

Silicon oxidation by aerial diffusion of active oxygen species from UV-irradiated TiO₂

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Abstract—Silicon oxidation by the aerial diffusion of active oxygen species from a UV-irradiated TiO₂ surface was evaluated and characterized. The key point was to confirm the oxidation possibility of inorganic materials such as silicon under a photocatalytic remote scheme. In this study, it was confirmed that the remote oxidation of silicon substrates would occur by the aerial diffusion of active oxygen species from UV-irradiated TiO₂ surfaces, and that the oxides have comparable properties to the thermally grown oxide. Remote oxidation using UV-irradiated TiO₂ is shown to be a viable alternative method for the fabrication of nano-scale silicon oxide.

Key words: Silicon Oxidation, Aerial Diffusion, Active Oxygen Species, TiO₂, Photocatalyst

INTRODUCTION

Semiconductor photocatalysts such as TiO₂ are known to exhibit a strong oxidizing ability. They have been used as self cleaning, deodorizing, self-sterilizing, and air cleaning coatings [1-3]. Some of these characteristics result from the photocatalytic generation of active oxygen species, which may include hydroxyl radical (OH•), superoxide anion (O₂^{•-}), hydrogen peroxide (H₂O₂), and singlet oxygen (¹O₂) [4,5]. During the photocatalytic process, the activated oxygen species on the surface, which are produced by electrons and holes generated under illumination, act as agents for oxidizing the organic or inorganic materials. Recently, the aerial diffusion of active oxygen species from UV-irradiated TiO₂ has been suggested and evaluated [5-12]. Tatsuma et al. [5-7] suggested the remote oxidation effect of TiO₂ on the patterning of a solid surface and the bleaching of organic compounds. In addition, it was reported that a photocatalytic reaction on the soot/TiO₂ interface can occur as a result of the air-borne diffusion of active oxygen species [11-13].

A simple and noncontact process based on remote oxidation for the modification of organic and inorganic surfaces in terms of their physical and chemical characteristics and their morphology would be very useful as a nano-level surface treatment, as it would not require complicated or expensive equipment. In this study, silicon oxidation by the aerial diffusion of active oxygen species from a UV-irradiated TiO₂ surface was evaluated and characterized. The key point of this study was to confirm the oxidation possibility of inorganic materials such as a silicon substrate under a photocatalytic remote scheme. This has not been reported thus far.

EXPERIMENTAL

TiO₂ aqueous sol (Nano solution, NSP-1000) was coated onto a quartz plate by spin coating at 1,500 rpm for 60 s. The thickness of the TiO₂ layer was adjusted to 100 nm after spin coating it two times. The TiO₂ film was dried at 100 °C and calcined at 400 °C for 30 min to obtain an anatase structure. Before TiO₂ film was used as a

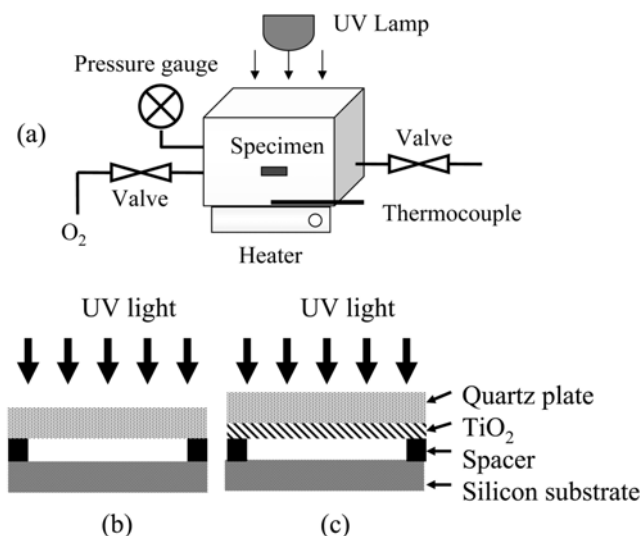


Fig. 1. Schematic illustration of the experimental apparatus (a) and specimens for (b) the control experiment and (c) the remote oxidation experiment.

