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A study of the self-aligned nanometre scale palladium clusters on silicon formation process

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Abstract. The possibility of the self-aligned formation of $Pd/Pd_2Si/Si$ nanostructures on a single-crystal silicon substrate is shown. A porous anodic oxide film of Al was used as a mask which determines the size and shape of the nanostructures. A thin Al film was first deposited on the silicon substrate and then transformed in a nanoporous oxide by the well known anodic treatment procedure in a sulfuric acid and water solution. It is shown by atomic force microscopy that nanoscale Pd clusters with diameters equal to the size of pores in anodic Al remain at the surface of silicon substrate after cathode deposition of Pd into the pores, vacuum thermal annealing and chemical etching of the Al_2O_3 mask. In addition, we determine the dependencies of the size and shape of the nanoclusters on the mask formation regimes and the Pd deposition conditions.

1. Introduction

The significant interest in the research of nanostructured material properties is due to their potential application in various electronic and optoelectronic devices. However, the traditional electronic lithography method used to create structures with nanometre element sizes requires very expensive equipment and is characterized by the long duration time of the fabrication process. Recently it was shown that the porous anodic oxide films of Al may be used as a self-organizing nanochannel mask for evaporation of various materials through it [1]. The structure of anodic porous Al is described as a closed packed array of channels. The sizes of, and the distances between these channels are determined by the conditions of oxide formation [2]. It is necessary to note recent results [3], where the technique of highly ordered porous oxide creation was offered. The opportunity for ordered porous anodic Al application as a mask for deposition metals by evaporation in a vacuum was also shown [1]. Unfortunately the methods offered [1, 3] require the realization of a complex and very precise process for mask manufacture and transferral to the substrate. In our opinion, such a procedure has considerably low productivity and cannot be used in mass-formation of the nanodot array.

The major advantage of this method in comparison with molecular beam epitaxy is that it is easy to fabricate metallic quantum dots on the semiconductor substrate. However, the disadvantage is that the density of quantum dots fabricated using this method is $\sim 10^{10}$ cm^{-2} which is approximately two orders lower than using molecular beam epitaxy [4].

In this paper we present a novel variation of the use of an anodic porous Al film as a mask in the self-aligned process of nanometre cluster $Pd/Pd_2Si/Si$ fabrication. Although we have not fabricated the ordered structure, we hope that the application of the preliminary preparation Al surface on a technique described in [3] will soon allow us to create the highly ordered structures by a simpler technique than in [1], where the complex process of fabricating the free-standing anodic porous Al film and transferring it to a substrate is required. In this paper we discuss the technique of the nanochannel-array formation directly onto a substrate, into which the deposition of metal is performed.

