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INFLUENCE OF SI CONDUCTIVITY TYPE ON IMMERSION DEPOSITION OF CU FILMS ON POROUS SI

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An immersion deposition of copper (Cu) on a porous silicon (PS) from an aqueous solution of the copper sulfate ($CuSO_4$) and hydrofluoric acid (HF) has been performed. The PS based on n^+- and p^+-silicon (Si) wafers has been used to study the Cu deposition depending on the conductivity type of the initial Si substrate. The PS/n^+-Si substrate has been found to allow the deposition of the nanostructured Cu films on the PS, while the PS/p^+-Si has been shown to provide the formation of the porous Cu films by the complete substitution of the Si atoms in the PS with the Cu atoms.

1. Introduction

Nanostructured metallic films present prospective nanomaterials due to their peculiar electrical, physic, chemical and optical properties, which are not typical for the bulk metals. Nanostructured Cu films are of the special interest.

First, it is connected with the extremely high electroconductivity of Cu causing the use of this metal as a basic material of the conductive interconnections [1]. However, the weak adhesion of the Cu interconnections to the bulk Si has been an important problem by nowadays. The nanostructured Cu films also has been drawing an attention as they possesses the surface plasmon resonance (SPR) in the visual range of the electromagnetic spectrum. Today this phenomenon is actively studied as, in particular, it opens the prospects of the significant improvement of the sensitivity of the Raman scattering. The SPR intensity strongly depends on the sizes, shape and mutual location of the Cu nanostructures, which compose the film. The Cu antibacterial activity also presents a remarkable feature, which has been widely applying in biomedicine [2]. The Cu films nanostructuring improves their antibacterial activity due to an increasing the specific surface area of the Cu structures.

The wide application of the nanostructured Cu films is both limited by their weak adhesion to the bulk Si and difficulties of the precise control of the structural parameters of such films, which is required to provide the reproducibility of their properties. The formation of the PS layer on the Si wafer before the Cu films deposition can solve these problems. The rough PS surface will improve the Cu film adhesion, while the managing nanoscaled sizes of the PS pores and Si crystallites will allow to form the Cu films with the required parameters.

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Presumably, the most various forms of the nanostructured Cu films can be fabricated by the immersion deposition of Cu in the PS from the aqueous solution of the Cu salt and HF. The previous study of the immersion deposition of Cu on the bulk Si has showed, that Cu deposits oxidizing the Si atoms [3]. The HF additive promotes removement of the Si oxide. Thus, the continuous Cu deposition and Si corrosion occur.

Despite the growing interest to the immersion Cu deposition on the PS, there has not been presented its complex study yet, including the influence of the conductivity type of the initial Si substrate on the redox process, which plays the major role in the growth of the Cu films.

2. Experimental

The antimony (n^+) and boron (p^+) doped 100 mm monocrystalline Si (100) wafers of the 0.01 – 0.03 Ohm·cm resistivity were used as initial substrates. The Si wafers were cleaned by using the RCA solution and cut into the samples of the 9 cm^2 area. Just before the PS formation, each sample was immersed into 5% HF solution to remove the native oxide. Immediately after that, the samples were fixed in the two-electrodes electrolytic cell made of Teflon. Uniform layers of the PS were formed by an electrochemical anodization of Si samples in HF-based solutions. The anodization of the n^+- and p^+- Si was performed according to the regimes presented in [4] and [5], respectively. After the anodizing the cell was filled with an aqueous solution of 0.025 M $CuSO_4$ mixed with HF (46 %) and C_3H_7OH in a ratio 200:1:8 by volume, that provided the Cu immersion deposition. The immersion time varied from a few seconds to a couple of hours depending on the experimental tasks.

A surface potential of the samples at the Cu deposition was registered with the Ag/AgCl reference electrode. The Lugging capillary was used to improve the accuracy of the potential measurements [6].

The morphology of the samples was studied with the scanning electron microscope (SEM) Hitachi S-4800. The elemental and phase compositions of the samples were studied by the energy dispersive X-ray (EDX) spectroscopy (with microscope Cambridge Instruments Stereoscan-360 equipped with the spectroanalyser Link Analytical AN 10000) and with X-ray diffractometer DRON-3 equipped with the Cu anode provided $K\alpha$ radiation (λ = 0,15406 nm).

3. Results and Discussion

The porosity and the thickness of the PS layers varied in the ranges 55 – 65 % and 2.5 – 2 μm respectively. The analysis of the SEM views of the PS samples revealed that they have a structure typical for the mesoporous media.

