

Cu-Si nanocomposites based on porous silicon matrix

BANDARENKA Hanna^{1, a}, SHAPEL Aliaksandr^{1, b} and BALUCANI Marco^{2, c}

¹Belarussian State University of Informatics and Radioelectronics, Microelectronic Department,
P. Brovka 6, 220013 Minsk, Belarus

²CNR-INFM University "Sapienza" of Rome, Electronic Department, via Eudossiana 18, 00184
Roma, Italy

^avitaly51@mail.ru, ^bvitaly@bsuir.edu.by, ^cbalucani@die.uniroma1.it

Keywords: Nanocomposites, Porous silicon, Copper particles, Displacement deposition

Abstract. Cu-Si nanocomposites formed by an immersion displacement deposition of Cu into porous silicon (PS) matrix have been experimentally studied. SEM and AES were used to investigate the structure and elemental composition of Cu-Si samples. The top part of the Cu-PS samples is shown to demonstrate the following structure: large faceted Cu grains at the top, a porous fine-grained copper film underneath the large grains, and the copper pointed rods extended from the surface into the PS layer. The top part of the silicon skeleton of the PS layer is converted into the copper by the etching followed by Cu displacement deposition. The porosity of the porous layer and displacement deposition times are found to form Cu-Si nanocomposites of various structures and various Cu-Si contents because of various extent of the silicon skeleton transformation into copper.

Introduction

Porous silicon (PS) is an artificially structured material which is usually formed by an electrochemical anodization of monocrystalline silicon. PS layer has a wide range of pore sizes from nanometers to submillimeters. Physical-chemical properties of PS are quite different from those of bulk silicon and strongly depend on the type and doping level of substrate, surface orientation and anodic treatment regimes. The open porous structure and a very large specific surface area of PS have motivated scientists to introduce different materials into the pores to fabricate composite structures for some technologically important areas of application like medical and biological sensors, MEMS, fuel cells, etc [1, 2]. Several approaches have been experimentally studied to deposit metals into PS including so-called dry and wet processes. Dry processes such as evaporation, a chemical vapor deposition and related techniques are widely used to deposit metals on bulk semiconductors. However, wet methods such as electrodeposition, electroless plating and immersion displacement deposition are more feasible and convenient for metal deposition into PS template [1, 2]. A metal displacement deposition from the solutions containing metal ions and fluoride agents has showed the very attractive results for the nanocomposites formation [2-5]. This method is a variant of the wet chemical deposition and based on the displacement reaction of silicon atoms by metal atoms. Principal advantages of such process are a deep penetration of metal atoms into the PS layer and the metal deposition on the oxide-free silicon surface. Copper ions in the aqueous solution containing fluoride ions have been found to interact with PS resulting in the formation of tiny Cu aggregates of dimensions from nanometers to tens of nanometers. As a result, binary Cu-PS composites based on PS can be made. Recently, a great attention has been devoted to the structural investigation of such Cu-PS composites and the determination of the mechanism of the displacement deposition of copper on porous silicon [3-6]. However, up to now the time transformation of a silicon skeleton of PS into copper to form Cu-PS composites is poorly known.

In this paper, we used scanning electron microscopy (SEM) to investigate the structural change of porous silicon layer during different times of PS samples immersion in solution containing copper and fluoride ions.

Experimental

Monocrystalline Sb-doped (111)-oriented Si wafers with resistivity of $0.01 \Omega\text{-cm}$ were used for fabrication of PS. Just before PS formation we did chemical cleaning of silicon samples in standard RCA solutions. Porous films were grown by an electrochemical anodization of Si samples in the fluoroplastic cell with an active electrode area of 3 cm^2 . Mixture of HF (45%), H_2O , and $\text{C}_3\text{H}_7\text{OH}$ in a 1:3:1 ratio by volume composed the anodic bath. The anodic current density of $60\text{-}100 \text{ mA/cm}^2$ was applied for 15-20 sec at room temperature. Such anodic regimes provided to fabricate PS layers of 1000 nm thickness and 55-85% porosity. Gravimetric method was used for the determination of PS porosity. After anodization the HF electrolyte was replaced by a $0.025 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.005 \text{ M HF}$ aqueous solution for different time-periods at room temperature and Cu film was deposited onto PS. SEM Hitachi S-4800 and AES PHI-660 were used to study the structure and elemental composition Cu-PS nanocomposites.

