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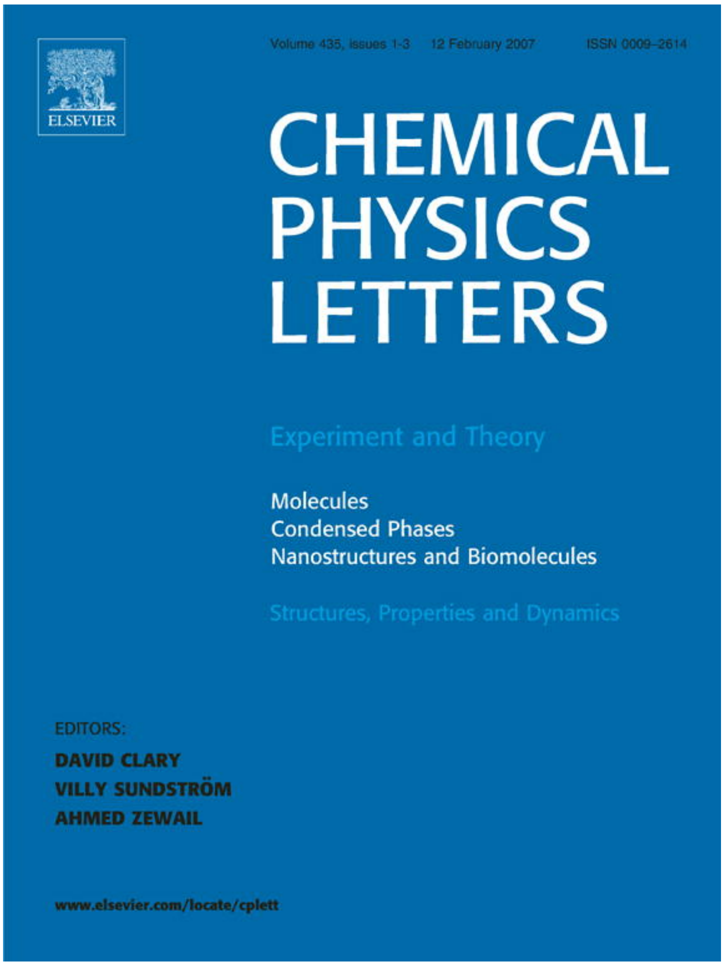

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Electrical and photoelectrical performances of nano-photodiode based on ZnO nanowires

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Abstract

A prototype nano-photodiode has been demonstrated based on heterojunctions between ZnO nanowires and p-Si substrate. The electrical and photoelectrical performances of the ZnO/Si structure have been characterized by a conducting atomic force microscopy at nanometer spatial resolution. The photoelectrical measurements demonstrate that the photodiode has high sensitivity and selectivity to UV light.
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Photodetector, such as photoconductor and photodiode, is a transducer capable of accepting an optical signal and producing an electrical output, which is an important component for integrating nanophotonics with nanoelectronics. Using low-dimensional nanostructures, nano-scale light sources have been made using nanodots [1], nanotubes [2], and nanowires (NWs) [3,4]. Nano-scale photodetector for light has been demonstrated using semiconducting NWs [5].

p–n photodiodes, as an alternative form of photodetectors, is based on carrier production in the high field junction region, and it has a response time considerably faster than that of a photoconductor and is typically in the order of nanoseconds. Internal noise in the photodiode is quite low, providing a high signal-to-noise ratio. On the other hand, the photodiode produces more linear response and higher sensitivity than the photoconductor [6]. Photodiodes are often used for accurate measurement of light intensity in science and industry as well as consumer electronics. They are also widely used in various medical applications, such as detectors for computed tomography [7], blood gas monitors [8], and immunoassay [9].

ZnO exhibits the most diverse and abundant configurations of nanostructures known so far, such as NWs [10], nanobelts [11], nanosprings [12], nanorings [13], nanobows [14], and nanohelices [15]. Numerous studies have demonstrated novel nanodevices and applications based on ZnO nanostructures, such as nanolaser [3], nanogenerator [16], and acoustic resonator [17]. In the field of photodetection, although a few studies have demonstrated novel photoconductor based on nanostructures recently [18,19], little work has been done in photodiode based on nanostructures.

In the present study, the electrical and photoelectrical performances of the nano-photodiode based on a heterojunction of n-ZnO NWs with p-Si substrate with spatial resolution at the nanometer scale have been investigated using a conducting atomic force microscopy (C-AFM). The photoelectrical measurements demonstrate that the photodiode has high sensitivity and selectivity of UV light. The heterojunction of ZnO/Si based on ZnO NWs could open new opportunities ranging from integrated photonics, such as the integration with nano-light-emitting diodes (nano-LEDs) and nanolasers, to bio-sensing by real-time near-field bioluminescent detection.

