Division of Materials Chemistry
- Inorganic Photonics Materials -

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Scope of Research

In this laboratory, amorphous and polycrystalline inorganic materials and organic-inorganic hybrid materials with various optical functions such as photorefractivity, optical nonlinearity, phptolumionescence and photocatalysis are the target materials, which are synthesized by sol-gel, melt-quenching and sintering methods and so on. Aiming at highly functional materials the structure-property relationship is investigated by X-ray diffraction techniques, high-resolution NMR, thermal analysis, various laser spectroscopies and quantum chemical calculations.

Research Activities (Year 2007)

Publications

Takahashi M, Maeda T, Uemura K, Yao J, Tokuda Y, Yoko T, Kaji H, Marcelli A, Innocenzi P: Photo-induced Formation of Wrinkled Microstructures with Long-range Order in Thin Oxide Films, *Advanced Materials*, **19 (24)**, 4343-4346 (2007).

Menaa B, Takahashi M, Innocenzi P, Yoko T: Crystallization in Hybrid Organic-inorganic Materials Induced by Self-organization in Basic Conditions, *Chem. Mat.* **19 (8)**, 1946-1953 (2007).

Kakiuchida H, Takahashi M, Tokuda Y, Masai H, Yoko T: Effect of Organic Group on Structure and Viscoelastic Properties of Organic-inorganic Polysiloxane Hybrid System, *J. Phys. Chem. B*, **111**, 982-988 (2007).

Mizuno M, Takahashi M, Tokuda Y, Yoko T: Substituent Effect on the Formation of Organically-modified Silicophosphate through Nonaqueous Acid-base Reaction, *J. Sol-Gel Sci. Technol.*, **44**, 47-52 (2007).

Presentations

Takahashi M, *et al.*, Photopolymerisation-Initiated Formation of Ordered Microstructure in Oxide Thin Films from Photo Monomer-Oxide Precursor System Photopolymerisation-Initiated Formation of Ordered Microstructure in Oxide Thin Films from Photo Monomer-Oxide Precursor System, XIV International Sol-Gel Conference, 6 September 2007, Montpellier, France.

Tanaka Y, Tokuda Y, Takahashi M, Yoko T, Durable Organic-inorganic Hybrid Silicophosphate Glass Prepared through Nonaqueous Acid-base Reaction, The Ceramics Society of Japan Fall Meeting, Aichi, Japan, 12 September 2007.

Grants

Takahashi M, The Kyoto University Foundation, International Collaborative Work “Self Organized Nano/micro Fabrication of Thin Oxide Films”, 10 October 2006–9 October 2007.

Tokuda Y, Fabrication of Pb-free Sealing Glass, JST, Research for Promoting Technological Seeds, 13 September 2006–28 February 2007.

Tokuda Y, Quantitative Structure Analysis of Amorphous Materials Using Solid State NMR Spectroscopy, 1 December 2007–30 November 2008, CASIO Science Promotion Foundation.

Photo-induced Formation of Wrinkled Microstructures with Long-range Order in Thin Oxide Films

Formation of ordered microstructures via spontaneous organization is in principle one of the simplest routes to produce controlled patterns in thin films. Here we show that patterned structures of oxide materials are indeed obtained through controlled processing of sol-gel films. We have induced wrinkling, through UV curing, in hybrid organic-inorganic films containing acrylamide monomers and titania precursors. Figure 1 shows the fabrication process of the present method. We have successfully controlled the wrinkling process by suppressing the evaporation of solvents to obtain a wet and soft film even several hours after deposition. The faster polymerization of the film surface generates a buckling effect to create patterns in the films. The removal of the organic polymer by thermal treatment leaves titania microstructures having a long-range order. This method of producing the micropatterned structures as shown in Figure 2 will find several applications in photonics.

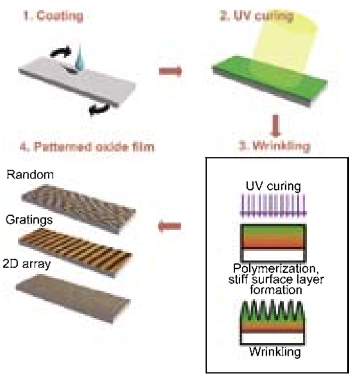

Figure 1. Schematic illustration of spontaneous formation of wrinkled patterns. 1. A hybrid acrylamide-titania film is deposited via spin-coating. 2. UV curing is applied to the film. 3. The formation of a stiff surface layer induces wrinkling on the films. 4. Thin oxide films with different wrinkled patterned structures are obtained by firing.

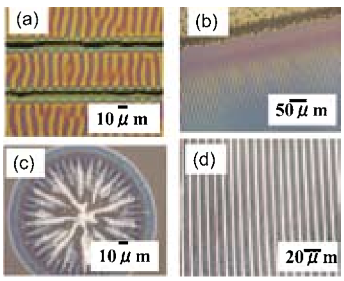

Figure 2. (a) ordered structure prepared on a patterned substrate (b) long range ordered structure fabricated by shaped UV light illumination, (c) dendrimer like structure fabricated by putting a droplet on the substrate, and (d) ordered structure fabricated by covering a part of the coating. Only black light (254nm, 5W) was used as a light source for fabricating these patterns.

Quantitative Structure Analysis of Quadrapolar Nuclei in Amorphous Material

MAS NMR is one of the powerful tools to obtain the structural information especially on dipolar nuclei (I = 1/2) in amorphous material. Unfortunately, quadrupolar nuclei (I ≥ 3/2) provide too broad MAS NMR spectra to be analyzed quantitatively, although half of the elements on earth have quadrupolar spin. Recently, Frydman et al. have developed MQMAS NMR for a better understanding of quadrupolar nuclei in a solid state material. However, it lacks quantitative information because the efficiency of multiquantum spin transition depends on the quadrupolar coupling constant.

In this work, we will provide a quantitative analysis of the local structure of quadrupolar nuclei in amorphous material based on the inverse analysis of MQMAS NMR spectroscopy and quantum chemical calculation. An observed spectrum and an inherent distribution of quadrupolar parameter, R, are related by the next equation

$$I(\varpi) = \int I_0(\varpi; R)\Pi(R)dR \qquad (1)$$

where $I(\varpi)$ is the observed spectrum, $I_0(\varpi;R)$ is the theoretical spectrum for R, $\Pi(R)$ is the distribution of R. Using equation (1), $\Pi(R)$ can be calculated based on the numerical approach with Tikhonov regularization (inverse analysis). The quantum chemical calculations make a direct correlation between R and structure parameter as follows,

$$C_q = e^2Q(q_{zz})/h \qquad (2)$$

where C_q is the quadrupolar coupling constant and q_{zz} is the electric field gradient. We are now trying to establish inverse analysis to extract the inherent structure distribution in inorganic glass from the measured NMR spectra.

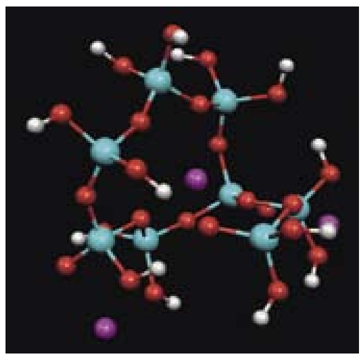

Figure 3. A model cluster of the local structure of sodium silicate glass. Quantum chemical calculation provides the electric field gradient tensor, q_{zz}, which is related to the quadrupolor coupling constant, C_q, as $C_q = e^2Q(q_{zz})/h$