Results and discussions

At first, let us turn to the structure of the initial porous silicon sample of 55% porosity fabricated by an electrochemical anodizing process. The top and cross-sectional views of such fresh PS layers are shown in Fig.1. The PS layer consists of a silicon skeleton and pore channels highly oriented perpendicular to the sample surface. The pore channel lengths are of 1000 nm. Fig.1 (a) demonstrates that pore channels are well separated from each other but the dendrites growth of side pores cannot be suppressed completely. Referring to the top view of the PS sample (Fig.1 (b)), a quasi-regular pore arrangement exhibiting a low degree of four-fold symmetry is observed. Entrances of the pore channels are sized in the range from 8 to 25 nm. The wall thickness of the silicon skeleton is about 10–25 nm. Referring to the international classification of porous media, the fabricated sample is a typical representative of mesoporous media.

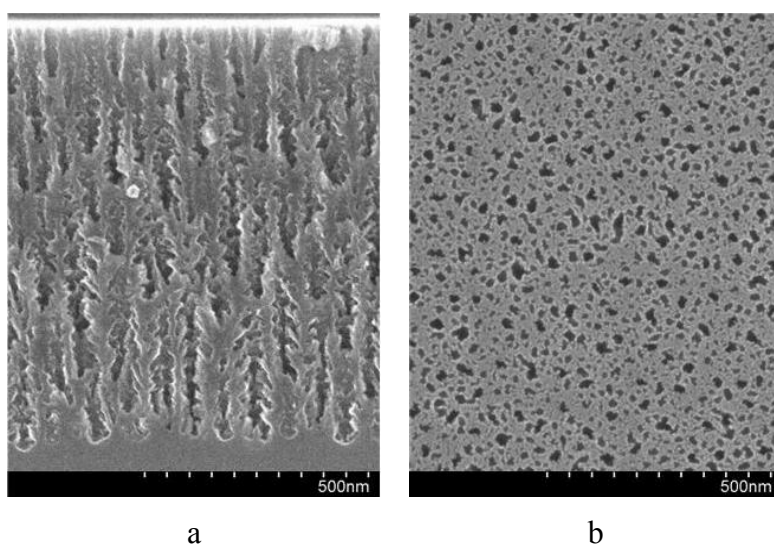


Fig.1 SEM cross-sectional (a) and top (b) views of fresh PS layer of 55% porosity and 1000 nm thickness

The solution for the copper displacement deposition contains CuSO_4 , HF and H_2O . When the PS samples are immersed in this solution, the solution agents should penetrate into the pore channels where then the copper deposition takes place by the displacement mechanism. There is a good reason to expect that the penetration of the solution agents inside the pore channels and the copper deposition are time-dependent and very sensitive to the pore aspect ratio.

To study the copper deposition kinetics, PS samples of 55% porosity were subjected to the immersion into the solution for different times. Fig.2 shows SEM cross-sectional and top views of PS samples that were treated with copper solution during 4 and 180 sec.

