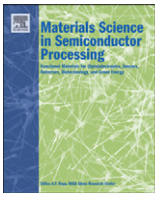
Materials Science in Semiconductor Processing 16 (2013) 520–524

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Short Communication

Surface photovoltage analysis of ZnO nanorods/p-Si heterostructure

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ARTICLE INFO

Keywords:
ZnO nanorod
Si
Surface photovoltage
Kelvin probe

ABSTRACT

In this work, n-type ZnO nanorods (NRs) were fabricated on a p-type Si substrate to form a ZnO NRs/Si structure using a low-temperature wet chemical bath deposition method. Kelvin-probe-based surface photovoltage (KP-based SPV) technology was used to study the behavior of surface photogenerated charges for the as-grown heterostructure. In general, the KP-based SPV response range of the ZnO NRs/Si structure was significantly expanded compared with the bare Si substrate, due to the incorporation of ZnO NRs. Moreover, the SPV response amplitude for ZnO NRs/Si structure also depended on the length and diameter of the NRs, and the corresponding mechanism was elucidated in terms of O_2 adsorption. The photovoltaic application of the ZnO NRs/Si based structure would benefit significantly from these achievements.

1. Introduction

With the increasing concern about the energy shortage and global warming, photovoltaic cells have recently attracted more attention as renewable energy sources. As a typical example of optoelectronic modules, Si solar cells have a dominant position because of their mature manufacturing technology and higher efficiency [1]. However, most of the solar energy in the UV region is consumed by the thermalization loss due to a 1.12 eV band gap of Si, which degrades the conversion efficiency of Si solar cells [2,3]. Thus, to remove the adverse effects, some heterostructures have been suggested to combine Si with other matching materials, such as ZnO, CdTe and organic materials [4–6]. Among them, the n-ZnO/p-Si heterostructure is especially attractive and has been extensively investigated due to the interesting physical properties of ZnO, including direct wide band gap (3.37 eV), large exciton binding energy (60 meV), and high quantum efficiency [7]. As a material, ZnO can be grown as thin films and nanostructures. ZnO nanorods (NRs)/p-Si heterostructure is preferred for photovoltaic applications, because its unique structure could provide more direct electrical pathways, and light scattering and trapping [8]. To date, although great progress has been made in the development of the ZnO NRs/p-Si heterojunction based structure, their photoelectric efficiency is still unsatisfactory for practical application [9–12]. Therefore, the fundamental understanding of the surface photogenerated charge is desirable and crucial for further improving the optoelectronic performance based on ZnO NRs/Si structure.

The Kelvin probe (KP) is a noncontact and nondestructive device for measuring the surface work function of semiconductor materials, which can be used to characterize the surface defect states with high surface sensitivity [13]. To date, KPs have been widely used for characterizing the surface photovoltage and the photogenerated charges of ZnO material in different structures, such as ZnO, ZnO/ITO (indium tin oxides), ZnO/P3HT (poly-3-hexyl-thiophene) and ZnO/CuPc (copper phthalocyanine) [14–19]. Their results have further demonstrated that the KP technique is a powerful method for characterizing ZnO with more surface defects. Nevertheless, so far there are few reports about the surface photogenerated charges of ZnO NRs/Si structure investigated by KP-based surface photovoltage (SPV) technology.

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1369-8001/$ - see front matter
http://dx.doi.org/10.1016/j.mssp.2012.10.016

In this study, controllable growth of p-type ZnO NRs was achieved on a p-type Si substrate via low-temperature wet chemical bath deposition (CBD) methods. The influence of the ZnO NRs/Si structure surface on photogenerated charges properties was systematically investigated using KP-based SPV technology. The results could help to improve the performance of photovoltaic devices based on a ZnO NRs/Si heterostructure.

2. Experiments

The p-Si (1 0 0) wafer was chosen as the substrate. After a standard cleaning process, the substrate was dipped in a 5% dilution of HF to remove residual oxide. For the growth of well-aligned ZnO NRs, the wet CBD method was used, which has been shown to be a high-performance growth technique for ZnO NRs due to its advantages such as low cost, lack of toxicity, and environmental friendliness [20]. Briefly, a thin ZnO seed layer was fabricated on the preprocessed substrate to promote vertically aligned NRs by radiofrequency magnetron sputtering. Subsequently, ZnO NRs were grown on the seed layer from the precursor solutions composed of equimolar zinc acetate ($C_4H_6O_4Zn \cdot 2H_2O$, 98%) and hexamethylenetetramine ($C_6H_{12}N_4$, 99%) in a sealed container. The detailed fabrication process has been described elsewhere [21]. Consequently, ZnO NRs/Si structures for KP-based SPV measurement were constituted.

