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MICROELECTRONIC AND NANOELECTRONIC TECHNOLOGY

Study of the Technology of the Plasma Nanostructuring of Silicon to Form Highly Efficient Emission Structures

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Abstract—New methods for silicon nanostructuring and the possibility of raising the aspect ratios of the structures being formed are considered. It is shown that the technology developed relates to self-formation methods and is an efficient tool for improving the quality of field-emission cathodes based on carbon nanotubes (CNTs) by increasing the Si–CNT contact area and raising the efficiency of the heat sink.

Keywords: silicon, nanostructuring, self-formation, carbon nanotubes.

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At present the nanostructuring of silicon and other functional layers and, in particular, those of SiC, Al, Ti, and Au is an area of research, which imparts new physical properties to the given materials, undergoing extensive development. Nanostructuring by pulsed laser or ion-beam irradiation can be used not only for light-emitting or light-absorbing devices and elements of the solar power industry, but also for other purposes. For example, the presence of a developed spread in the α-Si:*nc*-Si system can provide a positive effect in the development of gas sensors, catalytic devices, etc. [1–4]. In these cases, photoluminescence and/or electron-paramagnetic-resonance measurements can be used as a means of monitoring the evolution of the spread in the irradiated layers. We should note that lithographic methods fail to satisfy economic criteria and are frequently incompatible with the fabrication technology of devices based on nanostructured silicon.

Four areas of technological development can be distinguished in the field of surface texturing, those based on wet etching, dry etching, exposure to laser light, and ion-beam irradiation.

Wet etching is a highly productive method for silicon texturing, widely employed in the industrial manufacture of photoelectronic devices. This method is currently important for the following main reasons: the microtexture fails to provide zero surface reflectance, and the fraction of reflected light is rather high (6–8%), even with an antireflection coating.

† Deceased.

In contrast to the industrial method for the microtexturing of a silicon surface by wet etching, the approach based on silicon milling via high-power laser light in a chemically active medium requires that the solution of serious problems related to area scaling of the process. This approach is rather far from being industrially implemented in the manufacture of silicon solar-cell arrays or silicon–carbon nanoelecronic devices. The principle of the point-by-point treatment of a surface area with a laser spot 0.1 mm in size at a scanning velocity of 0.1 mm/s does not satisfy production requirements.

A possible replacement for the above methods in the production of solar cells is dry etching and, in particular, so-called maskless or automask reactive ion etching (RIE). The integration of RIE into the production process of solar cells is a modern trend. The term “black silicon” or “RIE grass” appeared in the mid-1990 s from the silicon microelectronics industry as a designation for the negative effect of the RIE of large-area silicon wafers. At the same time, the low reflectivity of a surface of this kind excited the interest of researchers and manufacturers of silicon solar cells. However, the maskless nature of RIE is its main shortcoming. Phenomena leading to local automasking are rather difficult to control. This is the reason for the irreproducibility and nonuniformity of the process both for the same wafer and from wafer to wafer.

The use of ion-beam irradiation of the surface of various auxiliary layers to form a nanostructured mask, with subsequent highly selective RIE of the functional layer is a subsequent stage in the development of nanostructuring technology. This nanostruc-

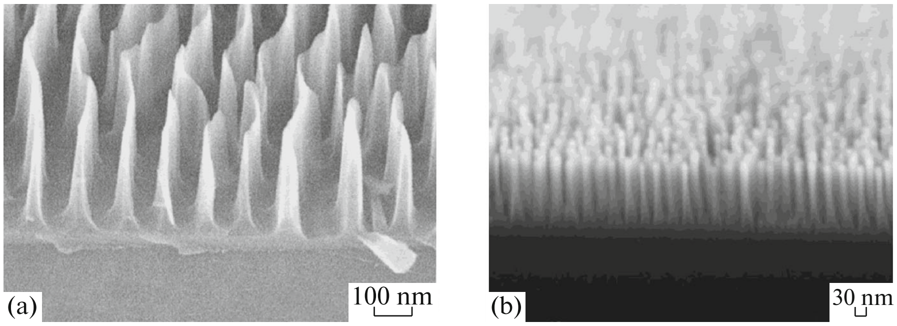

Fig. 1. Nanostructured arrays of varied morphology: (a) arrays of "ridges"; (b) arrays of "needles."

turing principle is applicable to any material capable of passing into a new state upon being irradiated with ion beams. The transition to the new state upon ion-beam irradiation enables the self-formation of nanostructured masks for further nanostructuring of the functional layer by highly selective precision etching in $HBr–O_2$, $Cl_2–O_2$ gas mixtures in reactors with a TCP source of dense plasma. Examples of a nanostructured silicon surface are presented in Fig. 1.

