J Mater Sci (2006) 41:5283–5286
DOI 10.1007/s10853-006-0267-5

Al-assisted anodic etched porous silicon

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Received: 7 April 2005 / Accepted: 7 October 2005 / Published online: 6 June 2006

Abstracts The photoluminescence (PL) properties and the surface morphologies of the porous silicon (PS) prepared from the wafers whose front sides were coated with or without Al film were studied. Furthermore, the Fourier Transforms Infrared (FTIR) and the Raman spectra were carried out. By introducing the Al film onto the front side of the wafer before the anodic etching, the surface morphology of the PS was quite different from that of conventional PS, which can be explained by the formation mechanism of the PS. The different PL properties of the PS may be attributed to the discrepancy in the structural configuration of the samples.

Introduction

Since the visible photoluminescence (PL) of electrochemically etched porous silicon was reported by Canham in 1990 [1], the porous silicon (PS) has been extensively studied in the last decade due to possible application in silicon-based opto-electronics, in chemical and biochemical sensing, as compliant substrates in expitaxial growth and for direct introduction of high mass biomacromolecules in mass spectrometry [2].

Two methods have mainly been applied for the preparation of PS: electrochemical and chemical (stain) etching. In stain etching, PS can be produced without any external electrochemical bias. However, there is an incubation time for the stain etching. But in some previous papers, the rapid stain etching method by the absence of an incubation time were reported, e.g., crystalline silicon was etched in mixed solution (HF/HNO_3 or HF/H_2O_2) in the presence of a metal film, such as Al, Au, Pt and Au/Pt [2–5]. The surface morphology and the emission property of porous silicon, which was prepared from the metal film coated single crystal, showed obvious difference from that of the porous silicon without coating. In anodic etching, metal films and metal ions were used to change the emission property of porous silicon. Chen et al. [6] used an ion coater to plate gold on the surface of silicon substrate before etching in order to fabricate stable Au–Si bonds on the PS surface to substitute for the easily broken Si–H and Si–O complexes. Kim et al. [7, 8] reported a simple method that Zn or Fe powders were dissolved in the electrolyte solution to prepare the full-color emitted porous silicon. Suh et al. [9] observed the blue PL from in situ Cu-doped porous silicon formed by electrochemical etching, which was aided by cuprous chloride. Copper is known to promote chemisorption of carbon dioxide at room temperature with the aid of absorbed oxygen to give a surface carbonate, and the blue PL of porous silicon was detected from carbonyl compound. In a recent paper, Biswajit Das et al. [10] carried out an experiment in which porous silicon could be fabricated through the nano scale pores of an anodized aluminum template formed on a silicon substrate. The aluminum template acted as a protective coating on the porous silicon surface, increasing its mechanical integrity.

In this paper, we compared the PL property and the surface morphology of porous silicon prepared from N-type single silicon wafers with and without metal coating. By introducing the Al film on the surface of silicon wafer before etching, the morphology of porous silicon

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exhibits obvious discrimination compared with that of the conventional porous silicon and the emission property of two-type porous silicon also shows the clear difference.

Experimental

The porous silicon samples were prepared with 1–10 Ω cm N-type (100) chemical polished Si wafers by electrochemical etching in a solution of HF–ethanol = 1:2 at a constant density of 10 mA/cm^2. Aluminum was sputtered onto the backside of the wafers for ohmic contact. The front side of some wafers was also coated by Al film before the anodic etching. The etching time was 10 min. After etching, the sample was cleaned by deionized water and dried in air. Uniform emission of porous silicon could be observed by naked eye under the illumination of UV light.

The samples were characterized by the PL spectroscopy, Fourier Transform Infrared (FTIR) measurement, Raman spectroscopy and the SEM observation. The PL spectra excited by a 360 nm wavelength were measured using a HITACHI F-4500 fluorescence spectrophotometer. The infrared absorption spectra were taken using a Bruker IFS 66 v/S FTIR spectroscope. The Raman spectra excited with 532 nm line were measured using a Nicolet Almege Raman Spectrometer. The morphology observations were carried out using a FEI SIRION FESEM. All the measurements were carried out at room temperature.

Results and discussions

Figure 1 shows the PL spectra of the porous silicon, which were prepared from the wafers with or without Al film coating. The electrochemical etching time was 10 min. It can be seen that the PL spectrum of the porous silicon prepared from the Al coated single crystal silicon exhibits two peaks, which are centered at 470 nm (blue emission) and 570 nm (green emission), respectively. The PL spectrum of the conventional porous silicon shows only one peak at 470 nm. The intensity of the blue emission from two-type samples is almost same.

