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Tungsten hydroxide /Porous Silicon composite Fabricated by the Liquid Phase Infiltration

Minoru Mizuhata, Yuki Mineyama, Takashi Hasegawa, and Hideshi Maki

Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University
1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan

It is well-known that porous silicon (PSi) is prepared by anodic oxidation from silicon wafer and utilized to near-infrared rugate filter and photoluminescence devices [1, 2]. The optical properties depends on the structure, porosity, and distance of the ordering structure, however, the photoluminescence properties of composite materials of Si and the other species have not studied very much. Previously, we reported that PSi/CeO_2 composite was fabricated on Si wafer and the photoluminescence was observed and discuss the influence comparing with the conventional porous Si. PL intensity depend on the pore size of PSi depended on its resistivity [3]. In order to prepare the PSi/metal oxide composite, electrodeposition method is useful method, however some oxide cannot be deposited directly, because silicon wafer is attacked during anodic deposition process in some case. In this study, we prepared PSi/ tungsten oxide composite using liquid phase infiltration (LPI) method [4] using metal-fluoro complex dissolved in water-acetone mixed solvent. Nanopore felt up by the reaction solution and tungsten hydroxide was deposited in nanopore structure of PSi.

P-type silicon(Si) wafer (Resistivity: 3-4 mΩ·cm) is electrolyzed in HF aqueous-ethanol mixed solution ($HF:H_2O:EtOH$ = 0.35:0.43:0.22) at 100 mA/cm^2 in dark-field [3] and porous silicon (PSi) was obtained. In LPI process, 20 mmol L^{-1} of tungsten-fluoro complex solution was prepared from WO_3 dissolving into aqueous HF solution. Typically, 70 mL of Acetone and 5 mL of 0.5 mol L^{-1} H_3BO_3 aqueous solution was mixed into 15 mL of reaction solution and PSi substrate is dipped in the reaction solution. After deposition reaction for 3-24 h, sample was rinsed in distilled water, dried in air at ambient temperature. Some sample was cut for observation of SEM-EDX, XRD, XPS etc. Deposition amount of tungsten hydroxide was measured by ICP-AES measurement.

In Fig. 1, SEM images and EDX line profile of typical PSi/tungsten oxide sample was shown. According to EDX profiles, W and O elements were observed at internal region of porous structure of PSi. Tungten oxide was deposited on not only surface of substrate but also inside of pore. On the other hand, in the case of using aqueous reaction solution, Tungsten oxide was deposited on the substrate mainly, which means the lack of infiltration of reaction solution. It is suggested that deposition rate depends on the surface hydrophilicity and surface energy of substrate. Acetone might lowered surface energy of substrate with its low tension. In Fig. 2, XPS profiles of W_{4f} for PSi/tangsten oxide are shown. As shown in Fig.2a, oxide was not deposited on the surface very much, however, it is suggested that internal deposition is predominantly preceded as shown in Fig.1a. In previous study, as-deposited oxide was hydrated and assigned as $H_2WO_4{\cdot}H_2O$[5]. Accoding to our results show no diffraction peaks due to nano-ordered reaction region. We are going to assign the structure on the pore structure for obtained samples.

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References

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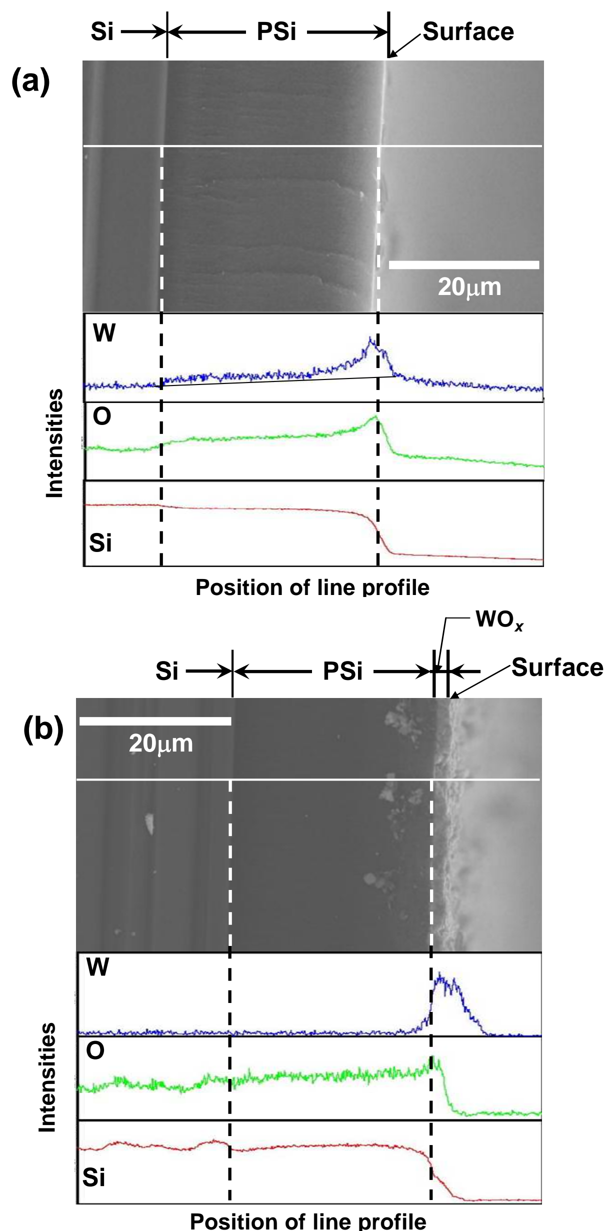

Fig.1. EDX line profile of PSi/tangsten hydoxide composite prepared by the LPI method for 6 hours. Solvent (a) water(30v/v)+acetone(70v/v), (b)water.

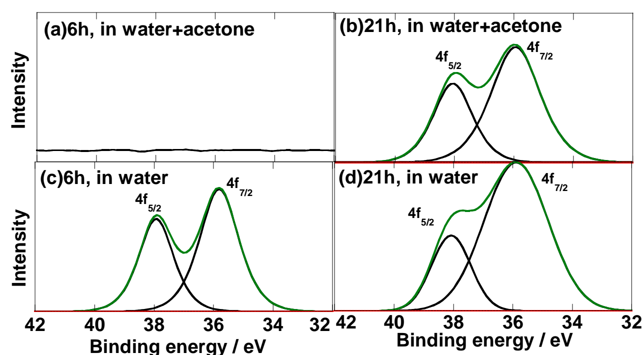

Fig.2. XPS profile of W 4f of PSi/tangsten hydoxide composite prepared by the LPI method for 6, 21 hours. Solvent (a,b) water(30v/v)+acetone(70v/v), (c,d)water.