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Copper deposition onto porous silicon by vacuum thermal evaporation

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Abstract. The morphology and composition of porous silicon samples with thermally evaporated copper coatings were studied using atomic-force microscopy (AFM), infrared spectroscopy (IR), and X-ray photoelectron spectroscopy (XPS). Our research demonstrated that nanocomposites obtained with this method involve both metallic copper and copper oxide. The results indicate that vacuum thermal deposition of copper promotes efficient penetration of this element into the porous silicon structure and retards the oxidation process of the porous layer during long-term storage in the atmosphere.

Keywords: porous silicon, composites, thin films, copper, vacuum-thermal sputtering

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Осаждение меди на пористом кремнии методом вакуумно-термического напыления

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Аннотация. Методами атомно-силовой микроскопии, инфракрасной и рентгеновской фотоэлектронной спектроскопии получены данные о морфологии и составе образцов пористого кремния с вакуумно-термическим напылением меди. Исследования показали, что нанокомпозиты, полученные с использованием данного метода, содержат как металлическую медь, так и оксид меди. Полученные результаты свидетельствуют о том, что вакуумно-термическое осаждение меди способствует эффективному проникновению этого элемента в пористую структуру кремния и замедляет процесс окисления пористого слоя при длительном хранении в атмосферных условиях.

Ключевые слова: пористый кремний, композиты, тонкие пленки, медь, вакуумно-термическое напыление

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Introduction

The development of technologies in nanoelectronics relies heavily on the use of advanced materials and novel synthesis methods. Among the promising materials for nanoelectronics are porous silicon structures and copper [1, 2]. Porous silicon demonstrates remarkable optical properties, a large specific surface area, and tunable porosity, making it highly attractive for applications in microelectronics, photonics, and sensing [3]. Copper, due to its high electrical conductivity and relatively low cost, is one of the most widely used materials in modern electronics [4].

Copper coatings on porous silicon can be fabricated by various methods, including chemical deposition from solution [2, 5], immersion plating [3], electrodeposition [5, 6], as well as physical and chemical vapour deposition [1, 4, 9]. Many of these approaches require complex technological equipment, strict process control, or the use of aggressive chemical media, which limits their scalability and cost-efficiency. In contrast, thermal deposition of copper offers several advantages: it is a simpler and more technologically feasible method that does not require plasma-based setups or complex chemical precursors [1, 3]. Previous studies have demonstrated that thermal deposition provides good adhesion of copper films to porous silicon substrates, allows precise control of film thickness, and can be integrated into existing microelectronic fabrication schemes [1, 7]. At the international level, research has shown the potential of copper–porous silicon systems in improving sensor sensitivity [4, 5], tailoring surface morphology [2, 8], and filling deep silicon pores uniformly with copper by electrodeposition [5, 6]. Porous silicon/copper nanocomposites have also been explored for enhanced photoluminescence and sensing applications [10]. Nevertheless, systematic studies of thermal deposition mechanisms and features remain limited, which makes this direction scientifically and technologically relevant [1, 3, 7].

The purpose of this work is to study the features of thermal copper deposition into porous silicon.

Materials and Methods

Porous silicon substrates (por-Si) were obtained from single-crystalline silicon (KEF 100; 0.2 Ohm·cm) [7]. Using thermal vacuum deposition technique, copper oxide film was sputtered on por-Si substrate. The process of deposition was employed with VUP-4 facility ($P = 0.5 \cdot 10^{-4} - 10^{-3}$ Torr, $\upsilon = 0.9^{-1}$ μm/min), etching time was 10 minutes. Morphology of the samples was studied by atomic-force microscopy (AFM) with Solver P47 PRO microscope. The studies of the chemical bonds and their potential deformations on the surface of porous silicon samples were made with the use of infrared spectroscopy technique (Vertex 70 Bruker). Spectra of X-ray photoelectron spectroscopy (XPS) of the original porous silicon and nanocomposite with the deposited copper were obtained with the use of laboratory spectrometer (SPECS FTI UrO RAS) according to the technique described in [9, 10].