The goal of our study is to examine the technology of the plasma nanostructuring of silicon to form highly efficient emission structures to be used in nanoelectronic devices. We use 100-mm heavily doped Si substrates with a thin (20–40 nm) thermal oxide. Nanostructuring is performed via the formation of an ultrathin nanostructured metallic mask and transfer of the resulting pattern to a lower-lying layer by the RIE processes developed in the study. This technique relates to self-formation methods because the nanostructuring effect is provided by a set of physical processes without the application of lithographic procedures.

The following nanostructuring pathway was developed:

(i) the deposition of metal layers (Ti, Ni, Cr, etc.) of nanoscale thickness onto the surface of Si/SiO_2;

(ii) thermal annealing in vacuum to facilitate the formation of nanoscale clusters;

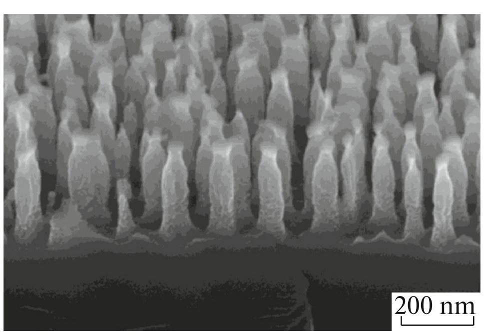

Fig. 2. Etching through a 5-nm-thick Ni mask (annealing without oxygen).

(iii) super-selective precision dry etching; and

(iiii) chemical removal of the mask.

The aspect ratio (AR, the ratio between the height of a structural element and its width) of nanostructured silicon is controlled by varying the thickness of the metallic layer, annealing parameters, and dry-etching modes. The procedure under study is regarded as a tool for improving the efficiency of field-emission cathodes based on carbon nanotubes (CNTs). In this case, the large-aspect nanostructuring of silicon solves the following problems:

—the area of the contact between CNTs and the conducting silicon surface or another conducting layer becomes larger;

—the adhesion of CNT bundles being formed in structures of this kind is improved;

—the heat transfer from CNTs to silicon is enhanced, which also improves the characteristics of the CNT field-emission cathodes being formed.

The process of silicon nanostructuring includes the formation of a nanostructured mask. The process is based on the clustering that occurs during thermal annealing in vacuum [5–7]. The size of the clusters and the distance between these depends on a number of factors:

—the thickness of the thin metallic film and characteristics of the material itself;

—the annealing temperature and duration in which clusters are formed from the deposited film;

—the state of the lower-lying functional layer determining the surface-tension coefficient of a cluster.

The cluster size is directly proportional to the surface-tension coefficient and inversely proportional to temperature. The surface-tension coefficient can be influenced by using special plasma processing included in the stage of thermal annealing in vacuum. In particular, plasma processing in oxygen enhances the surface hydrophilicity, and in a hydrogen-containing medium makes the surface more hydrophobic. These treatments can be included in the process of annealing to form clusters from a thin metallic film, with the structuring parameters thereby controlled.

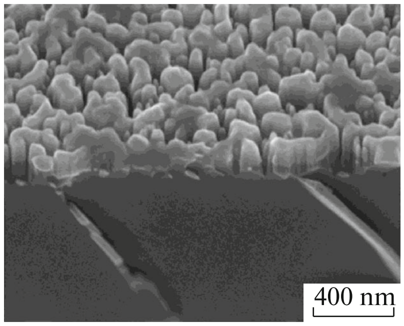

Fig. 3. Etching through a 7-nm-thick Ni mask (annealing with oxygen supplied).

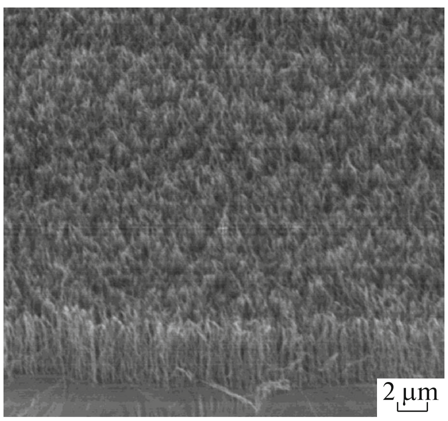

Fig. 4. Array of CNTs on a nanostructured silicon surface.