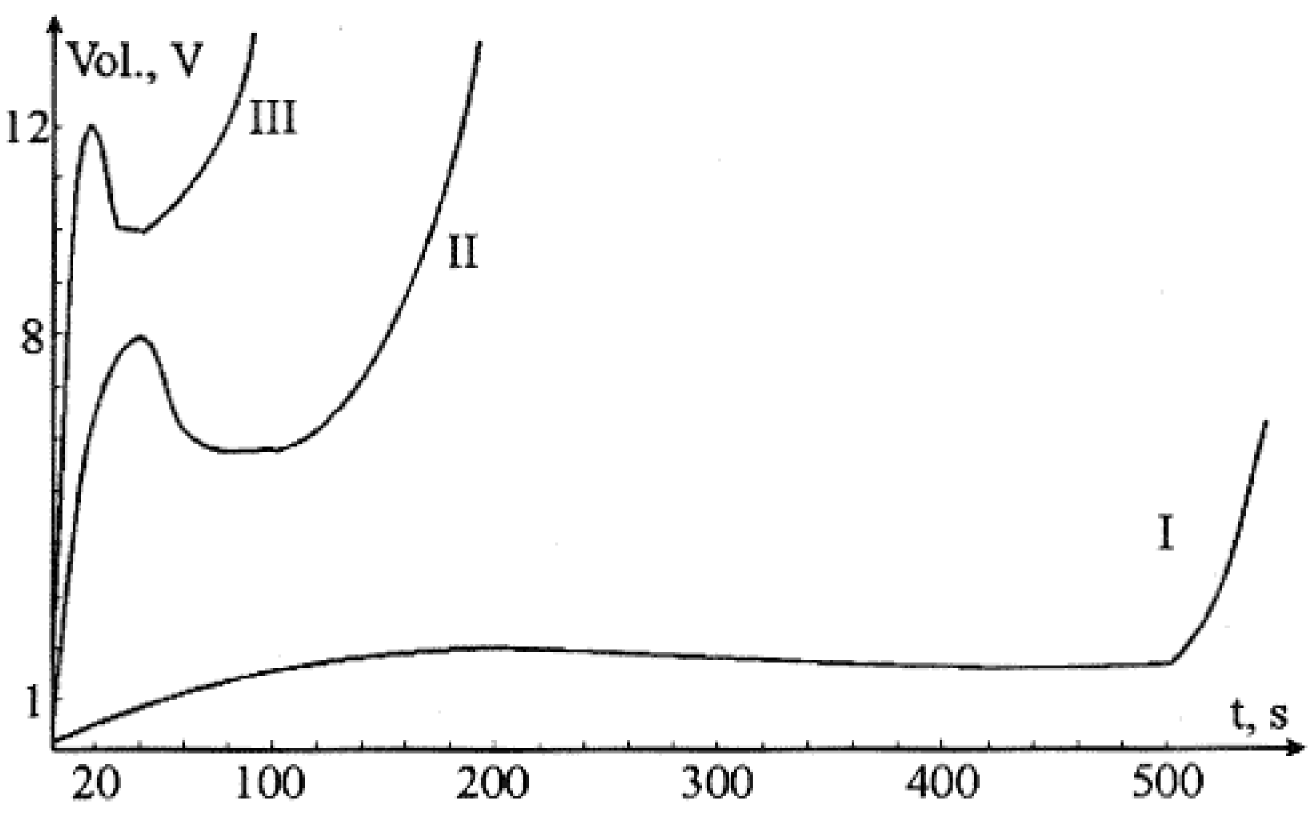

Figure 1. The time dependence of the oxidation voltage at various current densities: I—1 mA cm^{-2}, II—5 mA cm^{-2}, III—10 mA cm^{-2}.