Results and Discussion

AFM images of porous silicon samples before and after copper films deposition are presented in Fig. 1, as well as histograms of distribution of non-uniformities over the surface of samples. AFM images of the original porous silicon demonstrate the presence of non-uniformities with

different sizes (from 50 to 300 nm) on its surface, while the mean roughness of the surface is of ~70 nm. After copper film deposition mean roughness of the surface is reduced up to 6 nm, whereas histogram of distribution shows the presence of non-uniformities on the surface with the size of about 50 nm. Thus, the obtained results demonstrated that copper deposition on the surface of porous silicon in the process of its vacuum-thermal evaporation results in the formation of rather uniform continuous film that considerably smoothened relief of porous silicon.

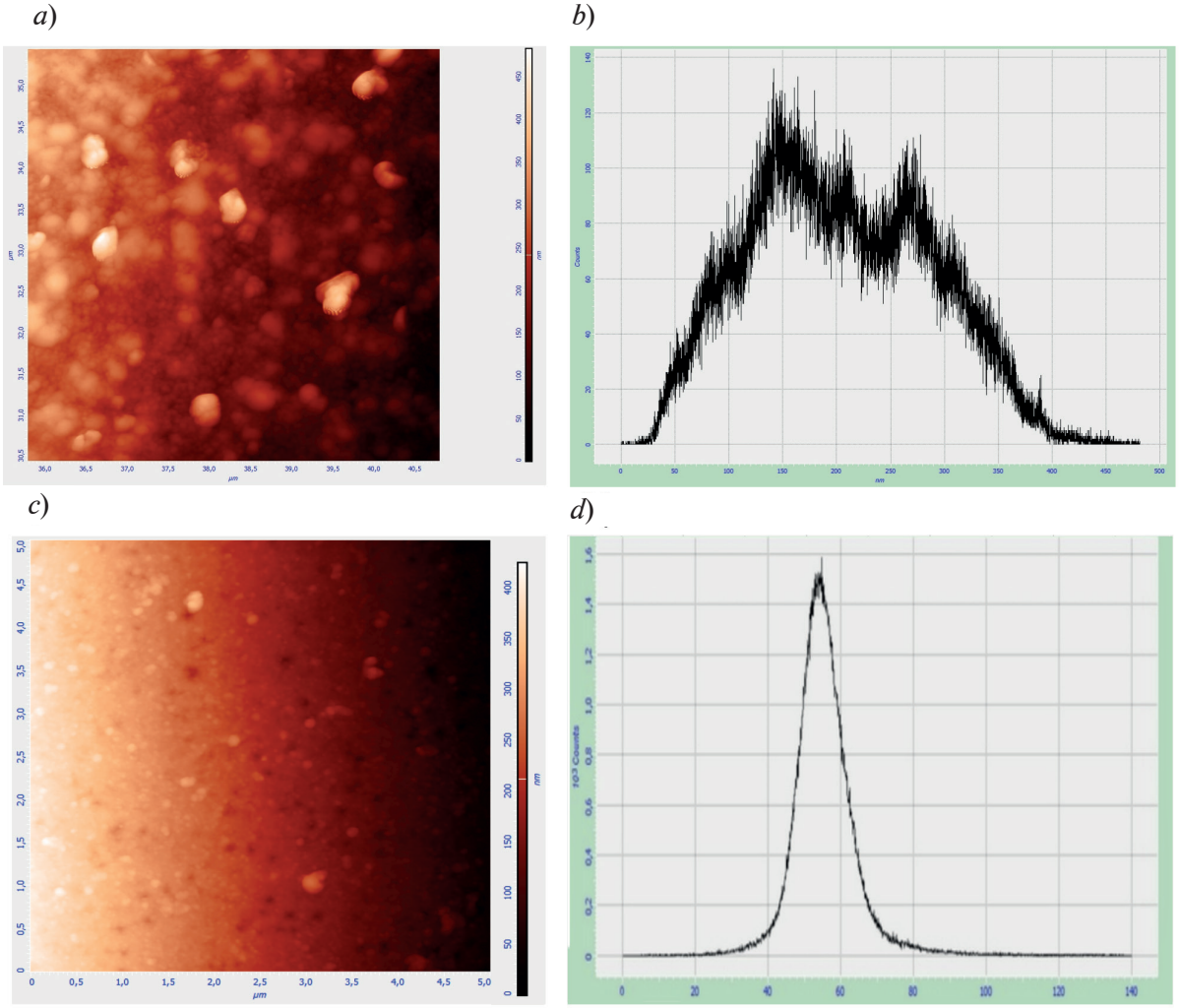

Fig. 1. AFM images of porous silicon samples: (*a*) surface of porous silicon, (*b*) histogram of particle size distribution on porous silicon, (*c*) surface of porous silicon with deposited copper, (*d*) histogram of copper particle sizes on porous silicon

IR transmittance spectra of the porous silicon samples as well as those with the deposited copper obtained by IR-spectroscopy with the use of ATR (Attenuated Total Reflection) attachment are presented in Fig. 2.

