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NANOSTRUCTURED SILICON FOR SOLAR CELLS

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ABSTRACT

Nanostructured black silicon wafers were obtained in a two-stage process of selective chemical etching initiated by metal nanoclusters. The obtained silicon wafer surfaces demonstrate the reflectance of 2-3% in the visible range. Surface-enhanced Raman scattering (SERS) effect was observed on silicon substrates coated with silver or cooper nanoclusters. Test substance of Rhodamine can be detected up to concentration of ~10-11 M by using nanostructured silicon substrates covered with silver nanoparticles. Dependence of average thickness of nanoparticles layer after the first stage of treatment as well as the thickness of the structured layer after the second stage of treatment on the concentration of AgNO3 in the solution was determined. It was shown that the depth of the structured layer is linearly dependent on the duration of the second stage etching up to etching time about 100 seconds. During the etching process, the formation rate of textured layer is twice faster in p-type silicon than in n-type silicon.

Keywords: nanostructured silicon, silver nanoclusters, textured surface

INTRODUCTION

The technology of nanostructured silicon can be used for creation of solar cell (SC) surface with low reflectance [1-5]. Rather low reflectance value in the visible range can be reached by creation of textured surface. However, the texturing leads to increasing surface resistance, which is an unwanted condition for SC manufacturing. Thus, it is crucial to develop low-cost technology for textured silicon surface production. This paper reports results of nanotexturing of silicon surface with low reflectance value for SC manufacturing.

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EXPERIMENTAL PART

Initial polished silicon wafers p-Si and n-Si, with the specific resistance of [illegible] Ohm*cm were thoroughly cleaned from dust and surface contaminations. In order to create a textured surface, the two-stage chemical treatment was applied [6-9].

For formation of shallow diffusion p-n-junctions, we prepared a dopant based on isopropyl alcohol, hydrochloric acid and tetraethoxysilane. In case of boron diffusion into n-Si, boric acid H_3BO_3 was added to the gel, for phosphorus diffusion into p-Si phosphoric acid was added to the gel, while the ratio of main components and dopants in gel varied. The gel was deposited using centrifugation.

Shallow diffusion p-n-junctions were created using a method of pulsed light annealing, which was conducted at the temperature of 950-1050 ^{0}C during 20 sec in constructed chamber for light annealing. Time of heating up to 950 ^{0}C was not more than 10 seconds. After that, back and front contacts were formed on the samples.

Morphology of samples' surface was studied by scanning electron microscopy (SEM) using electron microscope Quanta 200i 3D (FEI Company). Spectra of optical reflectance were measured on spectrophotometer UV-3600 (Shimadzu), Raman spectra were obtained using microscope equipped with the system of Raman signal registration NTegra Spectra (NT-MDT) with blue laser excitation at 473 nm. Current-voltage curves of obtained structures in the dark and at xenon lamp lighting were measured using potentiostat P-30J (Elins). The effectiveness of obtained SC was performed at halogen lamp illumination by measuring dark and illuminated current-voltage characteristics of SC and comparing it with the one of etalon SC with the known value of effectiveness.

RESULTS AND DISCUSSION

The first stage of texturing consisted of treatment in a water solution of hydrofluoric acid and metal salt – silver nitrate $AgNO_3$ or nitrate or chloride of copper. Varying parameters were a concentration of hydrofluoric acid solution, a concentration of metal salt and time of treatment.

In case of silver particles' synthesis with the use of silver nitrate, at the first stage silicon wafers were dipped into water solution of H_2O+HF+$AgNO_3$. During the experiments, we used H_2O:HF solutions with component ratio 4:1 and the concentration of $AgNO_3$ was 4, 6, 8 and 10 mmole/l. The usage of $AgNO_3$ concentration below [illegible] mmole/l led to unreproducible results, while at the concentration over 10 mmole/l thickness of the textured layer was too large for SC production.

It was found, that duration of the first stage from 10 to 20 seconds resulted in the formation of spherical-shaped silver nanoparticles on the silicon substrate. Increasing duration of the first stage led to the elongation of particles' shape and formation of additional layers of nanoparticles on the surface.

