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Non-heating atomic layer deposition of TiO_2 by using plasma excited water vapor

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Titanium oxide (TiO_2) is well known as an oxide coating material with a photocatalytic activity under the sunlight [1]. TiO_2 is also used as transparent conducting oxide films for dye-sensitized solar cells and organic-inorganic heterojunction solar cells [2]. Rutile TiO_2 has been also studied as a candidate of a high-k dielectric gate film for MOSFETs [3]. The growth temperature for the TiO_2 deposition has been desired to be decreased to room temperature (RT) because the devices mentioned above have been demanded to be fabricated on plastic or flexible substrates for organic electronics. In this work, we developed non-heating atomic layer deposition of TiO_2 at RT with tetrakis(dimethylamino) titanium (TDMAT) and plasma excited water vapor.

A p-type Si(100) substrate with a resistivity of 8-12 Ωcm was used as a sample. Prior to the experiment, the sample was cleaned with buffered HF acid and sulfuric acid-hydrogen peroxide mixture solutions. The Ti precursor of TDMAT was introduced with a variable leak valve. The reason for choosing TDMAT as the Ti precursor is because this molecule is possible to adsorb on the hydroxylated Si surface at RT. This was confirmed with an IR absorption spectroscopy. A plasma excited water vapor source was installed to the ALD chamber as shown in Fig. 1. The source gas for OH-radical is a mixture of H_2O vapor and Ar made by a water bubbler. The plasma was generated in a glass tube with an induction coil with a frequency of 13.56MHz and a RF power of 30 W. Before the ALD process, the substrate surface was treated with the plasma excited water vapor for 5 min to be terminated with Si-OH. For the TiO_2 deposition, we repeated the cycle of TDMAT saturation and plasma excited water vapor at RT. The TDMAT exposure was set to 1.0×10^{-2} Torr $\times$ 120 s. The saturation of TDMAT on the SiOH surface has been confirmed by the multiple-internal reflection IR absorption spectroscopy [4]. The plasma excited water vapor injection was set to 2 min. The oxidation state of the TiO_2 film was evaluated by X-ray photoelectron spectroscopy (XPS). The thickness of the grown film was measured by spectroscopic ellipsometry.

Figure 2 shows Ti2p spectra obtained from TiO_2 on Si grown by the present plasma assisted ALD. The stable TiO_2 peak of $Ti2p_{3/2}$ can be seen at 458.2 eV irrespective of ALD cycles. This indicates that pure TiO_2 was grown on the Si substrate reproducibly. Figure 3 shows the TiO_2 thickness as a function of the ALD cycle. The linear increase of TiO_2 thickness with the ALD cycle indicates that the TiO_2 is grown in the ALD mode. The growth rate is estimated to be 0.157 nm/cycle. This value is comparable with those released from the previous ALD studies [5]. From the intercept of the TiO_2 thickness at the y-axis, the initial deposition was made at 2.5nm. This implies that the TiO_2 film was grown on the Si surface with an extremely high rate. We tentatively assume that the naturally oxidized Si surface as the starting surface is very active to TDMAT molecules. It is also possible that the interfacial layer of SiO_2 produced at the initial treatment may affect the analysis of spectroscopic ellipsometry.

To conclude, we developed the non-heating, RT ALD of TiO_2. We are now evaluating the concentration of the residual carbon in the film. Although the grown film was amorphous, we are now examining if it is applicable for the photocatalytic film by annealing the sample to generate the anatase phase in TiO_2.

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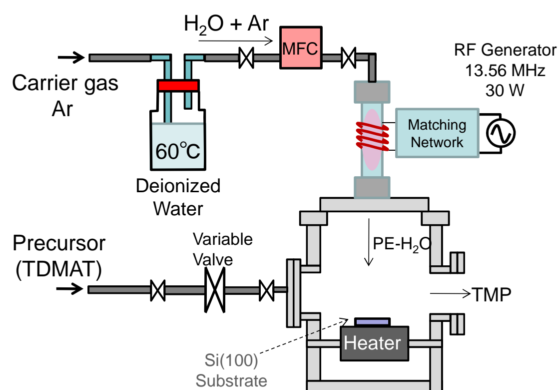

Fig. 1 Schematic of ALD chamber.

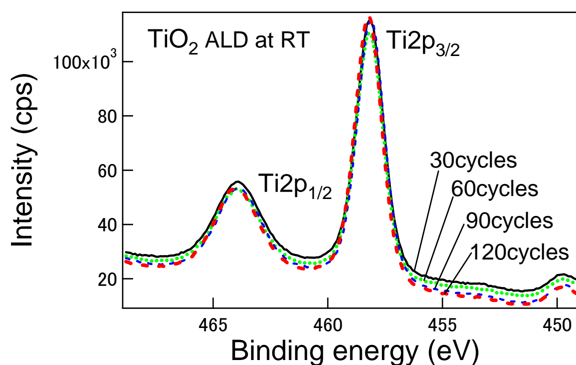

Fig. 2 Ti2p spectra obtained from TiO_2 on Si grown by the plasma excited ALD.

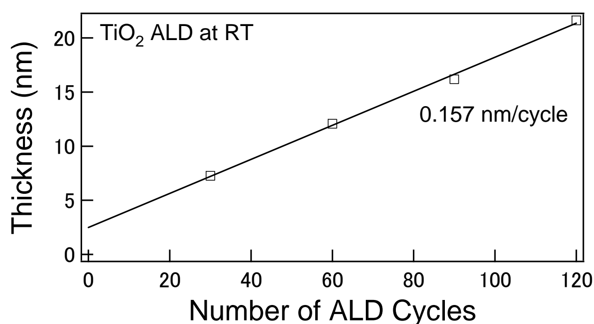

Fig. 3 TiO_2 thickness as a function of number of ALD cycles.