Characteristic features of the material are present in IR transmission spectrum (Fig. 2) of porous silicon which correspond to the valence Si-O-Si (1061 cm^{-1}) and non-valence Si-O-Si bonds (432 cm^{-1}), different bonds of Si-H_x type (624, 708 cm^{-1}). The sample also demonstrates adsorbed CO_2 (2355 cm^{-1}), which is present during spectrum survey in the air. One can also see the traces of hydrofluoric acid affect in the form of SiF_3 contamination (941 cm^{-1}) and the bonds of O_x-SiH_y type (863 cm^{-1}). Within the range of 2400–4000 cm^{-1} no any distinctions are observed except of the adsorbed water in the band range of 3400 cm^{-1}. From this figure it can be seen that while comparing IR spectra of porous silicon sample with that one where copper was deposited that majority of abrupt absorption jumps in the spectra were leveled. This can be

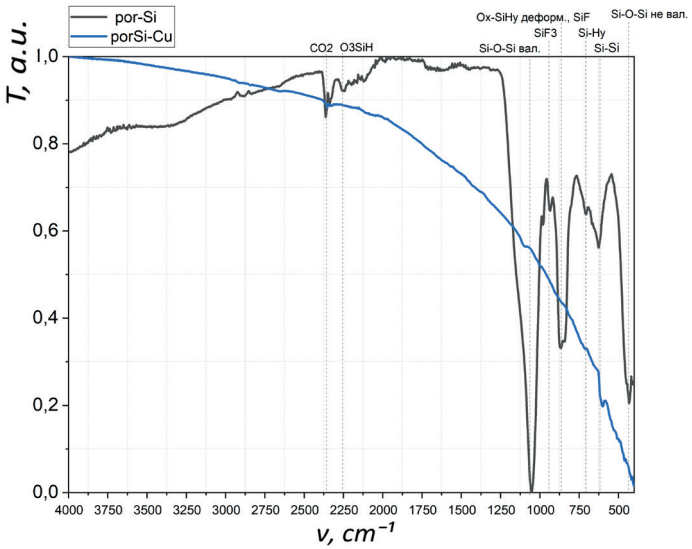

Fig 2. IR-absorption spectrum of por-Si and por-Si/Cu

Table

Absorption bands in IR-spectrum [3]

Wave number, cm^{-1}	Porous silicon
432	Si-O-Si non-valence
616	Si-Si
708	Si-Hy
863	Ox-SiHy deforms., SiF
941	SiF_3
1061	Si-O-Si valence.
2253	O_3SiH
2355	CO_2

explained by the fact that the absorption bands present in the porous silicon bound with oxide and other adsorbing bonds disappear because copper covering the substrate surface restrains its contact with the air and as a result, prevents oxide growth. Hardly observable peak in the range of Si-Si bond (616 cm^{-1}) remains as well. Disappearance of absorption bands can be explained by copper deposition which covers considerable number of silicon nanocrystals/clusters formed in porous silicon. These smallest particles reflect an incident radiation.

