

FORMATION OF POROUS SILICON LAYER WITH METALLIZATION PORES

Belousov I.V., Kuznetsov G.V., Skryshevsky V.A.

Kiev University, Radiophysics Department, Volodimirska st., 64, 01033 Kiev, UKRAINE,
e-mail: kuznetsov@uninet.kiev.ua

The methods of the metal introduction into the pore volume during the formation of porous silicon (PS) layers can be applied for doping of porous layers, the creation of semiconductor matrixes with metal nanoclusters in pores, the formation of sensors contact structures [1-2]. The problems associated with the necessity of joining on the silicon electrode both PS formations by anodization and metal deposition by cathodic process arises during the electrochemical growing of PS layers with metal nanoclusters. The metal introduction into pores is easier realized by the chemical PS formation, in particular, in mixture on the basis of hydrofluoric and nitric acids [3].

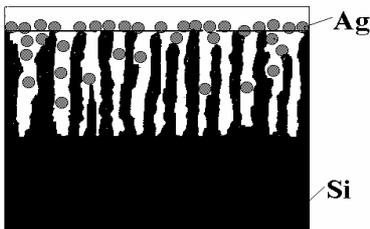


Fig.1. Formation of Ag-PS(Ag)-Si structure.

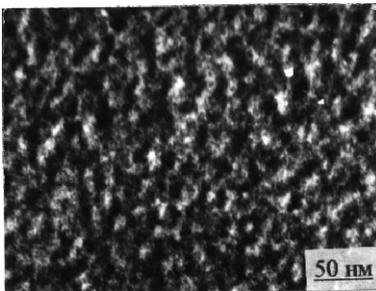


Fig.2. The scanning electron observations of silver modified porous

The formation and property of metal (silver) – PS(Ag) – silicon structures have been examined. The substrate n (p)-Si (100) with resistance of 1-10 Ohm.cm and thickness 300 μm are used. The chemical formation of the PS layer and simultaneous Ag deposition is provide in the solution: HF(48%): HNO₃(70%) : AgNO₃(1%) = 150:1:40. The PS layer formation is determined by the conditions of the transport of fluoride ions to the reaction zone. Their concentration depends on the concentration of hydrofluoric acid. The HF and H₂F₂ combinations dominate in the water solution of HF at pH<2, HF₂⁻ ions dominate at 2>pH<5 and F⁻ ions dominate at p>6. So at chemical PS layer growth we used solutions diluted of HF acid. The continuity of the PS layer growth is provided by the presence of insignificant amount of nitric acid in the etch solution. The production of the surface oxide stipulates the growth absorbed F⁻ ions and subsequent intensification of silicon etching. The concentration of HNO₃ is selected such a manner that the speed of SiO₂ oxide formation was considerably less than the speed of the production of the H₂SiF₆ soluble complex. Higher electrode potential of silver in comparison with silicon stipulated its deposition on the pore surface in the elementary state in high absorption and formation resulting of Ag nanoclusters. The duration of the chemical processing of silicon substrate is up to 1-2 min.

In Fig.1 the schematic view of the examined samples is shown. Electrical characteristics of such samples have been compared with the similar ones of test samples, in which the PS layer was formed by the treatment in (HF:HNO₃:H₂O = 150:1:40) electrolyte without AgNO₃. The morphology of the PS surface after Ag chemical deposition is characterized by the presence of the nanoclusters of semispherical shape. They correspond to the silver nucleation centers (Fig.2). The rise of the deposition time leads to the growth of the silver nucleation centers and increase of the surface-roughness. The time of chemical silicon treatment for the formation of the pore height d=1-2 μm is 30-60 sec. Auger electron spectroscopy (AES) results of the Si surface are presented in Fig.3. As seen the increase of the treatment time stipulates the growth of the dept penetration of Ag atoms into the substrate. The concentration of oxygen in the Si bulk is insignificant and does practically not depend on the treatment time.

