

The enhancement of photoluminescence from porous silicon with Si–Ti bond

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Abstract

Porous silicon (PS) was passivated with titanium by direct current sputtering. The enhancement and blueshift of photoluminescence (PL) peak were observed under the irradiation of ultraviolet light. X-ray photoelectron spectroscopy (XPS) results show that the formation of Si–Ti bond is responsible for the improvement of PL properties.

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1. Introduction

PS has high potential on the light-emitting devices (LEDs); however, PS always bears instability of PL properties, which is believed to originate from the chemical instability of the PS surface, namely, the Si–H bonds on the PS surface gradually break and the dangling bonds form in the ambient air [1–3].

In order to improve the PL efficiency and stability, lots of efforts have been made by passivating PS surface with N [4,5], O [6–8] and diamond-like carbon (DLC) [9]. Metal films, such as Au [10], Fe [3,11–13], were also tempted as passivation materials by plating. Few researchers adopted sputtering method to deposit Zn [14] and Cu [14,15] layer on PS; however, the results were not satisfactory, because sputtering doesn't result in effective bonding of silicon atoms with metal atoms. Furthermore, metal passivation on PS surface can result in non-radiative recombination nearby defects [12, 14].

In this work, we deposited titanium layer on PS by direct current sputtering, and obtained improved photo-

luminescence properties, the mechanism of titanium passivation was investigated.

2. Experimental

The silicon substrates used were (100) oriented, p-type wafers. The PS samples were prepared by electrochemical anodization in solution of $\text{HF}:\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}=1:1.5:2$ at a current density of 30 mA/cm^2 for 20 min, then 20 mA/cm^2 for 20 min. The PS sample was split into halves. One fragment acts as reference sample (sample A), the other fragment with bit of hydrofluoric acid left was passivated with titanium by sputtering (sample B), the role of hydrofluoric acid is to protect PS from oxidization. Ti films were deposited at room temperature with direct current power of 40 W at Ar pressure of 2.5 Pa. The sputtering time was 1 min. A sample with more hydrofluoric acid was prepared to prevent forming Si–Ti bond (sample C). In order to acquire instantaneous PL spectra, HITACHI F4500 Fluorescence spectrophotometer was used. The samples were exposed to an UV lamp with wavelength of 365 nm for 4 min. During the irradiation, PL spectra were acquired every 1 min at a scanning speed of 30000 nm/min (0.5 s/spectrum) from the beginning of irradiation. Time-scan was done by fixing the

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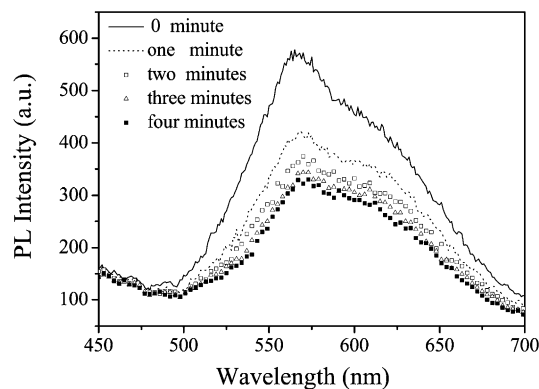


Fig. 1. The time-resolved PL spectra for sample A exposed to UV light at room temperature.

emission wavelength at the main PL peak. Perkin–Elmer PHI-1600 XPS was used to analyze the bonds on PS surface after UV irradiation.

3. Results and discussions

The normal PS without Ti passivation shows the unstable PL properties under the UV irradiation (Fig. 1). The peak at 564 nm shifted towards longer wavelengths and intensity reduced gradually, finally the PL peak located 571 nm and the intensity decreased 43%. As a comparison, the sample with Ti passivation (sample B) shows an extraordinary property (Fig. 2), PL peak shifted towards shorter wavelengths and the intensity increased with the UV irradiation; from the third minute on, PL became stable; at the end, the intensity of PL peak increased about 20% with a blueshift of 10 nm. The final PL intensity of sample B was two times higher than that of sample A. Time-scan of the samples is shown in Fig. 3, the intensity of sample B increased along with irradiation at the beginning, and then became stable, on the contrary, the PL intensity of sample A decreased for 32%, and that of sample C decreased for 18%.

Fig. 4 shows XPS results of Si 2p binding energy. For sample A, there exist strong Si–O peak (around 104 eV) and Si–Si peak (around 100 eV) [16,17], Si–Si peak and Si–O peak are from silicon nanocrystals in PS and the silicon oxidized layer on the PS surface, respectively. There is no obvious shoulder at lower-energy

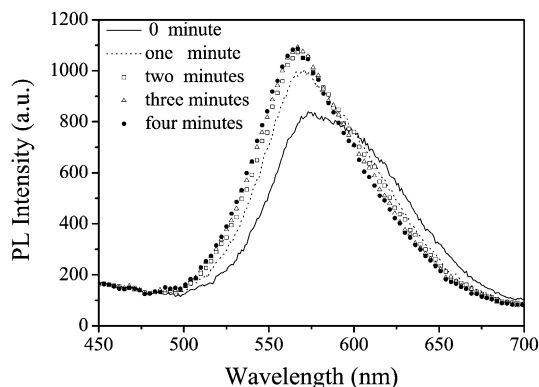


Fig. 2. The time-resolved PL spectra for sample B exposed to UV light at room temperature.