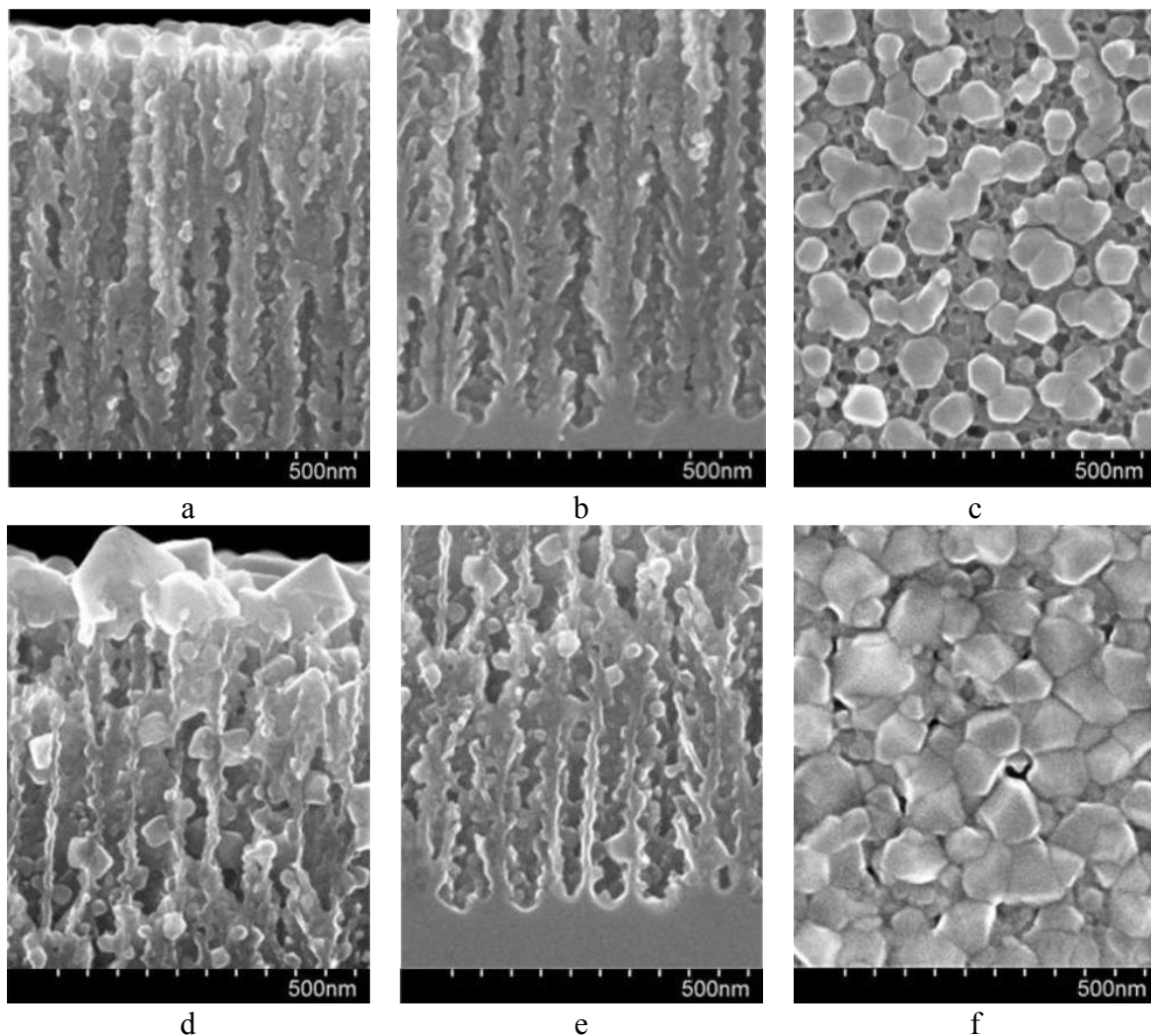


Fig.2 SEM cross-sectional (a, b, d, e) and top (c, f) views of PS samples of 55% porosity subjected to the immersion into the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{HF} + \text{H}_2\text{O}$ solution: (a, b, c) – 4 sec; (d, e, f) – 180 sec

As seen from Figs. 2 (a), (b), (c) at the initial stage of the deposition (4 sec of immersion), ball-shaped Cu particles are detected on the walls the silicon skeleton at all depth of the PS layer. Copper particle size comes smaller as the PS depth increases. At the bottom of PS pore channels Cu particle size is approximately 10 nm (fig.2 (b)) while at the surface regions it is about 25–30 nm (fig.2 (a)). A thin grainy Cu film of about 50-80 nm in thickness is observed at the PS near-surface region as a result of Cu particles coalescence. The top view image (fig.2 (c)) shows that this surface Cu film is porous and has grain sizes of the order of 20–25 nm. Cu grains of size 50-70 nm are observed on the surface of the mentioned Cu film. Some of them are joined together into chains consisted of 3–7 grains. Large Cu grains have a well-marked faceting to be indicative of copper crystals.

