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The excellent properties of titanium dioxide films (e.g. photocatalytic activity, hydrophilicity) largely depend on their phase composition, crystallinity and microstructure. Crystallization of amorphous films with different thickness (50-2000 nm) was investigated by in-situ isochronal and isothermal annealing at different temperatures and compared with the post-annealing of both amorphous and nanocrystalline films. The X'Pert Pro with MRI high-temperature chamber in parallel beam was used. The time dependences of crystallization were studied at low temperatures (180, 220°C). They could be well described by modified Avrami equation applied to the intensities of diffraction peaks $I = 1 - \exp[-b(t-t_0)^n]$. The exponent n was in the range 2-2.5 and slightly increasing with the film thickness. The initial time t_0 of crystallization (non-zero intensity) increases nearly exponentially with the decreasing thickness while the slope b increases significantly for thicker films. Typical time necessary for the crystallization of the whole film volume at the above temperature varied from several hours for thicker layers to about ten days for the thinnest films. Fast crystallization of the order of minutes appeared at 230 °C for thicker films and went up to 290°C for the thin film (below 100 nm). Weak texture was changing during the crystallization. Significant shifts of diffraction peaks with the temperature were observed and tensile residual stresses were confirmed by the $\sin^2\psi$ method for different diffraction peaks. They decrease with the increasing film thickness. Line profile analysis shown the growth of relatively large crystallites (100 nm) already at the beginning of crystallization. Reflectivity indicates increase of surface roughness with the thickness.

Keywords: titanium oxide compounds, thin films and multilayers, crystallization

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Compositional analysis of LaMnO₃-LaCoO₃-LaNiO₃ thin-film thermoelectric property diagrams

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High-throughput combinatorial mapping is a state-of-the-art screening technique for accelerating the selection and introduction of thermoelectric materials into the manufacturing process. A LaMnO₃-LaCoO₃-LaNiO₃ single-crystalline continuous spread combinatorial thin film library has been deposited onto a 50.8 mm diameter LaAlO₃ (100) substrate using home-grown targets via pulsed laser deposition (PLD). PLD occurred inside a vacuum chamber with a partial O₂ pressure of 13.3 Pa and at a heater temperature of 600 °C. Short duration KrF excimer laser beam pulses (25 ns) were used to strike the targets generating a plume of the vaporized materials which deposited onto the substrate. Inspired by our development of a high-throughput screening tool used to map out thermoelectric (TE) property variations as a function of wafer position, along with their technological importance, the cubic ($Pm-3m$) perovskite LaMO₃ ($M = \text{Mn, Co, Ni}$) materials have been selected to generate a ternary library, which has been analyzed by X-ray diffraction (XRD) using a General Area Detection Diffraction System with a grid matrix, and compositional mapping wavelength-dispersive spectrometry (WDS).

The phase diagram from the combination of the structural phase XRD data and compositional mapping WDS data, allows for a correlation with the TE properties (Seebeck coefficient, electrical conductivity, and power factor) obtained from the screening tool as a function of composition. The technique demonstrated here is expected to rapidly advance the exploration of thermoelectric perovskite oxides in comparison to conventional trial-and-error methods.

Keywords: thermoelectric materials, combinatorial library design, perovskite oxides

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Crystal structure and valence distribution of artificial superlattices [(LaMnO₃)_m(SrMnO₃)_m]_n

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The crystal structure and the valence distribution of Mn ions have been studied in the artificial superlattices, [(LaMnO₃)_m(SrMnO₃)_m]_n, utilizing X-ray scattering techniques. The high quality superlattices were fabricated, and all the films indicate an insulating behavior without reference to the periodicity m . The crystal structure of the films was determined by the structural analysis. The obtained stacking structure of [(LaMnO₃)_m(SrMnO₃)_m]_n is consistent with the designed structure. The periodicity slightly deviates from the designed value and m becomes non-integer value. The Mn valence distribution was evaluated in the films by the resonant X-ray scattering technique. In these artificial superlattices, as a result, the Mn valence state is dominated by the La/Sr layers and is the rectangular wave from 3+ to 4+. The charge modulation spreading over a few layers near the interface could not be observed. [(LaMnO₃)_m(SrMnO₃)_m]_n film with the rectangular wave of Mn valence state was elucidated to be intrinsically insulative.

Keywords: resonant X-ray scattering, charge ordering, superlattice structure

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Growth control of perovskite-related oxide thin films

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Perovskite-related oxides are materials showing interesting features. In order to realize functional devices taking advantage of these materials, top quality thin films for different applications are always necessary. However, it is not easy to grow such films and many criteria have to be fulfilled. The degree of complexity enhances significantly for multicomponent materials such as high-Tc superconductors, giant magnetoresistive materials, heterostructures,