



Copper deposition in microporous silicon using supercritical fluid



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ABSTRACT

Microporous silicon has been formed by anodization of p-type silicon. The pores with diameter less than 2 nm were filled with copper by using supercritical carbon dioxide fluid. The copper-filled layers were investigated with the field emission scanning electron microscopy, X-ray diffractometry, and energy-dispersive X-ray spectroscopy. Structural characterizations indicated that copper was continuously deposited into porous silicon down to a depth of about 0.5 μm. Electrical measurement confirmed this result. Copper-deposited layers exhibited much improved current density–potential curves.

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1. Introduction

The optoelectronic properties such as photoluminescence and electroluminescence of porous silicon (PS) make it attractive material candidate for luminescent devices [1], whereas the instability of PS electrical characteristics limits its application. The main reason of this instability is considered to be the chemical change (e.g. oxidation) of the air-exposed large surface of the PS nanostructure by the environment and/or electrical current. The luminescence [2–5] and electrical [6–8] characteristics of PS can be improved by using high-pressure water vapor annealing or electrochemical oxidation, as a result of efficient surface passivation or enhanced carrier localization in nanocrystals. Chemical modification by organic ligands [9–15], has also been shown to stabilize various PS functions.

Another problem affecting the electrical stability is the evolution of the physical contact between the silicon nanostructure and the top electrode. It easily deteriorates upon temperature-induced stress or material change. The addition of a stable carbon buffer layer, which was slightly penetrating into the PS pores, was shown to improve very much this particular aspect [16].

Filling PS layers with a metal is another approach to improve the electrical characteristics of the material. Several techniques for metal deposition into PS layers, using wet or dry, electrochemical or chemical method, have been reported [17–30]. In most of these works, metal filling was carried out in macroporous (pore diameter >50 nm) layers [19–26,28,29]. A few groups studied deposition in mesoporous (pore diameter 2–50 nm) layer [27,30].

Owing to typical material status of liquid–gas phase, supercritical CO₂ fluid (critical pressure 7.4 MPa, and critical temperature 31 °C) possesses unique characteristics such as high solvent capability, high diffusivity, and zero surface tension. Supercritical fluid deposition is an attractive technique for developing metals in nanostructured devices [29–37]. For example, different metals were deposited into multiwalled carbon nanotubes with diameter 7–9 nm [34].

Considering PS, Lin et al. [29] used micro-emulsion reaction in supercritical CO₂ fluid to deposit silver (Ag) into the PS (800–2000 nm in pore diameter). The disadvantage of this micro-emulsion reaction is (i) to leave water inside the voids and (ii) the formation of two separate phases (water and Ag nanoparticles) in small pores.

We have deposited continuous pure copper into mesoporous layer (pore diameter approx. 20 nm) by surface reaction of copper precursor with silicon substrate in the supercritical CO₂ fluid [30]. The maximum depth down to which copper could be deposited was about 1 μm. It would be interesting to know if copper could also be deposited into isotropic nano-porous silicon (also called microporous silicon), which exhibits much smaller pores (~2 nm) than mesoporous silicon. The narrower pores are considered to degrade the net diffusion amount of the supercritical CO₂ fluid and consequently diminish the deposition depth [36,37]. Microporous silicon also exhibits a sponge-like structure, as opposed to a columnar structure in the case of mesoporous silicon. It is expected to be less easy to deposit copper in such a complicated structure than in the much more opened and easy to access columnar pores. Since microporous silicon, and not mesoporous silicon, is used in electroluminescent devices, such a study is also very relevant for optoelectronic applications.

In this work, copper deposition was performed into microporous layers (pore diameter ≤2 nm) by using the same technique we used for mesoporous silicon. Metalized microporous layers with thickness

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of about 0.5 and 2 μm were investigated with field emission scanning electron microscopy (SEM), X-ray diffractometry, and energy-dispersive X-ray spectroscopy (EDX). The current density–potential curves were also measured and comparisons were made with reference samples.

2. Experimental details

PS layers were formed by anodization of a p-type, (100)-oriented, and 5–10 $\Omega\text{ cm}$ silicon substrates with an Al back contact. An electrolyte containing a mixture of aqueous HF (46 wt.%) and ethanol in the ratio 3:2 was used. Two types of layers with thickness of approximately 0.5 and 2 μm were obtained by etching 13 and 50 s, respectively, at a constant current density of 80 mA/cm^2 . Following formation, each sample was thoroughly rinsed with ethanol and dried in air for 1 h, and then was placed together with a precursor (25 mg) in a stainless-steel reactor (approx. 2 ml). A *bis*-diisobutylmethanatecopper (CB1479906, $\text{Cu}(\text{C}_9\text{H}_{12}\text{O}_2)_2$, abrv. $\text{Cu}(\text{dibm})_2$) was used as the precursor. The copper deposition was accomplished with a batch-type deposition system, shown in Fig. 1, through following three main procedures. At the first procedure, H_2 was flowed through the reactor to expel the air inside and continuously purged until the reactor pressure up to 1 MPa, and then gaseous CO_2 was purged to get mixture of H_2 and CO_2 . In the second procedure, liquid CO_2 was inserted to the reactor using a plunger pump for liquid chromatography to attain a reaction pressure of 10 MPa. Heating the reactor by 240 $^\circ\text{C}$ yields the supercritical fluid CO_2 . The supercritical condition at 10 MPa and 240 $^\circ\text{C}$ was maintained for 15 min. During this stage, the precursor dissolved completely in CO_2 and filled inside the nanostructure layer through H_2 reduction reaction: $\text{H}_2 + \text{Cu}(\text{dibm})_2 \rightarrow \text{Cu} + 2\text{H}(\text{dibm})$. Finally, the reactor was cooled to 40 $^\circ\text{C}$, and supercritical CO_2 fluid as well as by-products was vented as the gas.