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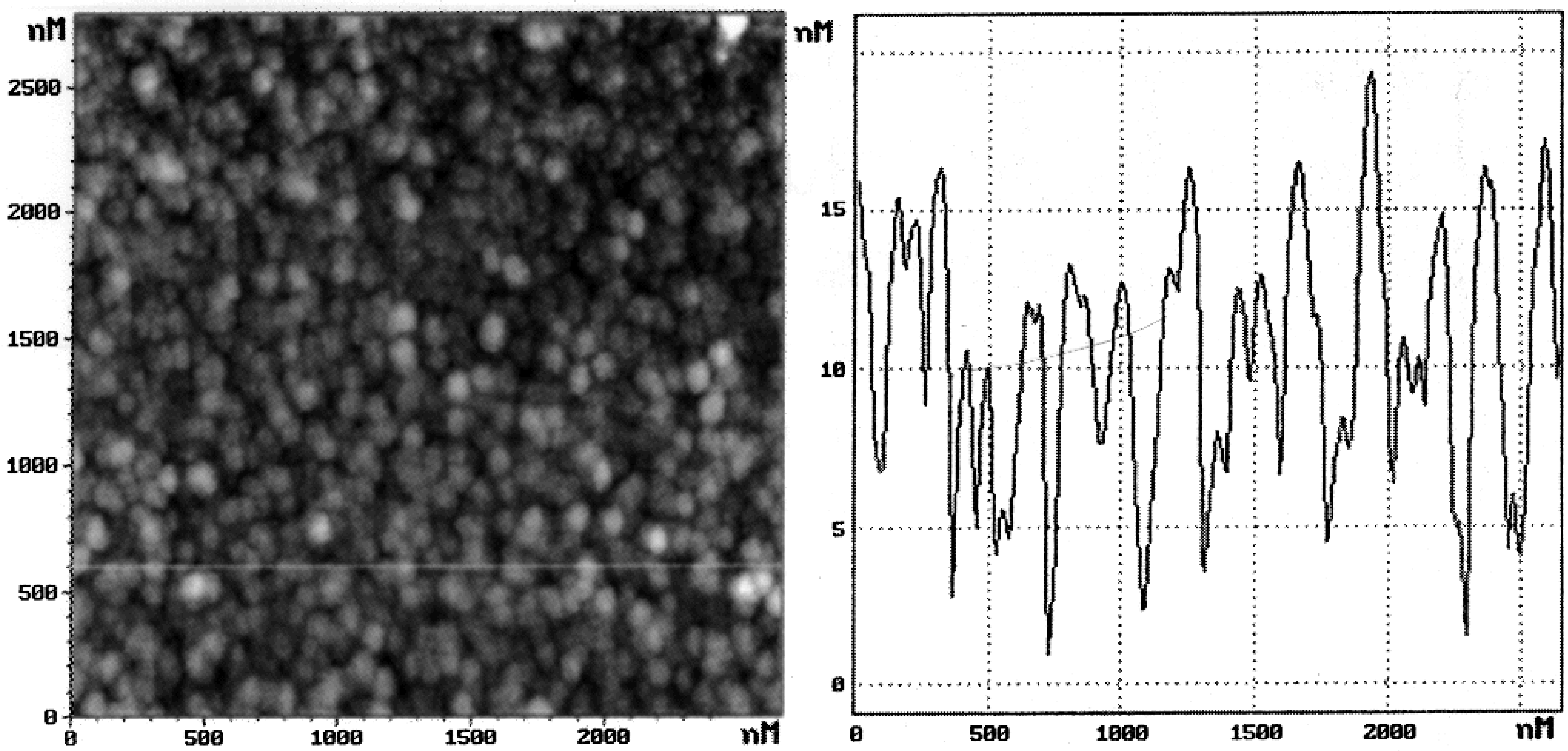

Figure 2. The AFM image of the common anodic porous alumina film surface in the left frame and the topography profile in the right frame.

2. Experiment

The anodic oxidation of the Al was carried out in a traditional way in a 10% (by volume) water solution of sulfuric acid at various current densities. Al was first deposited on a n-type silicon substrate with resistivity 4.5 Ω cm^{-1} and the surface orientation (100). The targets were fabricated from 99.999% Al. A deposition of Al was realized by a method of arc deposition [5, 6]. The Al film formed by this method has an amorphous structure. The thickness of the deposited film was 0.1 μm. Then the substrate was divided on samples of size 1 × 1 cm^2. The sample surface uncovered by Al was protected by a chemical proof insulating mask. Electrical contact to a processable surface of Al was carried out in an area, which was not further immersed in the electrolyte during anodization. After porous oxide formation the sample was placed in a 0.1 g l^{-1} water solution of $PdCl_2$. The Pd deposition was activated by cathodic bias of the sample. To form a reliable mechanical contact of Pd with the substrate the sample was thermally annealed in vacuum at a temperature of 350 °C for 10 min. According to [7], such a process results in the diffusion of the metal into the silicon and the formation of Pd_2Si at the metal/silicon interface. To remove the anodic oxide mask the samples were immersed in a 200 g l^{-1} water solution of CrO_3. Wet etching for a period of 5 min at 60 °C resulted in a selective dissolution of the oxide film.

Finally, the samples fabricated as above-described were examined by the commercial probe microscope P-47 SPM (NT-MDT, Russia, Zelenograd). The samples were investigated by silicon cantilevers with a force constant of 48 N m^{-1} on air.

3. Results and discussion

The experimental dependencies of a voltage drop between the cathode and anode as a function of anodization time are shown in figure 1. Three presented curves show results obtained under the anodization current densities of 1, 5 and 10 mA cm^{-2}, respectively. All of the curves consist of two parts: the initial part is a typical kinetic dependence for Al electrode under anode bias in the sulfuric acid and water solution and the final part of the curves where the increase of voltage drop is due to the complete transformation of Al into its oxide [8]. So, as one can see from figure 1 the anodization voltages were 2, 6 and 10 V. And the anodic current flow only occurs through the n-type semiconductor substrate. When the voltage reached the value of a factor of two higher than the maximum of the first stage of the process, the anodization was stopped.

