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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 X²Pert 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 ($Pm\bar{3}m$) 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-T_c superconductors, giant magnetoresistive materials, heterostructures,

other. This translates into a lower growth control level. Solution resides in identification of the specific details as well as of the general principles of growth and their personalized application towards preparation of optimized thin films of top quality. This is our approach and goal. Examples in this regard will be introduced.

Keywords: oxide thin films, perovskite, MOCVD

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Reactivity and optical property of diarylethene-gold nanoparticle complex in the film

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Gold nanoparticles covered with photochromic diarylethene polymers (Au-poly(DE)) or block copolymers with styrene were prepared. These nanoparticles expressed a bright red color because of their surface plasmon resonance absorption, and exhibited reversible photochromism upon alternate irradiation with ultraviolet light and visible light in the solid state as well as in solution. The photocyclization reactivity of the diarylethene chromophores around the gold nanoparticles decreased by shortening the distance between the surface of the gold nanoparticles and the diarylethene chromophore. Some effects of the gold nanoparticles on the optical properties of the diarylethene chromophores were evaluated by comparison of difference spectra between the UV-visible absorption spectra in the photostationary state and in the initial state under various conditions. In the case of Au-poly(DE) that has several-nanometer size of gold core synthesized by Brust' method, the effect was found to appear as a bathochromic shift in the absorption maximum of the diarylethene closed-ring form and the bathochromic shift depends on chain length of the diarylethene polymer and the ambient surroundings. On the other hand, in the case of Au-poly(DE) that has gold core size more than 10 nm synthesized by applying citrate reduction, the surface plasmon resonance absorption of Au-poly(DE) was altered by refractive index change in the diarylethene polymers that are caused by the photoisomerization of diarylethene chromophores. These results show that there are several interactions between the gold nanoparticles and the diarylethene chromophores, and these interactions strongly depend on the particle size, the distance from gold surface to the diarylethene chromophore, and the ambient surroundings.

Keywords: gold nanoparticle, photochromism, polymer

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Polyoxometalate Langmuir-Blodgett films toward two-dimensional molecular crystals

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Two-dimensional molecular crystal of polyoxometalate (POM) on

solid substrate is crucial to realizing POM-based molecular devices. Here, regular two-dimensional arrays of POMs with sub-nanometer size were constructed as Langmuir-Blodgett (LB) films by using dimethyldioctadecylammonium (DODA) as cationic partner. The film structure was evaluated by specular X-ray reflectivity (SXR) and grazing incidence X-ray diffraction (GIXD) measurements. Even ring-shaped and ball-shaped nanosized POMs were two-dimensionally arranged onto solid substrates. LB films of planer-shaped Anderson-type POM (hexatungstoantimonate, SbW₆) showed a well-ordered layered structure with a distance of 4.4 nm, in which POM molecules had a two-dimensional square lattice with a length of 1.4 nm. In the case of ellipsoid-shaped photoluminescent POM (decatungstoeuropate, EuW₁₀), the molecular ordering of POM anions was improved to form a regular two-dimensional array by using more concentrated solution of EuW₁₀ in the LB film fabrication. The better molecular arrangement leads to the stronger intensity of the emission by ⁵D₀ to ⁷F₁ transition and the longer emission lifetime. POM nanoring (Mo142, 3.9 nm) and nanoball (Mo132, 2.5 nm) having molecular size compared to small proteins were also incorporated in the built-up LB films having well-defined layered structure. The LB films contained densely packed two-dimensional arrays of Mo142 and Mo132 anions, and their molecular structures and electrochemical characteristics were retained. This verifies that the POM LB films are a promising option to fabricate functional thin films toward a two-dimensionally ordered molecular device.

Keywords: thin films and multilayers, X-ray reflectivity, grazing X-ray diffraction

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A study of polymer thin film formation on quartz substrate by X-ray grazing incidence techniques

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Thin films of carrageenan, polyvinylpyrrolidone (PVP) and carboxymethylcellulose (CMC) polymers were fabricated by spin-coating aqueous solution of the polymer onto quartz substrate. The thicknesses of the films were varied by varying the process parameters such as concentration of the polymer solution, spin speed and spin time of the spin-coating. Angle-dispersive total-reflection x-ray fluorescence (AD-TXRF) spectroscopy profiles of the three polymers showed film formation only in carrageenan and PVP. The CMC polymer showed an AD-TXRF profile of a bulk sample on top of the substrate. For both carrageenan and PVP, an increase in concentration yielded a corresponding increase in intensity of the fluorescent or scattered peaks. Thicknesses of the thin films were measured by x-ray reflectivity (XRR). For carrageenan, concentration of the polymer solution was the main determinant of final film thickness over other process parameters. The thickness of the films showed a linear relationship with the sulfur fluorescent intensity present in the polymer measured by AD-TXRF. For PVP, poor adhesion of the polymer onto the substrate yielded a limited number of thickness measurements from the XRR profiles.

Keywords: polymers, total reflection X-ray fluorescence, X-ray reflectivity