学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Fabrication of Polystyrene Colloidal Crystal Films by Electrophoretic Deposition and Structural Color Control

（電気泳動堆積法によるポリスチレンコロイド結晶の作製と構造色の制御）

Chapter 1　A colloidal crystal is an ordered array of colloid particles. The colloidal crystal film is promising for the different types of photonic materials, such as optical waveguides and sensors, due to its wide range of coloring derived from Bragg diffraction in the visible wavelength region. Colloidal crystal films have been synthesized by the various techniques. However, the low formation rate of the colloidal crystal films has still been one of the key issues in future industrialization for mass production. Recently, electrophoretic deposition (EPD) is becoming one of the promising candidates to realize the rapid colloidal crystal film fabrication. The EPD process is a widely used coating process for many industrial applications. This process is characterized by the migration of colloidal particles in a liquid under an electric field, i.e., electrophoresis, and the subsequent deposition onto an electrode. In 2000, the colloidal crystal films made of polystyrene (PS) particles with 200 - 300 nm diameters were fabricated for 30 minutes by the EPD technique. Since then, the research of colloidal crystal films was directed to faster fabrication and size enlargement. Nevertheless, they have still remained in the range between 30 minutes and 2 hours, and several cm^2 size, respectively. In this thesis, optimal conditions to fabricate the colloidal crystal films by the EPD technique were explored for the sake of fast and large size fabrication. For this purpose, growth mechanism of the colloidal crystal film was investigated in detail. The sensing applications of the colloidal cystal films were also examined.

Chapter 2　The optimal condition for the EPD colloidal crystal film formation was investigated in detail. The aqueous PS colloidal suspension was not appropriate due to the generation of gas bubbles during the electrolysis and formed only amorphous films. Dialysis and the application of a pulse voltage could avoid the gas bubble generation, however, particle self-assembly was still amorphous. As a suspension for the EPD process, the effectiveness of mixing ethanol (EtOH) and water was confirmed by testing several alcohols as solvents, and explained from the different viewpoints including hydrogen bond, van der Waals dispersion force, and mobility/freedom of PS particles. The higher the EtOH concentration, the better the colloidal crystal film formation. In the investigated range, the most preferable condition for the EPD colloidal crystal film formation was from the 92.5 vol% EtOH suspension. The substrate withdrawing rate from the suspension also significantly affected the EPD colloidal crystal film fabrication. Too slow and too fast withdrawing rates were not good. The most preferable rate was 3.0 mm/sec. The large area colloidal crystal film formation by the EPD technique was also demonstrated. Comparable quality of EPD colloidal crystal films fabricated on small area indium tin oxide (ITO)-coated glass (ITO/glass) and large area (over 50 cm^2) ITO-coated polyethylene terephthalate (PET) sheet (ITO/PET) substrates

was confirmed by the SEM observations and the reflectance spectra. These results demonstrate the advantage of the EPD technique for large scale production of colloidal crystal, considering the fast fabrication rate compared to the other conventional techniques. The growth rate of the colloidal crystal is extremely rapid (within one minute for 900 mm^2 area) compared with those of previous papers, such as oil covering and capillary deposition methods (several to hundreds of hours). This process has the potential for high-speed deposition of the colloidal crystalline thin films.

Chapter 3 A growth mechanism of the colloidal crystal films from the concentrated EtOH aqueous suspension was investigated. Closely packed colloidal crystal film was formed within 55 seconds. By the analysis of the reflection spectra and the optical microscope images, the growth mechanism from the colloidal suspension to the colloidal crystal film was found to consist of 4 stages. The 1st stage is a liquid film of the concentrated colloidal suspension on a substrate. By the progress of evaporation, the phase transition from disorder to order to form the non-closely packed colloidal crystal by self-assembly takes place. At the moment of the phase transition, the Bragg's diffraction peak is detected and the structural color appears. In the 2nd stage, the diffraction peak shifts toward the shorter wavelength direction (blue shift), due to the reduction of the interparticle distance of the non-close packed colloidal crystal. In the end, the closely packed colloidal crystal film is formed. In the 3rd stage, the liquid film covering on the colloidal crystal film evaporated and iridescence color due to thin-film interference is tentatively observed. In the 4th stage, the colloidal crystal film changes from wet to dry, by the evaporation of the interparticle EtOH aqueous solvent. The structural color changes from green to blue and the diffraction peak wavelength goes down with one more stage. This color change is dominated by thechange of the refractive index of the interparticle medium from the liquid to the air.

Chapter 4 The interparticle space of the colloidal crystal film was fulfilled by the PDMS (polydimethylsiloxane) elastomer to realize the soft photonic crystals. After filling the interparticle space with PDMS elastomer, the color changed from light blue to green due to the increase of the interparticle distance and the refractive index increase of the interparticle space. By the 4 times PDMS elastomer filling, the color changed to red with the further increase of the interparticle distance. By the tensile test of this film, the deformed area has shown green color with the shrinking of the interplanar distance although nondeformed area has not shown any color change. This result has shown the potential use of the colloidal crystal films with PDMS filling for the strain detection sensors.

Chapter 5 Swelling phenomena was investigated in detail by the different kinds of silicone oil and other organic compounds as solvents. By dripping these solvents onto the colloidal crystal film with PDMS filling, the structural color change was observed as a red shift (the diffraction peak shifts toward the longer wavelength). These red-shifted peaks again blueshifted to the original green color by drying up the volatile solvent. Since this phenomenon was reversible and repeatable, the possibility of the obtained colloidal crystal film with PDMS elastomer filling as volatile liquid sensor was shown. The swelling ratio for all solvents investigated was determined using the estimated interplanar distance. Generally, the swelling ratio of the solvents was inversely dependent on the solubility parameter. The highest swelling ratio, 1.6114, was obtained by the heptane, of which solubility parameter, 7.4 $cal^{1/2}cm^{-3/2}$, was very close to that of PDMS, 7.3 $cal^{1/2}cm^{-3/2}$.

Chapter 6 The general conclusions of my research and future prospects are given.