Figure 1 shows the surface morphology of silicon after the first stage of treatment in water solution of hydrofluoric acid with concentration of silver nitrate of 8 mmole/l. Treatment duration was 10 seconds. One can see the nanoparticles on the surface of

silicon substrate. On images of cleaved edge, it is seen that particles are located in one layer and have an average size of 50 nm. Elemental analysis showed that particles consisted of silver.

In case of formation of textured surface with copper nanoclusters, we used H_2O+HF+$Cu(NO_3)_2$ and H_2O+HF+$CuCl_2$ solutions with water and hydrofluoric acid ratio 4:1, with copper salt concentration from 10 mmole/l up to 20 mmole/l, duration of treatment was from 20 to 100 seconds. In figure 2 it is shown the morphology of silicon surface after the first stage of treatment in solution of hydrofluoric acid with copper nitrate (Fig.2 a) and copper chloride (Fig.2 b). Similar to the case of the usage of silver nitrate, nanoparticles are formed on the surface of silicon substrate. In this case, elemental analysis showed that the particles consisted of copper. Images of cleaved edge showed that the particles have the average diameter of ~80-180 nm.

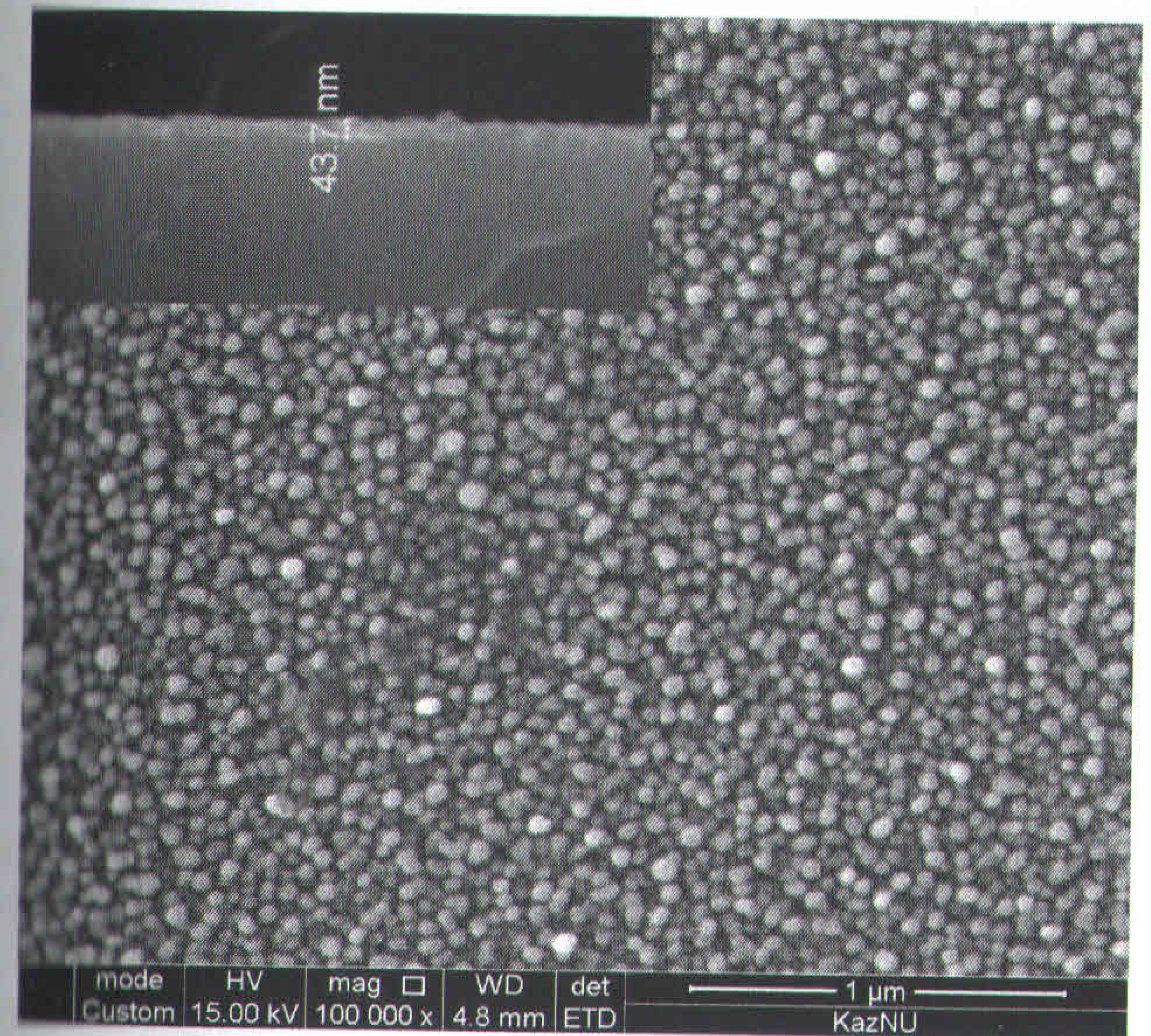

Figure 1 – Surface morphology of the samples obtained after the first stage treatment of silicon surface in 8 mmole/l solution of $AgNO_3$ in hydrofluoric acid during 10 seconds.

Obtained after the first stage of treatment silicon samples with metal nanoparticles on its surface can be used as substrates for detection of surface-enhanced Raman scattering (SERS effect) from organic molecules. It was revealed that after the first stage of treatment silicon substrates with metal nanoparticles on the surface exhibited SERS signal from test molecules of Rhodamine. In case of substrates with copper particles, noticeable SERS signal can be seen at Rhodamine concentration of 10^{-5} M, while in the

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case of silver particles – at Rhodamine concentration of 10^{-12} M, i.e. at Rhodamine concentration ~$5*10^{-10}$ gram per liter.

The second stage of formation of nanostructured surface is served for selective etching. On this stage, we used treatment in water solution of hydrofluoric acid and hydrogen peroxide for implementation of selective etching of silicon initiated by metal clusters. Generally, solution H_2O_2 : HF : H_2O=5 : 10 : 50 was used.