Figs. 2 (d), (e), (f) show SEM images of the PS samples subjected to the immersion into the solution during 180 s and demonstrate further conversion of the PS silicon skeleton to Cu due to displacement process. The 180 s immersion resulted in the nanocomposite formation with the structure and copper-silicon content varied within the layer thickness. Referring to Fig.2 (d, e), about 40% of the PS layer was converted into copper with practically full silicon skeleton

dissolution. The top part of the sample demonstrates the following structure: Cu crystal-like grains at the top (their size reached even to 150 nm), a porous fine-grained copper film underneath the large crystal-like grains, and the copper pointed rods extended from the surface into the PS layer. It is obvious long time of PS immersion to copper and fluoric ions solution led to single Cu crystals-like grains formation almost all depth of porous layer (fig.2 (e)). Abundant copper ball-shaped particles throughout the residual volume along with remains of etched silicon skeleton are observed below the copper pointed rods. As Fig.2 (f) suggests, large faceted Cu grains at the top coalesce to form low-porous polycrystalline Cu film.

The additional study into the elemental composition of the PS sample subjected to the immersion into the solution discussed for 180 s was made by AES with Ar ion sputtering. The copper content in the surface region of the PS layer was determined to be up to 95-97%, suggesting that the silicon skeleton of the PS layer is transformed into copper almost totally. At the 400 nm depth, the copper content is 40-50%, and the silicon content is 30-45%. At the 900–950 nm depth, the copper content is only 15–25%.

It is known that during the PS immersion into a $\text{CuSO}_4 + \text{HF}$ bath, oxidation-reduction reactions between copper ions from the solution and the silicon atoms from the silicon skeleton of the PS layer occur [3-6]. This is conditioned by the higher redox potential of Cu^{2+} ions than Si. Copper is reduced and deposited via electron exchange with silicon which is oxidized and dissolved in the fluoride-containing solution [7, 8]. The most important observation from this study for mesoporous silicon of the 55% porosity is the self-limiting copper replacement behavior resulting in a non-complete conversion of the Si skeleton into Cu. Our attempts at the increase of the silicon conversion into copper by the increase of the immersion time have not been successful for the PS samples of the 55% porosity. The initial silicon skeleton was not totally converted into copper even after long immersion time of 10-15 minutes. In our opinion, this is because of the difficulties of reagent diffusion through the pore channels after their filling with copper particles.

An increase of the PS porosity providing the better diffusion of reagents through porous layer was found to be more profitable. Fig.3 shows the cross-sectional and top views of PS sample of 85% porosity after the immersion into the solution for 180 sec. As Fig. 3 demonstrates, a considerable increase of the extent of the silicon skeleton transformation into copper takes place.

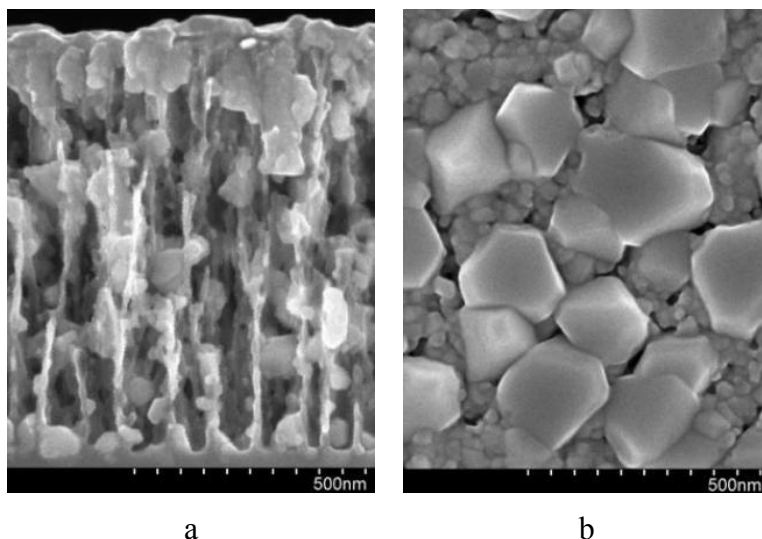


Fig.3 SEM cross-sectional (a) and top (b) views of PS sample of 85% porosity subjected to the immersion into the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{HF} + \text{H}_2\text{O}$ solution for 180 sec

