

Influence of surface Si–Ag bonds on photoluminescence of porous silicon

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(Received 17 January 2006; accepted 27 June 2006; published online 22 September 2006)

Porous silicon with surface Si–Ag bonds was prepared by depositing Ag on conventional electrochemically prepared porous silicon using electrodeposition method, and the influence of surface-bonded Ag on photoluminescence properties of the material was studied. Photoluminescence intensity of porous silicon increases with the amount of surface Si–Ag bonds formed during electrochemical deposition. Further treatment leads to increased amounts of Ag–O and Ag–Ag bonds on the material surface. Such layers of oxygen-bonded and metallic Ag are shown to retard the light emission from porous silicon. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2353397]

I. INTRODUCTION

Since the discovery of visible light emission from porous silicon (PS) over a decade ago, the material has been attracting many researchers in the field. The main driving force is its visible light-emission property at room temperature, which makes PS a good candidate for optoelectronic applications such as light-emitting devices.^{1–3} Additionally, its light emission is very sensitive to ambient conditions and this makes PS suitable for chemical and biochemical sensors.^{4,5} However, to meet product requirements in the above applications, the luminescence efficiency of PS must be high enough. This has demanded intense research efforts aiming at improving the luminescence intensity and stability.^{6–10}

In a previous study, we reported the preparation of Ag-passivated PS by the so-called “two-step method,”¹¹ which enabled higher photoluminescence (PL) intensity compared to that of conventional electrochemically prepared PS. The enhanced PL property was reported to result from the formation of Si–Ag bonds on the surface of PS. However, the conclusions were made based on the chemical composition measurements by energy-dispersive spectroscopy (EDS), which does not provide any direct evidence of Si–Ag bonding. Such a direct study of Si–Ag bonding on PS surface has not been reported to date.

In the present work, a simple electrochemical deposition technique was applied to prepare PS samples with different amounts of Ag on their surface. X-ray photoelectron spectroscopy (XPS) was used to evaluate Si–Ag bond structure. Based on the theory of binding energy, the existence of Si–Ag bonds is confirmed and their peak positions in XPS spectra are determined. Moreover, a close relation between PL intensity and the number of surface Si–Ag bonds was revealed.

II. SAMPLES AND METHODS

The initial material was *p*-type, *B*-doped, (100) oriented Si wafers with a resistivity of 10–12 Ω cm. Four PS samples were prepared by using normal electrochemical anodization. The solution used consisted of HF, C₂H₅OH, and H₂O with the volume ratio of 1:1.5:2, and the current density being 80 mA/cm² for 20 min. Sample 1, which was used as a control for comparison, did not undergo any further treatment. The other three (samples 2, 3, and 4) were then treated electrochemically at 1 mA/cm² in a 3 mM AgNO₃ solution for 1 s (sample 2), 5 s (sample 3), and 30 s (sample 4).

PL spectra were acquired with a Hitachi F4500 fluorescence spectrophotometer with excitation wavelength of 365 nm. A Philips XL30E microscope was used for EDS and scanning electron microscopy (SEM) analyses. Bond structure was investigated using a Nicolet 560 Fourier transform infrared (FTIR) spectrometer and Perkin-Elmer PHI-1600 XPS.

III. RESULTS AND DISCUSSION

Figure 1 presents PL spectra of the four samples. The sharp intense peaks around 730 nm originate from the frequency multiplication of the excitation source wavelength

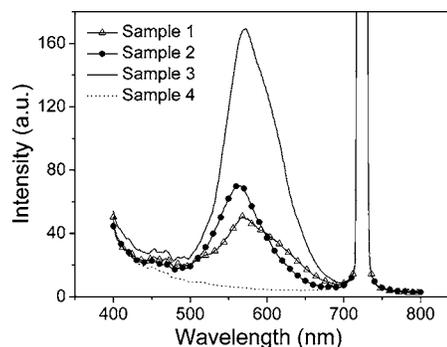


FIG. 1. PL spectra of samples 1–4.

