

Improved visible photoluminescence from porous silicon with surface Si–Ag bonds

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(Received 20 October 2004; accepted 9 March 2005; published online 19 April 2005)

Porous silicon with surface Si–Ag bonds was prepared by a two-step method combining chemical etching and electrochemical anodization. The microstructure was analyzed by scanning electron microscopy, and the bond structure was evaluated by energy dispersion spectroscopy and Fourier transform infrared spectroscopy. The material prepared by this technique gives strong photoluminescence with improved photostability. The improvements in properties are attributed to the existence of the surface Si–Ag bonds, which are more stable compared to Si–H bonds usually observed in convenient porous silicon fabricated by electrochemical anodization. © 2005 American Institute of Physics. [DOI: 10.1063/1.1920426]

Since Canham reported the emission of porous silicon (PS) under laser excitation in 1990,¹ PS has attracted considerable attention due to its potential applications in photoelectronic integration.^{2–4}

PS prepared by electrochemical anodization has been reported to show unstable in time photoluminescence (PL). Such a behavior has been attributed to the unstable character of its surface in air.^{5–7} As a result of interaction with oxygen, Si–H bonds on the surface of the PS are broken and the number of silicon dangling bonds increases. The accumulation of dangling bonds finally results in degradation and instability of PL intensity.⁸

A few passivation techniques have been proposed, including high temperature oxidation,⁹ NF₃ annealing,¹⁰ passivation by carbon films,¹¹ and thermal treatment with organic molecules.¹² These techniques are based on the idea of keeping away the contaminants from the dangling bonds in the PS skeleton by not exposing the opening bonds to the surrounding gas. On the other hand, mechanical methods, such as ultrasonic treatment, were applied to slow down the aging process.¹³

In this paper, we prepare PS by using a two-step technique, combining chemical etching and electrochemical anodization of a Si wafer. The first step (chemical etching) is based on microelectrochemical redox reaction in which both anodic and cathodic processes take place simultaneously at the Si surface;^{14,15} the second step is a conventional electrochemical anodization. Through such a two-step technique, we obtain a material demonstrating an intensive visible-light emitting property with enhanced stability.

The samples were prepared from *p*-type, *B*-doped (110) oriented Si wafers with a resistivity of 10–12 Ω cm. In the first step, a sample (hereafter, referred to as sample 1) was treated in an aqueous solution of HF and AgNO₃, the concentrations of HF and AgNO₃ are 3.0 and 0.014 mol/L, respectively. The treatment temperature and the etching time are 50 °C and 60 min, respectively. Following the chemical

etching step, the specimen was put into dilute nitric acid (HNO₃:H₂O=1:9 by volume) for four days to remove its silver coating. Then, after rinsing with deionized water, it underwent electrochemical anodization under the following conditions. The solution used consisted of HF, C₂H₅OH, and H₂O with the volume ratio of 1:1.5:2; and the current density was 30 and 20 mA/cm² for the first 30 and second 30 min, respectively. For comparison, another sample (sample 2) was prepared by using only electrochemical anodization under the above conditions.

The samples were studied by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) using a Philips XL30ESEM electron microscope equipped with an Oxford ISIS300 spectrometer. PL spectra were excited by the light of a Xe-150 lamp passing through a 365-nm filter. The infrared reflection spectra were collected by a Nicolet 560 Fourier transform infrared (FTIR) spectrometer.

Figure 1(a) shows the PL spectra of samples 1 and 2 (fitted with Gaussian curves). It is obvious that the PL intensity of the two-step fabricated sample 1 is more than three times stronger than that of conventional sample 2. The PL peak maximum of sample 1 has a shorter wavelength (about 60–70 nm) than that of sample 2, which we attribute to the different microstructures of the specimen surfaces (Fig. 2). The PL intensity of sample 1 degrades considerably slower than that of sample 2 [see Fig. 1(b)], which implies that sample 1 has higher photostability.

After the etching of the silicon wafer in the solution of HF and AgNO₃, the silicon wires with a Ag cap appeared as described in Ref. 15, most of silicon wires desquamated after the electrochemical etching. Figure 2 shows the surface morphology of samples 1 and 2. It is seen that the density of the pores in sample 1 is much higher than that in sample 2, and there are some Si wires still remaining on the surface of sample 1. On the other hand, according to the PL spectra in Fig. 1(a), it can be concluded that the nanocrystals in sample 1 are smaller than those in sample 2, as the PL wavelength is determined by the quantum confinement effect.¹ Therefore, one can conclude that there are more nanocrystals in sample 1.