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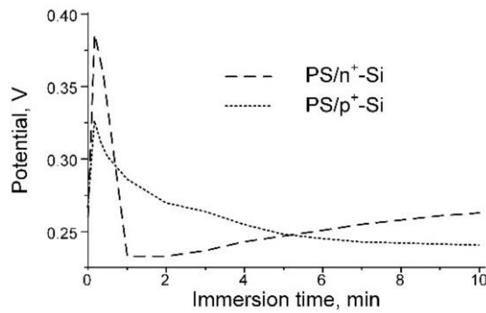

Figure 1. The PS surface potential dependences on the Cu immersion deposition time.

Figure 1 shows the dependence of the PS surface potential on the Cu immersion deposition time and the type of the Si conductivity. At the contact of the solution with the both samples, the potential sharply rises for 2 – 3 s due to the immediate change of the surface states. In the next 50 s the potential of the PS/n^+-Si greatly reduces and then constantly slightly increases. The final potential growth shows that the substrate is positively charged, i.e. loses the electrons of the dopant atoms. After the deposition for 15 – 20 min the Cu film separated from the sample. The surface of the sample had a rest of the PS/n^+-Si layer. The non-complete dissolution of the PS means that the Cu reduction indeed occurred due to the electrons of the dopant atoms delivered from the Si wafer. In contrast, the PS/p^+-Si potential gradually decreases. It continued for 120 min and then the Cu film separated. However, the PS layer was not observed on the Si sample, i.e. it was dissoluted during the Cu deposition. Thus, the Cu atoms deposited by taking the electrons from the Si atoms.

The XRD analysis of the PS/n^+-Si after the Cu deposition for 10 min showed that it contents the polycrystalline Cu deposit. The average size of the Cu crystallites estimated from the XRD spectrum was about 20 nm. The EDX analysis showed the Cu atoms are prevalently located on the external PS surface.

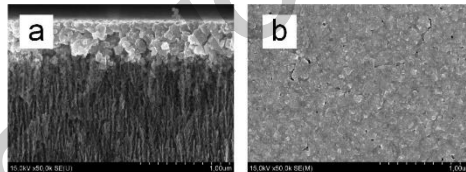

Figure 2. SEM images of the top (a) and cross sectional (b) views of the PS/n^+-Si after the Cu immersion deposition.

Figure 2 presents the SEM images of the studied sample allowing to summarize the immersion deposition led to the formation of the nano-structured Cu film on the external surface of the PS/n^+-Si. The film has the 500 nm thickness and consists of the polycrystalline Cu particles.

According to the XRD and EDX analyzes the film separated from the PS/p^+-Si includes 99 % of the Cu atoms and is polycrystalline in nature. Figure 3 shows SEM bottom, top and cross sectional views of this film. It consists of two layers and has the total thickness of about 8 μm. The bottom layer presents the Cu particles (100 – 150 nm) network which structure and thickness are similar to those of the initial PS. The upper layer

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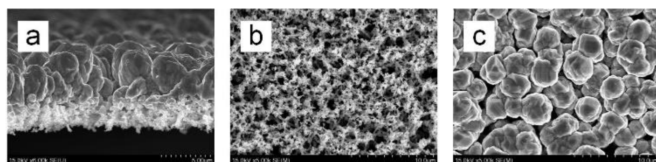

Figure 3. SEM images of the cross sectional (a), bottom (b) and top (c) views of the film separated from the PS/p^+-Si after the Cu immersion deposition.

consists of the Cu ellipsoid-like agglomerates and the pores, which are perpendicular to the film plane. The width and height of the agglomerates vary in the ranges 1.5 – 3 μm and 2.5 – 5 μm, respectively. Therefore, during the immersion deposition the Cu atoms firstly substitute the Si atoms in the PS. Secondly, the Cu atoms continue to deposit forming the porous Cu film. The film porosity was estimated as 65 %.

4. Summary

The Cu immersion deposition on the PS allows to fabricate different types of the nanostructured Cu films. It was revealed the Cu atoms prevalently deposit on the external surface of the PS/n^+-Si because of the excess of the electrons of the dopant atoms. On the other hand, the inner growth (inside the pores) of the Cu atoms was observed to dominate on the PS/p^+-Si due to the absence of the dopant atoms supplying the electrons. Therefore, using the PS/n^+-Si substrate provides the growth of the nanostructured Cu films on the PS without its full corrosion, while the PS/p^+-Si provides the formation of the porous Cu films by the complete substitution of the Si atoms of the PS with the Cu atoms.

Acknowledgments

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