Towards Perfectly Ordered Novel ZnO/Si Nano-Heterojunction Arrays

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The fabrication of a highly ordered novel ZnO/Si nano-heterojunction array is introduced. ZnO seed layer is first deposited on the Si (P<111>) surface. The nucleation sites are then defined by patterning the surface through focused ion beam (FIB) system. The ZnO nanorods are grown on the nucleation sites through hydrothermal process. The whole fabrication process is simple, facile and offers direct control of the space, length and aspect ratio of the array. It is found that ZnO/Si nanojunctions show an improved interface when subjected to heat treatment. The recrystallization of ZnO and the tensile lattice strain of Si developed during the heating process contribute the enhancement of their photoresponses to white light. The photoluminescence (PL) measurement result of nano-heterojunction arrays with different parameters is discussed.

1. Introduction

Nano-heterojunction semiconductor structures are material systems dominated by the interfacial properties of at least two dissimilar semiconductor material components which are in contact with each other at nanoscale. These interfaces can provide greater functionality than individual components. An example is the interface formed between unequal band gap semiconductors, which is responsible for the charge dynamics of the nano-heterojunction, including electron affinity and work function.[1] To date, a great deal of effort has been made to design, fabricate and characterize various nano-heterojunctions with the main focus on the interface in terms of its dimension, morphology, lattice mismatch, strain and defects.[2-4] The defects present at the interface between ZnO/Si junction, for instance, were reported to contribute to the emission of luminescence in the visible region.[5] Defect-free heterojunction interfaces enable the increase of the diode quantum efficiency for light-emitting diodes (LED).[6] Thus, manipulation of the interfaces of nano-heterojunctions allows us to tailor their properties for the desired technological applications, such as light emitters, photodetectors, transistors and thermoelectric devices.[7-9]
Wurtzite Zinc oxide has a direct wide band gap (3.37 eV), large exciton binding energy (60 meV) and excellent electronic and optical properties. It has strong absorption in the ultraviolet (UV) region, on the other hand, less than 30% of the UV light (wavelength shorter than 380 nm) is usable for commercial silicon solar cells. Meanwhile, ZnO is abundant, cheap, and friendly to the environment.

Aligned ZnO nanorods exhibit excellent light emitting and field emission performance. The fabrication and characterization of ordered heterojunctions between ZnO nanostructures with other semiconducting materials has been reported. The fabrication of ZnO nanostructures is facile and thoroughly investigated. Thus, ZnO is an attractive candidate as the UV absorber integrated in Si solar cells. Solar cells based on Si/ZnO heterojunctions have been demonstrated, though the conversion efficiency is still low (<0.2%).

In the present work, we introduce a simple way to grow ZnO nanorods on top of ordered Si nanoneedles, forming a perfect array of ZnO/Si nano-heterojunctions with controllable shape and size. The ordered Si nanoneedle array was first fabricated on the surface of a Si substrate coated with thin layer of ZnO with a thickness of approximately 50 nm using the method that we developed previously and described in detail in the literature. Subsequently, the growth of ZnO nanorods was carried out through a hydrothermal approach, in which zinic nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and hexamethylenetetramine (HMTA) were used as reactants. Finally, a perfect array of ZnO/Si nano-heterojunctions was obtained. In order to find out the effect of the microstructure of nano-heterojunctions on their electronic properties, the sample with ordered ZnO/Si nano-heterojunction array was annealed under 200 °C in the tube furnace with the argon (Ar) gas flow. Their crystallography and interfacial structure were view by high resolution transmission electron microscopy (HRTEM) with their photoresponses and PL properties being also evaluated.

2. Result and Discussion

Figure 1a is a secondary electron image of an ordered Si nanoneedle array captured in a focused ion beam/scanning electron microscope (FIB/SEM) system at an inclined angle of 52°. A thin layer of ZnO is visible on the top of each nanoneedle in the TEM. Supporting Information Figure S1a shows a bright-field TEM cross-sectional image of a nanoneedle, where the thickness of ZnO layer was measured to be ~50 nm. It is this thin layer that acts as a seed layer for the growth of ZnO nanorods above the individual nanoneedles, leading to a perfect ZnO/Si nano-heterojunction array. One example is shown in Figure 1b, where the ZnO nanorods appear crystalline and are oriented vertically relative to the surface of the Si substrate. It is also seen that there are a few ZnO nanorods located on the top of each Si nanoneedle. These nanorods are packed together and perfectly aligned with the Si nanoneedle structure array (see inset in Figure 1b). All the ZnO nanorods in the array have about the same height of ~800 nm. The length of ZnO nanorods could be controlled by simply changing the growth time and the solution concentration.

