Reciprocal space mapping of silver nanoparticle array re-assembly and oxidation

M. Jergel¹, P. Siffalovic¹, K. Vegso¹, M. Benkovicova¹, A. Vojtko¹, E. Majkova¹, H. Lee², C. Ku², M. Lin², U. Jeng²
¹Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia, ²National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Self-assembled metal oxide nanoparticle layers have attracted much attention recently due to potential applications in sensors. Here we report on a UV/ozone-driven re-assembly and oxidation of a self-assembled silver nanoparticle bilayer deposited by a modified Langmuir-Schaefer technique that was probed in-situ by simultaneous measurements of the small- and wide-angle X-ray scattering at grazing incidence (GISAXS, GIWAXS). The experiments were performed at BL23A endstation of NSRRC, Taiwan. Four distinct stages of the system response to the UV/ozone treatment were identified. In the first stage 0-120 s, a gradual extinction of Bragg rods and the nanoparticle short-range order due to a gradual surfactant removal is observed in GISAXS that is connected with an array densification and order improvement obeying the paracrystal model in the shrinking self-assembled regions. In the second stage 120-360 s, the original self-assembly goes to a total extinction while the integral intensity of Ag 111 diffraction in GIWAXS starts to decrease, suggesting the total surfactant removal. No nanoparticle short-range order is observed in stage III 360-730 s where AgO monoclinic phase due to the nanoparticle surface oxidation appears and pure Ag phase disappears. The initial AgO unit cell volume corresponding to the unstrained phase gradually expands by 4.6 % to the end of stage III. In stage IV 730-2000 s (end of measurements), new Bragg rods appear in GISAXS, suggesting a nanoparticle agglomeration with a typical correlation length of approximately 240 nm that was confirmed by ex-situ atomic force microscopy. The agglomeration does not reach saturation even after 2000 s while the AgO phase remains stable. These results have direct implications for tailored preparation of advanced sensors based on metal oxide nanoparticles. The work was supported by the projects APVV-0308-11, VEGA 2/0041/11, SAS-NSC JRP 2011/05, SAS-TUBITAK JRP 2013/6, COST MP1203 and COST CM1101.

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