Up to now, the emission mechanism of PS is still not clear. Several theories have been proposed to explain the origin of the PS luminescence. The popular one is that the luminescence results from the radiative recombination of quantum confined electrons and holes in columnar structures or undulating wires associated with the creation of pores and silicon nanoparticles. But, it was found in our experiments that the Raman spectra of the PS samples were almost the same as that of crystalline silicon, in which one peak was at around 515 cm^{-1}, as shown in Fig. 2. It illuminates that the quantum-confined effect was absent in our experiments [11]. The other important theory is that the PS luminescence results from surface confined molecular emitters, including complexes of silicon, oxygen and hydrogen [12], which is consistent with the experiments of this paper. Figure 3 shows the FTIR spectra of the samples subjected to anodic etching for 10 min. It can be seen that the intensity of the peak corresponding to the Si–O–Si bridge bonds at 1100 cm^{-1} is different each other, which may lead to the distinct PL spectra of two type samples. The other peaks at around 613, 1650, 2350 cm^{-1} are from the Si–Si bonds, the carbonyl group (C=O) and the Si–H stretching in O_3Si–H [13], respectively. It is supposed that the origin of the carbon could be related to the absorption from the ambient air. The FTIR spectra also illuminated that the Al film introducing into the anodic etched process can improve the degree of the oxidation on the surface of PS to change the emission property.

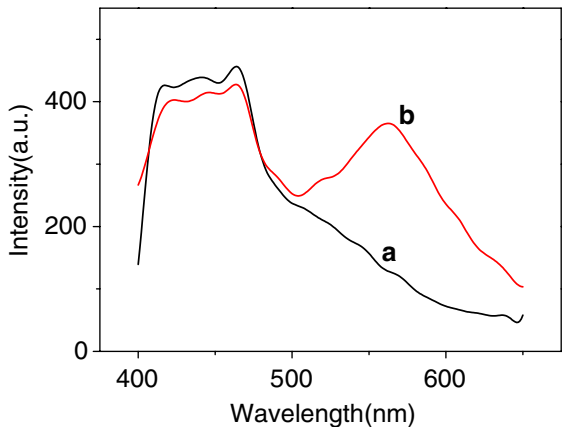

Fig. 1 PL spectra of the porous silicon prepared from the wafers without (**a**) and with (**b**) Al film coating. The electrochemical etching time was 10 min

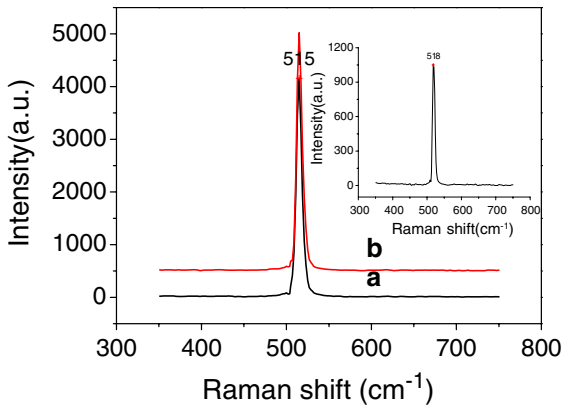

Fig. 2 Raman spectra of the porous silicon prepared from the wafers without (**a**) and with (**b**) Al film coating. The electrochemical etching time was 10 min. The inset is a Raman spectrum of single crystal silicon wafer

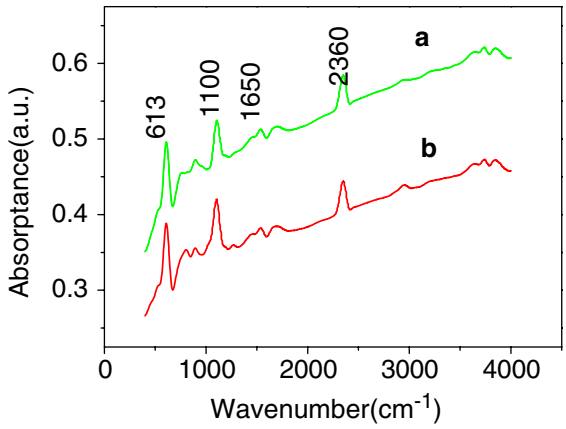

Fig. 3 FTIR spectra of the porous silicon prepared from the wafers without (**a**) and with (**b**) Al film coating. The electrochemical etching time was 10 min