The crystal structure of ZnO NRs on bare Si substrate was determined by X-ray diffractometry (XRD) on X'Pert Pro (PANalytical, Almelo, The Netherlands). Field-emission scanning electron microscopy (FESEM) on S-4800 (Hitachi, Tokyo, Japan) was used to observe the morphology of ZnO NRs/Si structure. KP-based SPV results were obtained by Scanning Kelvin Probe System SKP5050 (KP Technology Ltd., Wick, Caithness, UK) and a 250 W tungsten–halogen lamp source with a double additive grating scanning monochromator (Gemini180; Horiba, Kyoto, Japan). The width of the gold reference probe was 1.8 mm and the incident angle of light was about 45°. The scanning step of the KP system was set to be roughly 30 nm/min. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1(a) shows the typical XRD pattern for the ZnO NRs/Si structure. A dominant ZnO (0 0 2) diffraction peak accompanied with a rather weak ZnO (1 0 0) diffraction peak was observed, which indicated that the wurtzite polycrystalline ZnO NRs were achieved with the preferentially oriented growth along the c axis. No other compound peaks were detected besides those of ZnO.

Fig. 1(b)–(d) shows SEM images of ZnO NRs/Si structure as a function of growth time from 1 to 5 h. The insets are the corresponding cross-section images of ZnO NRs/Si structures. Vertically well-aligned ZnO NRs with a hexagonal prism shape were independent of the growth time. Besides, each NR had a uniform diameter distribution along its entire length, showing that the growth anisotropy was constantly kept during the growth process [21]. The average diameter and length of ZnO NRs increased from ~50 to ~150 nm and from ~150 to ~2500 nm, respectively, when the reaction time was increased from 1 to 5 h. Therefore, it is possible to control the length and diameter of ZnO NRs on bare Si substrate by simply adjusting the growth time.

To characterize surface-photogenerated charges for ZnO NRs/Si structures, the KP system was used to measure the contact potential difference (CPD), which is sensitive to surface charge changing [22,23]. In the KP-based SPV measurement, the CPD values from the surface of the samples were measured with respect to the reference gold probe in dark steady-state (Fig. 2). In general, the CPDs of both bare Si and ZnO NRs/Si structures exhibited a negative value, which indicated that their surface work function was less than that of the gold probe (5.1 eV). An evident shift to the higher CPD was observed in the ZnO NRs/Si structure compared with the bare Si substrate, which was attributed to the induced surface properties change of the ZnO NRs/Si structure, due to the incorporation of ZnO NRs. In addition, the degree of CPD shift was significantly influenced by the growth time of ZnO NRs, with the biggest shift achieved for the samples grown for 5 h. The detailed mechanism will be discussed later combined with PV spectra under illumination.

After CPD reached a steady state in the dark, KP-based SPV spectrum measurement was carried out by illumination with a wavelength from 1400 to 300 nm. Fig. 3 shows the KP-based SPV spectra under illumination, $-\Delta$CPD was used to show clearly the variation of surface charges in ZnO NRs/Si structures. The spectra can be reasonably divided into three distinct regions. In region I (illuminated with light in the range of 1250–1050 nm), a steep decrease in $-\Delta$CPD was observed for bare Si, whereas there was only a slight decrease in $-\Delta$CPD for ZnO NRs/Si structure, which indicated that bare Si surface was the dominant factor in determining the $-\Delta$CPD value. This can be understood by considering that the photon energy in this region was not high enough to excite ZnO NRs, which made a negligible contribution to the SPV response for ZnO NRs/Si structure in this region. In region II (illuminated with light in the range of 1050–420 nm), no significant change in $-\Delta$CPD was observed, which suggested nearly stable surface charges in ZnO NRs/Si structure. In region III (illuminated with light in the range of 420–300 nm), there was a marked positive response in $-\Delta$CPD for ZnO NRs/Si structure grown for 5 h, which indicates that the SPV response range for ZnO NRs/Si structure can be expanded because of the incorporation of ZnO NRs. Moreover, an enhanced SPV response amplitude was observed for the ZnO NRs with longer length and larger diameter.

According to the KP-based SPV spectra under illumination (Fig. 3), the marked SPV responses in ZnO NRs/Si structure were only observed in two regions, that is, in the IR region with bare Si being the dominant factor, and in the UV region with ZnO NRs being the dominant factor. Therefore, to investigate further the SPV response mechanism, the $-\Delta$CPD variation with time was recorded to exhibit clearly the surface charge evolution when the samples were illuminated with IR/UV light on and off. Fig. 4(a) shows the SPV response with 1050 nm light on and off. It can be seen that the SPV response of bare Si was rapidly decreased when illuminated with 1050 nm, and then it stabilized for some time when the