The optoelectronic performance of ZnO/Si nano-heterojunctions is mainly determined by their interfaces, which are the boundary separating ZnO and Si. To examine this interface, cross-sectional TEM samples for ZnO/Si nano-heterojunctions were prepared using FIB by lift-out method. An example of bright-field TEM images of several nano-heterojunctions is shown in Figure 2a. Each nano-heterojunction consists of ZnO and Si as proved in Figure 2b, which is an elemental distribution map performed using energy-filtered TEM technique across the middle nano-junction in Figure 2a. Each ZnO nanorod is found to be connected to Si by a thin layer. This layer is found to be amorphous by HRTEM, for example in Figure 2c, which is a HRTEM image of the area marked ‘A’ in Figure 2a. Its thickness is measured to be ~3 nm. This thin amorphous layer was introduced from the original Si substrate as a result of Si surface oxidation during deposition of the ZnO seed coating in the sputtering system (see Figure S1b).

The interface of the ZnO seed layer with the ZnO nanorods is visible (as marked by an arrow → and ‘C’ in Figure 2a) but not as clear as the amorphous layer. This is due to their close orientation relationship, which results in very little difference in diffraction contrast in the TEM image. The ZnO seed layer is polycrystalline (Figure 2c) but exhibits a preferential growth direction along <0 0 1>, as indicated by the X-ray diffraction (XRD) pattern (Figure S2) collected from the as-deposited ZnO seed layer. It is therefore reasonable that the ZnO nanorods are single crystals (Figure 2d, a HRTEM image of the marked area ‘B’ in Figure 2a) and were also grown along <0 0 1> direction. This interpretation is supported by the indexed fast fourier transform (FFT) sharp pattern (inset in Figure 2d) taken from the whole image of Figure 2d at a zone axis of [1 1 0] or [1 1 0]. On the other hand, this close orientation relationship brings about very low strain (close to zero) to the ZnO rod above the thin amorphous layer (Figures 2e,f), which are strain maps of the ZnO and Si lattices in Figure 2c.

$I$–$V$ curve measurements were carried out and results show that ZnO/Si nano-heterojunction array prior to heat-treatment presents diode characteristic (blue line in Figure 3a; rectification ratio = 11; ideality factor = 8.0) but is not as good as the heat-treated nano-heterojunction array (red line in Figure 3a; rectification ratio = 59; ideality factor = 4.6). This ideal response of current against forward and reverse bias indicates the perfection of the ZnO/Si
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A number of such nano-heterojunctions that are perfectly arranged across the Si substrate surface can provide a building block to fabricate various types of optoelectronic nanodevices, such as photodetectors or photovoltaic solar cells with significantly enhanced properties. For example, the blue line in Figure 3b is a plot of the photoresponse of nano-heterojunction array as a function of time when the white light was switched on and off repeatedly. Both “On” and “Off” currents in each cycle remain the same, which indicates the good reversibility and stability of the ZnO/Si nano-heterojunction optical switch. Meanwhile the device has a fast photoresponse with short rise and decay times which are below 1 s. The On/Off ratio is calculated to be around 2.6.

The photoresponse of the heat-treated nano-heterojunction array is shown as red line in Figure 3b, where the On/Off ratio rises up to around 3.3, almost 30% higher than nano-heterojunction without heat-treatment. This is due to the heating process that improves the ZnO and Si interface. The crystallinity of ZnO nanorods increases through the recrystallization of the polycrystalline ZnO during the heating, as demonstrated from the Morie fringes as well as the sharper interfacial edges of ZnO and Si lattices adjacent to the thin amorphous layer (Figure S3). This is also supported by the PL spectra shown in Figure S4, in which the broad visible band emission is significantly suppressed after the heat treatment, indicating fewer defects in the ZnO nanorods. In contrast to the non-heat-treated nanojunctions, the ZnO and Si lattice strains for the heat treated nanojunctions were performed using a high resolution image (Figure 4). It was found that the ZnO lattice strain still remains sufficiently low (Figure 4b). However, the Si lattice shows a tensile strain (Figure 4c). We value this tensile strain as it has been proven to enhance the carrier mobility and thus increase the photoresponse to white light.26,27

It is advantageous that the morphologies of nano-heterojunctions, dependent on the chosen parameters during their assembly, are easily controllable. For example, Figure 5a–d present four different morphological ZnO nanorods grown on the top of nanoneedles with the different sharpness brought about by different the patterning times of the ion beam on Si substrate (a: 210 s, b: 250 s, c: 300 s and d: 340 s).

