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The novel non-linear dc response of Ag thin films deposited on porous silicon: a fractal model explanation

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Abstract

We have observed a novel non-linear dc resistivity of Ag thin films deposited on porous silicon (PS) surfaces. We also found that as the porous silicon is oxidized in a HNO_3 solution, the dc resistivities of the Ag thin films become two orders of magnitude smaller, and behave linearly but are divided into three different regions. Each region exhibits different resistivities which drops abruptly at the thresholds. The resistivity decreases as the current increasing into a higher current region. The atomic force microscopy (AFM) image shows a self-affine structure of the PS surface with wires, hillocks and voids on various scales. After oxidation, the rough surface is smoothed down to simpler fractal hillock clusters. The silver clusters are deposited on the glazed surface in a fractal-like size distribution. A branched Koch curve fractal model is proposed in this study to model the tunneling between fractal-like silver clusters. It explains the stepwise linear fractal-like resistivity behavior.

1. Introduction

After Canham [1] reported the first strong visible photoluminescence (PL) of porous silicon (PS) at room temperature, many investigations have been devoted to put it into optoelectronic use. Since the surface morphology of porous silicon affects its photoluminescence, the morphology of the porous silicon surface has attracted extensive studies recently [2–15]. A rich variety of surface structures can be formed under different electrochemical processing conditions, such as random arrays of small interconnected pores, the reminiscence of the dendritic structures, and so forth. The phenomenon of PS formation for instance was discussed by Smith et al. [2,12], and they suggested that the PS forms a fractal structure. Furthermore, various methods have been adopted

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to characterize the surface nature, such as scanning electron microscopy (SEM) [3–5], AFM [6], transmission electron microscopy (TEM) [7,8], superconducting tunneling microscopy (STM) [9], X-ray diffraction (XRD) [10,11] and cross-section transmission electron microscopy (XTEM) [12]. Some studies corroborate the fractal nature of the porous silicon. Further experimental evidence has been provided by Raman spectra recently [13]. The PS surface morphology has also been simulated with the diffusion-limited aggregation scheme by some authors [14,15]. They have also discussed about the fractal structure of PS forming.

The transport properties of metallic thin films contacting to the rough surface of porous silicon is both fundamentally and technologically important in application. Yet the resistivity of metallic thin films deposited on rough substrates are less studied due to the lower reproducibility of the characteristics of samples. Recently we have measured the dc response of silver thin films deposited on porous silicon surfaces [14]. A novel non-linear dc resistivity is observed. While the PS sample is oxidized in a HNO_3 solution before depositing the Ag thin film, the behavior of the dc resistivity becomes linear, yet its resistivity drops stepwise in three current regions. This fascinating transport behavior may be produced from the fractal nature of the underlying porous silicon structures. To investigate these phenomena in detail, we study the PS surface directly with AFM. Our AFM measurement data are able to demonstrate the fractal structure of PS, and reveal the mechanism of the novel dc response in Ag thin films.

The origin of the non-linear dc conductivity of the metal/PS contact is similar to a general percolation problem. Gefen et al. [16] measured I–V characteristics of a two-dimensional system of thin gold films near a metal-insulator transition. Their I–V curves are initially linear and become non-linear with increasing bias. Ohtsuki and Keyes [17], on the other hand, studied the I–V characteristics of the binary mixture of a normal conductor and superconductor above the percolation threshold. Chakrabarty et al. [18] in turn, studied a carbon-wax mixture slightly above the percolation threshold. They also found non-linear I–V characteristics. The dynamic random-resistor network and the non-linear random-resistor network models are proposed to explain the non-linear phenomena. In the present study, we construct different kinds of random networks of conductor–semiconductor mixture on the PS surface. The high resistant semiconductor blocks will form another conducting mode as a tunneling channel is built due to charge accumulation. A fractal-like network of the Ag thin film on the anodized PS surface may explain the non-linear dc response. A branched Koch curve fractal model is proposed to model the tunneling between fractal-like silver clusters to explain the stepwise linear fractal-like resistivity behavior.