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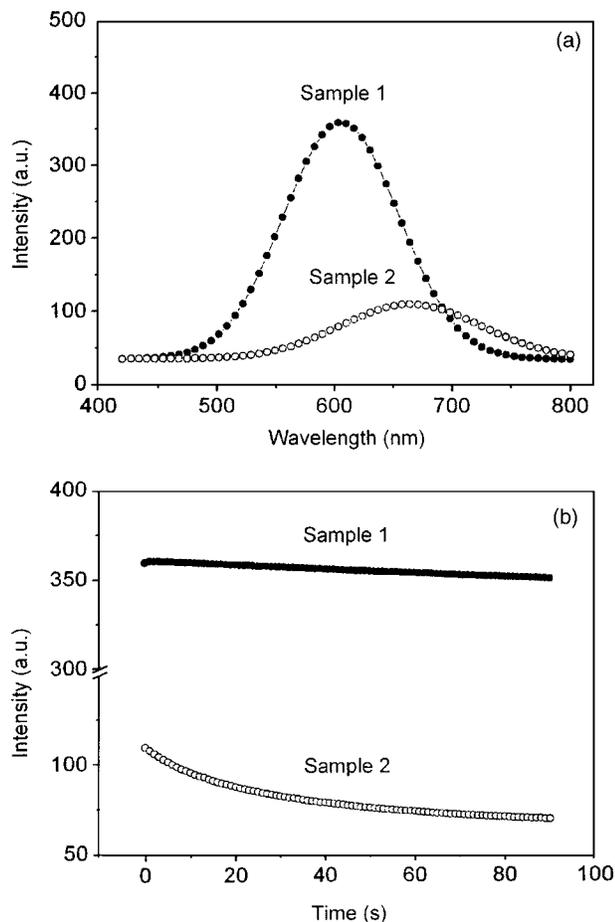


FIG. 1. (a) PL spectra of samples 1 and 2; (b) photostability of samples 1 and 2 under UV illumination.

