Topotactic Preparation of Preferentially Oriented $BaTiO_3$ and TiO_2 Thin Films on Polycrystalline Substrate

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A layered titanate $H_{1.08}Ti_{1.73}O_4$ oriented thin film on stainless steel and Ti metal substrates was prepared by using an exfoliation-restacking technique. The layered titanate film can be topotactically transformed to anatase and rutile thin films with preferred orientation along [103] and [110] directions, respectively, by heat-treatment, and to a $BaTiO_3$ thin film with preferred orientation along [110] direction by hydrothermal treatment in a $Ba(OH)_2$ solution.

Preferentially oriented thin films of metal oxides are high performance materials for electronic devices. For the preparations of the preferentially oriented thin films, usually epitaxial crystal growth techniques are utilized.[1–3] In these cases, a single crystal substrate and lattice matching between the substrate crystal and the film crystal are necessary, meaning the high cost for the preparation of the epitaxial films. If a polycrystalline or amorphous substrate can be used for the oriented thin films, a low cost thin film process is possible. Some studies have indicated that the oriented thin films can be obtained on polycrystalline substrates or single crystal substrates without lattice matching by controlling growth direction of film crystal.[4–6] However, the control of crystal growth direction on a polycrystalline substrate is not easy in normal cases.

Recently, we have studied the preparation of $BaTiO_3$ and anatase from a titanate with a layered structure, and found that plate-like $BaTiO_3$ and anatase particles with preferred orientation can be obtained by hydrothermal treatment of the plate-like titanate particles in $Ba(OH)_2$ solution and distilled water, respectively.[7] The structural transformations from the layered titanate to $BaTiO_3$ and anatase are topotactic reactions. This result implies that if a oriented layered titanate film can be prepared on a polycrystalline or an amorphous substrate, the oriented $BaTiO_3$ and TiO_2 films would be obtained by using the topotactic structural transformation reactions.

For the preparations of layered metal oxide thin films with preferred orientation, recently, exfoliation and layer-by-layer assenmbly techniques have developed.[8,9] Titania nanostructured films have been obtained by heat-treatment of a layered titanate film prepared by using the layer-by-layer assenmbly technique.[10]

In the present study, we descript preparation of an oriented layered titanate thin film on stainless steel and Ti metal substrates by using an exfoliation-restacking technique, and preparation of oriented $BaTiO_3$ and TiO_2 thin films from the layered titanate film by using topotactic structural transformation reactions.

A layered H^+-form titanate $H_{1.07}Ti_{1.73}O_4{\cdot}nH_2O$ (HTO) with a lepidocrocite-like layered structure was used as precursor, which was prepared from a layered titanate of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$, as described previously.[7] HTO powder sample was exfoliated into the nanosheets of elementary layer of its structure by reacting with a 0.1 M *n*-propylamine solution.[11] The titanium content in the resulted nanosheet colloidal solution was adjusted to 0.1 M. The HTO thin film was prepared by dipping the stainless steel substrate into the HTO nanosheet solution and then drying in air at room temperature. The HTO film with about 0.3 μm thickness was obtained by repeating the dipping and drying operation for 10 cycles. The HTO film has a layered structure with a basal spacing of 0.938 nm, which is larger than that of its precursor of HTO powder sample (0.922 nm) (Figure 1(b)). Only (0 k 0) diffraction peaks were observed, suggesting that the HTO nanosheets restack on the surface of the substrate and form a preferentially oriented film of the layered titanate after drying.

TiO_2 thin films can be obtained by heat-treatment of the HTO film in air. The HTO film retains the layered structure, but the intensity of the diffraction peaks decreased and the basal spacing changed to 0.933 nm after heat-treatment at 400 °C (Figure 1(c)). Anatase and rutile thin films were obtained after heat-treatment at 600 and 800 °C, respectively (Figure 1(d) and 1(e)). The anatase film shows much stronger (103) diffraction peak than that of the normal powder sample (anatase, JCPDS No. 21-1272), meaning (103) plane of anatase film parallels to the basal plane of the substrate. In the case of the rutile film, only (110) and (220) diffraction peaks were observed, indicating perfect preferred orientation along [110] direction. The preferred orientations

