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Schottky diodes based on electrospun polyaniline nanofibers: Effects of varying fiber diameter and doping level on device performance

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ABSTRACT

Electrospinning is used to fabricate Schottky diodes using polyaniline nanofibers and n-doped Si. By varying the fiber diameter, and also by varying the fiber doping level at a fixed diameter, we compare the device performance and examine the role of surface states on barrier height and charge transport. The diode electrical characteristics were analyzed using the standard thermionic emission model of a Schottky junction. Clear rectification is observed for diodes fabricated from thick fibers with significantly reduced rectification ratios for diodes fabricated from thinner ones. The surface states on the semiconductor exert a weaker influence on diodes fabricated from thinner fibers due to the reduced junction area, and for the thinnest fiber where the depletion width is expected to be negligible, the analysis suggests an additional charge transport mechanism other than thermionic emission at the junction. On the other hand, varying the fiber doping level lowers the diode rectification ratio but other diode parameters are relatively unaffected.

1. Introduction

Polyaniline is an organic conducting polymer that has been extensively investigated for the past two decades. Initial studies on this polymer focused on understanding charge transport mechanisms but later shifted to devices and sensor applications. Recent advances in fabricating polyaniline nanofibers [1,2] has extended previous research efforts that concentrated on thin films or other bulk forms of the polymer. An organic/inorganic Schottky diode is one of the simplest devices to fabricate and consists of a junction formed by a conducting polymer and an n-doped inorganic semiconductor (n-Si). This construction has been achieved in the past via electrochemical polymerization [3–6] or spin coating [7] of the polymer onto the semiconducting substrate. Using a simple electrospinning technique, we fabricate in air, and within seconds, Schottky diodes using polyaniline nanofibers and an inorganic n-doped semiconductor [8,9]. Under thermal equilibrium conditions with no applied external bias to the diode, the Fermi levels of the doped Si and that of polyaniline must be coincident leading to band bending at the junction via the flow of charge from the semiconductor into the polymer. This creates a depletion layer resulting in a potential barrier to charge flow from the polymer nanofiber trying to move into the semiconductor at the nanofiber/semiconductor interface. Fig. 1 shows the schematic band diagram of the relevant energy levels at the polymer nanofiber/n-Si interface. For typical Schottky diodes, charge flow is via thermionic emission over the barrier. Generally, the barrier height is determined by factors such as the polymer work function and the surface states on the semiconductor [10]. In this work, we fabricate and test Schottky nanodiodes using polyaniline nanofibers with different diameters and different doping levels, compare device performance and examine the role of these factors on barrier height and charge transport. As the fiber diameter decreases the diode exhibits poor rectification with the magnitude of the reverse bias currents comparable to that observed under forward bias implying a reduced barrier and an additional form of charge transport other than thermionic emission under normal operating conditions. Lowering the fiber doping level via exposure to NH_3 gas at a fixed fiber diameter decreases the rectification ratio while the other diode parameters are relatively unaffected. Raising the doping level (via annealing) leads to a recovery of the original diode behavior making the device operate as a reusable gas sensor as well.

2. Experimental

A commercially available n-doped Si wafer (⟨111⟩, 0.1–1.0 Ω cm) with a 200 nm thermally grown oxide layer was used as the

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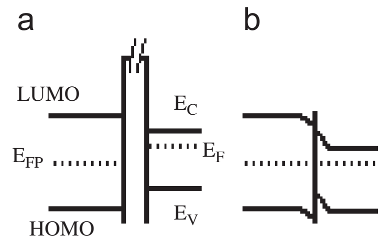

Fig. 1. Schematic energy band diagrams for the formation of the polyaniline/n-Si interface (a) before and (b) after contact. E_C and E_V are the conduction and valence band edge energies of the n-Si. E_F and E_{FP} are the Fermi energy levels of the n-Si and polyaniline, respectively. The LUMO and HOMO levels for polyaniline are also indicated. After contact, band bending helps to establish a constant Fermi energy level across the interface at thermal equilibrium.

