1B12   In-situ XRD study of oxidation process of copper nanoparticles

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The oxidation kinetics of bulk copper surfaces have been investigated over one century and summarized in several books and reviews, whereas relatively little is known about the oxidation of nano-particulate copper. Here we present our experimental data on the oxidation process of Cu nanoparticles observed by means of in-situ grazing incident x-ray diffraction (GIXRD) method under a controlled pressure and temperature. The Cu nanoparticles (mean size: ~12 nm) were generated by the inert-gas-aggregation method and deposited on a MgO substrate at 298 K. We confirmed from SEM and TEM observations along with BET measurements that the nanoparticles do not so highly coalesce with respect to the present experimental conditions (mean particle size, substrate temperature and deposition speed). From HRTEM observations the particles frequently showed the icosahedral morphology rather than the bulk crystalline structures.

Fig.1(a) shows the GIXRD pattern of the Cu nanoparticles under vacuum and Fig.1(b) shows the result after 10 h oxidation in dry air with the pressure of 13.3 Pa. The oxidation process initiated by introducing dry air was detected from the Cu_2O 111 diffraction peak evolution vs. time. It should be noted that no CuO phase has been detected in the present experiments. The XRD intensity ratio of Cu_2O 111 and Cu 111 diffraction peaks was used to derive the amount of Cu_2O. As can be seen in Fig. 2, the Cu_2O phase grows drastically up to the oxide thickness of ~0.5 nm, and then slows down up to reaching a saturated thickness of ~0.7 nm. The last process showed more like a stop of the oxidation. The whole oxidation process could be expressed not with a

Fig. 1. In-situ GIXRD pattern (CuKα) from Cu nanoparticles (a) under vacuum and (b) after 10 h oxidization in 13.3 Pa dry air.

single rate equation, but with two logarithmic rate equations. From the obtained rate equations, an additional increase of the oxide thickness after one year was estimated to be ~0.1 nm, indicating the protective oxidation behavior. This two-step oxidation process denotes that the Cu nanoparticle immediately forms a thin protective Cu_2O layer to prevent the further oxidation as soon as exposed by the atmospheric air.

The stress condition in the Cu nanoparticle during oxidation was investigated from the variation of the
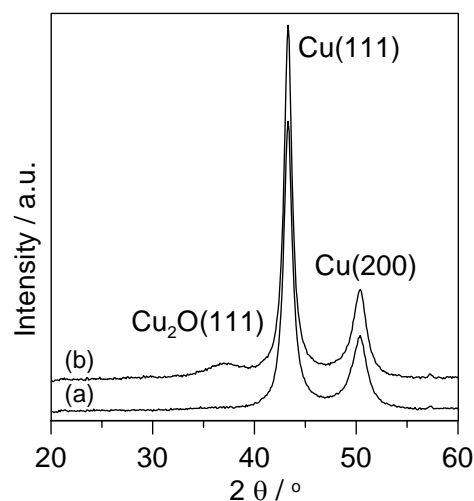
lattice constants of the Cu cores and the Cu_2O shells. The lattice constant of the Cu cores decreased rapidly during the fist stage oxidation, and then kept a constant value till end. Inversely, the lattice constant of the Cu_2O shells increased first and then also turned to a constant value. The two-step lattice constant change of the Cu cores and the Cu2O shells showed a strong correlation with the thickness change of the Cu_2O shell. In this work, both of the Cu_2O shells and Cu cores kept a smaller lattice constant than the bulk one, indicating the compressive condition of the Cu nanopartilces at room temperature. According to the recent study of molecular dynamics

Fig. 2. The x-ray intensity ratio of Cu_2O 111 to Cu 111 as a function of air exposure time.

simulations of the Si nanoparticle oxidation [1], grown SiO_2 surface layers bring an internal compressive stress in an unoxidized Si core, which was thought to be correlated with the self-protective oxidation of Si particles [2]. Thus, we consider the compressive stress observed in the present experiment plays an important role in inhibiting the further oxidation over a very thin oxide layer.
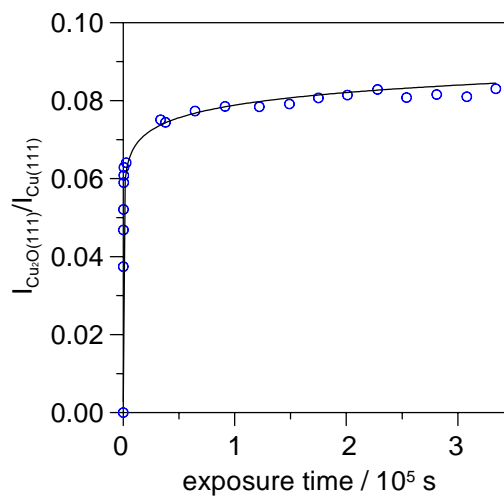
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