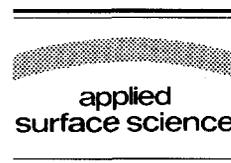




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Atomic force microscopy study on the surface structure of oxidized porous silicon

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Abstract

We study the surface structure of porous silicon (PS) using atomic force microscopy (AFM), before and after oxidation in a HNO_3 solution. The AFM image shows the PS surface with a self-affine random fractal structure of wires, hillocks and voids in various scales. After oxidization the wires and hillocks of PS structures are glazed with oxide and the voids are filled. PS structure is altered to a simple self-affine fractal structure of hillock clusters. The fractal dimension D of PS is around 2.3, which decreases with increasing oxidization to about 2.0 of a smooth surface for the saturated oxidization. Our direct observation of the fractal structure of PS from AFM data reveals a good explanation for the recently found novel nonlinear dc-response in Ag thin films deposited on PS. We find the fractal surface structure of oxidized PS responds to the stepwise avalanche electric breakdown of the resistivity of Ag thin films deposited on oxidized PS.

Since the first report [1] of the strong visible room temperature photoluminescence (PL) of porous silicon, many investigations have been devoted to realizing its optoelectronic applications. The transport properties of metal thin film contacting on PS is important from both fundamental and technological points of view. Recently the morphology structure of the PS rough surface has been studied extensively. Obviously, the surface morphology of PS has an important influence on its PL. Furthermore, the oxidation procedure can improve the PL stability and uniformity of PS [2–4]. The oxidized surface morphology of PS has also been intensively studied

[3–5]. The phenomenon of PS formation had been discussed by Smith et al. before [6–8]. They suggested a fractal structure of the PS formation. Very recently, Roy and Sood [9] simulated the PS surface morphology with the diffusion-limited aggregation scheme, and Mattai et al. [10] performed an experimental study by Raman scattering. Their results show PS exhibiting the fractal structure. Recently we have measured the dc-response of Ag thin films deposited on PS [11]. A nonlinear dc-conductivity of the Ag thin films deposited on PS was found. Furthermore, after the PS sample is oxidized in HNO_3 solution, the nonlinear dc-resistance of Ag thin films exhibits a fractal-like property depending on the PS structure. And we proposed a branched Koch curve fractal model to explain the novel electric transport phenomena [12]. According to our model, the nonlinear

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dc-response may be explained with a fractal-like network of the Ag thin film deposited on PS surface. For a detailed understanding of this fractal-like phenomena, we further study the PS surface structure with AFM, which reveals detailed, three dimensional images of PS surface topography. And the AFM data does reveal a self-affine fractal structure of PS surface, which may correspond to the novel dc-response of Ag thin films deposited on oxidized PS.

In this work the PS sample is fabricated by anodization of the p-type boron doped (100) single-crystal Si with resistivity of 5–8 Ω cm. Aluminum ohmic contacts are made on the backside of PS before electro-chemical etching. The anodization is performed by a constant current of 10 mA/cm² in the electrolyte of HF/C₂H₅OH = 1:1 solution at 30°C for 8 s to 30 min. We oxidize PS by immersing samples in HNO₃ acid with the concentration from 0.1 M to 1 M, and for 1 to 10 min. Before and after oxidation, all PS samples are monitored using a transmission Fourier transform infrared spectroscopy (FTIR) (Bomem 150 series). The morphology of PS surface, before and after oxidation, is imaged by AFM (Digital Instruments, NanoScope III) in contact mode with a commercial silicon nitride tip of radius about 30 nm. For some PS samples contaminated by particles, AFM images are taken with a tapping mode instead. With the AFM software (Digital Instruments) the surface roughness profiles are analyzed in terms of a ‘fractal dimension’ D which is referred to as fractal-based roughness [13]. D increases with the roughness of the surface. The method for determining D involves the use of a box dimension. Through the box counting the fractal dimension D is defined in terms of $N \propto b^{-D}$. In brief, this method overlays a profilometer curve with a uniform grid or a set of ‘boxes’ of side length, b , and a count is made of the nonempty boxes, N . The box size b is changed and the count is repeated. Finally, the counts are plotted against each box size on a log–log scale to obtain a boxcount plot, and the slope of the least-squares-fit line of the resulting curve gives the fractal dimension. The analyzation of surface roughness profiles using fractal theory has been illustrated an advantage in characterizing the surface complexity [13,14].