Analysis of the survey XPS (X-ray Photoelectron Spectroscopy) spectra allows determining the chemical composition of the material surface. Figure 3, *a* presents the XPS Si 2p spectrum of the initial porous silicon (por-Si). The obtained data are in good agreement with literature values [7, 9]. The surface layer of porous silicon typically consists of silicon dioxide (Si 2p, $E_b \approx 103.5$ eV), silicon sub-oxides (Si 2p, $E_b \approx 100.5$–103 eV), and non-oxidized silicon in crystalline or amorphous state (Si 2p, $E_b \approx 99.5$ eV). It is also known that with increasing storage time, the amount of oxide phases grows, especially in the near-surface region. For the composite sample por-Si/Cu, the XPS Si 2p spectrum (Fig. 3, *b*) shows a similar component distribution to that of the initial substrate, with silicon dioxide dominating and a small contribution of sub-oxide at ≈ 101.5 eV, whereas the signal of elemental silicon at ≈ 99.5 eV is absent. The XPS Cu 2p spectrum of the por-Si/Cu sample (Fig. 3, *c*) indicates that the surface is mainly composed of metallic copper (Cu $2p_{3/2}$, $E_b \approx 933$ eV) with a minor contribution from copper oxide CuO (Cu $2p_{3/2}$, $E_b \approx 935$ eV).

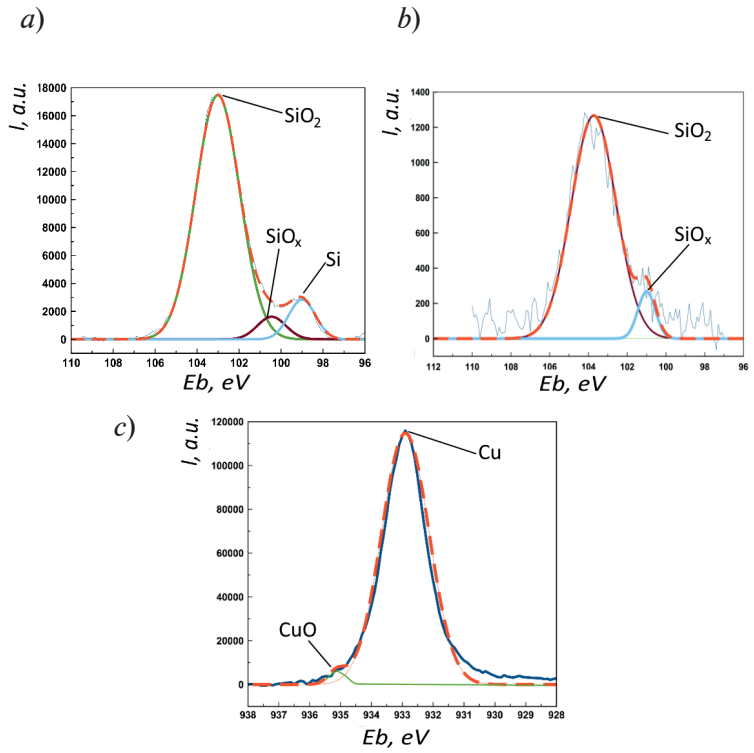

Fig. 3. XPS Si2p spectrum of the original porous silicon (*a*), Si2p spectrum of por-Si/Cu (*b*); Cu2p spectrum of por-Si/Cu (*c*) along with their decomposition into the components

Conclusion

Nanostructures composites of porous silicon with the deposited layer of copper oxide were obtained in the work using vacuum-thermal evaporation technique. The obtained results demonstrated that applying vacuum-thermal evaporation of copper forms steady continuous film repetitive porous silicon relief. Nanocomposites of porous silicon with the deposited copper obtained by vacuum-thermal deposition involve the phases of metallic copper and copper oxide. According to IR-spectroscopy data vacuum-thermal copper deposition retards the oxidation process of porous silicon during its long-term storage in the atmosphere.

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