2. Experiment

In this work, the PS sample is fabricated by anodizing the p-type boron-doped (100) single-crystal Si with resistivity of $10\,\Omega\cdot$cm. Aluminum ohmic contacts are made on the backside of the wafer before electrochemical etching. The anodization is performed

by a constant current of 10 mA/cm^2 in the electrolyte of HF/C_2H_5OH= 1 : 1 solution at 30°C for 1 to 30 minutes. The structure of the PS surface is changed through the oxidation treatment by immersing the sample in HNO_3 acid for 10 minutes. Before and after oxidation, the PS samples are examined by FTIR (Fourier transformation infra-red), XRD and PL to characterize their quality. The chemical properties of the PS surface can be monitored by FTIR. The surface coverage of the PS layer is fully oxidized, and does not contain the main peaks of SiH, SiH_2, SiH_3 stretching modes between 2000 and 2300 cm^{-1}. About 200 Å thick silver thin films are deposited on the PS by the dc magnetron sputtering method. The thickness of the Ag film is calibrated by a long-time deposition experiment. The XRD analysis shows a silicon-like peak for both anodized and oxidized PS. XRD cannot find a heterogeneous Ag track due to PS pores. Since the deposited film is only about 200Å on PS, the Ag thin film morphology is therefore almost the same as that of the PS surface. The morphology of the PS surface, before and after oxidation, and the deposited Ag thin films, are then characterized by AFM (Digital Instruments, NanoScope III).

The I–V measurement is performed with a standard four-point probe method on the line pattern of the Ag thin films, 0.35 mm wide and 10 mm long. The data are measured point by point with computer controlling. The current source (Kethley 220) supplies a fast rising current by increasing voltage until the current reaches the preset value. During the measurement, the voltage is monitored (as a constant value) for some hundreds of ms, then the current source is switched off for 1–2 seconds, allowing the sample to cool down for the next measurement. In this way we can avoid temperature effects. Hence all samples have similar I–V curves.

3. Results and discussion

In the present work the porous silicon surfaces have been examined by the AFM directly. Typical surface patterns of anodized PS for 5 and 30 minutes are shown in Figs. 1 and 2, respectively. Our AFM data show that the surface morphology of the PS depends on the time duration of anodization. The geometrical features of the AFM images show self-affine surface structures with wires, hillocks and voids on various scales. While the anodized PS sample is oxidized in a HNO_3 solution, the wires and hillocks on the surface are glazed with oxide and the voids are filled, the PS structure changes to simpler

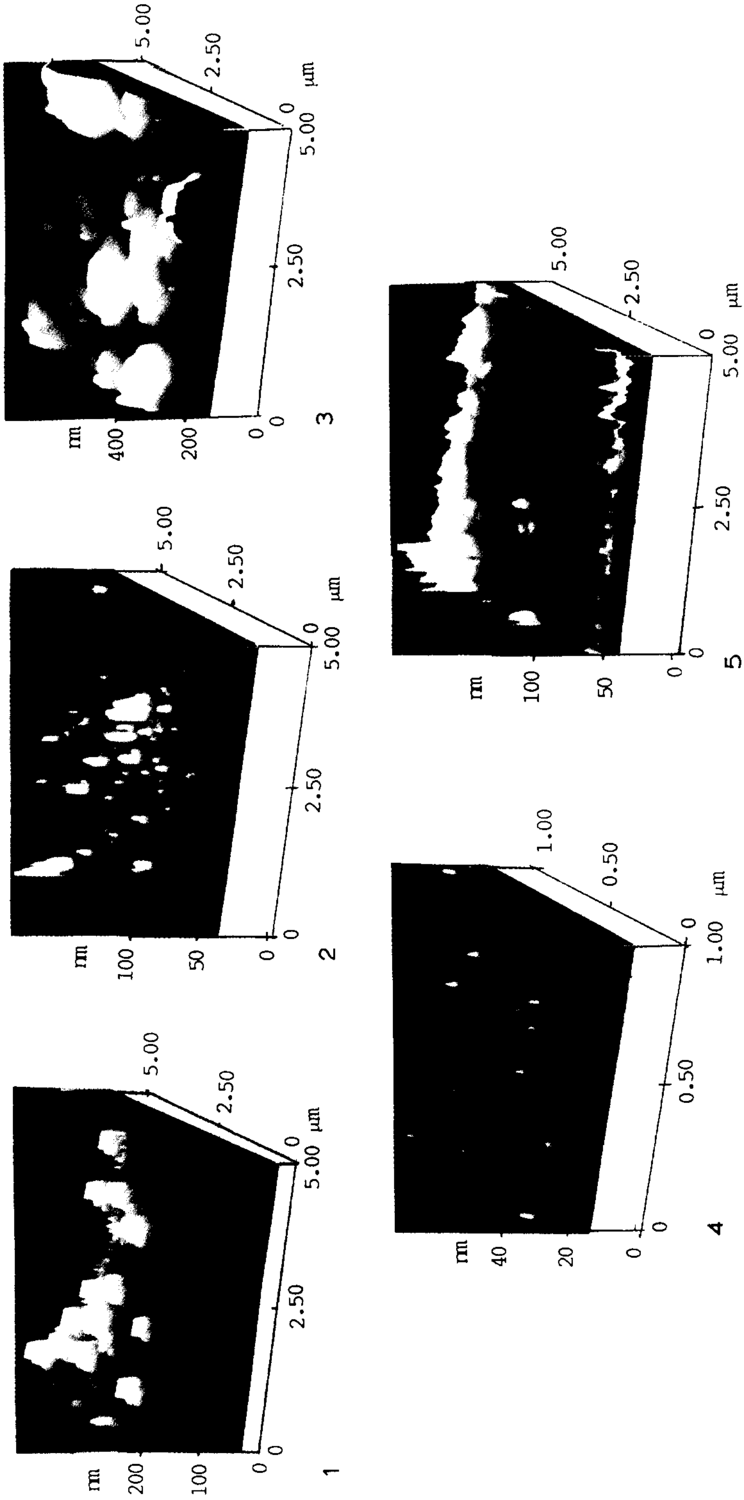
Fig. 1. AFM photograph of the porous silicon anodized for 5 minutes.

