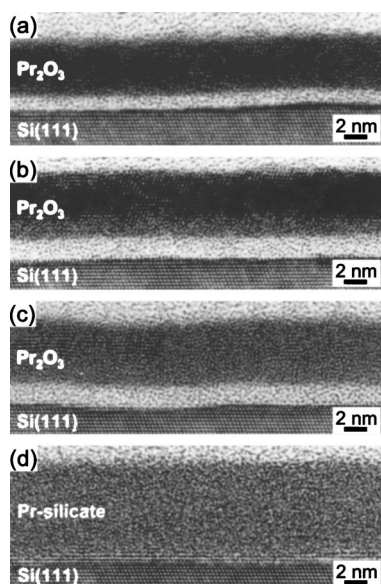


FIG. 1. Cross-sectional $\langle 110 \rangle$ high-resolution TEM images of as-deposited (a) 300-O/300-V, (b) 500-O/300-V, (c) 500-O/500-V films, and (d) a 500-O/300-V film after PDA at 1000 °C.

Several samples of as-deposited Pr-oxide films were prepared with systematic variations in the first-deposition temperature, and the second-deposition temperature under either vacuum or O₂ ambients. The following is an example of the sample notation adopted. A Pr-oxide film formed by the first deposition at 300 °C in vacuum followed by the second deposition at 500 °C in O₂ ambient was noted as a 500-O/300-V film. Figures 1(a)–1(c) show high-resolution TEM images of three typical as-deposited films. As seen in Fig. 1(a), the 300-O/300-V film exhibits lattice fringes of a Pr₂O₃ phase, having a cubic manganese oxide structure; the epitaxial relationship is Pr₂O₃(111)//Si(111) with twin symmetry. Note that an amorphous layer with a thickness of ~ 1.3 nm is formed at the Pr₂O₃/Si interface. Since it was confirmed from *in situ* RHEED observations that a 1×1 surface was explicitly maintained at all deposition processes, the interfacial amorphization possibly occurs not from the surface but the Pr₂O₃/Si interface during the epitaxy of the Pr₂O₃ layers. Comparison between the 300-O/300-V and the 500-O/300-V samples shown in Figs. 1(a) and 1(b), respectively, shows that the thickness of the interfacial amorphous layer increased at the increased second-deposition temperature. Furthermore, as shown in Fig. 1(c), the interfacial amorphization pronounced by increasing the first-deposition temperature up to 500 °C severely influences a growth manner of the second Pr₂O₃ layer so that the Pr₂O₃ is partially prevented from epitaxy, resulting in the amorphous structure. We have also confirmed that O₂ introduction during the second deposition promotes the amorphization at the Pr₂O₃/Si interface: the interfacial layer of the 500-O/500-V film shown in Fig. 1(c) was found to be thicker than that of the 500-V/500-V film (not shown) which was ~ 1.5 nm. Therefore, as far as the interfacial layer growth, lower temperature at the first deposition and reduced O₂ pressure lead to thinner interfacial layers resulting in better crystallinity of the second layers.

Although as-deposited films exhibit two separated phases typically consisting of Pr oxide and interfacial layers, it was found that PDA at 1000 °C drastically modified the film into a single homogeneous amorphous layer of Pr sili-

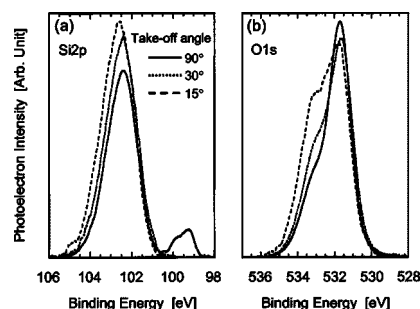


FIG. 2. Photoelectron spectra taken with take-off angles of 90°, 30°, and 15° of (a) Si 2*p* and (b) O 1*s* for the PDA-treated 500-O/300-V film.

