Photoelectric characteristics of silicon P–N junction with nanopillar texture: Analysis of X-ray photoelectron spectroscopy*

Liu Jing(刘 静)[a)b)], Wang Jia-Ou(王嘉鸥)[a)], Yi Fu-Ting(伊福廷)[a)†],
Wu Rui(吴 蕊)[a)], Zhang Nian(张 念)[a)b)], and Ibrahim Kurash(奎热西)[a)]

[a)] *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*
[b)] *University of Chinese Academy of Sciences, Beijing* 100049, *China*

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Silicon nanopillars are fabricated by inductively coupled plasma (ICP) dry etching with the cesium chloride (CsCl) islands as masks originally from self-assembly. Wafers with nanopillar texture or planar surface are subjected to phosphorus (P) diffusion by liquid dopant source ($POCl_3$) at 870 °C to form P–N junctions with a depth of 300 nm. The X-ray photoelectron spectroscopy (XPS) is used to measure the Si 2p core levels of P–N junction wafer with nanopillar texture and planar surface. With a visible light excitation, the P–N junction produces a new electric potential for photoelectric characteristic, which causes the Si 2p core level to have a energy shift compared with the spectrum without the visible light. The energy shift of the Si 2p core level is −0.27 eV for the planar P–N junction and −0.18 eV for the nanopillar one. The difference in Si 2p energy shift is due to more space lattice defects and chemical bond breaks for nanopillar compared with the planar one.

Keywords: X-ray photoelectron spectroscopy (XPS), photoelectric characteristic, P–N junction, silicon nanopillar

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1. Introduction

Due to abundant Si source, mature technology, low cost, and stable properties, the silicon-based devices are dominant in commercial semiconductor market, such as solar cell, light-emitting diodes, and optical fiber for communication.[1–3] Silicon P–N junction is one of the basic circuit elements in various photonic and photovolatic devices, which has great effect on the performance of these devices.[4,5] Silicon nanopillar array has become more and more attractive due to their unique electrical and optical properties, making them a potential candidate for photovoltaic applications as antireflection and nanopillar P–N junction structures.[6,7] Many methods have been employed to fabricate nano structures, such as e-beam and laser interference lithography,[8,9] nanoimprint lithography,[10,11] self–assembly lithography,[12–14] and so on. Various silicon nanopillar/nanowire P–N junctions have been investigated for their unipue optoelectronic properties at the nanometer scale, which are usually detected by testing the final devices, for example *I–V* curve testing for nanopillar based solar cell.[15,16] However, the final device testing results are always affected by some other important factors, for example ohmic contact between metal electrode and nanopillar surface for nanopillar-based solar cell, which cannot reveal the properties of P–N junction directly.

In this work, the P–N junction with silicon nanopillars are finished by dry etching and phosphorus diffusion. By dry etching, the silicon nanopillars are fabricated with the masks of cesium chloride (CsCl) islands originating from the simple self-assembly method.[17–19] By phosphorus diffusion with liquid dopant source at 870 °C, the P–N junctions with a depth of 0.3 μm are formed. The X-ray photoelectron spectroscopy (XPS), as a powerful tool for the electronic states and chemical shift of surface material testing,[20–22] is used to measure the Si 2p core levels of P–N junction with nanopillar texture or planar wafer. Under a visible light, the P–N junction produces a new electric potential for photoelectric characteristics to have a shift for the Si 2p core level.

