

Advanced Optoelectronic Devices based on Si Quantum Dots/Si Nanowires Hetero-structures

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Abstract. Si quantum dots are currently extensively studied since they can be used to develop many kinds of optoelectronic devices. In this report, we review the fabrication of Si quantum dots (Si QD) /Si nanowires (Si NWs) hetero-structures by deposition of Si QDs/SiO₂ or Si QDs/SiC multilayers on Si NWs arrays. The electroluminescence and photovoltaic devices based on the formed hetero-structures have been prepared and the improved performance is confirmed. It is also found that the surface recombination via the surface defects states on the Si NWs, especially the ones obtained by the long-time etching, may deteriorate the device properties though they exhibit the better anti-reflection characteristics. The possible surface passivation approaches are briefly discussed.

1. Introduction

Nano-crystalline Si quantum dots (Si QDs) have attracted more and more attention in recently years since they can be applied in many kinds of nano-electronic and optoelectronic devices such as next generation of solar cells, non-volatile memories and Si-based light emitting devices [1-3]. It is currently an open question to further improve device performance of the Si QDs-based devices. One of the interesting topics is to introduce the novel micro- and/or nano-structures to make the efficient photon management, in which Si-based nanowires structures are one of the potential candidates. For example, it was reported that the enhanced optical absorption and photoluminescence from Si QDs can be achieved by using SiO_x nanowires due to the anti-reflection characteristics of the nanostructures [4]. Meanwhile, Si nanowires (Si NWs) fabricated by the metal-assisted chemical etching method were used to get radial p-n junction solar cells, such as crystalline Si NWs cells, a-Si/Si NWs shell/core cells, and organic polymers/Si NWs hybrid cells [5-7]. Si NWs structures can significantly reduce the surface light reflection as well as enhance the incident optical absorption and in turn improve the device performance, which is more suitable for Si-QDs-based optoelectronic devices because the active layer in such devices is usually very thin.

Here, we report the fabrication of hetero-structures containing Si QDs-based multilayers on Si NWs array prepared by the metal-assisted chemical etching technique. The anti-reflection and absorption enhancement behaviors of obtained hetero-structures are demonstrated. The photovoltaic devices and electroluminescence devices based on the Si QD /Si NWs hetero-structures are prepared. Compared with the flat devices, the device performance is obviously improved by using the Si QD /Si NWs hetero-structures. Moreover, it was found that the influence of surface defects states becomes significance with



increasing the etching time during the formation of Si NWs as revealed by ESR measurements. The possible passivation techniques are proposed to reduce the surface defects states and in turn to further improve the device properties.

2. Experimental

Si QDs/SiO₂(or SiC) multilayers with various dot sizes were prepared by annealing amorphous Si/SiO₂ (or SiC) stacked structures with controllable amorphous Si sublayer thickness, which were deposited in conventional plasma enhanced chemical vapor deposition (PECVD) system. The detailed preparation parameters and procedures can be found elsewhere [8-9]. The optical bandgaps have been deduced based on the measured optical absorption spectra according to Tauc's plots and we found that the optical bandgap is shifted with the dot size, which provides a flexible way to design the corresponding Si-based photonic and opto-electronic devices.

In order to get Si NWs, the wet electroless etching technique was used to etch the p-type or n-type Cz silicon (100) wafers. The tree-like Si NW arrays were formed due to the selectively anisotropic etching of silicon substrate in aqueous HF solution induced by the Ag nanoparticles. To remove the capped silver, the as-prepared samples were finally dipped into a 30 wt% HNO₃ aqueous solution for 60 s. It is found that the depth of formed Si NW structures is increased by controlling the etching time. We deposited the Si QDs based multilayers on flat and Si NWs arrays to obtain the prototype device structures, especially the photovoltaic devices and light emitting devices.

3. Results and Discussion

The structures of Si NWs were characterized by field emission scanning electron microscopy (SEM, Sigma Zeiss). Figure 1 (a) and (b) show the top-view and cross-sectional SEM images of the Si NW arrays after etching for 8min. The vertically aligned nanowires are clearly identified with high density. The depth of Si NWs is about 450nm while the average diameter is about 50nm after 8min etching. After preparation of Si QDs-based multilayers on the Si NWs array, the top morphologies are still kept due to the good conformal deposition characteristics of Si-based thin films in PECVD system, which was revealed by cross-sectional transmission electron microscopy (not shown in here).