photocatalyst, the TiO₂ film surface was irradiated with a black-light UV lamp (60 W) for more than 10 hr in order to clean the surface. P-type silicon specimen with (100)-oriented was dipped into a dilute HF solution to remove its native oxide on the surface before each experiment. The step was confirmed by a sheet-off inspection and a spectroscopic ellipsometer (Nano View, SE MG1000-V). The effects of active oxygen species on the silicon oxidation were compared with a controlled specimen, as shown in Fig. 1. Covering with a quartz plate coated with TiO₂ was a basic scheme, where a polyimide spacer of 20 μm was inserted between the silicon substrate and quartz plate. UV sources with intensities of 1.8, 8, and 25 mW/cm² were used. To control the process ambient, a specific process scheme was used as shown in Fig. 1(a), where the silicon substrates were uniformly heated at the desired process temperatures and dry oxygen was fed into the reactor chamber with 1 atm. The oxide thickness on the silicon surface was measured with a spectroscopic ellipsometer.

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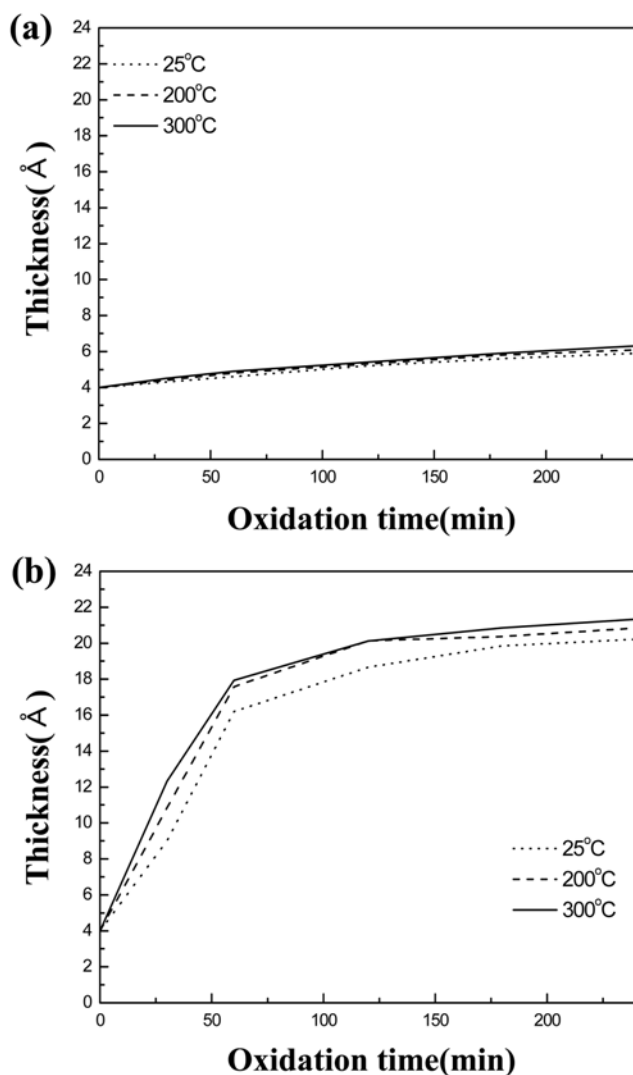


Fig. 2. Effect of the process temperature on the growth thickness of the surface oxide according to the exposure time; (a) on the control specimens and (b) on the remote oxidation specimens. The UV intensity of 8 mW/cm^2 was used, and the thickness was measured by using a spectroscopic ellipsometer.