The HF acid stipulates the opportunity of metal deposition with the direct substitution of Si atoms on the substrate. The anodic and cathodic processes take place simultaneously and the charge

exchange is realized through the substrate. The Si surface is released from the oxide in the presence of fluoride-hydrogen combination and the cathodic metal deposition is realized of with the simultaneous renewal of oxidant. The Si surface in the HF solution becomes hydrophobic one that promotes to Ag ion absorption. Metal ions deposited and from nucleation centers simultaneously with the etch resulting in the PS layer formation with metal nanoclusters into pores. They are the centers of the charge exchange and they initiate the chemical deposition without the initial activation of the Si surface [4]. The chemical reaction is written as:

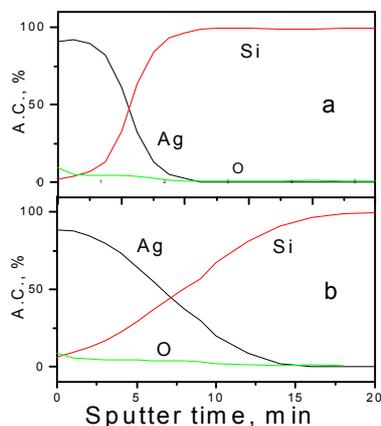
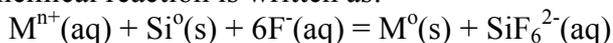


Fig.3. AES depth profiles of atomic compositions after formation PS(Ag) layer: a - 20 s; b - 40 s.

The results of measurements of the resistance of Ag chemical deposited layer were compared with those of Ag layers obtained by vacuum thermal evaporation on Si substrate before and after formation of the PS layer. The comparison shows that the resistance of metal evaporated on PS layers is large than those on mono Si. The transition from Ag nanoclusters to the solid Ag layer on PS is observed for the thickness up to ~ 20 nm. One of the possible mechanisms of the current transport at the sizes and distances between nanoclusters ~ 10 nm is the charge tunneling through carriers the substrate. Is the number of the trap centers is significant then electrons tunnel to these centers as quickly as possible in comparison between with by nanoclusters. This fact is stipulated by higher possibility of multi step tunneling.

The current dependence from the applied bias for Ag-PS-Si structures is rectifying one ϕ_b the potential barrier has been formed in

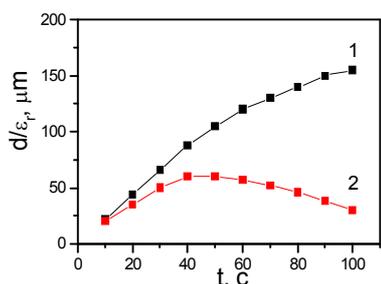


Fig.4. The change of dielectric layer thickness with the time chemical treatment:
1 - without AgNO₃;
2 - presence AgNO₃

the examined structures. The results of the determination of the intermediate dielectric layer thickness at metal-semiconductor interface in the Ag-PS-pSi structures using capacitance-voltage measurements are presented in Fig.4 (ϵ_r - is the relative dielectric constant, d - is the layer thickness). The PS thickness increases after chemical treatment in the solution without AgNO₃. The initial linear growth becomes slowed at the increase of the duration of the chemical treatment and it approaches to the dependence typical for diffusion processes: $d \sim t^{1/2}$. The presence of AgNO₃ in the solution leads to the decrease of the effective thickness of the intermediate dielectric layer at the growth of treatment time that is stipulated by the increasing penetration of Ag atoms into the PS layer. The analysis shows that in the range of high voltage $eV \gg \phi_b$ volt-ampere characteristic is fitted by $\ln I \sim V^{1/2}$. The shape of this characteristic does depend on thickness,

the dielectric, area and material of the upper electrode at the room temperature. The conductance of the intermediate dielectric layer may to be determined by the bulk processes. At electrical fields 10^5 - 10^6 V/cm namely the Poole-Frenkel emission accelerated by the field of thermoexcited electrons from the deep traps into the conductance band of the dielectric.

REFERENCES

1. Pearlstein F. in Lowenheim F.A.(ed). Modern Electroplating. -N.-Y. -Wiley (1974). -170p.
2. Gupta A., Jain V.K., Jalvania C.R., Singhal G.K., Arora O.P., Puri P.P., Singh R., Pal M., Kumar V. Semicond. Sci. Technol. 10, 698 (1995)
3. Kuznetsov G.V., Skryshevsky V.A., Tsyganova A.I., Vdovenkova T.A., Gorostiza P., Sanz F. Journal Electrochemical Society **148**, 8, 528 (2001)
4. Nagahara L.A., Ohmori T., Hashimoto K., Fujishima A. J. Vac. Sci. Techn. **A11**,763 (1993)