The samples before and after supercritical CO_2 fluid chemical deposition were investigated in terms of a SEM (Hitachi, S-4500) with operating voltage of 15 kV. The metalized layers were characterized with an X-ray diffractometer (Shimadzu, XRD-6000) with the θ - 2θ arrangement using Cu $K\alpha$ radiation and a SEM EDX (JEOL, JSM-6500 F). The current density–potential curves were measured by source measure unit (Keithley, 2401) for PS samples metal-deposited using supercritical CO_2 fluid and sputtering to compare effects of the deposition.

3. Results and discussion

Fig. 2 shows cross-sectional electron micrograph images of as-formed microporous silicon (etching time 13 s) and the same sample after copper deposition. The individual pores cannot be distinguished

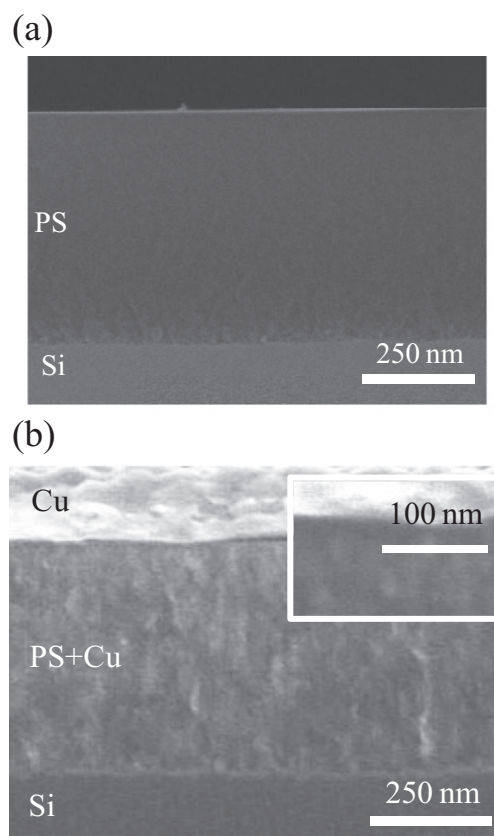


Fig. 2. Cross-sectional electron micrograph images of microporous silicon formed with p-type silicon. The thickness of the PS layer is approximately 0.5 μm . (a) As-formed PS layer. (b) PS layer after copper deposition. The insets show top part of PS layer with higher magnification.

because of the resolution limitation of the SEM. From the difference of image gray level between PS and silicon substrate, the thickness of the porous layer was estimated as approximately 0.5 μm . Compared with the as-formed PS layer shown in Fig. 2(a), PS in which copper was deposited appears uniformly much lighter gray, indicating that the micropores were filled with copper continuously from top to bottom. To examine components produced by copper deposition, the X-ray diffraction (XRD) patterns of both metalized samples were obtained with Cu $K\alpha$ radiation (1.54 Å). Cu and Si peaks were clearly observed in the

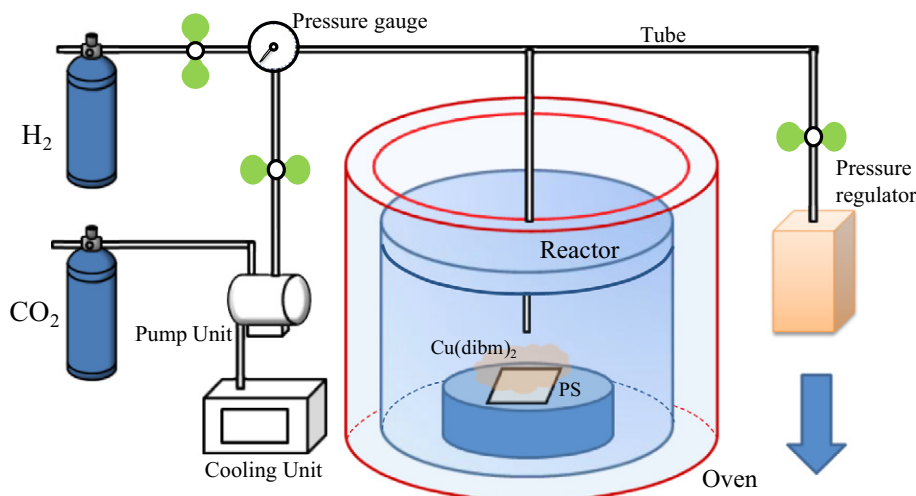


Fig. 1. A schematic diagram of supercritical fluid deposition experimental apparatus.

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