A typical atomic force microscopy (AFM) image of the processed samples (surface image and topography profile through the white line on the surface image) is shown in figure 2.

It is well known that the porous anodic oxide of Al consists of a thin oxide film at the bottom of the pores (barrier film) and the oxide pore walls (porous film) [2]. The thickness of the barrier film is considerably less than that of the porous film. Therefore, under cathode bias from such a type of electrode, current generally flows through the pore bottom, and Pd fills the pores from the bottom to top.

The AFM images of the sample surface after cathode pore filling by Pd, vacuum annealing, and selective etching of the oxide mask are shown in figure 3. The images show the influence of the porous oxide formation conditions on the final sample surface morphology. The lower the oxide formation current density, the higher the density of the Pd cluster on the silicon surface.

Optical microscopy has shown that for complete oxidation of Al it is necessary to carry out the process up to the moment when the voltage drop on the final part of the curve presented in figure 1 exceeds the corresponding value on the initial part of the curve by a factor of two. On the basis of the data in figure 1 it is assumed that at a smaller current density it is possible to stop the oxidation process at a significantly smaller voltage value in an electrochemical circuit. The voltage increase at the second stage of anodic oxidation

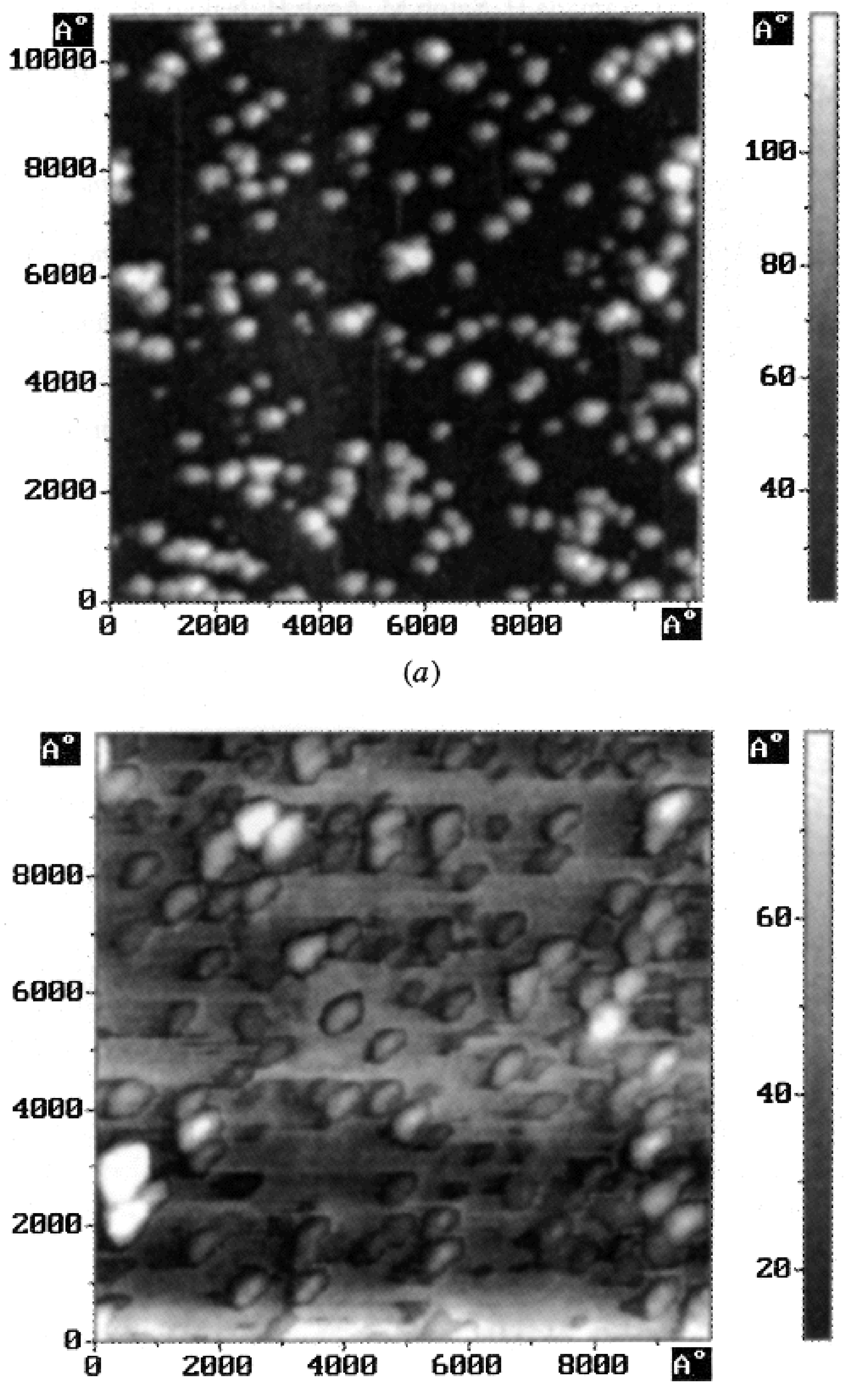

Figure 3. (*a*) The AFM image of the final sample surface morphology at 1 mA cm^{-2} oxide formation current density. (*b*) The AFM image of the final sample surface morphology at 5 mA cm^{-2} oxide formation current density.