In addition, by introducing the Al film on the front side of the wafers before the anodic etching, the surface morphology of porous silicon is quite different with that of conventional porous silicon, so the different PL properties of the porous silicon may also be attributed to difference in the structural configuration of the samples [14]. Figure 4 shows the SEM images of the porous silicon prepared from the wafers with and without Al film coating, which were subjected to anodic etching for 10 min. The cross-sectional analysis of the surface shows the columnar structure on the porous silicon. The surface of the porous silicon is very flat with interconnected pores. The uniform distributed and high-density pores were observed on the surface of porous silicon when introducing the Al film on the surface of wafer before etching, as shown in Fig. 4(b). On the surface of the conventional porous silicon, the pores only appear on the location of surface defects so the density of pores is low and the distribution of the pores is irregular, as shown in Fig. 4(a). The etched rate on the surface of Al film coated wafer is higher than that on the surface of the conventional wafers because the diameter of the pores of the former is larger than that of the latter, which can explain by the theory of the formation mechanism of the porous silicon. Malinovska et al. [3] suggested that Al film deposited on the Si surface could be reacted with HNO_3 to produce the required holes for the start of the chemical etching of Si. In our experimental, before the external bias was applied, the metal dissolution observation as the behavior reported in Ref. [5]. The stain etching was started, which produces the characteristic sharp tips of the structures. This assumes can be proved by the SEM images, as shown in Fig. 5. Figure 5 gives the SEM images of the chemical etched wafers without and with Al film coated about 10 s. Due to the coated the Al film, the notches are shown in the surface of the wafers after the

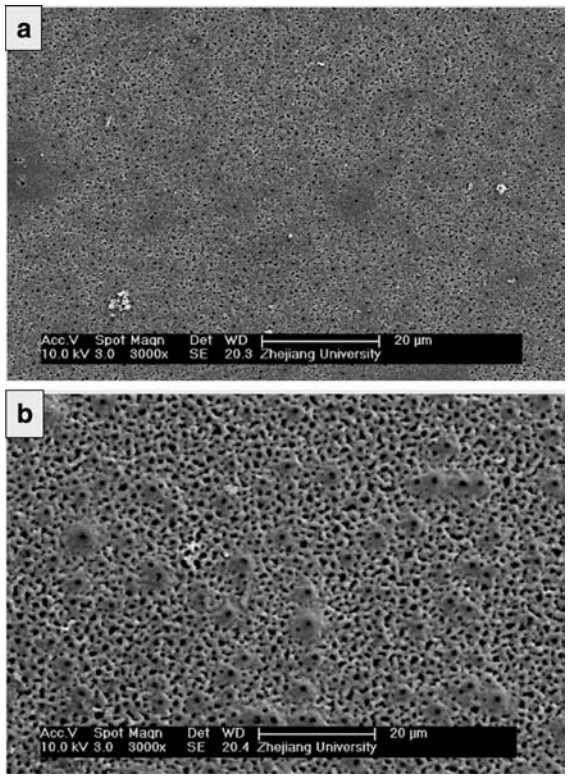

Fig. 4 SEM images of the porous silicon prepared from the wafers without (**a**) and with (**b**) coating. The electrochemical etching time was 10 min

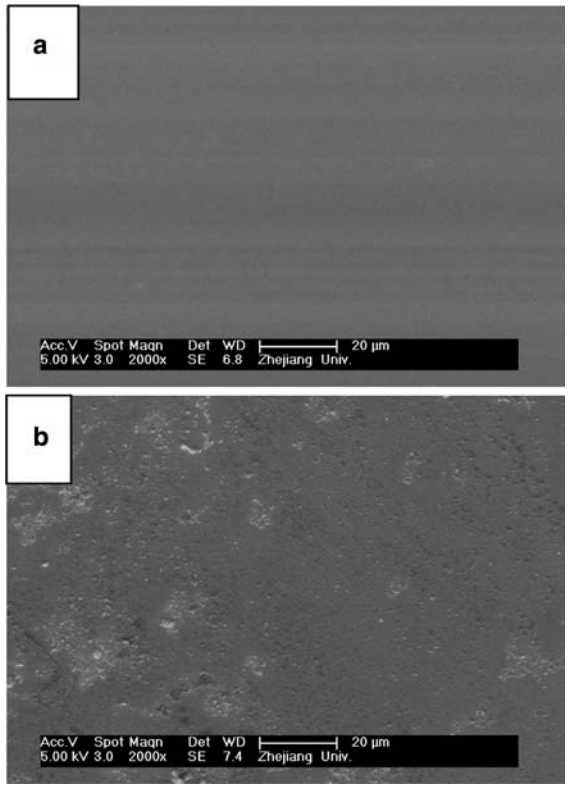

Fig. 5 SEM images of the porous silicon without (**a**) and with (**b**) Al film coating. The stain etching time was 10 s

chemical etched for 10 s. Because the uniform Al film was coated on the front side of the wafer, the nucleus of the pores are almost heterogeneously distributed on the surface. When the anodic etching was started, the pores were evolved from the sharp tips of the structures so the wafer coated by Al film can possess of the high-etched rate.

Conclusions

The present experiments have shown the PL properties and the surface morphology of porous silicon anodic etched from the wafers without and with Al film coated. Due to the Al-assisted anodic etched or not, the surface morphology of two-type porous silicon is quite different to each other, which lead to the difference of the PL properties.

Acknowledgement The authors would like to thank the Natural Science Foundation of China (No. 60225010) and the Key Project of Chinese Ministry of Education for financial supports.

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