cate for all samples. Figure 1(d) shows a cross-sectional high-resolution TEM image of the 500-O/300-V film after PDA. A mottled contrast with no crystalline lattice fringes is clearly observed, indicating the occurrence of complete amorphization through the film. Furthermore, no interfacial layers are seen and the roughness of the interface was measured as being in the range of one to two biatomic layers. Detailed chemical composition analysis using XPS revealed the film to have a composition ratio of Pr:Si:O:N = 23:16:54:6. It was thus interpreted that the deposited Pr oxide undergoes solid-phase intermixing with Si from the substrate during high-temperature annealing to form Pr silicate. It should be noticed that the Pr:O ratio increased from 2:3 for the initial Pr₂O₃ to 23:54 for the Pr silicate. This additional oxygen probably comes from the interfacial layer formed in the as-deposited film.

The take-off angle dependence of Si 2*p* and O 1*s* photoelectron spectra for the PDA-treated 500-O/300-V film are shown in Figs. 2(a) and 2(b), respectively. The Si 2*p* spectrum for a take-off angle of 90° had a main peak at 102.4 eV, originating from a Si³⁺ suboxide binding state in Pr silicate, as well as a Si bulk peak at 99.3 eV. Note that the main peak intensity increased with reduction in the take-off angle from 90° to 15°. In Fig. 2(b), the O 1*s* spectrum had a main peak at 531.7 eV, attributed to oxygen bonded in a Si-O-Pr configuration of Pr silicate⁸ together with a subpeak, assigned to oxygen in Si-O-Si, with a binding energy of ~ 1.3 eV higher than the main peak. The dependence of the take-off angle is also seen in this spectrum, where relative intensity of the subpeak increased at lower take-off angles. These results indicate a higher concentration of the Si-O bonding in regions closer to the film surface. On the other hand, it was confirmed that the peak profile of Pr 3*d*_{5/2} (not shown) was almost independent of the take-off angle. Such a difference in Pr and Si distributions through the film allows us to interpret that Si out-diffusion from the substrate into the Pr-oxide layer is dominant, rather than Pr in-diffusion during intermixing to form Pr-silicate layers. This phenomenon is also supported by the fact that no particular thickness increase was seen when comparing the as-deposited film [Fig. 1(b)] and the PDA-treated film [Fig. 1(d)]. The ease of intermixing seems to be reasonable in the light of the previous studies that show reactions between Pr₂O₃ films on Si substrates⁹ and other lanthanoids oxides after postannealing.^{10–12}

Turning to the *I-V* and *C-V* characteristics measured for various samples, a systematic correlation between *I-V* and *C-V* characteristics for each sample was not observed in the as-deposited films. However, a drastic reduction of leakage current density was noted in the 500-O/300-V film, as shown

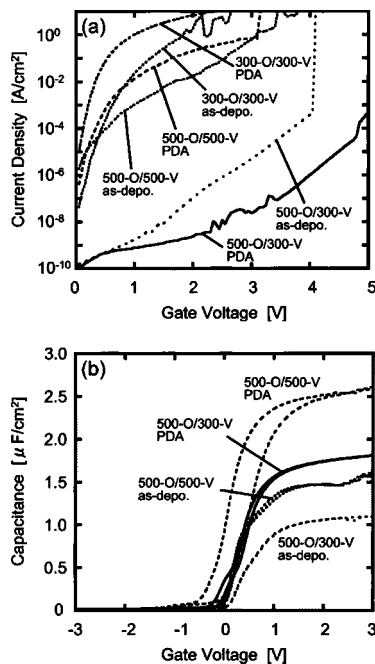


FIG. 3. (a) I - V and (b) C - V curves of typical as-deposited and PDA-treated films. The capacitance was measured at 100 Hz.