2. Experimental

Nanopillar arrays with P–N junctions are fabricated on a P-type (1–10 Ω·cm), polished (100)-oriented silicon substrate with an initial thickness of 350 μm. Firstly, a CsCl film is deposited by heat evaporation onto the cleaned wafer surface in high vacuum system (0.01 Pa) (Fig. 1(a)). Secondly, the vacuum chamber is filled with fixed humidity gas, and CsCl on the substrate starts to grow up, forming CsCl nanoisland arrays by absorbing water in the air (Fig. 1(b)). Thirdly, the dry etching with inductively coupled plasma (ICP) is used to obtain silicon nanopillar arrays (Fig. 1(c)) with the mask of CsCl nanoislands. Fourthly, the substrate is put in water to dissolve the CsCl resist (Fig. 1(d)), and the silicon nanopillar arrays are successfully prepared.[17] Then, the wafer with nanopillar

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†Corresponding author. E-mail: yift@ihep.ac.cn
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surface texture is subjected to phosphorus diffusion by liquid dopant source ($POCl_3$) at 870 °C to form the P–N junction having a sheet resistance of 40 Ω/□, a phosphorus density of 10^{18}/cm^3, and a depth of 0.3 μm. Finally, back surface P–N junction is removed by ICP dry etching under the condition of SF_6:He=120:10 sccm, excitation power of 500 watt, bias power of 30 watt, and chamber pressure of 4.6 Pa for 5 min (Fig. 1(f)). The silicon P–N junction with planar surface is just carried out phosphorus diffusion and back P–N junction removal process.

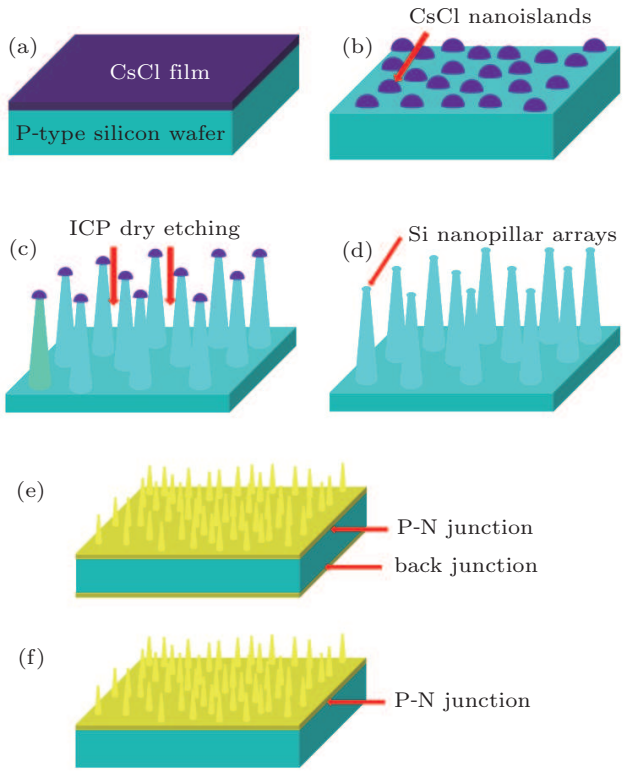


Fig. 1. (color online) Fabrication process of the silicon P–N junction with nanopillar texture: (a) deposition of CsCl film, (b) development for CsCl nanoislands, (c) ICP dry etching, (d) removal of the CsCl resist, (e) phosphorus diffusion for P–N junction, and (f) removing P–N junction back.

All the XPS experiments are carried out at the Beijing Synchrotron Radiation Facility (BSRF), at the beamline 4B9B. The energy of incident photon is 500 eV and the energy step is set to 30 meV. All spectra are normalized by the incident beam current. The visible light is supplied by an incandescent lamp. The two kinds of samples used for measurement are the silicon P–N junctions with planar surface and nanopillar texture. Both the samples are measured under the conditions of back or front surface connected with earth by copper conductive adhesive tape respectively shown in Fig. 2. A silicon planar wafer without P–N junction is also measured under the condition of back surface connecting with earth for comparison. Before the XPS experiment, all the samples are immersed in the dilute HF (HF:H_2O = 1:4 by volume) for 5 min to remove the silica layer on the surface, and ultrasonic cleaned in alcohol and acetone solution, respectively. The morphology of the silicon nanopillar is represented by scanning electron microscope (SEM, Hitachi-4800).