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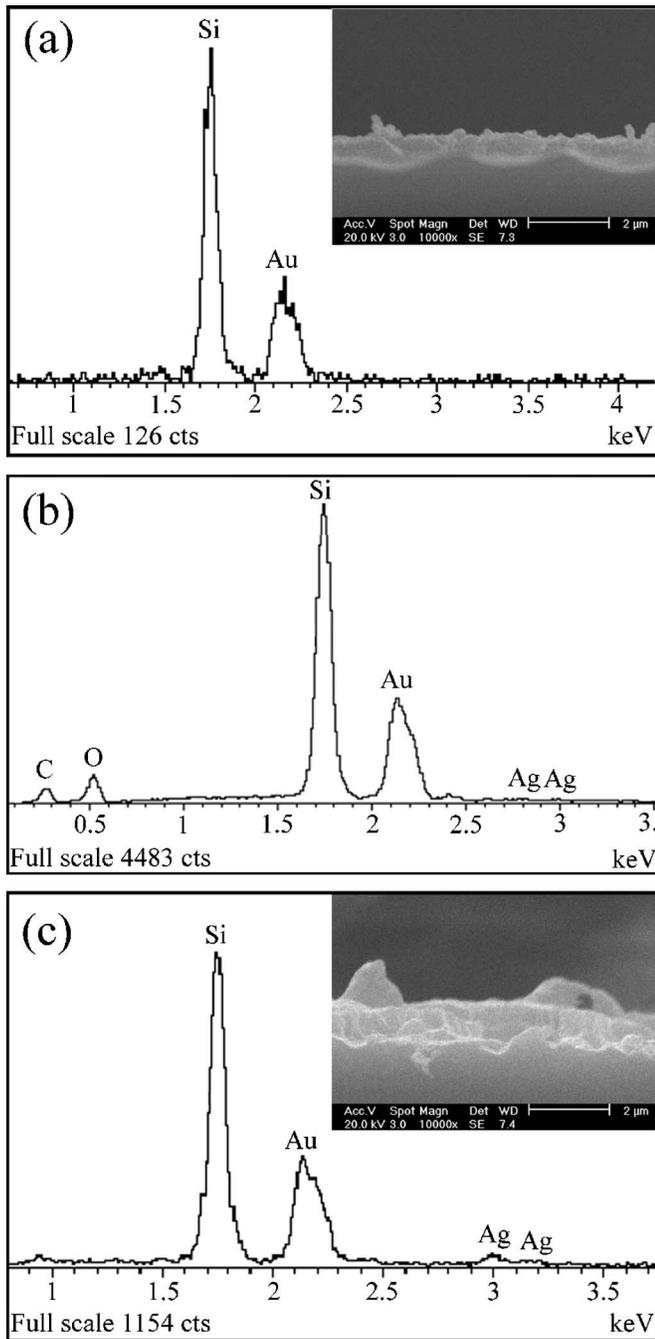


FIG. 2. EDS spectra of samples 1(a), 2(b), and 3(c). The insets are cross-section images of the corresponding samples.

(365 nm). It is clear that the PL intensity of the control (sample 1) is lower than those of samples 2 and 3, while no light emission from sample 4 is detected.

Figure 2 shows EDS spectra of samples 1, 2, and 3, and cross section images of samples 1 (control PS) and 3 with the strongest PL being inserted into corresponding spectra. While no significant difference in morphology can be found in SEM images, the EDS results confirm that Ag has been deposited on the surface of samples 2 and 3 [Figs. 2(b) and 2(c)] and no Ag in sample 1 [Fig. 2(a)]. The Au signals are from the sputter-deposited layer prior to SEM observation. Using Si peaks as a reference, it is possible to see that the Ag peak intensity grows from sample 2 to sample 3, thus implying increase in amount of surface Ag with treatment time.

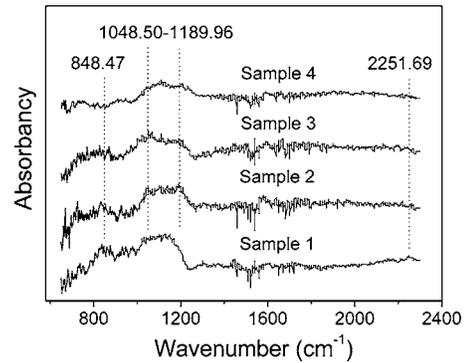


FIG. 3. FTIR spectra of samples 1–4.

