Control of Size and Two Dimensional Ordering of Au Nano-particle Using Block Copolymer Thin Film as Nano-reactors

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(Introduction) In order to control the size and two dimensional alignments of Au clusters and/or nano-particles, the micro-phase separated structure of amphiphilic liquid crystalline di-block copolymer was used as nano-reactors. Liquid crystalline amphiphilic di-block copolymer consisted of poly(ethylene oxide) and polymethacrylate having mesogenic group as ester group form a hexagonally packed PEO cylinders selectively in wide ranges of copolymer fraction and temperature due to the thermodynamic effect of liquid crystal formation. PEO nano-cylinders are controllable to align normal to the silicon wafer surface. [1, 2] In this study, the location of Au ions and Au nano-particle in a nano-reactors were determined by grazing incidence small angle X-ray scattering (GISAXS), X-ray reflectivity (XRR) and atomic forth microscopy (AFM).

(Experiments) PEO_{114-b-PMA(Az)_{40}} and PEO_{272-b-PMA(Az)_{17}} were used as nano-reactors in this study. Thin film of PEO_{ae-b-PMA(Az)_{n}} were prepared on the silicon wafer by spin coating from toluene solution. PEO_{ae-b-PMA(Az)_{n}} thin film was immersed in aqueous solution of ethylene diamine Au complex at room temperature. After immersing PEO_{ae-b-PMA(Az)_{n}} thin film, the amount of doped Au ions were determined from the melting temperature depression of PEO in nano-reactor and the critical angle of total reflection of X-ray. The reduction of Au ions was carried out in hydrogen atmosphere (H_{2}/N_{2} = 1/9) at 80 °C. Grazing incident small angle X-ray scattering (GISAXS) was measured GI optics at FSBL03XU, SPring-8, Hyogo, in order to evaluate the structure change of nano-reactors after doping and reduction of Au ions. The wavelength of X-ray was 0.1 nm^{-1} and the camera length was 2000 mm. X-ray reflectivity (XRR) was measured by Rigaku TTR X-ray optics. Atomic forth microscopic (AFM) observation was carried out by SII Nanotechnology Co Ltd E-sweep using cantilever with 5 N/m at 123-167 kHz. Transmission electron microscopic (TEM) observation was carried out by JEOL JEM-3200FS.

(Results) Fig.1 showed TEM image of the two dimensional alignment of Au nano-particles which were obtained by the reduction of Au ions in the hydrophilic PEO nano-cylinders of PEO_{114-b-PMA(Az)_{40}}. Two dimensional alignments of Au nano-particles were the result of highly ordered hexagonally packed PEO cylinders perpendicular to the substrate surface. The average diameter of Au nano-particles was 3.7 ± 0.2 nm, however one cylinder had two or three nano-particles. The control of amount of doped Au ions in each cylinders and the mild reduction process were required to control the size of Au nano-particles.

The alignment of PEO nano-cylinders were scarcely changed after the doping Au ions judging from the GISAXS and AFM observations. GISAX profiles were analyzed by the distorted wave Born approximation, the distribution of cylinder size (Δd/d) was 0.1 and 0.15 before and after doping Au ions, respectively. This result suggested that the amount of doped Au ions in each PEO cylinders was almost the same. AFM phase images for PEO_{272-b-PMA(Az)_{17}} before and after doping Au ions, the phase difference between PEO cylinder and PMA(Az) matrix became smaller due to the stiffness increment of PEO cylinders absorbed Au ions. From the fitting of XRR profiles of PEO_{114-b-PMA(Az)_{40}} thin film doped Au ions, the doped Au ions localized at the upper region of PEO cylinders. XRR profiles fitting analysis was also carried out for PEO_{114-b-PMA(Az)_{40}} thin film after reduction of Au ions. Au nano-particles existed on the top of PEO cylinders, which were observed by AFM.

References