

3P039 Study on formation of small, thin and smooth islands of TiO₂ on silicon substrate

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Small, thin and smooth islands are a convenient system to perform quantitative studies on the bulk defect influence on the surface properties of TiO₂. **The essential requirements** to prepare islands are producing the objects with a small volume and with the countable amount of defects; variable and controllable thickness; small roughness. The convenient methods to realize such conditions are selective deposition of TiO₂ by chemical vapor deposition (CVD) and liquid phase deposition (LPD) using self-assembled monolayer (SAM) as a mask for growth. In both cases the reaction of TiCl₄ (TC) molecules with silanol groups of the irradiated area of the SAM and with water molecules, which were adsorbed on patterned SAM or remained in the solution, plays the significant role in the formation of TiO₂ films.

SAMs of octadecyltrimethoxy-silane (ODS) were prepared on photochemically cleaned Si (100) wafers by CVD, where the molecules react with silanol and are fixed on the substrate. The SAMs were selectively decomposed to form silanol regions by UV irradiation (low-pressure mercury lamp) through a mesh for transmission electron microscopy (a pitch size is 12.5 μm) in Ar atmosphere. It generates SAM-silanol (hydrophobic/hydrophilic) pattern. The morphology and hydrophobicity of the irradiated and non-irradiated surfaces were measured by atomic force microscopy (AFM) and water contact angle measurements.

TiO₂ islands were prepared on the patterned SAM by LPD method using a toluene solution containing TC under Ar atmosphere. Series of experiments were done with varying precursor concentration, deposition time and temperature to improve the characteristics of TiO₂ islands. The TiO₂ islands were also prepared by CVD method by the sequential exposure-evacuation cycles of TiCl₄ vapor and H₂O vapor at different temperatures in a vacuum apparatus. The thin films and islands of TiO₂ were investigated by AFM, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Surface roughness was evaluated by root mean square (RMS) expressed as $[(Z_i - Z_{ave})^2/n]^{1/2}$, where Z_i is the height at point "i" (nm), Z_{ave} is the average of Z (height) (nm), and n is the number of data points. The thickness of the films was estimated from XPS data of the Ti_{2p} / Si_{2p} peak ratio or by AFM. The semi-infinite specimen (Si substrate) with uniform TiO₂ overlayer of thickness (t) model was assumed for calculations from XPS data.

Very smooth, fully covered ODS-SAMs were successfully prepared by CVD. It is essential for following growth of smooth, separated TiO₂ islands on the patterned SAM. The smoothness of SAM was confirmed by AFM RMS data on with (~ 0.15 nm) and without (~ 0.1 nm) SAM samples. Thus, SAM repeated the surface shape of the substrate. The water contact angle measurements of the SAM covered Si substrate have shown a value ~105°, which is in good agreement with those reported in the literature. It corresponds to hydrophobic surface covered with high concentration of ODS molecules. Changes in the water contact angle of the ODS-SAM covered surface showed that the ODS monolayer was decomposed after irradiation by UV light (183 nm) during 30 min in Ar atmosphere. The water contact angle became less than 5° indicating that photoirradiated surface became completely hydrophilic covered with OH groups. The confirmation of the patterned SAM surface was achieved after deposition of the TiO₂ thin film by AFM and SEM.

XPS measurements of the thin TiO₂ films prepared by LPD (varying deposition time, concentration of TC and temperature) have shown that the thickness becomes saturated at very small value 1-2 nm which was unacceptable. Such tendency can be explained by the presence of the thin water layer on the silicon surface at the initial stage. The consumption of the water molecules through hydrolysis of TC leads to suppression the TiO₂ layer formation.

We have expected the selective deposition of TiO₂ on the patterned SAM by LPD, but the formation of TiO₂ occurred in the whole area regardless of the type of surface functional group. The SAM surface may have a negative charge due to partial ionization of the remained (after reaction with ODS) silanol groups (SiOH) to $-SiO^-$, while TiO₂ particles have a negative charge due to oxygen