RESULTS AND DISCUSSION

The oxidation of the silicon substrate was processed at the process temperatures of 25°C , 200°C and 300°C under UV intensity of 8 mW/cm^2 . The effect of aerial-diffusion of the active oxygen species from the UV-irradiated TiO_2 surface can be clearly known via a comparison of the oxidation rate of the controlled substrate, as shown in Fig. 2. In the oxidation thickness of the specimen covered with a TiO_2 -coated quartz, there was no apparent difference according to the process temperature. Furthermore, a similar tendency in the behavior of oxide growth was shown in Fig. 2(b), but all the oxides had a tendency to be saturated at approximately $20 \text{ \AA}$, whereas that of a controlled specimen were less than $6 \text{ \AA}$ at the process time of 200 min, as shown in Fig. 2(a). From these results, it became evident that the remote oxidation of inorganic material surface occurs as a result of the aerial-diffusion of active oxygen species

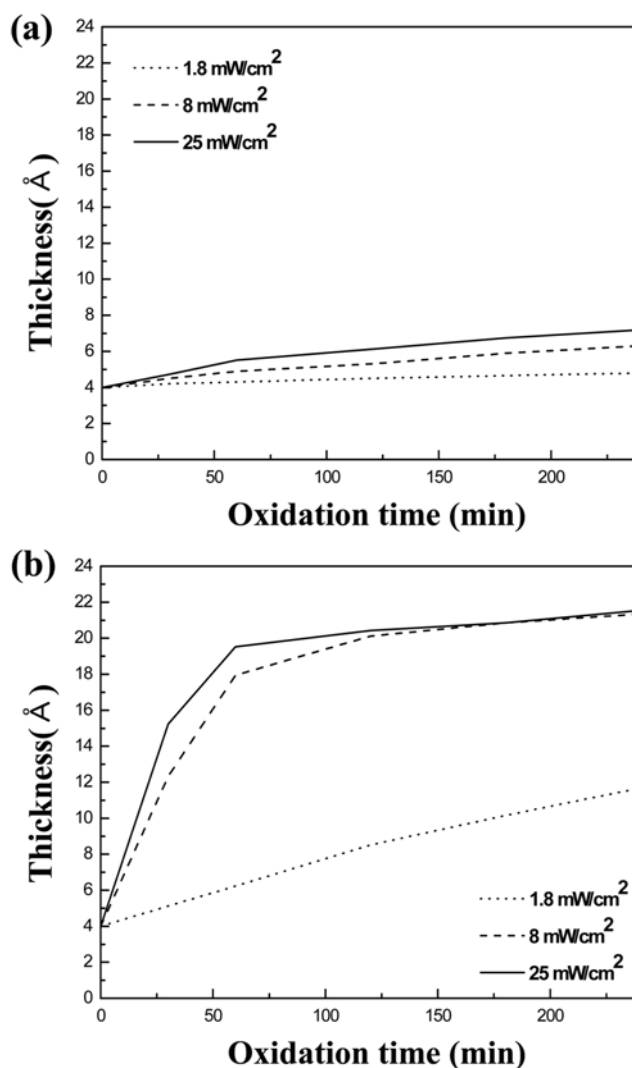


Fig. 3. Effect of the UV intensity on the growth thickness of the surface oxide according to the exposure time; (a) on the control specimens and (b) on the remote oxidation specimens. The process temperature was fixed at 300°C , and the thickness was measured by using a spectroscopic ellipsometer.

from the UV-irradiated TiO_2 . Also, it showed that the process temperature is not a significant factor for the remote oxidation of silicon surface. The oxidation rate at the process temperature of 300°C can be controlled by the UV intensity, as shown in Fig. 3. In a comparison of the oxidation rates under the variation of UV intensities, the oxidation rate at UV intensity of 25 mW/cm^2 showed an eight-fold increase compared to that at 1.8 mW/cm^2 in an early stage. A similar observation was made for the removal of an octadecyltriethoxysilane (ODS) [6]; the removal of ODS was faster under a stronger UV light, suggesting that the rate of the remote oxidation of ODS is controlled by the supply of photons. Then, we could recognize that a thinner TiO_2 layer prepared on quartz is recommended in order to enhance the absorption of UV light at the TiO_2 . In addition, the methods for improving the remote oxidation activity could be found from several previous reports. If a TiO_2 coating is negatively charged and/or a silicon substrate is positively charged, the remote oxidation of silicon would be enhanced, as the deprotonated forms of