results from the silicon anodic oxide formation. The well known Güntherschulze–Betz [8] relationship between the anodic current density which flows through the oxide and the voltage in an electrochemical circuit predicts the formation of thinner silicon anode oxide under porous Al at lower anodic current density. In contrast to metals, the thickness of the anodic oxide film on a semiconductor cannot be defined directly from the value of the final voltage because of an electric field redistribution between the oxide and semiconductor. This redistribution of electric field results in the influence of the electrical properties of the semiconductor on the final oxide thickness and causes the oxide thickness inhomogeneity. Therefore, during the consequent cathodic deposition of Pd the metal precipitates faster in areas where this dielectric layer is thinner. Moreover, if the oxide thickness has a high nonuniformity the metal does not grow at the local porous surface regions.

For each AFM image we calculated the average diameter of metal clusters determined from the base cluster diameter. The random error of average diameter determination is connected with the artifacts of the images presented in figures 3(*a*) and (*b*), which are related to the tip shape. We found the correlation between the average diameters and current densities of porous oxide formation, which is presented in figure 4(*a*). The increase of cluster diameter under an increase of porous Al formation current density is confirmed by the well known dependence of pore diameter from porous oxide formation conditions [2, 8]. Therefore, these results demonstrate an opportunity to control cluster array topology by means of a choice of self-organizing dielectric matrix parameters.