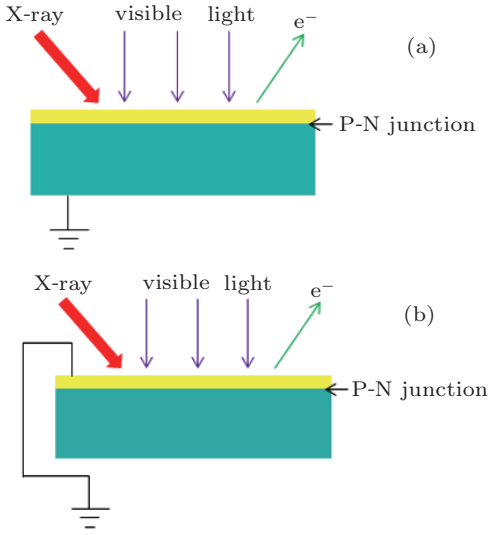


Fig. 2. (color online) Schematic of XPS with (a) back and (b) front surface of samples connecting with earth.

3. Result and discussion

3.1. Si 2p core level shift of planar wafer with P–N junction

The back of planar sample with P–N junction is connected with earth to keep the electric potential of back surface zero during the XPS testing (Fig. 2(a)). When the incandescent lamp is turn on, the Si $2p_{1/2}$ and Si $2p_{3/2}$ core level has a −0.27 eV shift instantaneously (the minus "−" stands for the shift to lower binging energy). When turning the incandescent lamp off, the −0.27 eV energy shift of the core level disappears immediately. There should be a new electric potential φ when visible light excitation from the photoelectric characteristics of P–N junction with φ_A of −0.27 eV for planar P–N junction.

When the visible light shines on the P–N junction surface, free electron–hole pairs are produced for photoelectric effect and the P–N junction separates the electrons and holes. The holes are transported to the P-type surface in the wafer, while the electrons are transported to the N-type surface on the wafer surface to produce a new electric potential φ. The electric potential of N-type surface is lower than that of the P-type surface, so φ is negative and the value is related to the electron–hole pairs produced by photoelectric effect and separated by P–N junction. The free electrons are emitted to the vacuum level continuously by X-ray photons and supplied by earth through the back P–N junction surface continuously to be a steady state. When the visible light disappears, φ disappears instantaneously.

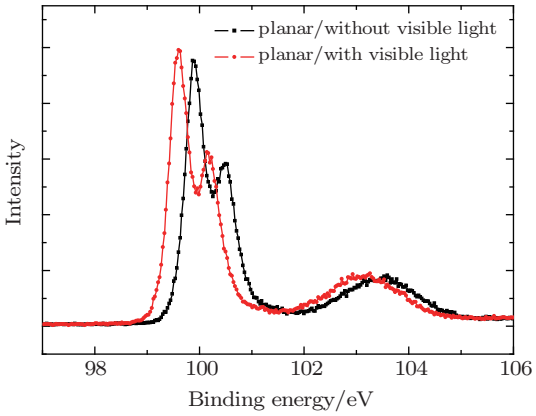


Fig. 3. (color online) Si 2p core level spectra with a photon energy ($h\gamma$) of 500 eV. The back of planar sample is connected with the earth.

When the front of the planar sample is connected with the earth through copper conductive adhesive tape to keep the electric potential of front surface zero, the eletrons can be supplied to N-type surface directly (Fig. 2(b)). With the visible light excitation, electron–hole pairs can be produced and separated, but the N-type surface of P–N junction still keeps zero electric potential for earth connecting. Therefore, there is no Si 2p core level energy shift with or without visible light excitation (Fig. 4).

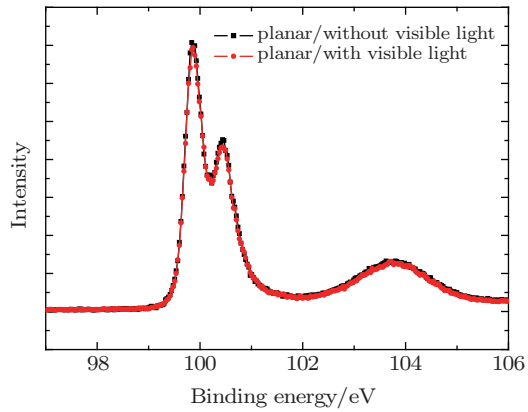


Fig. 4. (color online) Si 2p core level spectra with a photon energy ($h\gamma$) of 500 eV. The front of planar sample is connected with the earth.