Fig. 1a and b present the AFM images of as anodized PS for 8 s and 30 min. In Fig. 1a the

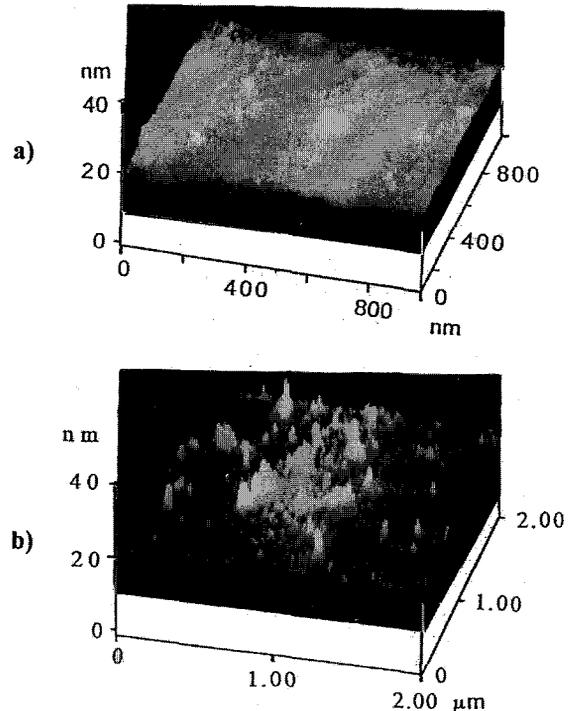


Fig. 1. Three-dimensional AFM image of the as anodized porous silicon surface structure formed on p-type (5–8 Ω , <100>) Si, $I = 10$ mA/cm² for: (a) $t = 8$ s and (b) $t = 30$ min. The PS layer thickness and roughness are not monotonically proportional to the anodization time.

shallow hillocks have just formed a cluster-like surface in this early anodization phase. As the anodization time increases, the PS surface layer becomes thicker and rougher. However, the thickness and roughness of PS are not monotonically increased with the anodization time. The wires and hillocks of the PS are continuously removed and new ones will start to form. In Fig. 1b shows the 30 min as anodized PS with a thickness of only ≈ 40 nm. This figure displays similar hillock structures in large and small scales, which manifests self-affine fractal. The morphology of as anodized PS is strongly dependent on doping, conductivity [6], and on the anodization conditions [3], such as current density, irradiation of the light, etc. The influence on the morphology is due to the electro-chemical etching reactions in which the corrosion and diffusion take place between the PS surface layer and the electrolyte. The transport processes such as surface diffusion, charge migration

in bulk, and convection, also have great impact on the texture of the PS layer. This work concerns the AFM analysis on the oxidized PS surface.

Fig. 2a and b show AFM images of 5 min anodized PS with light and saturated oxidizations, respectively. Fig. 2a displays a self-affine structure, too. This PS layer is much thicker than that of the 30 min anodized (Fig. 1b). We observe AFM photographs with different fractal structures in the PS surface which varied throughout the oxidization procedure. In Fig. 2b the AFM image shows the PS forming big oxide clusters after saturated oxidation. The structures of oxidized PS, the wires and hillocks, are glazed with oxide and the voids also are filled. And the PS structure changes to simpler fractal hillock clusters. Its fractal dimension D is nearly ≈ 2.0 , just like a smooth surface. To demonstrate the self-affine fractal feature AFM images are taken of one PS sample, of 20 min anodized and 10 min oxidized in $1/8$ M HNO_3 , in two scales. Fig. 3a

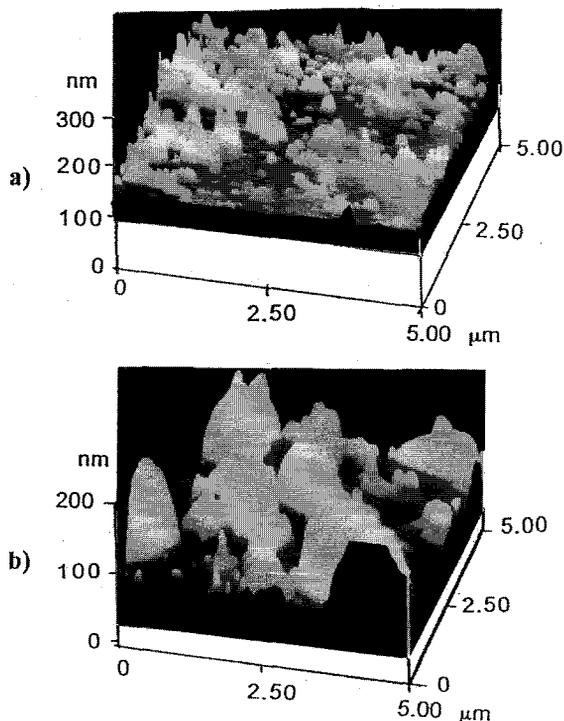


Fig. 2. AFM photograph of the 5 min anodized porous silicon and oxidized for: (a) in $1/8$ M HNO_3 for 3 min, (b) in 1 M HNO_3 for 10 min.