To investigate the relationship between the improved PL intensity and bond structure on the surface of PS, FTIR and XPS measurements have been performed. FTIR results are shown in Fig. 3. It is clearly seen that the intensity of absorption bands at 848.47 and 2251.69 cm^{-1} , which are attributed to Si–H bonds,¹² decreases in samples 2 and 3 and vanishes in sample 4. At the same time, the wide absorption bands between 1048.5 and 1189.96 cm^{-1} , standing for Si–O–Si bonds,¹³ remain essentially unchanged in all the spectra. Therefore, it can be concluded that the enhanced PL intensity is not related to Si–H or Si–O–Si surface bonds.

XPS Si $2p$ spectra of the four samples are shown in Fig. 4. All of the samples exhibit peaks for Si–Si bonds (around 101 eV).¹⁴ They also show peaks at higher energy: for samples 1 and 2, the peak around 106 eV is ascribed to Si–O bonds;^{14,15} for samples 3 and 4, the peak around 108 eV is ascribed to Si–F bonds.¹⁶ In addition, for samples 3 and 4, there is a well seen shoulder at the lower-energy side (around 99 eV) of the Si⁰ peak, which suggests Si bonding with some atoms with lower electronegativity compared to that of Si. In the present experiment, only Ag meets the above requirement, thus the shoulder at ~ 99 eV can be attributed to Si–Ag bonds. This assumption is well consistent with the spectra in Fig. 4. Indeed, the spectrum of the control (sample 1) with no Ag deposited demonstrates a valley at ~ 99 eV. Then in sample 2, which was treated in the AgNO_3 solution for 1 s, the valley around 99 eV disappears, thus implying formation of some Si–Ag bonds. Further electrochemical treatment for 5 and 30 s leads to more pronounced Si–Ag components in the spectra of samples 3 and 4, respectively.

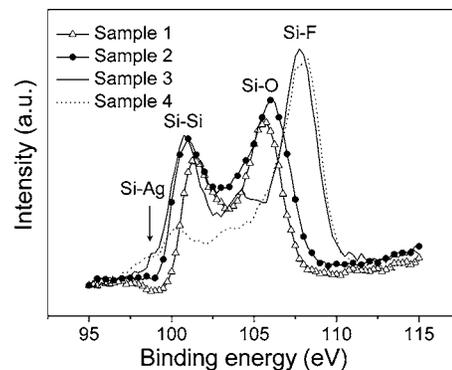


FIG. 4. XPS Si $2p$ spectra of samples 1–4.

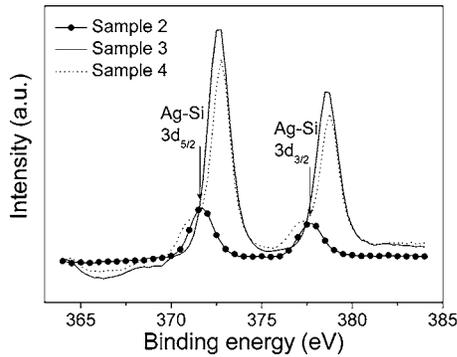


FIG. 5. XPS Ag 3d spectra of samples 1–4.

Based on Fig. 4, the effective area of the Si–Ag peaks and the amount of Ag-bonded Si increase with deposition time.