Fig. 2. AFM photograph of the porous silicon anodized for 30 minutes.

Fig. 3. AFM photograph of the porous silicon anodized for 10 minutes and oxidized in HNO_3 for 5 minutes.

Fig. 4. AFM photograph of the porous silicon with Ag coating thin film, the PS is anodized for 10 minutes.

Fig. 5. AFM photograph of the porous silicon with Ag coating thin film, the PS is anodized for 10 minutes and oxidized in HNO_3 solution for another 10 minutes.



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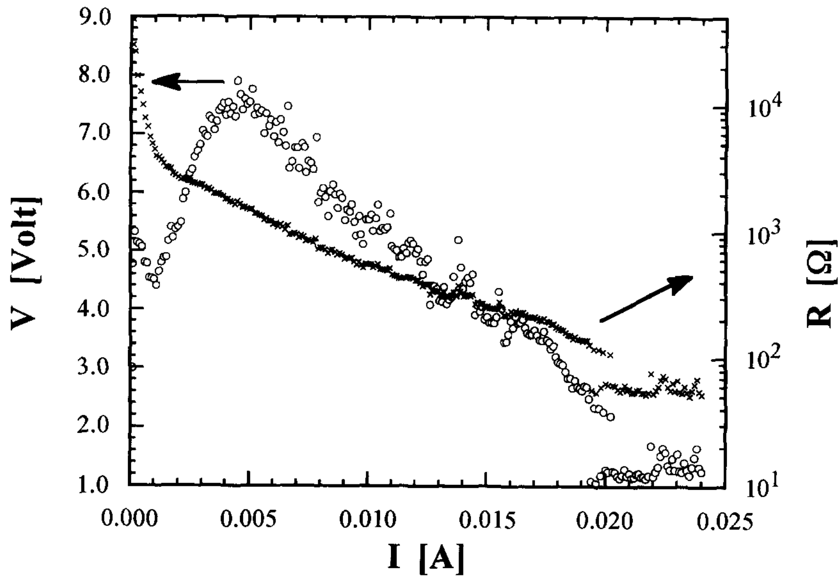

Fig. 6. The dc I–V curve of the Ag thin film on anodized PS for 10 minutes. The dc resistivities of the Ag thin film show the non-linear behavior.

fractal hillock clusters. Fig. 3 shows a typical surface pattern of the anodized PS sample of Fig. 1 after 10 minutes oxidation in a HNO_3 solution. Compared to the anodized PS, the surface of PS after oxidation in HNO_3 becomes less rough. It is noted that the typical fractal nature remains after the oxidation treatment in our research, even the PS surface morphology becomes smoother. Some studies report that oxidation treatment leads to the stabilization and enhancement of the PS photoluminescence [19,20]. Our oxidized PS samples also demonstrate enhanced PL intensity [21]. Figs. 4 and 5 show the porous silicon surfaces with silver coating thin films. The substrate PS samples of Fig. 4 are anodized for 10 minutes, while that of Fig. 5 is oxidized in a HNO_3 solution for another 10 minutes. The AFM photographs demonstrate that the deposited thin Ag films on both PS substrates also remain fractal-like.