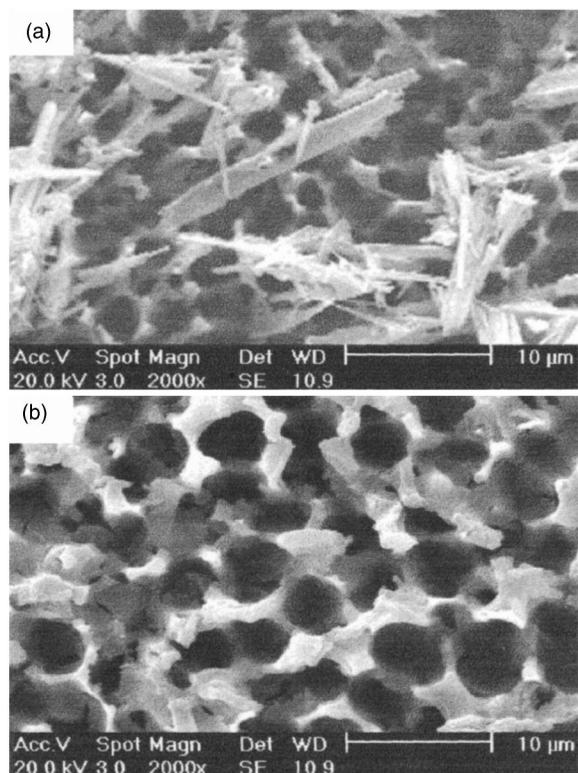


FIG. 2. Surface morphology of samples (a) 1 and (b) 2

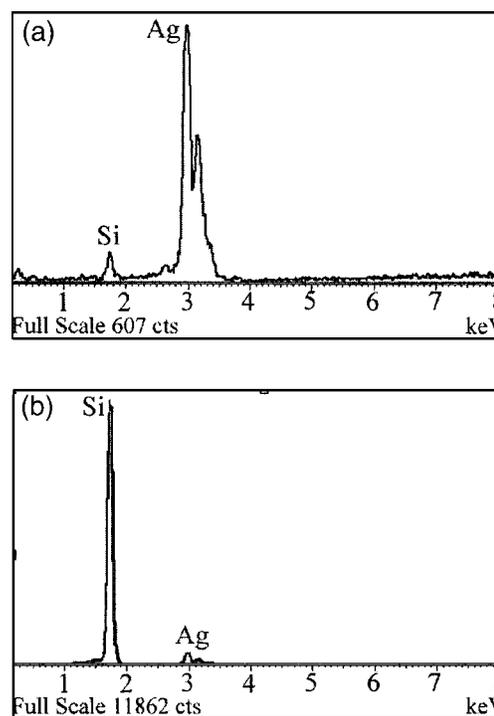


FIG. 3. EDS spectra on the surface of sample 1: (a) just after the first step (chemical etching) and (b) after the second step (electrochemical anodization).

The increase in the number of Si nanocrystals could be one of the reasons for the increase in PL intensity of sample 1; however, it could not cause the improvement in the photostability observed in Fig. 1(b). In order to find out the origin of the different intensities and, in particular, stability of the PL spectra of PS prepared by the two-step method and by electrochemical anodization, EDS and FTIR analyses of the specimens have been performed.

Figure 3 shows the EDS spectra of the surface of sample 1, which indicates the change of Ag content just after the first step (chemical etching) and after the second step (electrochemical anodization). It is seen that a large quantity of Ag deposited on the surface of the silicon wires after the chemical etching; after the electrochemical anodization, there is still a small quantity of Ag remaining in the specimen. Such traces of Ag atoms have not been detected in the EDS spectrum of sample 2, which has not undergone chemical etching

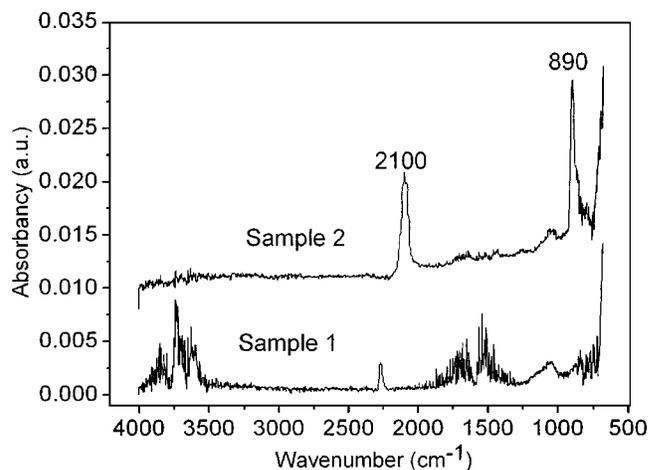


FIG. 4. FTIR spectra of samples 1 and 2.

in presence of Ag ions. The FTIR results are shown in Fig. 4, where the absorption bands at 2100 and 890 cm^{-1} in sample 2 are much stronger than those in sample 1. These absorption bands have been attributed to Si–H stretching and deformation vibration modes, respectively.^{2,16} Thus, it can be concluded that the surface–bond configurations of the PS prepared by the two-step method and by electrochemical anodization are quite different.

In the case of sample 1 with Ag atoms, the latter can readily terminate the surface dangling bonds, replacing less stable Si–H bonds and forming more stable Si–Ag bonds.¹⁷ Ag is expected to be distributed on the surface of PS and, thus, passivate the material against oxygen in the air. The FTIR spectra in Fig. 4 indicate a considerable decrease in the number of Si–H bonds in the two-step fabricated PS, which can support the above assumption. It has been previously reported that Si–Au bonds are more stable than Si–H bonds and thus allow for improvement of the PL stability.⁸ Since the chemical properties of Ag are similar to those of Au, Si–Ag bonds are also expected to passivate the PS surface. Namely, stable Si–Ag bonds can suppress formation of Si dangling bonds and result in more intensive and stable visible luminescence than that of PS prepared by conventional electrochemical anodization.

In conclusion, we have obtained the PS prepared by a two-step method that combines chemical etching and electrochemical anodization. The material demonstrates PL with higher intensity and enhanced stability in comparison to that of conventional PS prepared by electrochemical anodization. The improvements are believed to be the results of the difference in microstructure of pores and Si–Ag bonds on the surface of the material prepared in two stages.

This work is partially supported by the Natural Science Foundation of China (Grant No. 50402010), Natural Science Foundation of Tianjin city (Grant No. F104012) and the 985 Project of Tianjin University.

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