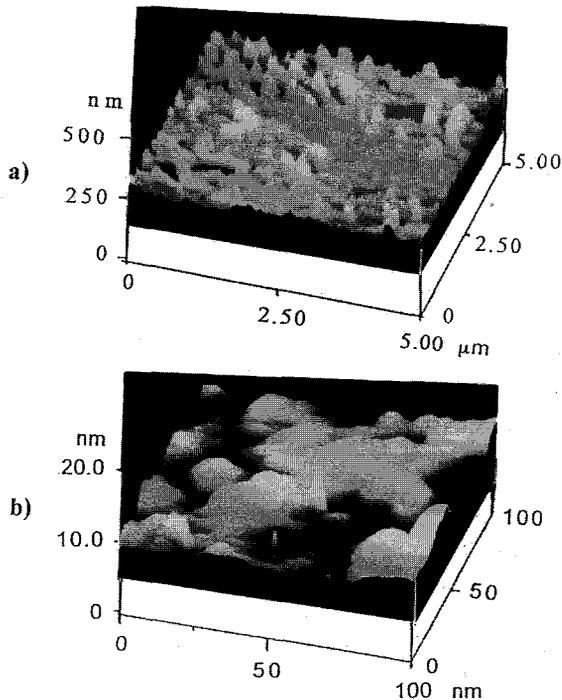


Fig. 3. (a) AFM photograph of the 20 min anodized porous silicon oxidized in $1/4$ M HNO_3 for 3 min. (b) Higher resolution AFM image of the same sample as in (a).

shows the PS structure in $5 \mu\text{m} \times 5 \mu\text{m}$ area and Fig. 3b in $0.1 \mu\text{m} \times 0.1 \mu\text{m}$ area. The smallest PS wire we can see is about 5 nm wide in Fig. 3b. They show self-affine structures and have the same fractal dimension.

All samples show fractal structures. In measuring their fractal dimension, we find they have different values. The fractal dimension D determines the relative amounts of the surface irregularities at different distance scales. The fractal dimension D is around 2.3 for the as anodized and lightly oxidized PS. The maxima of fractal dimensions occur at the medium range of the oxidization for different anodization times. The PS surface of saturated oxidation is very smooth with a fractal dimension approaching $D \approx 2.0$ (in Fig. 2b). In spite of different structures of as anodized PS surface, the PS samples, after oxidization, acquire similar fractal structures with the fractal dimensions $D \approx 2.0$ for saturately oxidized PS samples. That can be understood with the AFM images, since after oxidization the wires and hillocks of PS

structures are glazed with oxide and the voids are filled. A further study of the correlation among the PS structure feature, roughness, and anodization conditions is still in progress.

The AFM data is consistent with earlier proposed branched Koch curve structure model for dc-conductivity of the Ag thin films deposited on PS. We proposed the conductivity due to the percolation of Ag conducting particles or clusters and the tunneling effect among the clusters in Ag thin film under an influence of fractal nature of the PS surface structure. The total resistance of Ag thin film is formed by connecting the resistor in series. When PS is oxidized, the fractal structure is smoothed to forming simpler fractal clusters. Therefore, the electrical path of Ag film on PS surface can be simplified with the branched Koch curve [12].

In summary, in this AFM study on the oxidized PS structure, the AFM data reveals a fractal structure of the surface layer for as anodized and oxidized PS. After oxidation in HNO_3 , the PS surface is reduced to a simpler fractal structure. In a higher resolution AFM image we observe a self-affine fractal feature. The AFM data is consistent with our earlier proposed branched Koch curve fractal model for the dc fractal-like response of Ag thin films deposited on PS. The fractal dimension is around $D \approx 2.3$ for as anodized and lightly oxidized PS, and exhibits a maximum in medium oxidization range. And for saturately oxidized PS the fractal dimension approximates $D \approx 2.0$, which can be explained by the AFM data.

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