It is clear from data discussed that Cu-PS composites of various structures and various Cu-Si contents can be formed by changing the porosity of the porous layer and displacement deposition

times. Physical-chemical properties of these composites are obvious to differ considerably depending on their structure and will be a subject of our research in the near future.

Nevertheless, we already utilize mechanical properties of Cu-PS composites. We have discovered that the adhesion of the copper layer deposited into porous silicon can be varied over wide limits by varying the PS porosity from 30 to 85 %. For example, Cu-PS composites formed in the 45–50% porous and 0.3–0.5 μm thick PS layer by the method discussed for 2–3 min demonstrate the very high adhesion of the copper layer. It is order of magnitude higher than the adhesion of copper films deposited on the silicon surface by any other known techniques. As the PS porosity increases from 60 to 85 %, the adhesion of the copper layer decreases down to very low values at the porosity more than 85 %. We utilized such Cu-PS composites with the controlled adhesion in the Layer Transfer technology for MEMS [9, 10].

Summary

Thus, the experimental study into the copper deposition kinetics in porous silicon from the solution consisted of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{HF} + \text{H}_2\text{O}$ has shown that the copper deposition takes place by the displacement mechanism. The top part of the samples is shown to demonstrate the following structure: large faceted Cu grains at the top, a porous fine-grained copper film underneath the large grains, and the copper pointed rods extended from the surface into the PS layer. The top part of the silicon skeleton of the PS layer is converted into the copper pointed rods by the etching of the skeleton and further Cu displacement deposition. Cu-PS composites of various structures and various Cu-Si contents can be formed by changing the porosity of the porous layer and displacement deposition times.

References

- [1] R. Herino: *Materials Science and Engineering: B* Vol. 69 (2000), p. 70.
- [2] I. Coulthard, R. Sammynaiken, S. Naftel, P. Zhang and T. Sham: *Phys. Stat. Sol. (a)* Vol. 182 (2000), p. 157.
- [3] D. Hamm, T. Sakka and Y. H. Ogata: *Phys. Stat. Sol. (c)* Vol. 2 (2005), p. 3334.
- [4] A. Bondarenko, in: *Proceedings of the International Conference Nanomeeting-2007*, World Scientific Publishing Co. Pte. Ltd. (2007), p. 497.
- [5] H. Bandarenka, M. Balucani, R. Crescenzi and A. Ferrari : *Superlattices and Microstructures* Available online 24 January 2008, in press.
- [6] J. Sasano, R. Murota, Y. Yamauchi, T. Sakka and Y. H. Ogata: *J. Electroanal. Chem.* Vol. 559 (2003), p. 125.
- [7] F. W. Kern, Jr., M. Itano, I. Kawanabe, M. Miyashita, R. W. Rosenberg, and T. Ohmi, in: *Proceedings of the 11th Workshop on ULSI Ultra Clean Technology* (1991), p. 23.
- [8] H. Morinaga, M. Suyama and T. Ohmi: *J. Electrochem. Soc.* Vol. 141 (1994), p. 2834.
- [9] V. Bondarenko, M. Balucani, in: *Conference Abstracts of NATO ARW Nanoscaled semiconductor-on-insulator structures and devices*, Sudak, Crimea, Ukraine (2007), p. 15.
- [10] M. Balucani, V. Bondarenko, in: *Proceedings of the 1st International Scientific Conference Nanostructured Materials-2008*, Minsk, Belarus (2008), p. 533.

Nanocomposite Materials

doi:10.4028/3-908454-10-7

Cu-Si Nanocomposites Based on Porous Silicon Matrix

doi:10.4028/3-908454-10-7.222