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REVIEWS AND SHORT NOTES

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SYNTHESIS OF POROUS SILICON WITH SILVER NANOPARTICLES BY ION IMPLANTATION

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New experiments on the formation of porous silicon (PSi) layers with Ag nanoparticles by low-energy high-dose Ag-ion implantation are presented and a comparison of morphology and electron backscattering diffraction pattern of PSi formed by implantation and thermal annealing are considered. Metal-ion implantation is suggested to be effective technique for a formation of porous semiconductor layers with metal nanoparticles.

1. Introduction

At present time porous silicon (PSi) is considering in practice as a key material in many industrial sectors as electronics, sensors and photonics. PSi layer was first obtained in the mid-1950s at Bell Labs [1]. By now there are two main technological methods for production of PSi structures: electrochemical etching and chemical stain etching. Thus, PSi could be chemically created on crystalline silicon under appropriate conditions with typical feature porous sizes in the order of a few nanometers [2]. Both the porosity and the pore morphology of PSi are greatly influenced by the electrochemical and chemical stain etching parameters.

Additionally, the interest to PSi nanostructures containing silver nanoparticles (AgNPs) was recently found. It was initiated because noble metal nanoparticles with localized surface plasmon modes demonstrate a specific option to enhance the recombination rate of the light Si emitter to increase the efficiency of photoluminescence [3] or surface enhancement Raman scattering [4]. Silver nanoparticles are the subject of specific increasing interests due to their strongest plasmon resonance in the visible spectrum [5].

Instead of using simple Si as the flat substrate for the AgNPs deposition on the top of a sample, the ion implantation technique can be used to form AgNPs in a volume of semiconductors as in the case of ion-irradiated silica glass or polymers [5]. Such new technological way based on low-energy ion implantation for creation of PSi layers with AgNPs on the crystalline surface of semiconductor wafers, which was developed in [6,7], is combined with thermal annealing technique at the present work.

2. Experimental details

A (100)-oriented single crystalline c-Si wafer as the substrate was used for Ag^+-ion implantation to create PSi structures. The substrate was cleaned in a wet chemical etching process. The semiconductor wafers were implanted with Ag^+ ions at the energy of 30 keV and the ion current density of 8 $\mu A/cm^2$ with the dose of $1.5 \cdot 10^{17}$ ion/cm^2 using the ion implanter ILU-3 at residual vacuum of 10^{-5} Torr and room temperature of the irradiated substrate. Depth distribution profiles of Ag atoms and the damage level in implanted semiconductors were modeled using the free simulation-program the Stopping and Range of Ions in Matter (SRIM-2013). Thermal annealing was realized with vacuum evaporate device VUP-5M during 30 min at 600 °C. Local structure and surface sample morphology were analyzed with scanning electron microscopy (SEM) Merlin (Carl Zeiss), which combined with a detector of electron backscattering diffraction (EBSD) Norlys HKL (Oxford Instruments). EBSD measurements were performed at the accelerating electron voltage of 20 keV and tilt angle 70 deg to the sample surface.

3. Results and discussion

According to the SRIM simulations, during ion bombardment an excess vacancy-rich region and accumulation of implanted ions can be formed close to the surface of the irradiated matrix. A mean penetration range (R_p^{Ag}) of 30 keV Ag^+-ions into Si substrates are about 26.3 nm with a longitudinal straggling (ΔR_p^{Ag}) of 8 nm in the Gaussian depth distribution. Thus, the assumed thickness of the modified Si surface layer ($R_p + 2\Delta R_p$) is about 42.3 nm. It was assumed [8] that during ion implantation various porous semiconductor structures could be resulted from nucleation of small voids in the irradiated materials by vacancy generation.

In contrast to unimplanted c-Si (Fig. 1a) the PSi surface after Ag-ion implantation shows the black hole network appeared on Si surface (Fig. 2a). Such structure consists of near cellular holes partitioned by rather thin walls with thicknesses about 30-60 nm. Uniform pore distribution with distinguished sharp holes over surfaces of the implanted samples is observed. The size of pores is in the range from 100 to 130 nm. A white spots in these SEM figures corresponds to material with higher density against to Si that suggests them to be AgNPs with average size of 10 nm [6,7].