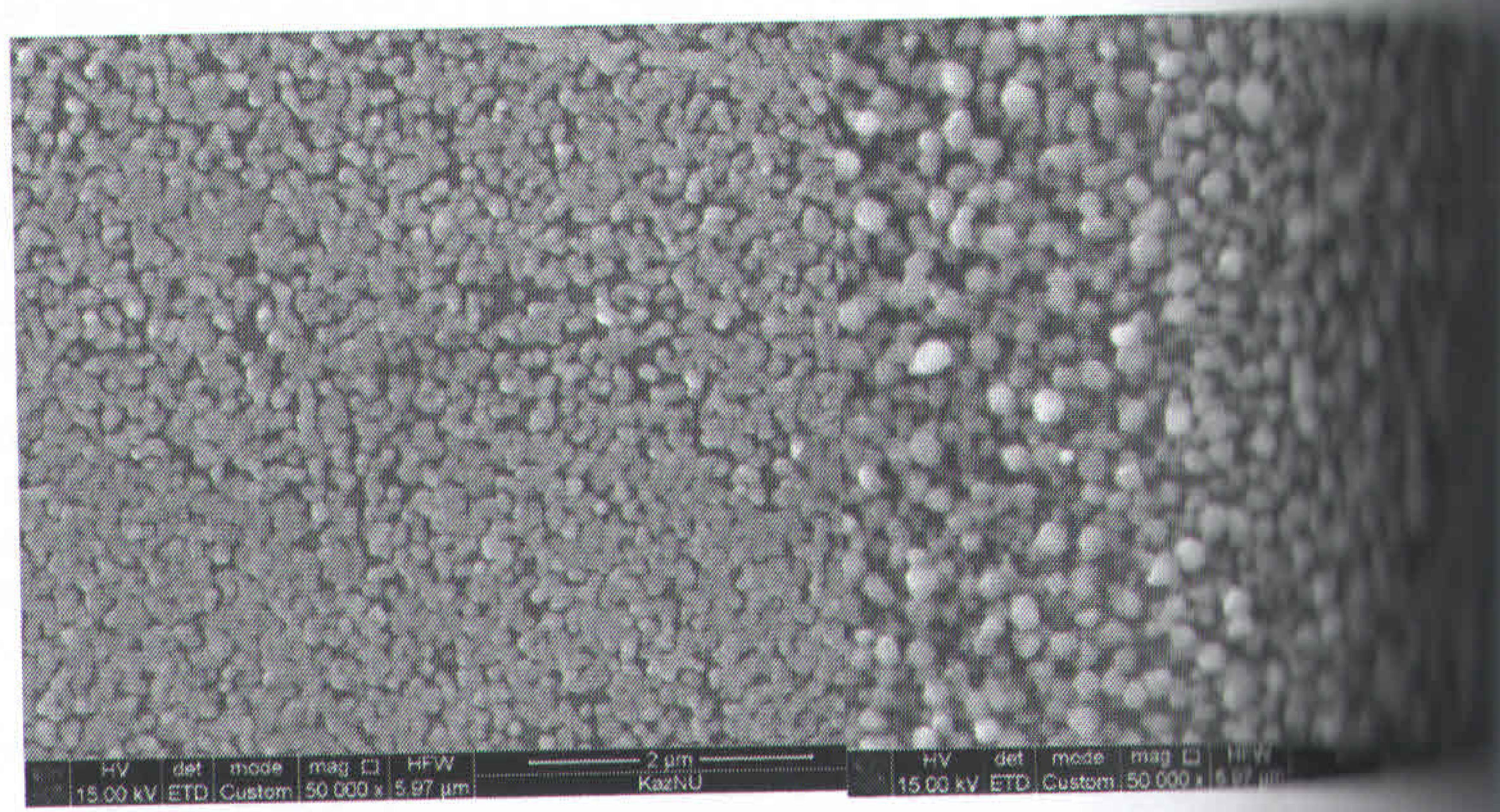

Figure 2 – Surface morphology of samples obtained after the first treatment stage of silicon surface: in solution of hydrofluoric acid with 10 mmole/l of copper nitrate for 100 seconds (left), in solution of hydrofluoric acid with 20 mmole/l of $CuCl_2$ within seconds (right)

Surface morphology of p-type silicon after two stages of treatment consists of pillars with cross-sectional sizes of about 50-100 nm. On the cleaved edge of the sample it is seen that height of structured layer is approximately 300 nm.

We have studied the dependence of the average thickness of the layer consisted of nanoparticles after first stage treatment and thickness of structured layer after second stage treatment on the concentration of silver nitrate in solution at the first stage treatment. It is found that at the concentration of $AgNO_3$ 8 mmole/l one can obtain minimal size of nanoparticles, however average size of particles slightly varies when concentration of $AgNO_3$ changes within 4-8 mmole/l, and only when concentration of $AgNO_3$ rises up to 10 mmole/l particle size begins to grow rapidly.

Etching conditions were defined, at which the thickness of structured layer slightly changes at varying etching duration and composition of the etching solution. This shows that the method of two-stage treatment is a convenient technique for repeatable formation of structured layer, as the results slightly depend on the concentration of copper salt and duration of the first stage. The main parameter that defines the depth of structured layer is duration of the second stage.

Silicon surfaces obtained after the second stage of treatment demonstrate low optical reflectance (Fig.3). Spectra of optical reflectance for the samples in the range 200-1000 nm show sufficient decrease of reflectance from ~30% down to ~2-3% in the wide range of wavelength. Minimal reflectance was reached at $AgNO_3$ concentration of 8 mmole/l on the first stage of treatment, at duration of the first stage of 20 seconds and 100 seconds for the second stage.