substrate and formed part of the diode construction. After prepatterning gold electrodes over the oxide via standard lithography and the lift-off techniques the substrate was cleaved in air through the electrodes. The exposed cleaved surface has the edge of the gold electrode separated from the doped Si by the insulating oxide layer. A doped polyaniline nanofiber was then deposited over the wafer edge via electrospinning and completed the Schottky diode construction. The polyaniline nanofiber was prepared as follows: 100 mg of emeraldine base polyaniline was doped with 129 mg of camphorsulfonic acid (PANi-HCSA) and dissolved in 10 ml $CHCl_3$ for a period of 4 h. The resulting deep green solution was filtered and a small amount (<10 wt%) of polyethylene oxide (PEO) was added to the solution and stirred for an additional 2 h. PEO was added to assist in fiber formation, and the solution was then filtered using a 0.45 μm PTFE syringe filter. Using a very simple electrospinning technique reported earlier [1] individual, charged, dry and flexible polyaniline nanofibers were deposited over the wafer edge making contacts to the gold and the doped Si and that are stable with no apparent degradation or oxidation. The resulting Schottky diode is formed along the vertical edge of the cleaved substrate at the nanofiber-doped Si interface. Such a vertical orientation may offer higher levels of integration in circuitry than that provided by in-plane horizontal structures. External electrical contacts to the diode were made via the use of gold wire (diameter ~25 μm) and silver paint. The diode was then mounted inside a closed chamber that was evacuated using a simple roughing pump, and its current–voltage (I–V) characteristics were measured in vacuum ($\sim 10^{-2}$ Torr) at room temperature using a Keithley Model 6517A electrometer. Varying the doping level of the fiber was achieved by placing the device in a closed chamber with ports for gas inlet and outlet. In the as prepared diode, the electrospun fiber is fully doped and is maintained that way by flowing dry N_2 gas over the device during the measurement, while lowering the fiber doping level was achieved by flowing NH_3 gas (obtained by bubbling the same N_2 gas into a concentrated NH_4OH solution) over the device for 45 s before turning it off and then performing the measurement. Fig. 2(a) shows a schematic of the device together with the external electrical circuit, and Fig. 2(b) shows a scanning electron microscope image of a polyaniline nanofiber at the wafer edge in a typical device.

3. Results and discussion

Fig. 3(a–c) shows the I–V characteristic curves at 300 K of diodes fabricated from polyaniline nanofibers having diameters 70, 50 and 30 nm, respectively, when the positive terminal of V_B was connected to the gold electrode for each device. When the positive terminal of V_B was connected to the doped Si terminal for each device, it was forward biased in the third quadrant thereby confirming the formation of Schottky barriers at the polymer/n-doped semiconductor junction. The diode rectification, defined as the ratio (I_{ON}/I_{OFF}) was calculated at bias voltages of ± 1 V. The diode resistances in the forward bias regime prior to turn-on and in the on state are also calculated. Table 1 shows the variation of these parameters as a function of fiber diameter. As expected, the resistances are seen to increase as the fiber diameter gets smaller due to reduced cross-section area for charge transport. The diode resistances are also higher in the presence of NH_3, as this gas de-dopes polyaniline making it more of an insulator.

In order to quantitatively analyze the diode characteristics we assume the standard thermionic emission model of a Schottky junction as follows[11]:

$$J = J_s\left[\exp\left(\frac{qV_B}{nkT}\right) - 1\right] \tag{1}$$

$$J_s = A^* T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \tag{2}$$

where J is the current density, J_s is the saturation current density, q is the electron charge, k is the Boltzmann constant, T is the absolute temperature, ϕ_B is the barrier height and n is the ideality factor which takes into account corrections to the original simple model e.g. image-force barrier lowering. The Richardson's constant ($A^* = (4\pi q m^* k^2)/h^3$) is calculated to be 120 A/K^2-cm^2 assuming m^* is the bare electron mass. Using the data in Fig. 3(a) as an example, the inset to this figure shows a representative semilogarithmic plot of the diode current versus applied voltage under forward bias conditions. At low biases a linear variation of the current is observed consistent with Eq. (1), while the deviation from linearity at higher bias voltages generally is related to ohmic losses due to the diode series resistance. Extrapolating the linear portion of the semi-log plot to zero bias yields a saturation current density of 6.5×10^{-2} A/cm^2 and the diode ideality factor calculated from the slope of the linear portion of this plot as follows:

$$n = \frac{q}{kT}\left(\frac{\partial V_B}{\partial \ln J}\right) \tag{3}$$

is $n\sim4$. Using these equations we calculate the barrier height of 0.49 eV while the rectification ratio is low and the ideality factor high compared to all inorganic Schottky diodes ($n = 1$ represents the ideal value), nevertheless the present design, size and the simple fabrication method via electrospinning makes this technique attractive in the mass production of such diodes.

In a similar manner, the data in Fig. 3(b and c) were analyzed and the results tabulated as a function of fiber diameter. Table 1 shows that as the fiber diameter is reduced, the diode series resistance increases, reducing the rectification ratio and the diode turn-on voltage decreases, becoming difficult to define for the 30 nm diameter fiber diode. As the fiber diameter gets smaller, the junction area also diminishes. The surface states on the semiconductor will therefore have a reduced influence on the Fermi level pinning at the interface and hence band bending is expected to be minimal since the depletion width in the semiconductor is also reduced. The effect of this is reflected in Fig. 3(c) where the magnitude of the reverse bias currents are comparable to that observed under forward bias implying a reduced Schottky barrier. In the case of a Schottky contact where the diode size is smaller than the depletion width, tunneling currents become significant and the potential profile in the diode is described by [12]

$$V(x) = \frac{a}{x} V_S, \quad \text{for } x \gg a \tag{4}$$