in Fig. 3(a). Moreover, in this sample, further reduction of leakage current density and a significant increase in capacitance [Fig. 3(b)] could be achieved due to PDA: a dielectric constant and a leakage current density are found to be, respectively, 19.7 and 3×10^{-9} A cm $^{-2}$ at +1 V relative to the flatband voltage (V_{FB}) for an equivalent oxide thickness (EOT) of 1.9 nm. A correlation was also sought between the current leakage property in as-deposited and PDA-treated films. As a result, the leakage characteristic after PDA was found to be critically determined by the as-grown nature: the superior characteristics of as-deposited films were carried over into the PDA-treated film although the crystallographic structure and the chemical composition of the film were completely changed by atomic intermixing of Pr oxide and Si. We tentatively consider that oxygen strictly incorporated into the crystalline Pr $_2$ O $_3$ lattice sites, promoted by the epitaxy at a relatively higher deposition temperature, plays a crucial role in realizing lower leakage current density even after PDA.

Energy-band profiles of Pr-silicate/Si systems have been also evaluated by XPS. The band-gap energy can be determined from analyzing an energy-loss spectrum for O 1s.¹³ Figure 4(a) shows an O 1s energy-loss spectrum of the PDA-treated 500-O/300-V film, where the band gap is determined from the threshold energy to be 6.50 ± 0.05 eV. On the other hand, from the valence-band spectra of Pr silicate and a Si(111) surface, a valence-band offset of the Pr-silicate/Si(111) systems can be derived. Figure 4(b) shows spectra for both the PDA-treated 500-O/300-V film and an atomically flat hydrogen-terminated Si(111) surface, where the binding energy for each spectrum was calibrated using a Si $2p_{0+3/2}$ peak position. The difference of valence-band edges at which density of states starts to emerge allows the observation of a valence-band offset between the Pr silicate and Si(111) as 2.75 eV. A simple calculation using this value and the band gap of Si leads to a conduction-band offset of 2.63 eV. The fact that the Pr-silicate/Si system has suitable band

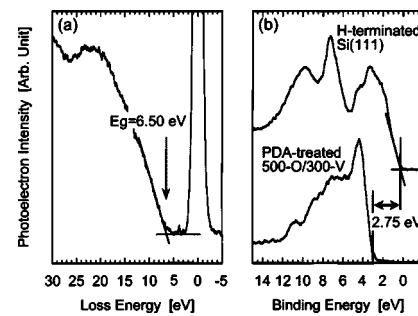


FIG. 4. (a) Photoelectron energy-loss spectrum of O 1s for the PDA-treated 500-O/300-V film taken at a take-off angle of 90°. The contribution of peak intensity from the Si-O bonding state was subtracted from the original spectrum. (b) Valence-band spectra of the PDA-treated 500-O/300-V film and a hydrogen-terminated Si(111) surface taken at a take-off angle of 90°.

offsets with quite high symmetry is one of the possible reasons why such a low leakage current density was obtained for this system.

Finally, we discuss the potential of Pr silicate as a gate dielectric material alternative to SiO $_2$ on the basis of the aforementioned structural and electrical properties. It has been previously reported that crystalline Pr $_2$ O $_3$ films epitaxially grown on Si exhibit excellent performance, especially, in terms of their EOT and the leakage current density.¹⁴ In the Pr silicate reported here, although homogeneity in film texture is retained by forming amorphous structures, superior electrical properties are confined to a rather narrow process window. In practice, the effective capacitance and leakage-current properties of films were all shown to be critically dependent on the deposition temperature and the growth ambient. Nevertheless, the characteristics of Pr silicate obtained here appeared to be attractive; the dielectric constant was higher than that of other silicate materials, such as Hf and Zr silicate,³ the large band gap displayed quite symmetric band alignment with respect to Si, and the low leakage-current density was comparable to the epitaxial Pr $_2$ O $_3$.¹⁵ Furthermore, high thermal stability in direct contact with Si, which is often argued for other materials, is obviously achieved. All of these factors imply that Pr silicate prepared by the current method could be a promising candidate for gate dielectrics, compatible with the next generation of MOS devices.

¹For a review, see A. I. Kingon, J.-P. Maria, and S. K. Streiffer, *Nature* (London) **406**, 1032 (2000), and references therein.

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