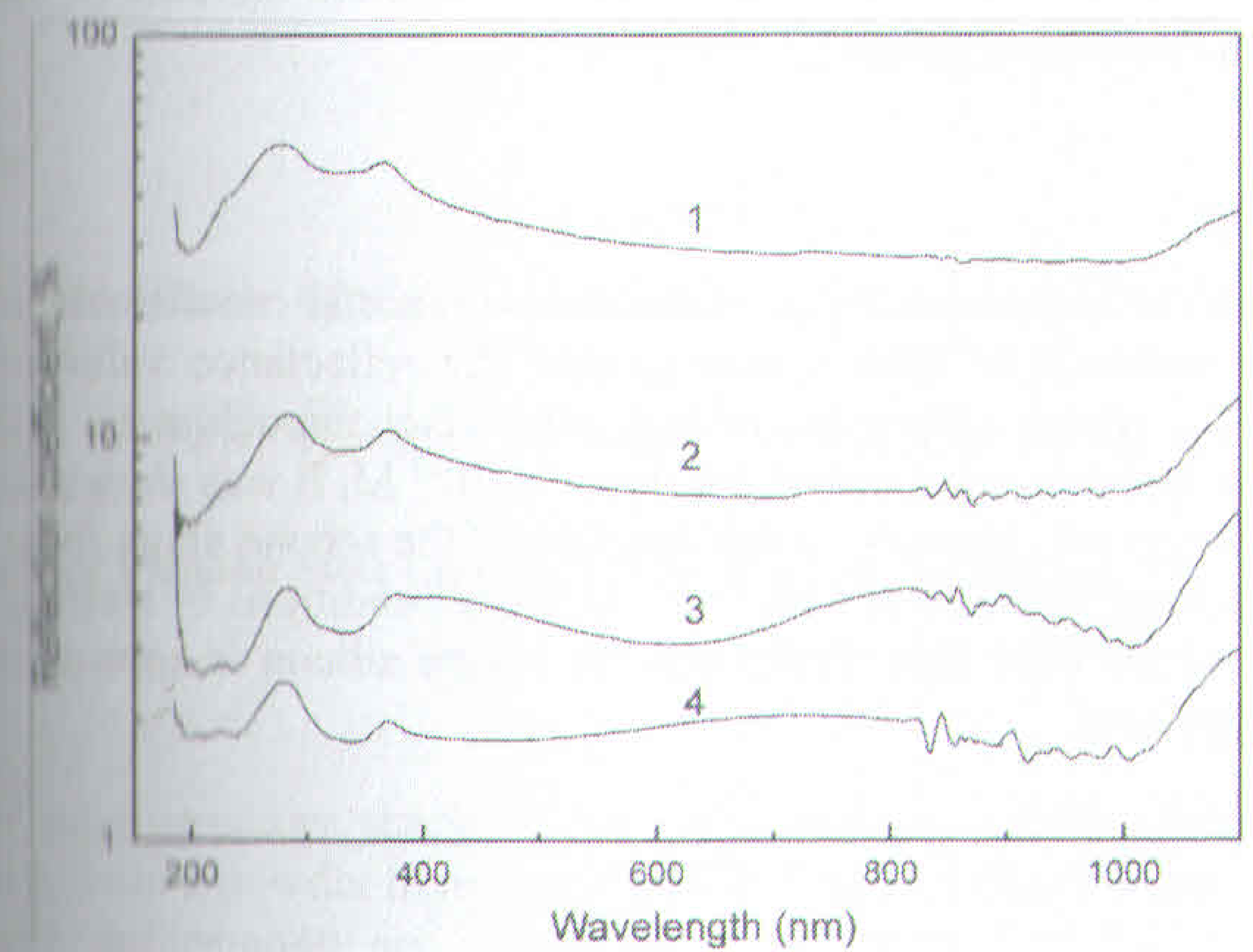

Figure 3 – Spectra of optical reflectance of samples: initial silicon wafer (1) and after etching at the second stage duration of 40 sec (2), 50 sec (3) and 60 sec (4).