The ZnO NW arrays used for the experiments were grown using a vapor–liquid–solid process [20]. For fabricating heterojunction n-ZnO/p-Si photodiode, the sub-

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strate-bound ZnO NWs were mechanically scrapped off and sonicated in ethanol and deposited on boron doped Si(1 1 1) substrate, which has a resistivity of 0.01–0.018 Ω cm and 510–540 nm in thickness. The Si wafers were cleaned chemically by a standard Radio Corporation of America (RCA) cleaning process, which is the industry standard for removing contaminants from wafers before contacting with ZnO. To obtain good contact between ZnO and Si, a heat treatment was carried out in a rapid thermal annealing apparatus at 300 °C for 30 s in N_2 ambient.

Electrical and photoelectrical measurements of heterojunctions between ZnO NWs and p-Si substrate were made using a standard commercial instrument (OMICRON ultra-high-vacuum variable temperature atomic force microscopy (AFM)). The pressure in the analysis chamber was below 5×10^{-11} mbar during the experiments. C-AFM measurements were carried out in contact mode using silicon cantilevers with constant loading forces in the range between 30 nN and 50 nN. To protect the tip from failing, the maximum of injection current was limited to less than 50 nA during C-AFM measurements. The AFM tip was precoated with a PtIr layer, provided by the manufacturer (Nanosensors), and subsequently coated with a Ti/Au (30 nm/30 nm) film by electron beam evaporation for obtaining ohmic contact between Ti and ZnO. 30-nm-thickness Pt was also sputtered onto the backside of the p-type Si substrate to obtain ohmic contact. C-AFM tip is used to apply voltage and measure the current through the NW and Si substrate. The light source for photoelectrical characterization was fixed at wavelengths of 254 nm and 365 nm. The illumination power was controlled at 4 W (UVP, UVGL-25).

By controlling the experimental condition, ZnO NW arrays were first grown on (11–20) Al_2O_3 substrate surface using Au as catalyst. The scanning electron microscopy images of the as-grown ZnO NWs on an Al_2O_3 substrate, displaying well-aligned distribution and uniformity in diameter. The structure of the ZnO NWs has been characterized by transmission electron microscopy, showing the phase of NWs is hexagonal wurtzite structure and the growth direction of ZnO NW arrays is [0 0 0 1] [20].

The current–voltage (*I–V*) curves measured for a ZnO NW deposited on an insulating layer and connected by a pair of Ti/Au electrodes, and a boron-doped Si substrate connected by a pair of Pt electrodes indicate that the linear trend shows the establishment of Ohmic contacts. After ensuring Ohmic characteristics for the metal–semiconductor interface, *I–V* characteristics of the Si/ZnO heterojunction could be measured.

An undoped ZnO NW usually shows n-type characteristics due to the presence of zinc interstitials and/or oxygen vacancies. Considerable studies on ZnO-based optoelectronic thin-film devices were carried out by fabricating heterojunctions employing as-grown n-type ZnO with other p-type materials [21,22]. After fabricating heterojunction based on ZnO NWs, electrical measurements were performed in C-AFM, as shown in Fig. 1. One of the main features of the C-AFM is precisely locating the objects by using topographic imaging. The C-AFM probe was positioned directly onto the NW, and used to apply voltage and measure the current through the NW and Si substrate, as shown in Fig. 2a. We particularly probed vertical electron transport as a function of location along the ZnO NW. Studies of the *I–V* characteristics of the fabricated n-ZnO NW and p-Si structure revealed a good p–n heterojunction. Fig. 2b shows the *I–V* characteristics in the absence of light illumination at room temperature, taken from ‘a’, ‘b’, and ‘c’ points on the NW. There is no difference in *I–V* curves along the ZnO NW, indicating good contact between the ZnO NWs and Si substrate. A pronounced rectifying diode-like behavior with a threshold voltage of ~1.5 V is clearly observed. A small reverse leakage current less than 0.2 nA was observed at −3 V reversed bias. The forward current was as high as 50 nA at 2 V forward bias.

