## Epitaxial growth of β-Bi<sub>2</sub>O<sub>3</sub> thin films with mist CVD

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Bi<sub>2</sub>O<sub>3</sub> is a wide gap semiconductor forming at least six polymorphs with a variety of functionalities [1]. Among the six phases,  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> has relatively narrow bandgap and shows excellent photocatalytic activity [2]. In equilibrium conditions, thermal treatment at high temperature is necessary to synthesize metastable  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> [1]. Although a number of works have focused on the growth of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> thin films with non-thermal equilibrium processes [2], epitaxial growth of flat thin films is still challenging and has never been achieved as far as we know. In this study, we adopted mist chemical vapor deposition (CVD) method for epitaxial growth of metastable β-Bi<sub>2</sub>O<sub>3</sub>, where mist CVD is usually a low temperature process in atmospheric pressure.

 $\beta$ -Bi<sub>2</sub>O<sub>3</sub> thin films were grown on yttria-stabilized zirconia (YSZ) (111) and sapphire (0001) single crystal substrates at different temperatures from 350 to 550 °C under N<sub>2</sub> gas flow. 2-ethylhexanoic acid solution containing 25 wt.% of bismuth (III) 2-ethylhexanoate diluted with N,N-dimethylformamide was used as a precursor according to ref. 3. X-ray diffraction exhibited epitaxial growth of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> (201) with multiple domains on both YSZ and sapphire substrates (Fig. 1a). At 350 °C of growth temperature, the full widths at half maximum of rocking curves of the 201 peak were as small as 0.065° and 0.070° on YSZ and sapphire substrates, respectively, indicating their good crystallinity. In addition, flat surfaces with root-mean-square roughness less than 2.10 nm were observed with atomic force microscope (Fig. 1b). With increasing growth temperature, however, the thin films gradually aggerated and finally formed nanoparticles. A possible origin for the stabilization of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> is the close Bi-O bond length in the bismuth 2-ethylhexanoate to that of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, which would promote transformation into the oxide. These results indicate that mist CVD is suitable for low temperature epitaxial growth of metastable  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> thin films with high quality.

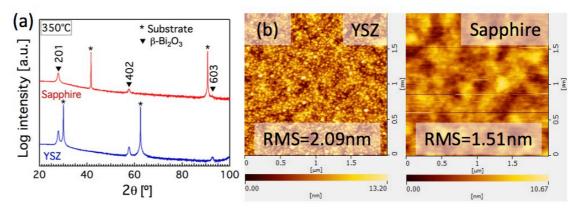


Fig. 1 (a) X-ray diffraction patterns and (b) atomic force microscope images of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> epitaxial thin films on YSZ (111) and sapphire (0001) substrates.

References: [1] D. Michel et al., *Chem. Rev.* **107**, 80 (2007). [2] P. Dulce et al., *Sci. Rep.* **6**, 39561 (2010). [3] S. Yao et al., *Jpn. J. Appl. Phys.* **54**, 063001 (2015).