Fig. 6 shows the non-linear behavior for the dc I–V curve of the Ag thin film on anodized PS of Fig. 1. Fig. 7 shows the dc I–V curve for the oxidized sample of Fig. 3. The dc resistivities of the Ag thin film become two orders of magnitude smaller, and behave linearly but are divided into three different regions. The resistivity drops abruptly at the threshold, and decreases from one constant value to a smaller constant value as the current increases into a higher current region. Each region exhibits different resistivities. The I–V results are reproducible for different samples.

Gefen et al. [16] measured the I–V characteristics of a two-dimensional system of thin gold films near a metal-insulator transition. Their I–V curves are initially linear and become non-linear with increasing bias. Ohtsuki and Keyes [17] studied the I–V characteristics of the binary mixture of a normal conductor and superconductor above the percolation threshold. Chakrabarty et al. [18] studied a carbon-wax mixture slightly

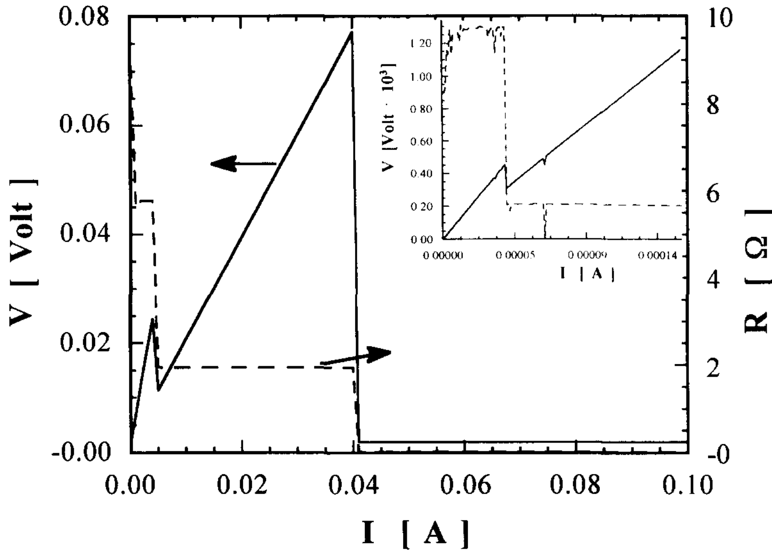

Fig. 7. The dc $I-V$ curve for the oxidized sample of Fig. 3. The dc resistivities of the Ag thin film behave linearly but are divided into three different regions. The insert shows the behavior in a small current region.

above the percolation threshold, and found that the $I-V$ characteristics of a carbon-wax mixture are non-linear. For low-resistance samples, the $I-V$ curves are smooth with a quadratic term besides the linear one. They also found a stepwise resistance for high-resistance samples. The dynamic random-resistor network and the non-linear random-resistor network models are proposed in this work to explain the non-linear phenomena.

To discuss the results of the dc response in our investigation, we should first consider the material picture. Here the AFM data ascertain the fractal nature of PS with and without thin silver deposit. Instead of considering the PS surface self-affine wires and hillocks, we propose that the voids consist of various hierarchies of pores. The silver will permeate into the pores, and the PS surface forms a heterogeneous structure of randomly distributed silver clusters. The conducting silver thin film is blocked by crystalline silicon filaments and also by the glanuar boundary. The high resistant semiconductor silicon blocks and the glanuar boundary could form another conducting mode as a tunneling channel is built due to charge accumulation with increasing current. The $I-V$ diagram of a thin Ag film on anodized PS, as shown in Fig. 6, demonstrates that the voltage first increases with increasing current, then gradually decreases in the high-current region. It exhibits a non-linear behavior. Considering the fact that metallic silver forms random fractal-like clusters on the anodized PS surface, it makes the silver thin film a random network. The Ag thin film is seriously blocked in the low-current region, and is similar to the percolation situation with high resistance. After passing the threshold, the charge accumulation begins to relax with the occurrence of the tunneling modes, and the voltage will gradually decreases due to the electrical short circuit. Hence the random fractal-like network of the Ag thin film on the anodized PS surface may explain the non-linear dc