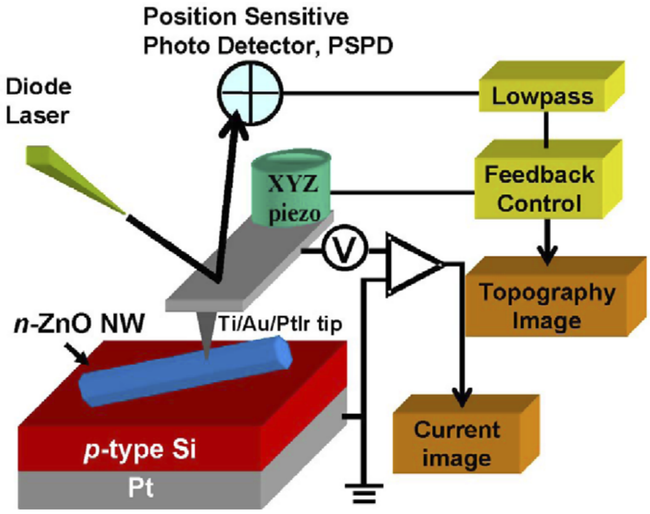

Fig. 1. Schematic diagrams of the vertical *I–V* measurements of nano-photodiode by C-AFM in the absence of any input optical signal at room temperature. C-AFM tip is used to apply voltage and measure the current through the NW and Si substrate.

The mechanism of the NW-based n-ZnO/p-Si diode is described as follows. Before n-ZnO and p-Si are in contact, the n-ZnO NW has a high concentration of electrons and few holes, while the p-Si is rich in holes but with few electrons. Upon contacting, diffusion of carriers would take place at the interface because of the large carrier concentration gradient at the junction. Thus holes diffuse from the p-Si side into the n-ZnO side, and electrons diffuse from n-ZnO into p-Si. Although the electrons and holes can move to the opposite side of the junction, the donors and acceptors are fixed in space. When electrons diffuse from the n-ZnO to the p-Si side, they leave behind uncompensated donor ions in the n-ZnO material, and holes leaving the p-Si region create uncompensated acceptors. The diffusion of electrons and holes from the vicinity of the junction establishes a region of positive space charge near the n side

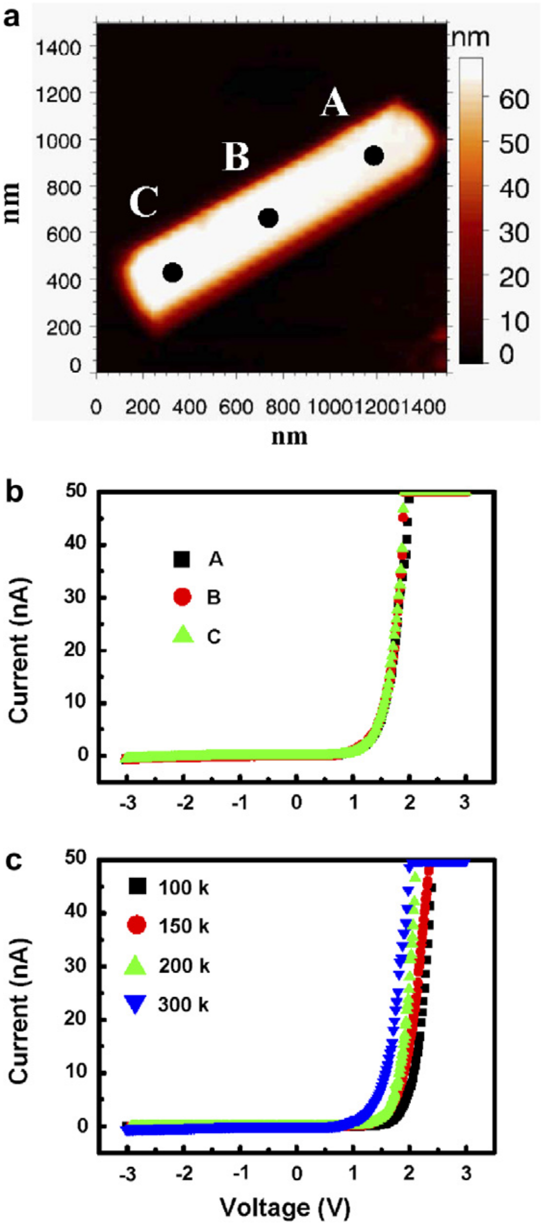

Fig. 2. (a) AFM topography image of nano-photodiode based on ZnO nanowires. (b) Electron transport characteristics of nano-photodiode at different positions along the ZnO NW. (c) Temperature-dependent *I–V* characteristics for n-ZnO/p-Si nano-photodiode were recorded at 100 K, 150 K, 200 K, and 300 K.