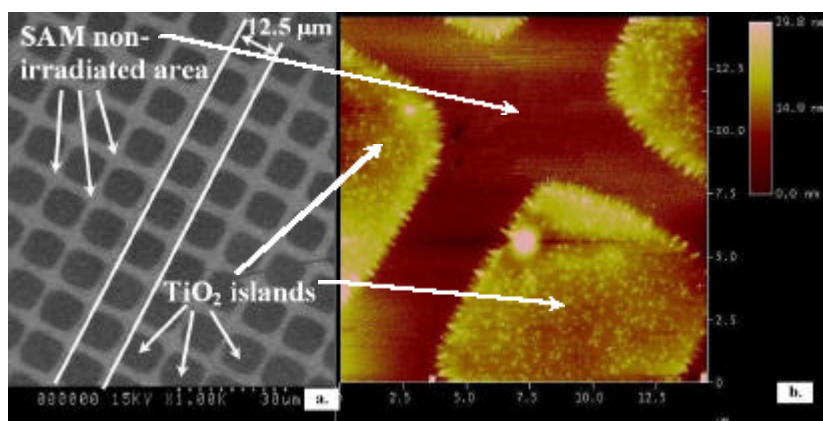


Fig. 1 SEM (a) and AFM (b) images of a patterned TiO₂ thin film prepared by CVD (1 cycle)

vacancies. Thus, it is possible to propose that the deposition on the non-irradiated area can be associated with the small particles of TiO₂ came to the surface from the solution by the electrostatic interaction.

As was mentioned in introduction, very smooth thin films are required. The films with small roughness were tried to prepare by LPD

varying deposition time and concentration of TC. The smallest RMS value which

could be achieved was about 0.7 nm but it did not satisfy the requirements.

We supposed that CVD method by the sequential exposure-evacuation cycles of TiCl₄ gas and H₂O vapor makes it possible to obtain the selective deposition of the smooth islands since the deposition should occur only in the silanol area. The TiO₂ islands were acquired as shown in **Fig. 1**. The pitch size on the SEM and AFM images corresponds to the pitch size of the mesh. The water layer becomes thinner and formation of the TiO₂ islands occurred only in the hydrophilic area. The thickness of TiO₂ layer increased almost proportional to the number of cycles. Thickness per a cycle

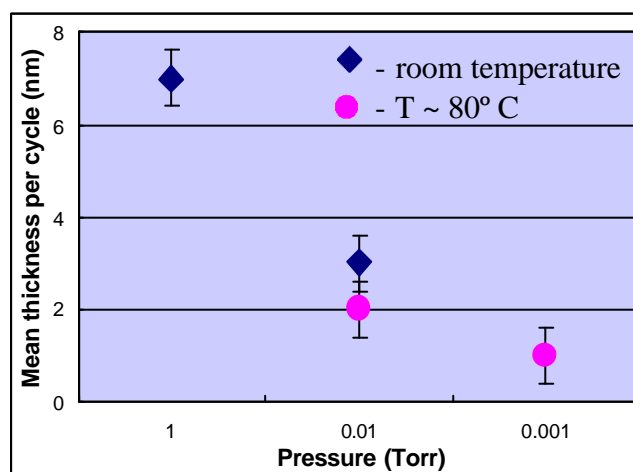


Fig. 2 TiO₂ film's mean thickness grown per a CVD cycle depending on evacuation pressure and deposition temperature

was evaluated at different evacuation pressure and deposition temperature by XPS and AFM as shown in **Fig. 2**.

However, AFM measurements showed that formation of TiO₂ occurred on the whole surface for thicker films. One possibility to explain this effect is when the thickness of the TiO₂ thin film exceeds the thickness of the SAM layer the lateral growth takes place. It means maximum island thickness is determined by the thickness of SAM (~ 2nm). But it was found that the TiO₂ can be removed from the SAM regions by ultrasonication and the separated islands were observed for thick

ultrasonication. Such difference could be explained by lower elasticity of the thick film than the thinner one. Thus, by using ultrasonic treatment on non-chemical bonded TiO₂ layer on the intermediate (SAM) area can be removed for the thick film.

Quality of the films prepared at higher temperature (~ 80 °C) and lower pressure was sufficient for our purpose. RMS value was about 0.3 nm. It is possible to explain by the decreasing of thickness of the water layer. After evacuation at higher temperature almost no water remained on the hydrophilic areas and TiO₂ layer after reaction of TC with the surface or remained water becomes more uniform.

Growth of TiO₂ by LPD was not region-selective on the patterned SAM. The small thickness and unacceptable roughness also prevent one from obtaining an appropriate system for investigation of the bulk defect influence on the surface properties.

The smooth thin islands of TiO₂ were obtained by CVD. The deposition of TiO₂ was selectively occurred in the silanol region which has high hydrophilicity. The thickness and roughness of thin films can be controlled by the selection of growth parameters. By increasing the deposition temperature in CVD very smooth (RMS ~ 0.3 nm) films with controllable thickness were obtained.