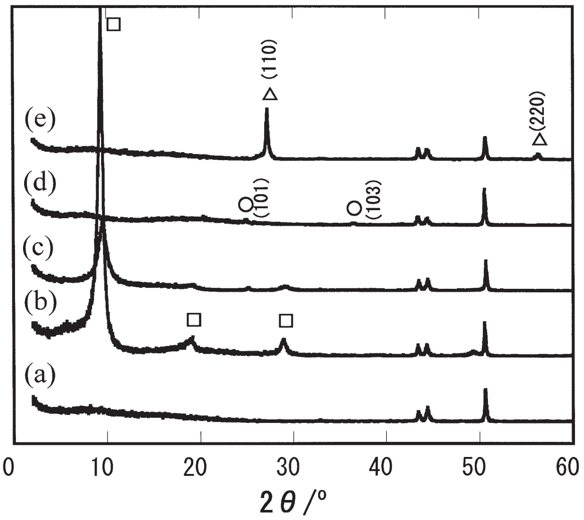

Figure 1. X-ray diffraction patterns of (a) stainless steel substrate, (b) HTO film, and the films obtained by heat-treatment of the HTO film at (c) 400, (d) 600, and (e) 800 °C for 2 h in air, respectively. Squares, circles, and triangles indicate layered titanate, anatase, rutile phases, respectively.

suggest that the formations of anatase and rutile from the layered titanate are dehydration topotactic structural transformation reactions.

A $BaTiO_3$ film was prepared by hydrothermal treatment of the HTO film in a $Ba(OH)_2$ solution. Before the hydrothermal treatment, the HTO film was heated at 400 °C, to prevent the dissolution of the HTO film by re-exfoliation reaction when the film was immersed in the solution. The $BaTiO_3$ film with a cubic phase ($BaTiO_3$, JCPDS No. 31–174) can be obtained after the hydrothermal treatment in a 0.1 M $Ba(OH)_2$ solution at 150 °C in a Teflon-lined, sealed stainless steel vessel (Figure 2(d)). The X-ray diffraction patterns showed very strong (110) diffraction peak and very weak peaks for other diffractions, indicating that $BaTiO_3$ film with a preferred orientation along [110] direction was obtained. This result suggests that the formation of $BaTiO_3$ phase is a topotactic structural transformation reaction, where Ba^{2+} migrate into the crystal bulk through the interlayer pathway and react with the TiO_6 octahedral layers of HTO in the crystal bulk to form $BaTiO_3$ in situ.[7]

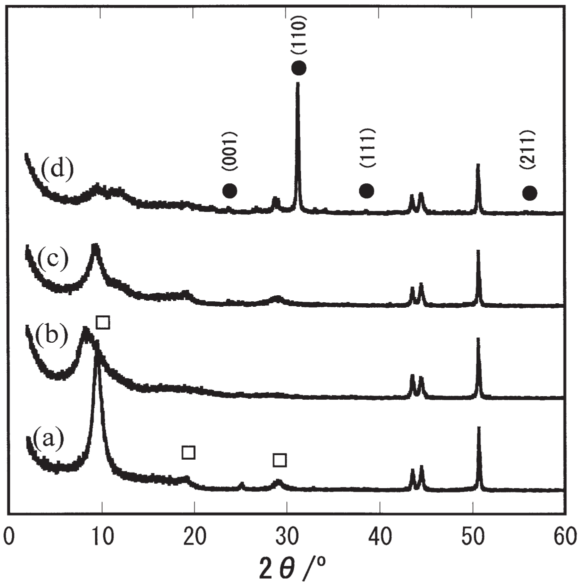

Figure 2. X-ray diffraction patterns of (a) the HTO film after heat-treatment at 400 °C, and the films obtained by the hydrothermal treatment of the HTO film at 150 °C for 20 h in (b) distilled water, (c) 0.01 M, and (d) 0.1 M $Ba(OH)_2$ solutions, respectively. Squares and circles indicate layered titanate and $BaTiO_3$ phases, respectively.

The $BaTiO_3$ film with preferred orientation along [110] direction can be prepared also on Ti metal substrate by using similar method, indicating the orientation direction is not dependent on the properties of the substrate, but on the structure of HTO precursor. Preliminary capacitance and dielectric loss measurements were carried out on the $BaTiO_3$ film with 0.31 μm thickness at an applied voltage of 0.1 V and 25 °C. The dielectric constants and the dielectric losses are 570 and 11% at 10^2 Hz, and 440 and 18% at 10^4 Hz of frequency, respectively. It is notable that the dielectric constant is higher than that of $BaTiO_3$ films prepared by other methods in same frequency range.[12–15]

In conclusion, the oriented $BaTiO_3$ and TiO_2 thin films could be prepared by using topotactic structural transformation reactions from the layered titanate precursor film. The preferred orientation direction of the films is dependent on the structure of the precursor, but not on the properties of the substrate.

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