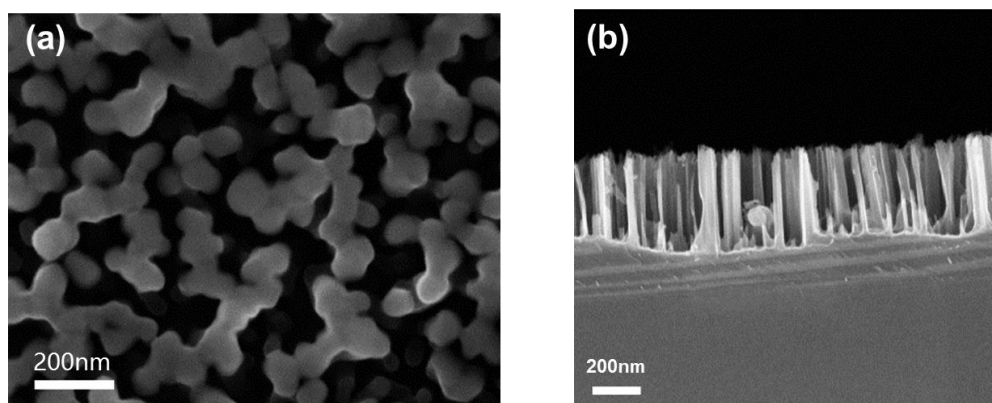


Figure 1. Top (a) and side (b) SEM images of Si NWs after 8 min etching.

A broadband anti-reflection property of Si QDs/Si NWs hetero-structures is found and the reflectance is gradually suppressed with increasing the etching depth of Si NWs. The typical reflection spectra for flat Si substrate, Si NWs array and Si QDs/Si NWs hetero-structures are given in Fig.2. It is found that the reflectance of flat Si substrate is quite high (>30%) in the wavelength range from 200-1100nm. However, the Si NWs array exhibits the reduced reflection in the whole measurement range. In the

wavelength range of 200-700nm (UV-visible light range), the reflectance is even less than 5%. After deposition of Si QDs/SiO₂ or Si QDS/SiC multilayers on Si NWs array, the reflection spectrum is slightly changed as shown in Fig.2. The good anti-reflection characteristics of Si NW arrays can be explained in terms of the formation of graded-index layer from the substrate to the top surface which can suppress the reflection obviously. Another important factor is the strong light scattering effect in the Si NWs array, which trap the light due to the increased optical path [10-12]. As a consequence, the optical absorption is significantly enhanced. It is found that the mean absorption weighted by AM 1.5G solar spectrum in the wavelength range from 300 to 1200 nm for Si QDs/SiC multilayers on Si NWs can reach as high as 88.9%, which is enhanced by 46% compared with the flat one [8,13-14].

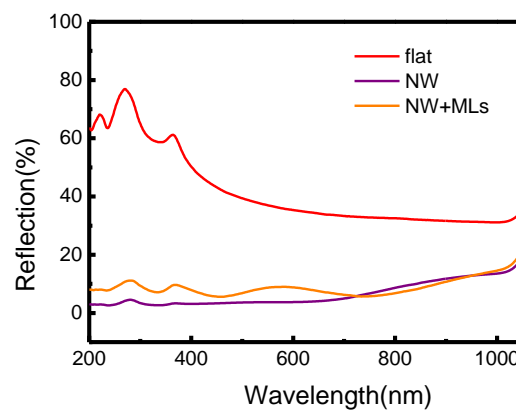


Figure 2. Reflection spectra for flat Si substrate, Si NWs array and Si QDs/Si NWs hetero-structures.

In order to get the device based on Si QDs, the Si QDs (4nm)/SiC (2nm) multilayers and p-type a-Si layer are successively deposited on both flat n-Si wafers and wafers with vertically aligned Si NW arrays to form p-i-n solar cell structures. Figure 3 shows the schematic diagram of device structures. The rectification characteristics are clearly observed, which indicates that the p-i-n structures are well formed by the present approach [8,13]. It is found that the external quantum efficiency (EQE) of Si QDs/Si NWs hetero-structured cell is obviously enhanced over a wide spectral range of 500-1000 nm compared with that of flat reference cell. Meanwhile, the power conversion efficiency based on Si QDs/Si NWs hetero-structures exhibits the best value of 11.3%.

