Nanofabrication and Characterization of Iron Compounds with Focused Electron beam

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The production of nanometer-sized oxide structures is of significant interest due to the potential application to nanoelectronics, nanomagnetics and optoelectronics. Several techniques have been proposed to produce iron oxide nanostructures [1]. It is important to place nano-dots or nano-wires at desired positions for the production of nanodevices. Electron beam-induced deposition (EBID) is a promising technique to produce nanometer-sized dots and wires in a position controlled manner [2]. The resolution of EBID is now reaching down to sub-nanometers [3]. The shape and position of the nanostructures can easily be controlled by controlling the beam position using a computer. Recently, Shimojo et al. reported that carbon-free crystalline iron oxide was deposited at room temperature by EBID [4]. In this paper, to reveal the mechanisms of the formation of crystalline iron oxide, effects of water and oxygen addition to iron pentacarbonyl on nanostructure are studied.

EBID was carried out in a 30kV FE-SEM (JSM-7800UHV) with a custom made gas introduction system. The details of the gas introduction system were described elsewhere [4]. A schematic illustration of the deposition system is shown in Fig. 1. The electron beam current was 0.8 nA with a beam diameter of 4 nm. The base pressure of the chamber was 2x10^{-6} Pa. Two cylinders, either 1) iron pentacarbonyl (Fe(CO)5) and water (H2O) or 2) Fe(CO)5 and oxygen (O2) were connected. The electron beam position was controlled by an external deflector voltage input using a computer with digital-analogue converters.

A high resolution TEM image and a diffraction pattern of nanorods formed using a mixture of Fe(CO)5 and H2O vapors are shown in Figs. 2(a) and 2(b). The partial pressure ratio [H2O]/[Fe(CO)5] was 1.0. It was confirmed that crystalline Fe3O4 iron oxide was formed, by analyzing the diffraction pattern. No amorphous carbon is observed in the nanorods. As the nanorods formed only from Fe(CO)5 are amorphous containing iron, carbon and oxygen, it is suggested that oxygen radicals formed from water molecules remove carbon and oxidize iron. The composition of the deposits as a function of partial pressure ratio, [H2O]/[Fe(CO)5] is shown in Fig. 2(c). The carbon content decreased with increasing the partial pressure ratio, and reached almost zero at partial pressure ratio of 1.0 or more. The ratio of Fe and O became constant at partial pressure ratio of more than 1.0. Fig. 3 shows a high resolution TEM image of a nanorod formed with Fe(CO)5 mixed with O2 at a partial pressure ratio [O2]/[Fe(CO)5] of 1.0. Fast Fourier transforms of parts of the high resolution image near the surface and inside regions are also shown. Both reveal that small crystals exist near the surface but the inside is amorphous. The relative atomic ratio of Fe:O:C in the nanorods was about 1.0:0.6:0.4, according to the measurements of electron energy loss spectroscopy. This suggests that a large amount of carbon still exists inside the nanorod. This indicates that oxygen addition slightly reduces the carbon content, which leads to the formation of crystalline oxide near the surface, but does not affect drastically like water vapor addition.

References

FIG. 1. Schematic drawing of a 30 kV FE-SEM with dual gas introduction system for EBID with a gas of iron carbonyl.

FIG. 2. High resolution TEM image (a) and a diffraction pattern (b) of nanorods formed at a partial pressure ratio of 1.0, and the composition of the deposits as a function of partial pressure ratio (c), using a mixture of Fe(CO)$_5$ and H$_2$O.

FIG. 3. High resolution TEM image (a) of a nanorod formed with Fe(CO)$_5$ mixed with O$_2$ at a partial pressure ratio [O$_2$]/[Fe(CO)$_5$] of 1.0. Fast Fourier transforms of parts of the high resolution image near the surface (b) and inside (c) regions.