the active oxygen species are apt to be transported as a result of the electrostatic forces [5]. Also, the surface fluorination of TiO_2 , facilitating the desorption of active oxygen species from a UV-irradiated TiO_2 surface would enhance the remote photocatalytic oxidation activity [14]. The oxide on the silicon surface grown by the remote oxidation at the temperature of 300°C , the UV intensity of $8\text{ mW}/\text{cm}^2$, and the process time of 200 min was monitored by using TEM pictures, as shown in Fig. 4. The thickness of the remote oxide was

approximately $20\text{ \AA}$ and appeared very clean and smooth feature, whereas a native oxide layer on the silicon revealed very rough and irregular surface morphology, as shown in Fig. 4(a).

The oxide grown by the UV-irradiated TiO_2 scheme has nearly identical chemical properties to a thermally grown oxide, according to a comparison of the binding energies of the key elements from X-ray photoelectron spectroscopy (Thermo VG, Sigma Probe) analysis, as shown in Fig. 5. The thermally grown oxide on a cleaned

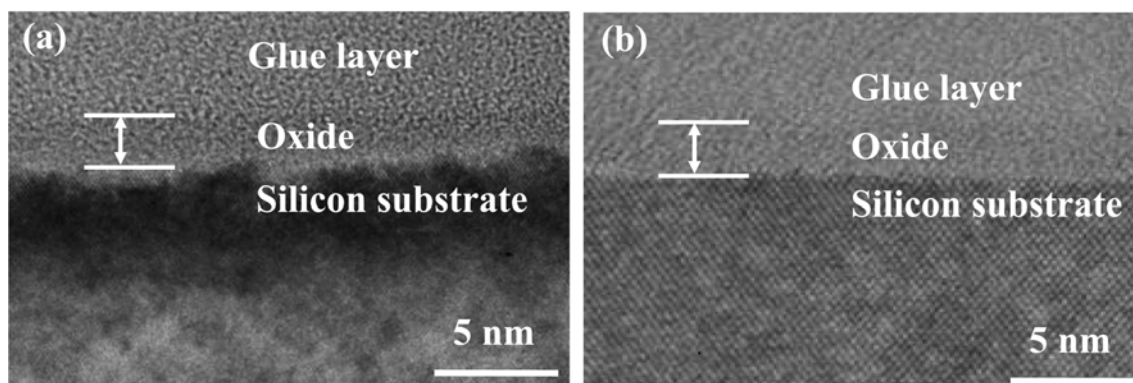


Fig. 4. Cross section TEM photographs of (a) the native oxide on a silicon substrate and (b) the silicon oxide grown by the remote oxidation at the temperature of 300°C , the UV intensity of $8\text{ mW}/\text{cm}^2$, and the process time of 200 min.

