Fabrication of nanostructured Ge films by He plasma sputtering

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Li ion batteries are developed as a promising power source for portable electronics, hybrid electrical vehicles and electric vehicles. Increasing the capacity of negative electrode of Li ion battery is attractive route to lower battery weight and volume. Li ion batteries with nano-structured electrodes significantly improve the charge/discharge capability. There has been increasing in using nano-materials for advanced negative electrode of Li ion battery, particularly for increasing the energy density by using high specific capacity materials. An attractive alternative material for the graphite electrode is Si, large due to its wide abundance and order of magnitude higher charge storage capacity (theoretical values of 4,200 mAh/g for Si vs 372 mAh/g for graphite). However, the insertion of Li into Si to form the fully lithiated silicide $Li_{4.4}Si$ is associated with a large volume change of > 400%, which can cause the material to pulverize and lose contact with the current collector, resulting in a decrease in charge storage capacity over time. Ge is also one of most promising materials for negative electrode, due to its higher charge storage capacity of 1,600 mAh/g, where the insertion of Li into Ge to form the fully lithiated $Li_{4.4}Ge$ is associated with a volume change of > 200%. Intense research activities are currently undertaken in the field of Si and Ge materials to realize the high capacity electrode related above-mentioned problems [1].

The Ge films were fabricated on a copper disk using 13.56-MHz radio-frequency (rf) magnetron sputtering. The copper disk had a diameter and thickness of 15 mm and 80 μm, respectively, and was placed at the center (r = 0) of the substrate holder and 30 mm from center (r = 30 mm), where the on-axis and off-axis sputtering deposition can be performed, respectively. The sputtering target was a polycrystalline Ge disk (1 inch diameter) with a purity of 99.99 %. An rf power of 60 W was supplied to the sputtering target for plasma production. He gas was supplied from the direction from the target to the substrate holder at a flow rate of 15 to 200 sccm. The He gas pressure was set to a relatively high value of 0.1 Torr. The distance between the target and the substrate holder was 20 mm. The substrate holder was not heated or cooled during film deposition.

Figures 1(a) and 1(b) show surface and cross-sectional SEM images of films deposited at center of the substrate holder. Ge nanoparticle film was fabricated in a single step process using low temperature plasma under the He-gas pressure condition of 0.1 Torr. Average size of nanoparticles was roughly estimated to be 100 nm from the surface SEM image. The porous structure with abundant pores was clearly observed in the film from the cross-sectional SEM image as found in Fig. 1(b). We evaluated the porosity of the deposited Ge films. Here, we measured the mass density ρ of the deposited films and compared it with the bulk Ge density of 5.32 g/cm^3. The porosity, which was calculated as $((5.32 - \rho)/5.32)$ 100 (%), was as high as 34%. Figures 1(c) and 1(d) show surface and cross-sectional SEM images of films deposited at 30 mm from center of the substrate holder (off-axis deposition). The nanoparticle became the half-smaller 56 nm, and the film changed to more dense structure. It must be emphasized that the porosity of the dense nanoparticle film was still as high as 30%. Our result indicates that the He-gas condition leads to a high porosity film composed of Ge nanoparticles.

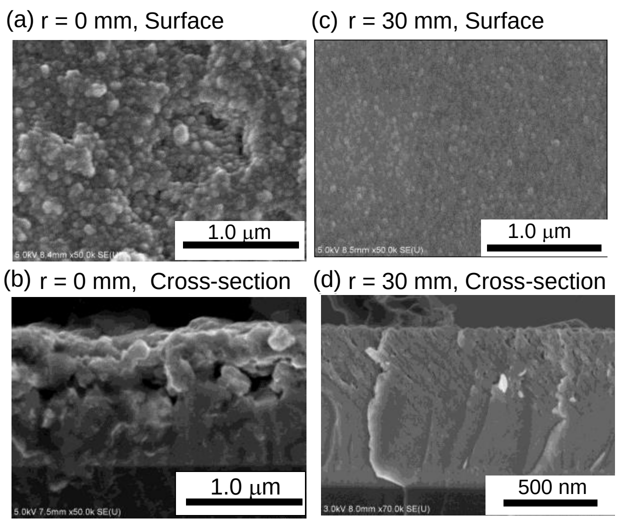

Figure 1. SEM surface and cross-sectional image of Ge films deposited at substrate position of (a)(b) 0 mm (on-axis position) and (c)(d) 30 mm (off-axis position). The film was deposited at He gas pressure and flow rate of 0.1 Torr and 15 sccm.

Reference

[1] M. Shiratani, K. Kamataki, G. Uchida, K. Koga, H. Seo, N. Itagaki, T.Ishihara, MRS Proceedings, 1678, mrss14-1678-n08-58 (2014).