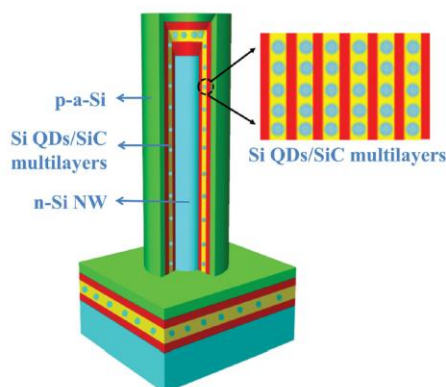


Figure 3. Schematic diagram of photovoltaic device structures containing Si QDs/SiC multilayers deposited on n-Si NWs. The out layer is p-type a-Si film.

We also fabricated the light emitting devices containing Si quantum dots/SiO₂ multilayers deposited on Si nanowire arrays. The enhanced electroluminescence has been achieved as shown in Fig. 4. It is found that the electroluminescence intensity is obviously enhanced by using Si QDs/Si NWs hetero-structures compared with that of flat device. At the same injection current (100mA), the integrated electroluminescence intensity is increased by 4-folds and the output power density is in an order of $\mu\text{W}/\text{cm}^2$. However, it is found that the electroluminescence is first enhanced with increasing the depth of the Si nanowires and then reduced for further increasing the depth though it exhibits the lowest reflectance ($\sim 3\%$). The electron spin resonance (ESR) measurements suggest that the surface defect states may increase after long time etching. Figure 5 is the ESR spectrum of Si NWs sample after 8min etching. It is found that the ESR signal with g value of 2.005 can be observed, which is assigned to Si dangling bonds (P_b - centres) [15]. It is suggested that the surface of Si NWs contain the defects states, which can act as the non-radiative recombination centres to reduce the electroluminescence intensity.

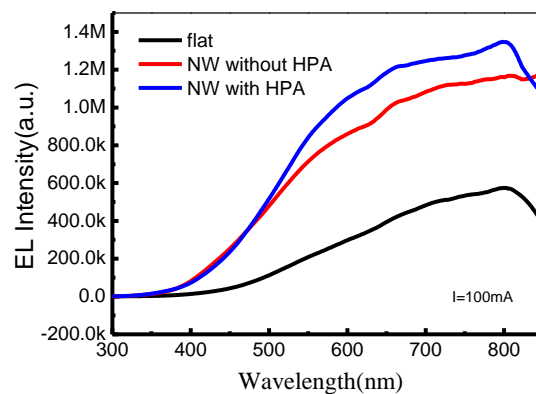


Figure 4. Electroluminescence spectra for flat Si substrate, Si NWs array and Si QDs/Si NWs hetero-structures. The data are collected at the same injection current of 100 mA.

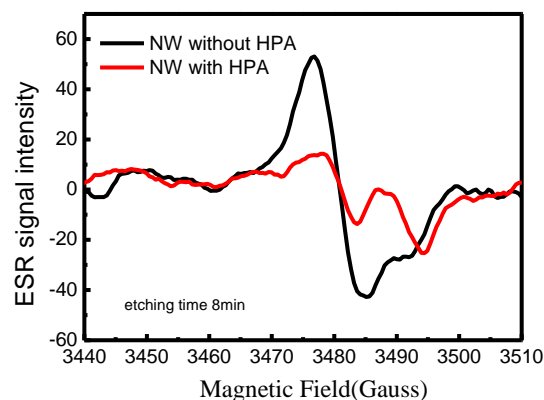


Figure 5. ESR spectra for Si NWs array before and after hydrogen plasma annealing.

In order to reduce the surface states and to further improve the device performance, we proposed the possible passivation techniques such as hydrogen plasma annealing (HPA) treatments or deposition of Al_2O_3 passivation layer. As shown in Fig. 5, the ESR signals related to the dangling bonds are significantly suppressed after HPA treatment. The same passivation effect is also demonstrated by using Al_2O_3 layer. The reduction of surface defects states is indeed improve the device properties. As given in Fig.4, the electroluminescence intensity is further enhanced after HPA treatment and the integrated luminescence intensity is 5 folds stronger than that of flat one and the output power density exceeds $1.0 \mu\text{W}/\text{cm}^2$. Meanwhile, we also found that the turn-on voltage of device is reduce to 3.5V and the operation voltage is about 10V, which is compatible with the requirements of Si-based optoelectronic integrated circuits.

4. Conclusions

The Si QDs/Si NWs hetero-structures with good anti-reflection and optical absorption characteristics were fabricated. Based on the hetero-structures, the prepared optoelectronic devices exhibited the enhanced performance. The hydrogen plasma annealing or Al_2O_3 passivation can significantly suppressed the surface defects states of Si NWs and the device properties can be further improved.

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