

Topotactic metallization of ruthenate nanosheet crystallites

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Introduction

Nano-sized metals such as nanoparticle, nanorod and nanowire have been extensively studied in science and technology. As they mostly offer intriguing physical and chemical properties associated with the size and shape on a nanometer scale, it is of essential importance to develop unique structure and dimension of metal nanomaterials for many applications including electronics, optics and magnetic devices as well as catalysis. In this study, we examined structural transformation of ruthenate nanosheets, obtained via total exfoliation of layered ruthenate, under reducing atmosphere by means of grazing-incidence X-ray diffraction analysis.

Experimental

Layered ruthenate, NaRuO₂, with α -NaFeO₂-related structure was chemically delaminated into elemental host layer, i.e. RuO₂^{0.2-} nanosheet, having a thickness of ~ 1 nm through soft-chemical process [1]. Sub-monolayer films in which the ruthenate nanosheets lay flat to Si substrate were fabricated via electrostatic self-assembling with cationic polymer. Then, the obtained films were heated at more than 200°C for 1h under 10% hydrogen gas flow. In-plane diffraction pattern of these films was measured by a four-axis diffractometer equipped with NaI scintillation counter at the BL-6C in Photon Factory.

Results and Discussion

Synchrotron radiation in-plane XRD patterns for as-grown and heated samples are displayed in Fig. 1. The as-grown film exhibited three diffraction peaks at 3.94, 6.85 and 7.85 nm⁻¹, which are assignable to 2D hexagonal cell of $a = 0.2929(6)$ nm [1]. After heating at 200°C, only two peaks at 4.20 and 7.30 nm⁻¹ were detected. Judging from metallization of bulk precursor in the same heating condition, they can be indexed as 100 and 110 of hcp-Ru with c -axis orientation, respectively. On further heating up to 400°C, the pattern appears to remain more or less unchanged except for negligible upsurge at 4.8 nm⁻¹. However, the expanded peak profile around 7.2 nm⁻¹ indicates a distinct change. The 110 peak of hcp-Ru in Fig. 1b shifted to larger $1/d$ value after heating at 300°C and above. And the resultant 110 peak centered at 7.36 nm⁻¹ is consistent with that of bulk hcp-Ru with a -axis of 0.27 nm. This indicates that hcp-Ru at early stage of transformation seems to have a structural strain, which stems from the precursor having a larger 2D periodic structure of Ru atom as a hexagonal template. Such a

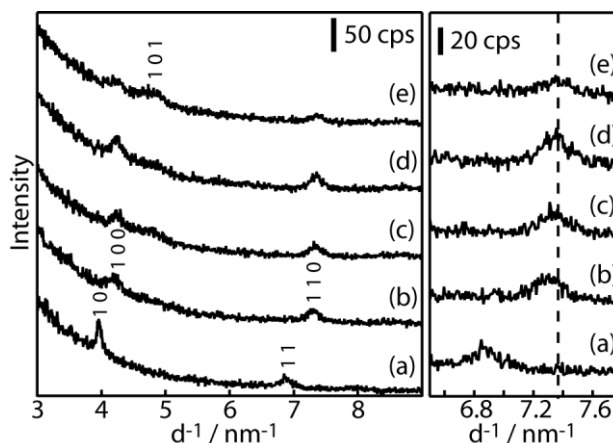


Fig. 1 In-plane XRD patterns for (a) as-grown film and samples heated at (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C under reducing atmosphere. Right panel shows the magnified profile around 7.2 nm⁻¹.

strain can be entirely relaxed by further heating. Here, it should be noted that 500°C-heated sample showed a strong peak assignable to 101 of hcp-Ru. This is because excessive atomic diffusion induced by high temperature leads to a formation of randomly oriented hcp-Ru polycrystalline phase as seen in the case with multilayers of titania nanosheets [2]. As a result, it is found that the ruthenate nanosheets metalize into hcp-Ru oriented along the c -axis through hydrogen reduction at below 400°C.

Interestingly, AFM observation (not shown) revealed that lateral morphology of the ruthenate nanosheets was preserved after the metallization. On the other hand, their sheet thickness decreased from ~ 1.3 nm to ~ 0.6 nm. This can be explained by the removal of oxygen atoms from the ruthenate nanosheet in the reduction process. These results suggest that topotactic metallization took place. This structural behavior may be peculiar to noble metal of which surface is easily reduced by heated hydrogen gas. The metal nanosheets obtained in this study would be attractive not only for fundamental science but also for various applications using metal.

References

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