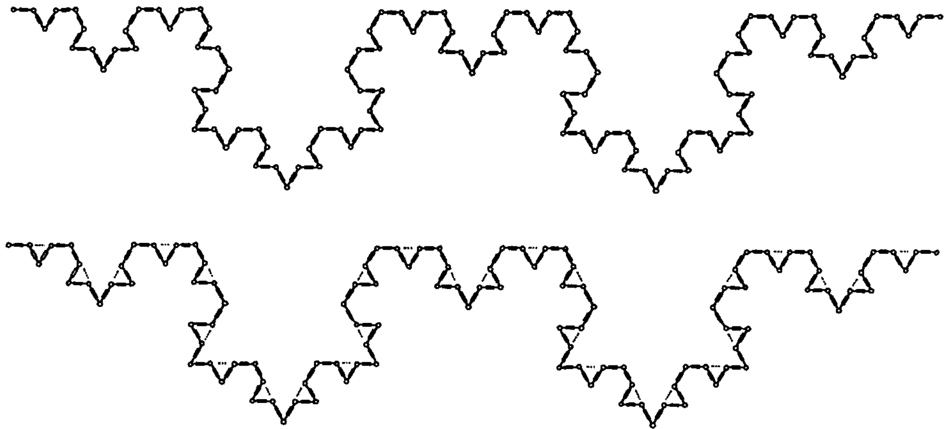

Fig. 8. A deterministic branched Koch curve fractal model to describe the tunneling effect between fractal-like silver clusters. The electrical path is represented by a Koch curve. The small circles at every junction represent the accumulating charge. The tunneling effect between fractal-like silver clusters is represented by the branched Koch curve with the dotted lines.

response.

However, while PS is oxidized in a HNO_3 solution, its surface smooths into a simpler fractal structure as shown in Fig. 3. The deposited thin silver may nucleate on the glazed surface on similar scales. Because the smooth surface has few pores, the deposited silver may span to form a better conducting film. The resistivity as shown in Fig. 7 is about two orders of magnitude smaller than that in Fig. 6. We simplify the electrical path of the Ag film on the PS surface by a Koch curve with a small circle at every junction to represent the accumulating charge at the glanuar boundary of the Ag thin film or at the silicon blocks. As shown in Fig. 8, a deterministic branched Koch curve fractal model is proposed to describe the tunneling effect between fractal-like silver clusters. With increasing accumulating charge, an avalanche electric breakdown occurs between the silver clusters of the same hierarchy. This phenomenon is represented by the branched Koch curve with the dotted lines. It leads to a drop of voltage. There are three stages of resistivities due to different hierarchies of fractal structures exhibited in Fig. 7. The branched Koch curve model could explain the stepwise linear fractal-like resistivity behavior. Hence the fractal evidence might provide an explanation for the mechanism of the novel dc response in Ag thin films deposited on anodized PS with and without oxidation.

4. Conclusion

We present an AFM study on the structure of the PS surface, and propose a fractal model to explain the novel dc response of the Ag thin film deposited on such a rough surface. The geometrical fractal features of the PS surface is related to the experimental data of the dc response of the Ag thin film deposited on PS. The random fractal-like

network of the Ag thin film on the anodized PS surface could explain the novel non-linear dc response. The origin of the non-linear dc resistivity of the metal/PS contact is similar to a general percolation problem. While the substrate PS has been oxidized before the Ag deposition, the resistivity becomes linear, and drops stepwise on a fractal-like scale. These results can be produced with the smeared fractal nature demonstrated by the AFM data. The proposed branched Koch curve model could explain the stepwise linear resistivity behavior. Fractal evidence might provide an explanation for the mechanism of the observed novel dc response of Ag thin films of PS. Further detailed investigations of the novel properties of Ag thin films on porous silicon are in progress.

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