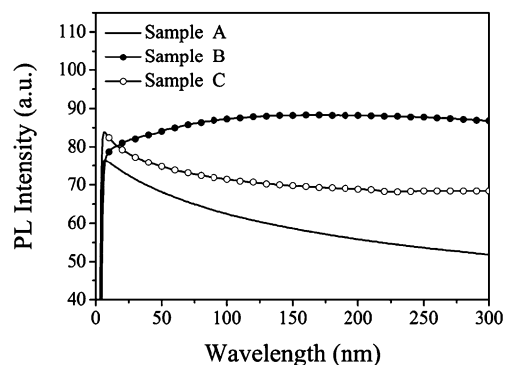


Fig. 3. Time-scan photoluminescence spectra for samples A, B, C.

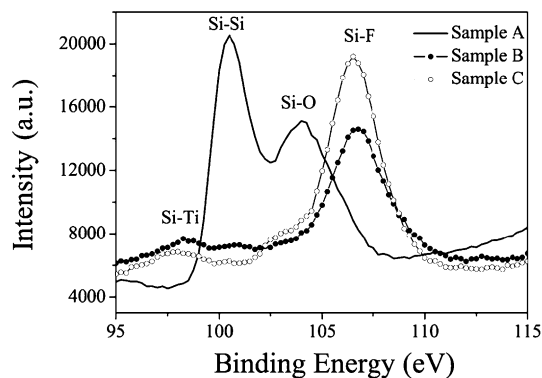


Fig. 4. XPS results of Si 2p binding energy.

side of Si–Si peak, which suggests there are not many Si–H bonds (about 99 eV [18]) on PS surface. Above results indicate that the change of PL properties of sample A is due to the instability of surface bonds: photons can accelerate desorption of H atoms from unstable Si–H bond and formation of Si–O bond [19–21]. The PL red-shift and intensity reduction of sample A were then attributed to the breakage of Si–H bond and the formation of Si–O bonds [22].

As for sample B and sample C, there exist intensive XPS peaks in Fig. 4 related to Si–F bond of SiF_4 (106.6 eV) [23], because Ti films prevented silicon fluoride from volatilizing. Ti 2p binding energy was shown in Fig. 5. For TiO_2 thin film or exposed surface of TiO_2 , the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ binding energies locate around 459.5 eV and 465 eV respectively [24–26].

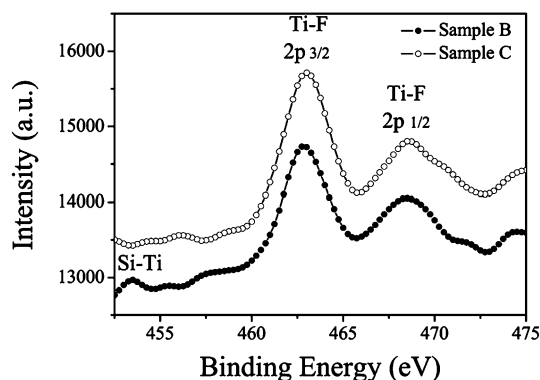


Fig. 5. XPS results of Ti 2p binding energy.

Therefore, the peak at 462.4 eV in Fig. 5 is attributed to Ti 2p_{3/2} and the peak at 468.2 eV to Ti 2p_{1/2}. The binding energies of passivated layer are higher than that of titanium dioxide, which is due to the different bond type.

Since there is a large amount of F atoms in sample B and C, which can be deduced from Fig. 4, we supposed most of titanium atoms are bonded with F atoms. The Pauling electronegativity value for F (4.0) is larger than that for O (3.65), thereby, the effective positive charge on the Ti atom of the Ti–F bond is larger than that of the Ti–O bond. As a consequence, the photoelectrons from the Ti 2p core level of Ti–F should appear at higher binding energy in comparison with Ti–O.

The XPS results show that Si–F and Ti–F bonds are on the surface of both sample B and sample C. The PL intensity of sample C did not increase although the stability was somewhat enhanced, which indicates the Si–F and Ti–F bonds are not decisive on the improvement of PL properties.

The peak around 98.8 (Fig. 4) and 453.9 eV (Fig. 5) in spectrum of sample B are from Si–Ti bond [27,28], but the peaks did not appear in the spectrum of sample C. It suggests that the formation of UV induced Si–Ti bond is the way of passivation instead of UV induced surface oxidization [29,30]. Since excessive hydrofluoric acid was used for sample C before the sputtering, all of titanium atoms were consumed to form Ti–F bonds. On the contrary, for sample B, the amount of hydrofluoric acid was limited, and extra titanium atoms were left after the chemical reaction. During UV light irradiation, Si–H bonds broke and the residual Ti atoms formed Si–Ti bonds with Si dangling bonds caused by H desorption. The blueshift and the increase of PL peak of sample B were consistent with the increase of the number of Si–Ti bonds. Therefore, the Si–Ti bonds contributed to the improvement of the PL prosperities.

4. Conclusions

PS was passivated by sputtering titanium films. After irradiated by ultraviolet light, the final PL intensity of passivated sample was two times higher than that of non-passivated one. The formation of Si–Ti bond was demonstrated to be responsible for the improvement of PL properties.

Acknowledgements

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