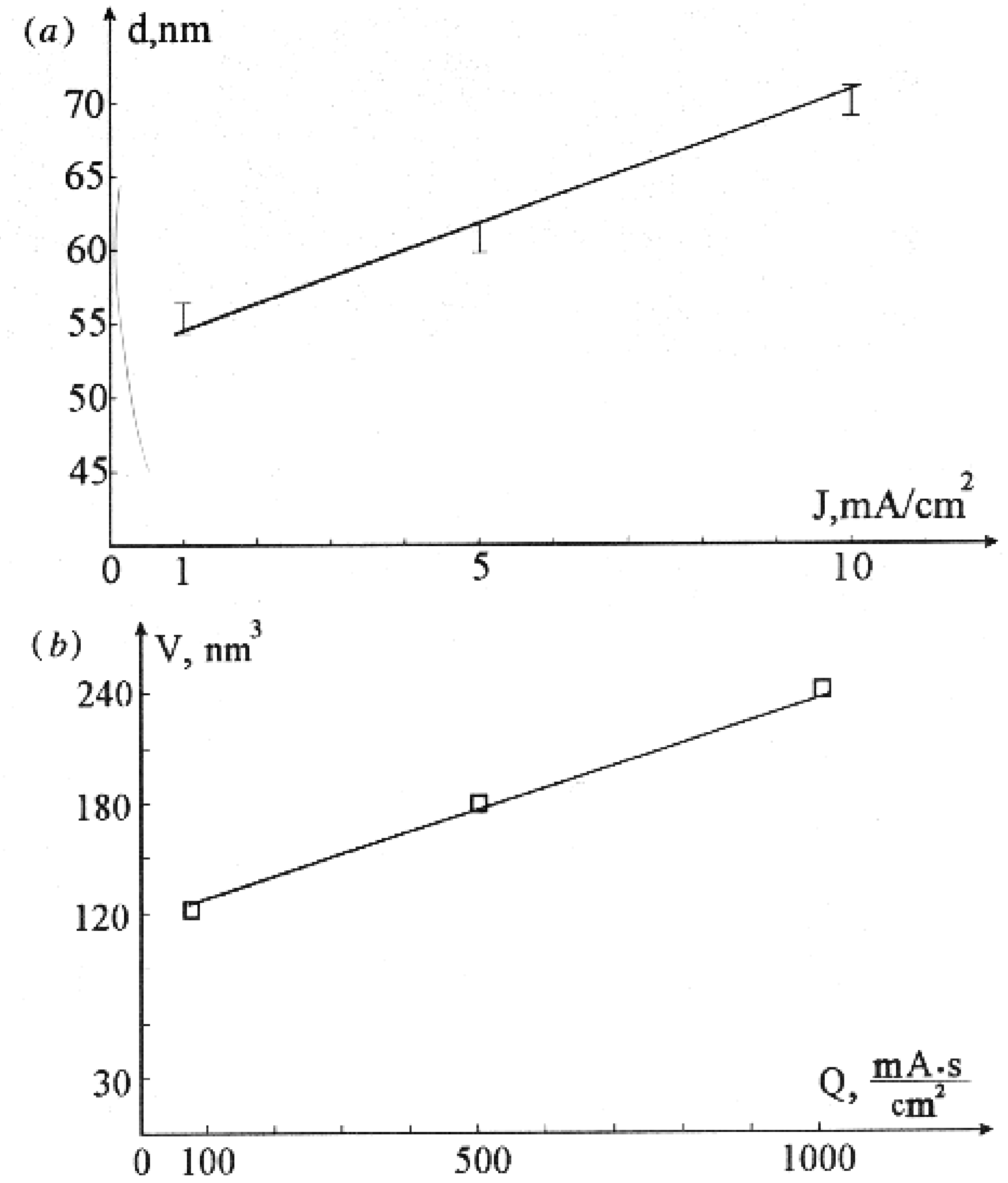

Figure 4. (*a*) The dependence of the cluster diameter on the current density. (*b*) The dependence of the cluster volume on the magnitude of electricity expended.

The dependence of the cluster volume on the quantity of electricity spent on their formation was investigated (figure 4(*b*)). The linearity of the received dependence can testify that at least the delivery of the Pd ions to a silicon surface is not complicated by diffusion processes. Otherwise, the most probable dependence $V = f(Q^{1/2})$ would be observed [9]. It is necessary to note that at a zero charge volume there is already some volume of nanometre cluster. This fact is explained by the difference between the volumes of Pd and Pd_2Si which form during thermal annealing.

The observed linear dependence of cluster volume on the charge also allows one to carry out the exact control of the nanostructure sizes. For example, at a known average diameter of pores it is possible to exactly control the cluster's height. It suggests the possibility of fabrication of structures such as quantum dots $d \gg h$, and quantum wires $d \ll h$ by the method mentioned above.

4. Conclusion

The research carried out has shown the possibility of the self-aligned fabrication of a Pd cluster system on a monocrystalline silicon surface covered with an anodic porous Al film. It is shown that the quality of obtained structures depends essentially on the conditions of the anodic porous oxide mask preparation. The degree of surface filling by clusters depends on the thickness of the Al oxide film. The possibility of exact size control was found to be determined by the linearity of the dependence of the deposited metal volume on the magnitude of electricity expended.

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