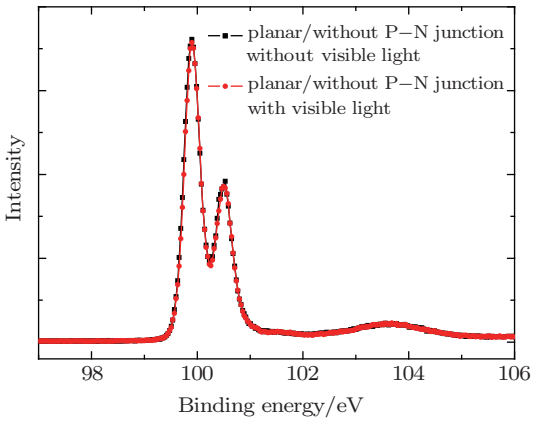


Fig. 5. (color online) Si 2p core level spectra with a photon energy ($h\gamma$) of 500 eV for the planar sample without P–N junction. The back of the sample is connected with the earth.

To exclude other possibilities for Si 2p core level energy shift, a similar measurement having the back connected with earth is carried out on a silicon planar wafer without the formation of P–N junction. From Fig. 5, there is no energy shift and the new electric potential φ cannot be produced by visible light excitation without P–N junction. This phenomenon proves that the silicon P–N junction is the core for the energy shift with visible light excitation.

3.2. Si 2p core level shift of nanopillar texture wafer with P–N junction

Figure 6(a) shows the CsCl nanoislands with an average diameter of 400 nm, which are prepared from 200-nm-thick CsCl films after developing under 40% humidity for 30 min. With these nanoislands acting as masks, silicon nanopillars of circular cone morphology (300 nm in average diameter and 1.5 μm in height) are produced by ICP dry etching under the condition of SF_6:He = 120:10 sccm, excitation power of 500 watt, bias power of 30 watt, and chamber pressure of 4.6 Pa for 5 min (Fig. 6(b)). This nanopillar textured wafer is diffused phosphorus for 300 nm depth P–N junction and tested by XPS with or without visible light.

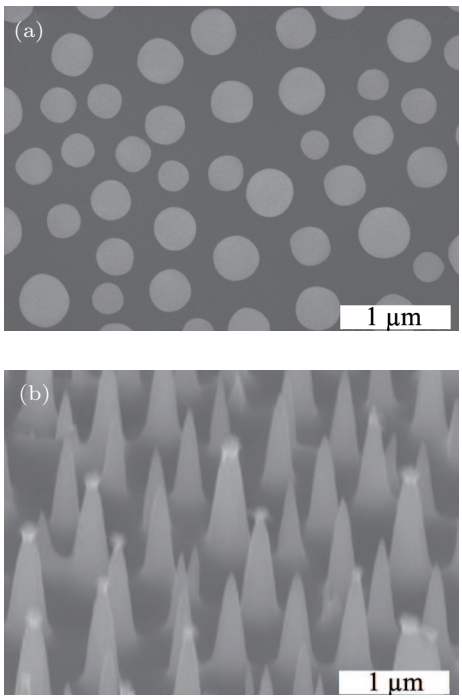


Fig. 6. SEM images of (a) CsCl nanoislands with an average diameter of 400 nm, and (b) silicon nanopillar of circular cone morphology with an average diameter of 300 nm and height of 1.5 μm.