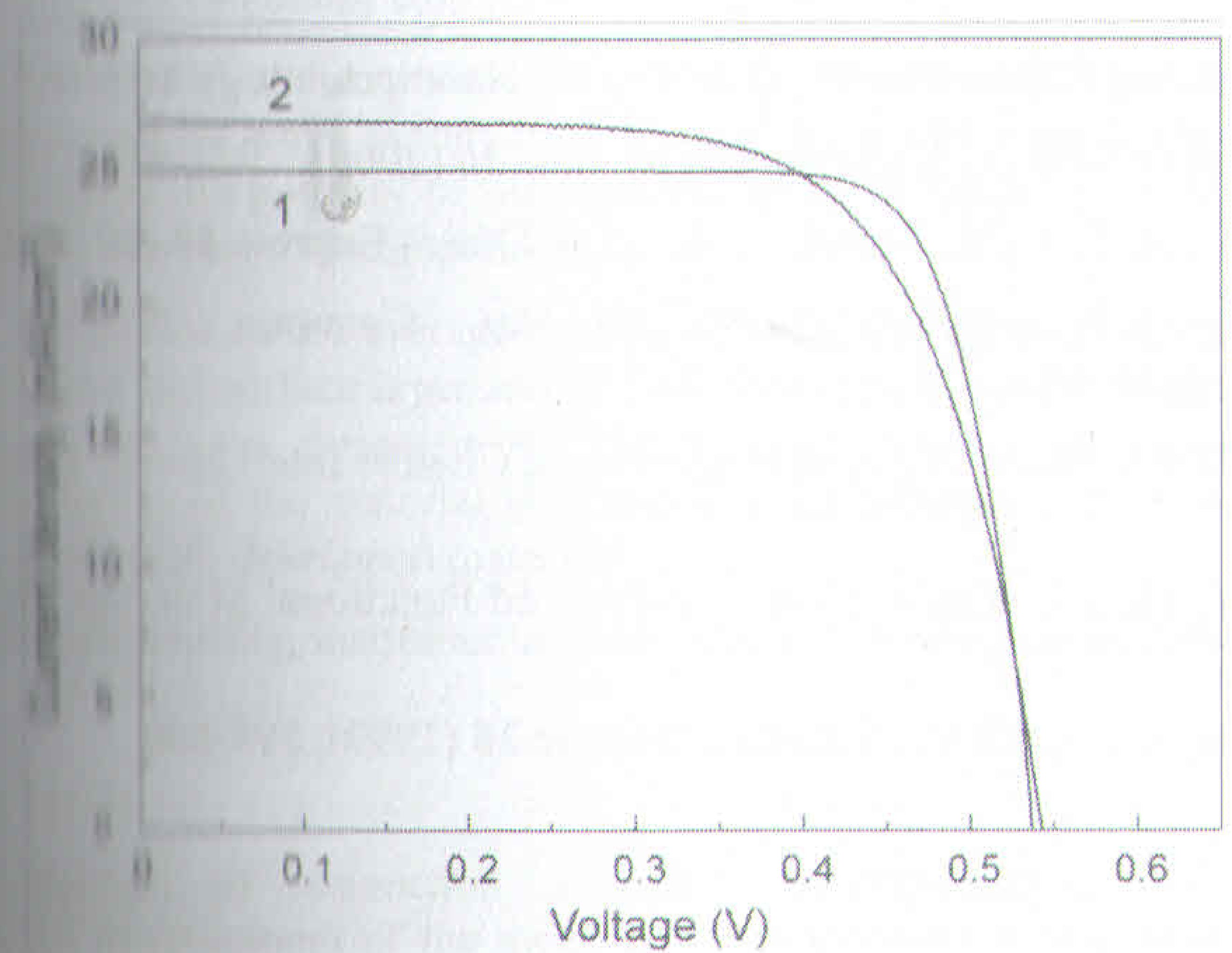

Figure 4 – Current-voltage characteristics of control SC (1) and textured SC (2) under

10.5593/sgem2017/61

NANOSTRUCTURING AND HETEROGENEOUS HARDENING OF TOOL MATERIALS FROM HIGH-SPEED STEEL POWDER

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ABSTRACT

The results of microstructure study, X-ray microanalysis, microhardness, porosity of sintered samples from a powder high-speed steel before and after hardening by the wave intensive plastic deformation are presented. It has been established that the basic elements in the composition of sintered samples from tungsten powders are C, O, Mo, S, V, Cr, Fe, W.

Based on the analysis of the sintered samples microstructure, it was determined that the there is a uniform distribution of solid carbide in the base material volume.

Based on the theoretical and experimental research, it was established that the use of hardening processing by wave deformation for tool materials from high-speed powder will allow to reduce the porosity of the material up to 10 times, thereby increasing of tensile strength in bending and compression.

Also there is an increase of the average microhardness value of hardened material in 1,8 times in the surface and surface layer and in 1,45 times at a distance equal to 7 mm from the place of strain wave propagation. The marked increase in the physical and mechanical properties of the material will improve the strength and wear resistance of cutting tools, made from developed materials.

Keywords: nanostructuring, instrumental materials, powder high-speed steel

INTRODUCTION

In the last decade, in connection with the development of science-intensive technologies, the development of the metal-working industry, which contributes to the creation of machines and mechanisms of the new generation, becomes of decisive importance. The modern level of technical solutions urgently requires the use of instrumental materials with high physical and mechanical properties. From the working capacity of the instrument, a successful solution to the problem of ensuring the specified

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