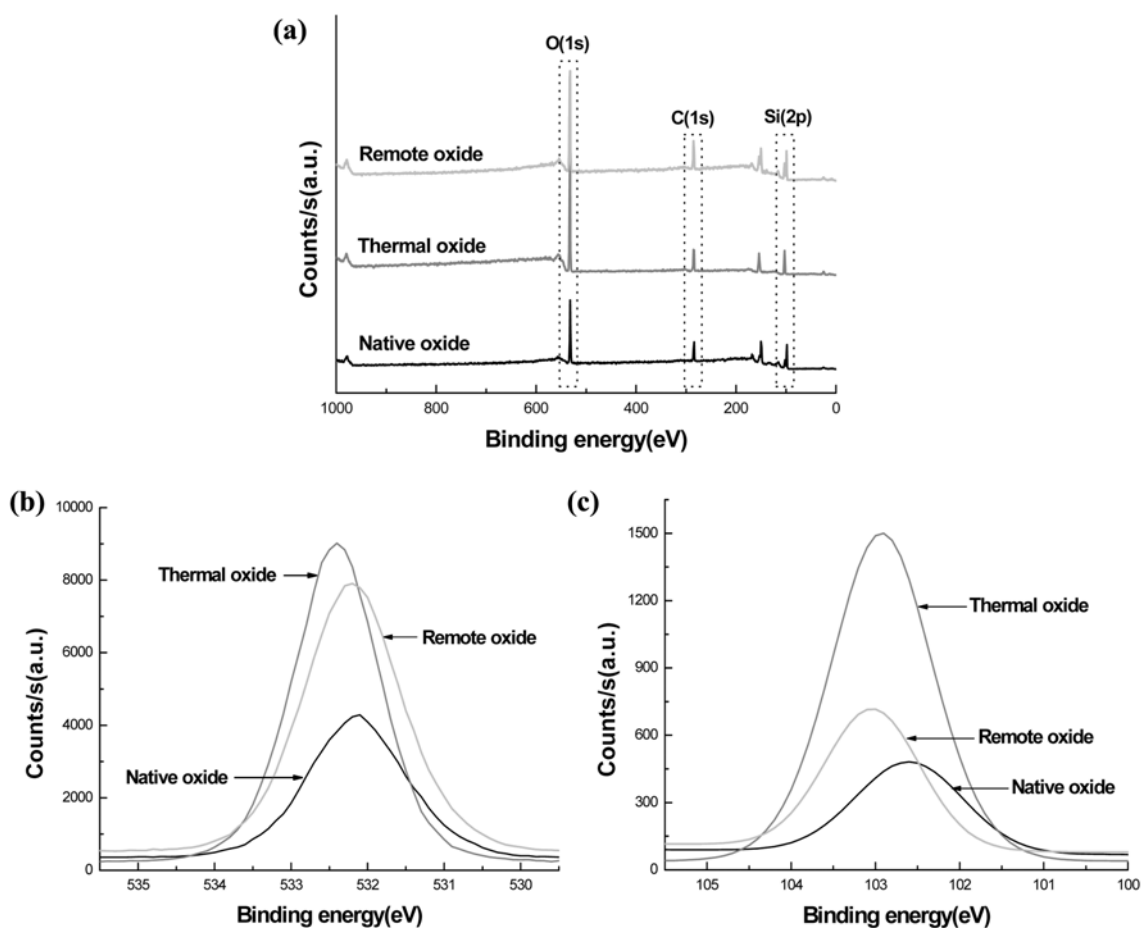


Fig. 5. Comparison of XPS spectra of the oxides from remote oxidation, thermal oxide, and native oxide at (a) the wide scan, (b) O 1s, and (c) Si 2p.

p-type silicon wafer with a thickness of 100 nm was prepared at 950 °C under an ambient of oxygen, whereas the oxide on a bare p-type silicon wafer was adopted as the native oxide in this study. The binding energies of Si(2p) and O(1s) for the remote oxide were determined to be 103.0 and 532.2 eV, respectively. These values are very close to those for a thermally grown oxide of 102.9 and 532.4 eV, confirming that a stoichiometric silicon oxide was formed. However, the peaks of native oxide were located in somewhat different values of binding energies compared to those of the thermally grown oxide. This shows that the oxide grown by remote oxidation has superior properties to the native oxide and is comparable to a thermally grown oxide, as confirmed by the measurement of the refractive index of each layer. Among the peaks of binding energy, the peak related to carbon might come from contamination during the specimen handling after experiment. The refractive index of the grown oxide was in the range of 1.457 to 1.459, which is close to the refractive index of a thermally grown oxide at 1.462 [15]. Thus, it is evident that the physical and chemical properties of the oxide by aerial-diffusion are comparable with those of the thermal oxides. This implies that the application area is extendable to nano-level advanced technologies.

SUMMARY

Remote oxidation of silicon substrates is possible with the aerial diffusion of active oxygen species from a UV-irradiated TiO₂ surface. The oxide thickness was approximately 20 Å, which was saturated under the current experimental conditions regardless of variations in the temperature, pressure and UV intensity. However, the properties of the oxides grown by remote oxidation were comparable to those of a thermally grown oxide. The remote oxidation of silicon through UV-irradiated TiO₂ is believed to be a viable method

for the fabrication of nano scale silicon oxide layers.

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