PL spectra were acquired from the aligned ZnO/Si nano-heterojunctions to investigate their collective optical properties. The PL measurements were performed at room temperature using a 325 nm He-Cd laser as the excitation light source. The 2400 lines mm⁻¹ was selected for the measurement. The integration time was set to be 10 min. Figure 5e shows the characteristic PL spectra of the nanoarray samples with different patterning times. In the spectrum, curves a–d in Figure 5 were collected from the nano-heterojunctions. All PL spectra contain a UV emission band centered at 380 nm as well as a wide green to red band. The sharp UV peak is the near band-gap emission of ZnO, while the broad visible band emission is attributed to the recombination of photo-generated holes with singly ionized charge states at the defects in the ZnO nanorods, such as oxygen vacancies.28,29 The relationship of the diameter of the top Si needle, the average diameter of the ZnO nanorods and the corresponding ratio between the height of UV peak and the visible peak is shown in Figure 5f. It is observed that with decreasing the top Si cone size, the ZnO nanorods become thinner and the relevant ratio of the peaks (UV band/visible band) in PL is also found to be smaller. This phenomenon can be explained by the size effect in relation to the surface recombination.30 ZnO nanorods with smaller diameter have larger specific surface area, which leads to higher
surface luminescence. This result indicates that through the control of the patterning time, we are able to control the diameter of the ZnO nanorods grown in the nano-heterojunctions, and then modify the PL properties. The correlation between the morphologies and the PL properties of the nano-heterojunctions will be further investigated in the future.

3. Conclusion

In this work, we have presented a novel approach for the production of highly ordered and vertically aligned ZnO/Si nano-heterojunctions. The space, height and aspect ratio of the nano-heterojunction could be controlled through tailoring the ion beam parameters (e.g., ion current and energy), the reaction time of the hydrothermal process and the concentration of the aqueous solution. The crystallography and the interface structure were studied by TEM. The photoresponses to white light before and after heat treatment, and PL properties of nano-heterojunctions with different morphologies, were measured. The well designed and highly controllable ZnO/Si nano-heterojunctions are building blocks to fabricate devices with the enhanced optoelectronic efficiency for multi-functional applications.

4. Experimental Section

**Fabrication of the Silicon Nanoarrays:** ZnO seed layer with thickness of \( \approx 50 \) nm was coated on the surface of conductive p-type Si (001) as the substrate through a radio frequency (RF) magnetron sputtering system. XRD and SEM energy-dispersive X-ray spectroscopy (EDX) were performed to characterize the ZnO seed layer. Subsequently, a nanoarray structure of silicon, with ZnO seed layer on the top, was fabricated in the FIB system (FEI Nova Nanolab 600i). FIB is usually used to prepare thin-film samples in semiconductor industry or material science. In this article, ion beam was used to pattern the surface of the Si substrate,\(^{[22]}\) with the energy of 30 keV and the current of 0.46 nA (The current was an important parameter which would determine the profile of the Si arrays. Normally a larger beam current means a larger spot size). The ion beam was perpendicular to the surface of the ZnO/Si substrate. A square mesh pattern...
of 20 μm x 20 μm was scanned with the adjacent controllable space, dwell time of 1 μs, overlay 50%, and pitch of 17.50 nm. The total scan period was controlled to adjust the aspect ratio of the arrays.

**Growth of ZnO Nanorods:** Zn(NO$_3$)$_2$·6H$_2$O and HMTA were first dissolved in deionized water (DI water) respectively. Then these two solutions were mixed and stirred. ZnO/Si substrate with the rinse in DI water and finally dried in air at room temperature. The heating rate was set to be 3 °C min$^{-1}$ and the cooling rate was 10 °C min$^{-1}$.

**Heat Treatment:** Heat treatment of the samples after the growth of ZnO nanorods was carried out under 200 °C for one hour in the tube furnace with the Ar gas flow. The heating rate was set to be 3 °C min$^{-1}$ and the cooling rate was 10 °C min$^{-1}$.

**Characterization:** SEM images were collected in the dual beam FIB system (FEI Nova Nanolab 600i). TEM (JEOL 2010F) was employed to study the interface of the nano-heterojunction. PL measurement was performed on Renishaw with a Kimmom IK5751-G UV laser (325 nm). Keithley 4200 Micromanipulator was used to examine the electrical properties and photoresponse of the nano-heterojunctions.

**Strain Analysis:** Geometric phase analysis method was employed to map the strain fields with HRTEM images of ZnO and Si in Figure 2c, which were processed using commercial software GPA Phase developed by the Gatan DigitalMicrograph environment.

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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