of the junction and negative charge near the p side. An electric field is built up at the interface. At zero voltage bias, the energy gaps (E_g) for ZnO and Si are 3.27 eV and 1.12 eV, respectively. The electron affinity for ZnO is taken as 4.35 eV, and the electron affinity of Si is 3.95 eV. The energy barrier ΔE_c for electrons is $\Delta E_c = \chi_{ZnO} - \chi_{Si} = (4.35 - 3.95)$ eV $= 0.4$ eV, while the energy barrier ΔE_v for holes is $\Delta E_v = E_{g,ZnO} + \Delta E_c - E_{g,Si} = (3.27 + 0.4 - 1.12)$ eV $= 2.55$ eV. Thus, the energy barrier for holes (ΔE_v) is six times more than the barrier for electrons (ΔE_c). i.e. when a reverse bias is applied, holes attempting to move and encounter ΔE_v, yielding a low current. In contrast, when a forward bias is applied, the electron only need overcome a much smaller potential barrier (ΔE_c), thus giving rise to the rectifying effect. These arguments are for the ideal case, and direct measurements are required to determine the exact band structure of the heterojunction.

The *I–V* characteristics show thermally activated diode-like rectifying behavior, as indicated in Fig. 2c. It demonstrates that the small reverse current is slightly temperature-dependent. However, the magnitude of the forward current at a given voltage decreases significantly with decreasing temperature. This behavior is consistent with tunneling through a barrier out of occupied levels whose population is slightly modified by the nonzero temperature, and a potential barrier that allows increased penetration with increasing forward voltage [23].

In addition, ZnO NW-based nano-photodiodes were designed to be responsive to optical input. Photodiodes usually have extremely high resistance when reverse biased. This resistance is reduced when light of an appropriate frequency illuminates on the junction to create additional free electron–hole pairs. Hence, a reverse biased diode can be used as a detector by monitoring the current running through it. The *I–V* characteristics are shown in Fig. 3, where clear rectifying behavior can be observed both in the dark and under UV illumination conditions (365 nm and 245 nm). Distinct response to UV illumination can be seen from Fig. 3 in the reverse biased condition due to the photogeneration of additional electron–hole pairs. The magnitude of photocurrent increases with the increase of applied reverse bias due to enhanced carrier collection. The photocurrents for 365 nm and 245 nm are 0.93 nA and 1.27 nA, respectively, with the −3 V reversed bias. On the other hand, the dark leakage current for the ZnO photodiodes is weak (0.6 nA in the −3 V reversed bias). This behavior indicates that ZnO photodiodes can sensitively detect UV light to produce the measurable photocurrent response. Compared to 365-nm light source, higher reverse photocurrent was produced with 254-nm energy. The possible mechanism could be proposed as follows. Under a reverse bias condition,

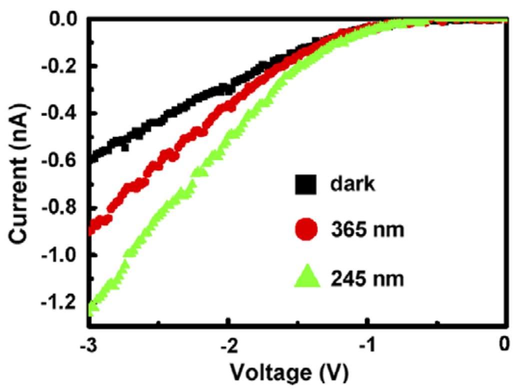

Fig. 3. Photocurrent versus reverse-bias voltage (photo *I–V*) curves for two UV wavelengths of illuminations. Dark *I–V* curve is also indicated as a reference. All of the curves demonstrate a strong rectifying behavior.

$$I_{ph} = I_n + I_p = q\Delta n \upsilon_n + q\Delta p \upsilon_p \quad (1)$$

where I_{ph} is the total photocurrent, I_n the photocurrent by electrons, I_p the photocurrent by holes, q the electronic charge, Δn and Δp the average photon generated electrons and holes, respectively, υ_n and υ_p the average velocities of electrons and holes, respectively, in a given depletion field. It is likely that UV photons with higher energies create more electron–hole pairs in the depletion region, leading to a higher I_{ph} in Eq. (1). ZnO NWs possessing cambered surface area and small diameter on the surface of Si could make the entire junction (n-ZnO and p-Si depletion region) effective for receiving the illumination of incident photons with little damping in intensity caused by the penetration-depth.

In summary, we have demonstrated the electrical performances of a nano-photodiode based on a heterojunction of n-ZnO NW with p-Si substrate with spatial resolution at the nanoscale using C-AFM. The temperature-dependent transport has been investigated. The photoelectrical measurements demonstrate that the heterojunction based on ZnO NW has high sensitivity and selectivity with UV light. This study presents the potential of using NWs in diverse areas, ranging from integrated photonics, such as the integration with nano-LEDs and nanolasers, to bio-sensing by real-time near-filed bioluminescent detection.

Acknowledgments

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