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A Study of Dewetting on (001) Rutile using AFM

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Thin SiO_2 films on (001) rutile TiO_2 surfaces have been observed to dewet and form classic droplet patterns on the surface after high-temperature annealing. [1-2] The proposed driving forces for the formation of these droplet patterns include surface tension, temperature gradients and composition gradients, (including gradients formed from the dissolution and precipitation of the TiO_2 substrate into the SiO_2 glassy film [2-3]). Additionally, film thicknesses and substrate orientation may also affect the type of patterns formed during dewetting. Liquid phase sintering (LPS) depends on the wetting/dewetting behavior of the glassy-phase additive. [4] Films dewet to minimize the liquid/vapor interface area. [5]

When a substrate coated with a surface film is at a higher temperature than the surrounding atmosphere the Rayleigh instability results. [6] The thickness variations cause the film to break apart into droplets. [5] For thicker films on a planar substrate, dewetting via the Rayleigh instability occurs more slowly. [5]

Plasma-enhanced chemical-vapor deposition (PECVD) was performed with a SiH_4 precursor pumped into the chamber at 200 standard cc/min (sccm) and N_2O pumped at 400 sccm. Chamber pressure was 900 mTorr and 20 W of power was used to drive the deposition. The SiO_2 films were deposited at 200°C. The system was purged with N_2 before and after deposition. Film thicknesses were approximately 100 and 200 nm. The samples were annealed at 1600°C, just above the SiO_2/TiO_2 eutectic temperature, for 1 h and allowed to cool in an air atmosphere. Samples were heat treated in high-purity alumina crucibles. The alumina powder served as an impurity getter. Visible light microscopy (VLM-Olympus BH2) and atomic force microscopy (AFM-Digital Instruments equipped with Nanoscope III using Si_3N_4 cantilevers in contact mode) were used to characterize the films.

The films were expected to dewet in a densely branching, cell-like network with a uniform distribution of droplets on the (001) TiO_2 surface similar to that investigated by Gilliss, et al. [2] During the anneal of the initial 200 nm thick films, SiO_2 droplets formed on the substrate surfaces. An AFM montage, shown in figure 1, shows a dewetting front with 175 nm high droplets. The film is retracting and leaving droplets behind instead of rewetting the substrate. By tracing the droplet patterns in figure 1, the front's motion across the substrate surface may be mapped. Dissolution of Ti into the glass is believed to provide the driving force necessary to initiate turbulent flow in the film. [2, 7] After the uniform composition change of the entire film, the film's density is also altered, causing the film to contract on the surface. [8]

In thinner PECVD films, (~100 nm), a different droplet behavior was observed. SiO_2 nanodroplets were found to form on top of the rutile surface facets. Tubes of glass form on the facet crests instead of facet valleys, shown in figure 2, due to electrostatic potentials of the oxygen or titanium surface-

terminated facets and the need to lower the liquid's surface energy, as in the Rayleigh instability. The deposited film is initially uniform. Upon thermal treatment, the film becomes liquid and surface reconstruction of the slightly miscut substrate begins. The newly formed facets cause the film to become non-uniform in thickness, and thus, set up the Rayleigh instability in the film. On cooling, amorphous silica tubes and droplets form on top of the facets.

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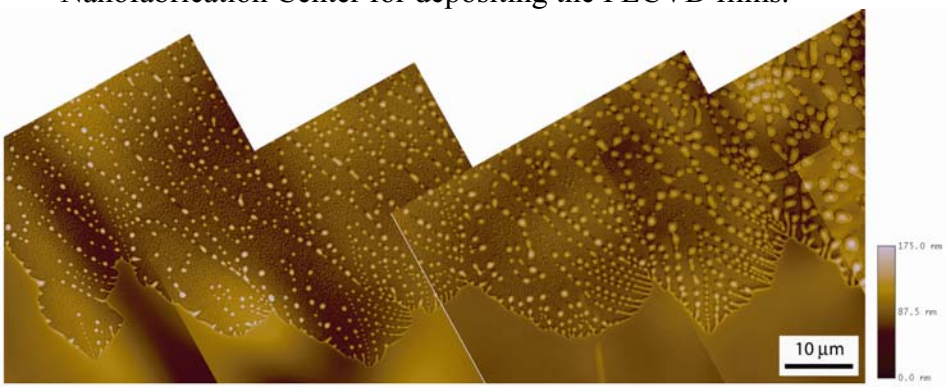

Fig. 1. Contact-mode AFM montage image of a dewetting front in a 200 nm thick SiO_2 film on (001) TiO_2. The continuous film has dewet into numerous droplets up to 175 nm high forming regular patterns.

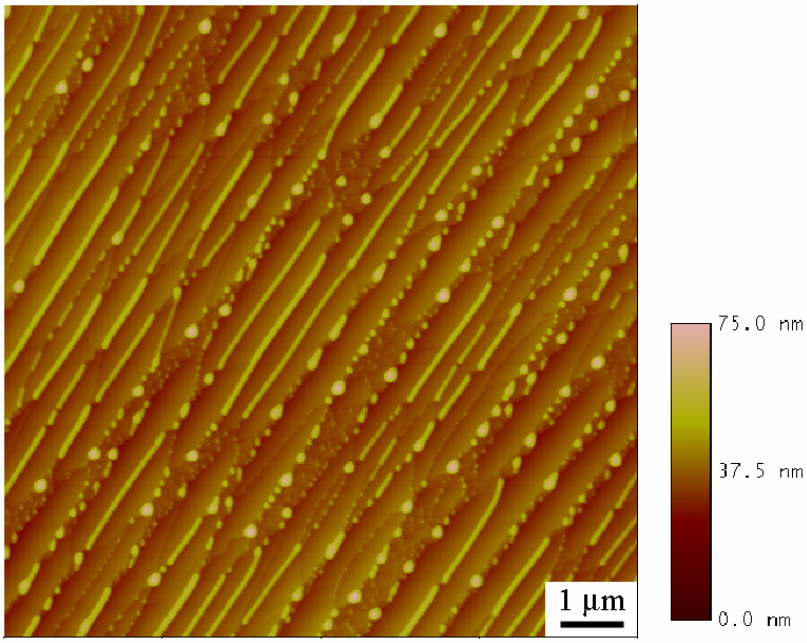

Fig. 2. Droplets are sitting on top of the reconstructed (001) TiO_2 surface facet junctions.

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