In practice, EBDS analysis is used for characterization of various crystallographic structural parameters of materials [9]. Experimental EBDS pattern of c-Si shows typical monocrystalline Kikuchi structure (Fig. 1b). Electrum beam during EBSD penetrates into Si dipper than PSi layer. Thus EBDS image of PSi seems as a superposition of low intensity Kikuchi band of the substrate c-Si and diffusely ring from the formed PSi layer (Fig. 2b).

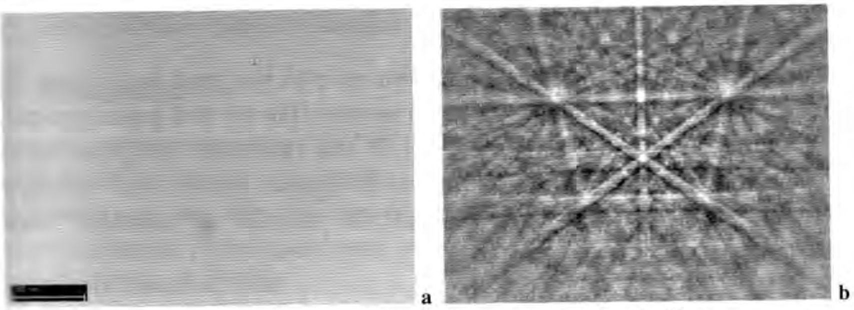

Figure 1. (a) SEM and (b) EBSD images of unimplanted c-Si.

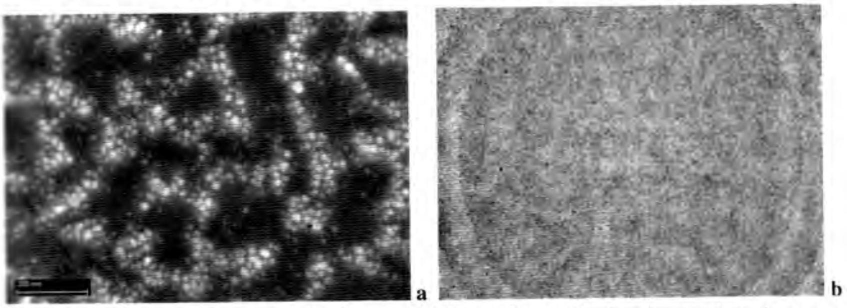

Figure 2. (a) SEM and (b) EBSD images of PSi layer formed by Ag+-ion implantation.

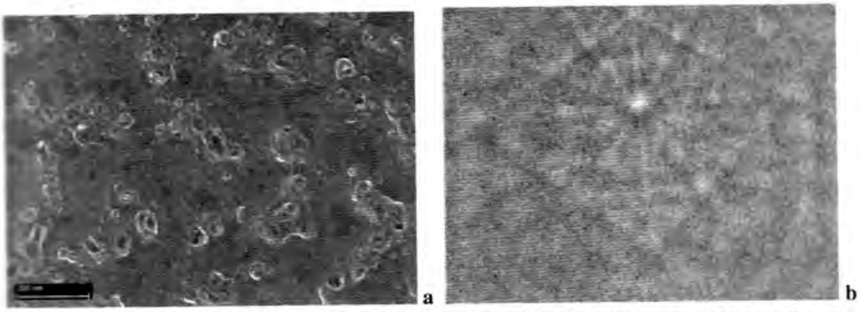

Figure 3. (a) SEM and (b) EBSD images of PSi layer formed by Ag+-ion implantation and thermal annealing.

Thermal annealing was carried out at 600 °C in vacuum in order to recrystallize PSi structure. As seen from Fig. 3a the SEM image of PSi layer after annealing procedure demonstrates some consistence with PSi created by implantation. However, porous network is partly destroyed by heating of the sample. EBSD pattern in Fig. 3b shows reconstruction of the Kikuchi band of annealed PSi to cubic syngony. Unfortunately, computer analysis of the Kikuchi band indicates an appearance of crystallographic orientation in the modified PSi to be different from (100) of unimplanted c-Si.

4. Conclusion

Low-energy high-dose Ag-ion implantation of c-Si was used to fabricate PSi layers and later modified by annealing in vacuum. For the first time a structural EBSD analysis of PSi was carried out. It was concluded that after Ag-ion implantation the surface PSi layer is amorphous which can be partly recrystallized by annealing. Crystallographic structure of annealed PSi is different from unimplanted c-Si (100).

Acknowledgments

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