The nanostructuring of silicon includes the process of precision dry etching of the lower-lying layers (SiO_2, Si_3N_4, Si, Si^*, α-Si, etc.), which is successfully performed using modern plasma-chemical etching equipment. The basic physicochemical mechanisms and physical principles of the precision transfer of an image were reflected in, e.g., [8, 9]. Taking into account the required parameters of the silicon nanostructuring process and using nanoscale clusters as a mask, we developed a two-stage process for silicon etching in a dense-reactor plasma with a TCP source: etching of SiO_2 (Si_3N_4) with a CHF_3–CF_4–He working-gas mixture in the first stage, and etching of Si (Si^*, α-Si) with a Cl_2–O_2–CF_4 gas mixture in the second. Examples of etched areas of nanostructured silicon are presented in Figs. 2 and 3.

It was found that the density of the mask pattern can be controlled by varying the nickel-layer thickness d from 2 to 10 nm and the annealing duration. It was determined that, with the layer made thicker and the annealing duration longer, a less dense mask pattern is obtained. This, in turn, makes it possible to create a large-aspect (AR of up to 10:1) nanostructured silicon array with a column-to-column distance sufficient for the further synthesis of CNTs within the silicon structure. A nanostructured silicon array and a CNT array grown on structured silicon are shown in Figs. 2–4.

To synthesize a CNT array on the surface of nanostructured silicon, we preliminarily deposited a catalytic layer, performed ion treatment to remove the catalyst from the upper part of the structure, and synthesized CNTs by plasma-enhanced chemical-vapor deposition (PECVD) using a NanoFab 800 Agile installation (PlasmaLab System 100 platform, Oxford Instr., UK).

Over the course of the study, we measured the emission from two modifications of samples with CNT arrays synthesized on nanostructured silicon. The measurements were performed using a high-vacuum stand equipped with a system for the precise positioning of an electrode (anode) along three axes with an accuracy as high as 50 nm. The procedures used for synthesis and emission measurements were described

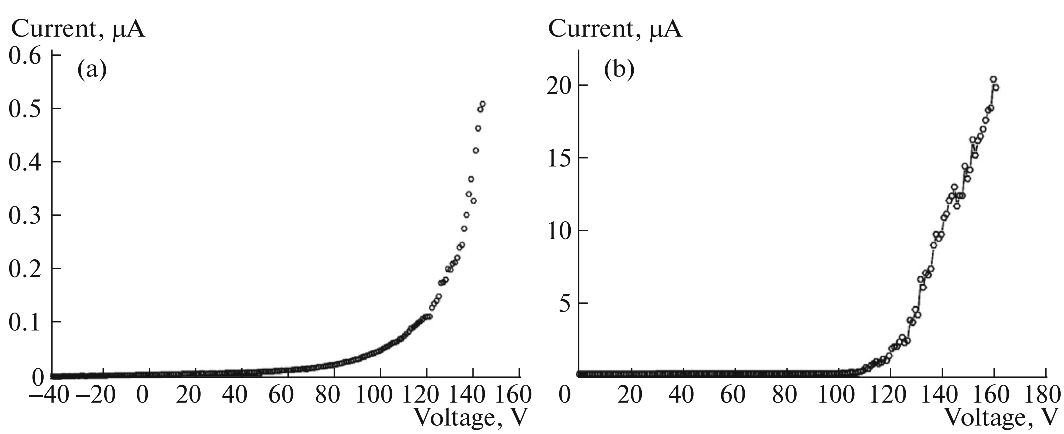

Fig. 5. *I*–*V* characteristics of samples: (a) sample with a continuous array of CNTs on a smooth silicon surface, the distance from the array surface to the electrode (anode) is 3 μm; (b) sample with an array on structured silicon, the distance to the anode is 6 μm.

in [10]. The first modification is an array synthesized on a smooth silicon surface. The current—voltage (*I*—*V*) characteristic of a sample of this kind is shown in Fig. 5a. The emission threshold occurs at 30 V/μm.

The second modification is represented by arrays grown on nanostructured silicon. The *I*—*V* characteristic of the sample is shown in Fig. 5b. In this configuration, the emission threshold begins at 20 V/μm. The emission current becomes several times higher and the emission stability is improved.

Thus, the threshold voltages substantially decrease and the emission currents increase if the silicon surface on which a CNT array is deposited is subjected to nanostructuring. This will enable the development of nanoelectronic emission devices with better operating characteristics. In further studies, we will optimize the geometric parameters of structures of this kind to obtain better electrical characteristics.

The study demonstrated that the controlled nanostructuring of silicon is possible via clustering and highly selective anisotropic dry etching and the nanostructuring technique is effective for improving the electrical characteristics of emission elements in devices of vacuum nanoelectronics.

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