The above trend can be also followed by analyzing the Ag 3d spectra of the samples containing deposited Ag (shown in Fig. 5). For sample 2, there are two symmetric peaks at 372 and 378 eV in the spectrum. At the same time, the two peaks of sample 3 are asymmetric, which means the peaks are contributed by a few different components. The curve-fitted Ag 3d spectrum of sample 3 is shown in Fig. 6. It is seen that the spectrum can be well interpreted based on the contribution from two species, Ag–O and Ag–Si. As for sample 4, there are two shoulders beside the asymmetric peaks in Fig. 5. Therefore, in addition to the Ag–O and Ag–Si components used to curve-fit the spectrum of sample 3, one more peak, attributed to Ag–Ag bonds, is used to curve-fit the spectrum of sample 4 (see Fig. 7). According to Refs. 17–19 the peaks at 371 and 377 eV arise from $\text{Ag}^0 3d_{5/2}$ and $\text{Ag}^0 3d_{3/2}$, while those at 373 and 379 eV from Ag–O $3d_{5/2}$ and Ag–O $3d_{3/2}$. The peaks at 372 and 378 eV between the peaks of Ag–Ag and those of Ag–O must arise from bonds of Ag with the element whose electronegativity is between Ag and O. Such bonds can be ascribed to Ag–Si, and the two peaks are from Ag–Si $3d_{5/2}$ and Ag–Si $3d_{3/2}$. Thus, the detailed analysis of electron states related to Ag in the samples allows us to conclude that mainly Si-bonded Ag was deposited after 1 s (sample 2), then Si- and O-bonded Ag atoms are detected after 5 s (sample 3), and finally longer treatment for 30 s (sample 4) leads to additional formation of metallic Ag deposit on PS surface.

The above FTIR and XPS results can be used to explain

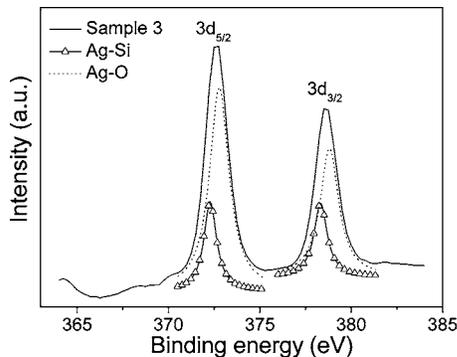


FIG. 6. Interpretation of the XPS Ag 3d spectrum of sample 3 assuming contributions from Ag–Si and Ag–O.

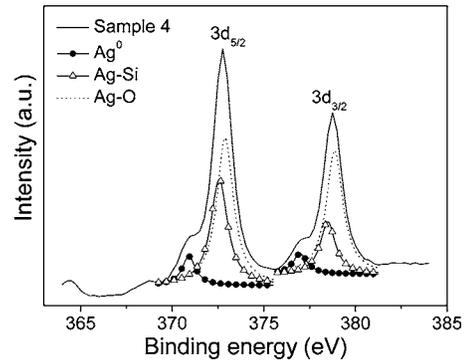


FIG. 7. Interpretation of the XPS Ag 3d spectrum of sample 4 assuming contributions from Ag–Si, Ag–O, and Ag–Ag.

the PL spectra presented in Fig. 1. Sample 1 represents a conventional PS which emits comparatively weak PL. It was proved that the amount of Si–H bonds on the surface of PS is proportional to the concentration of H^+ in the solution.²⁰ In the process of electrochemical deposition, the concentration of H^+ is much lower than that during the electrochemical anodization because there is only some residual HF when Ag deposit is formed. Therefore, Si–H bonds tend to break, leaving Si dangling bonds under such conditions.²⁰ In sample 2, the Ag atoms are combined with Si dangling bonds forming stable Si–Ag bonds²¹ and passivating PS surface, which led to somewhat increased PL. Because of too short deposition time (1 s), the amount of Si–Ag bonds in sample 2 is limited and far from saturation. As the deposition time was increased to 5 s, the amount of Si–Ag bonds in sample 3 is larger than that in sample 2, which leads to more enhanced surface passivation and further rise of PL intensity. The observed PL intensity is more than three times higher compared to that of the control PS. Finally, in sample 4, although there is a large number of Si–Ag bonds formed, the deposited layer is too thick, containing a surface layer with metallic and oxidized Ag that suppresses light emission significantly.

IV. CONCLUSIONS

In this work, the effect of Ag electrochemically deposited on porous Si on the photoluminescence of the latter is investigated. The enhancement in photoluminescence of the materials is shown to be related to the number of surface Si–Ag bonds, while no obvious influence of Si–H and Si–O–Si bonds was observed. Increase in a Ag deposition time results in a larger amount of surface Si–Ag bonds. However, as the electrochemical deposition proceeds, later Ag–O and Ag–Ag bonds also form in the deposit, which suppresses further improvement in photoluminescence intensity.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Foundation of China (No. 50402010), Natural Science Foundation of Tianjin city (No. 043800711), and Project 985 of Tianjin University.

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