For the nanopillar texture P–N junction surface, the Si 2p core level still has an energy shift to lower binding energy under the visible light, with the new electric potential φ_B equal to −0.18 eV (Fig. 7). However, the energy shift for the nanopillar texture is smaller than that for the planar one (−0.27 eV). Although accompanied by lower visible light reflection, the nanopillar morphology[17] has more space lattice defects and

chemical bond breaks for ICP dry etching to cause recombination of electron–hole pairs. Therefore, the electric potential produced by the nanopillar P–N junction is lower than the planar one. The front of nanopillar sample is connected with earth by copper conductive adhesive tape, and there is no Si 2p core level shift with or without visible light excitation acting as the planar sample. This proves that the core level energy shift is decided by the P–N junction's property. For silicon solar cell, the theory of nanopillar texture surface reducing the open circuit voltage can be demonstrated by the XPS results, and the surface passivation must be considered to improve the open circuit voltage of nanopillar textured solar cells.[23,24]

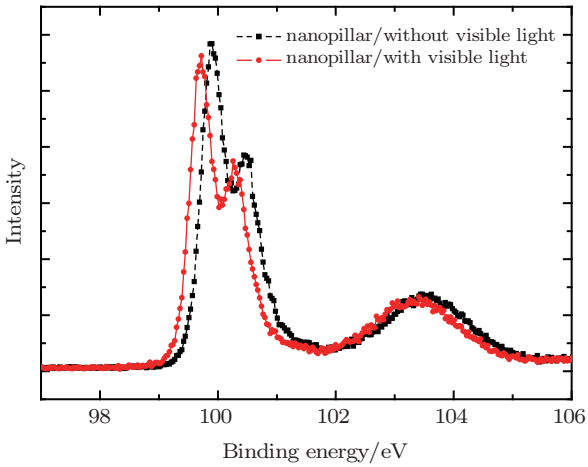


Fig. 7. (color online) Si 2p core level spectra with a photon energy ($h\gamma$) of 500 eV. The back of nanopillar sample is connected with the earth.

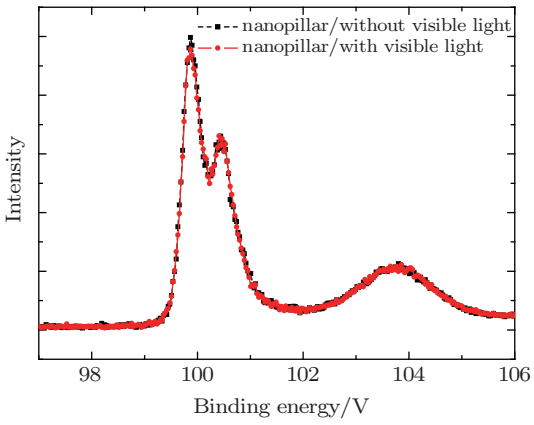


Fig. 8. (color online) Si 2p core level spectra with a photon energy ($h\gamma$) of 500 eV. The front of nanopillar sample is connected with the earth.

4. Conclusions

In this work, CsCl island self-assembly lithography and ICP dry etching method are used to make silicon nanopillars on polished silicon wafer surface. The silicon nanopillar and planar wafers are subjected to phosphorus diffusion by liquid dopant source at 870 °C to form a 300-nm-thick P–N junction. The X-ray photoelectron spectroscopy is used to measure the Si 2p core levels of P–N junction with nanopillar texture and planar wafer. Under a visible light excitation, the P–N junction of back connected with earth produces a negative electric potential from photoelectric characteristics to have a energy shift for the Si 2p core level. When the visible light is removed, the shift of core level and the new electric potential disappear instantaneously. For the planar P–N junction, the energy shift of Si 2p core level is −0.27 eV, while for the nanopillar P–N junction, it is only −0.18 eV when excited by the same visible light. The nanopillar morphology brings more space lattice defects and chemical bonds breaks compared with the planar one which leads to the lower electric potential. Hence, for the silicon solar cell, the theory of nanopillar texture reducing the open circuit voltage can be demonstrated by the XPS results, and surface passivation must be considered to improve the open circuit voltage of nanopillar textured solar cells.

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