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This is an **author produced version** of a paper published in:

IEEE Electron Device Letters 36.8 (2015): 814 - 816

DOI: <http://dx.doi.org/10.1109/LED.2015.2442678>

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Low Leakage Current ZnO Nanowire Schottky Photodiodes Built by Dielectrophoretic Contact

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Abstract— This work presents the characterization results of nanowire (NW) Schottky photodiodes fabricated from the dielectrophoretic contact between a ZnO NW and a Cu electrode. The device counter-electrode is fabricated using Pt focused ion beam deposition. The current-voltage characteristics exhibit rectifying properties with a leakage current as low as 40 pA at -40 V. The fitting of the forward characteristics reveals a barrier height lowering under UV illumination along with a large reduction of the series resistance. At forward bias, responsivities of about 10^5 A/W are obtained above the bandgap energy. Under reverse bias, the responsivity reduces up to 10^4 A/W, but a higher ultraviolet/visible contrast and a faster response are observed. In those conditions, the barrier height lowering is fostered by the drift of photogenerated holes towards the interface with the Cu electrode, yielding lower barrier height values under illumination.

Index Terms— Dielectrophoresis, nanowires, Schottky photodiodes, ultraviolet photodetectors, ZnO.

I. INTRODUCTION

Zinc Oxide (ZnO) has received a great deal of attention in the last decade thanks to their excellent electrical, mechanical and optical properties [1]. Many publications have addressed the characterization of ZnO nanowire (NW) photodetectors, exhibiting strong UV selectivity and high photoconductive gains in comparison to bulk photodetectors [2]-[4]. The latter has been attributed to the broadening of the conductive volume inside the NW upon illumination with UV light. The broadening occurs when electrons trapped at surface levels are released to the conductive volume of the NW. Unfortunately, this phenomenon is typically associated with long recovery times after illumination. Different authors have tried to solve this issue fabricating Schottky barrier contacts. Operated in photoconductive mode, the devices present shorter recovery times than photoconductors. Effective rectifying behaviors have been obtained from Schottky barrier contacts fabricated from the deposition of a ZnO NW onto a metal electrode pre-patterned on a substrate [5], [6]. In those devices, the reduction of the potential barrier is a key factor in the device performance.

In this work, we present the use of Schottky barrier contacts formed by dielectrophoretic assembly of NWs on top of a Cu

electrode. Its high thermal and electrical conductivity make this metal attractive for improving heat dissipation and increase the operation voltage at reverse biases.

II. FABRICATION

ZnO NWs are grown on sapphire substrates from the carbo-thermal reduction of ZnO powder using vapor phase transport without a metal catalyst, at 900 °C and atmospheric pressure in a horizontal tube furnace. Vertically aligned NWs are obtained with diameters between 300 and 700 nm and lengths up to 90 μ m. The sample is sonicated in ethanol for about 10 s to provoke NW scission. Three 5-10 μ L droplets are casted on a glass substrate that is pre-patterned with a pair of coplanar Cu electrodes separated a 50 μ m distance. An AC bias is applied between the pair of electrodes during drop-casting to exert an attracting force on the nanowires by dielectrophoresis (DEP). The DEP experiments are run under a frequency of 100 kHz and a peak-to-peak voltage of 15 V. Due to the large interelectrode distance, the process produces the assembly of the NWs on the edges of one of the Cu contacts, while the open end of the NWs rests on the glass area (Fig. 1). The contact of the NW on the

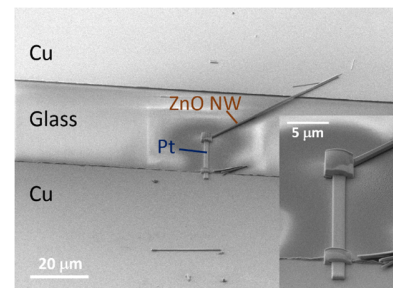


Fig. 1. Single NW device assembled between a Cu electrode and a Pt pad deposited by focused ion beam. Inset: closer image of the Pt pad.

Cu electrode is done through the m-plane facets of the wurtzitic structure.

In order to complete the device structure with an ohmic contact on the open NW end, a focused ion beam (FIB) system is used to deposit Pt from a gas precursor using Ga ions. The FIB deposition of this metal on ZnO NWs produces low

This work was supported by the Banco Santander-UAM Cooperation Program between Universidad Autónoma de Madrid and The University of Alabama. J. L. Pau is with the Electronics and Semiconductors Group, Departamento de Física Aplicada, Universidad Autónoma de Madrid, c/Francisco Tomás y Valiente 7, Madrid 28049, Spain (e-mail: josepau@uam.es).

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resistivity contacts with linear characteristics [7], [8]. The NW characterized in this work has a diameter of about 700 nm and a length of 60 μm . The Pt pad is reinforced with additional deposits on the electrode edge and on the NW tip (inset, Fig. 1).

III. CHARACTERIZATION AND DISCUSSION

The samples are characterized using a HP4145B Parameter Analyzer. The measurements under illumination are done using a Xe lamp coupled to an Oriel monochromator.

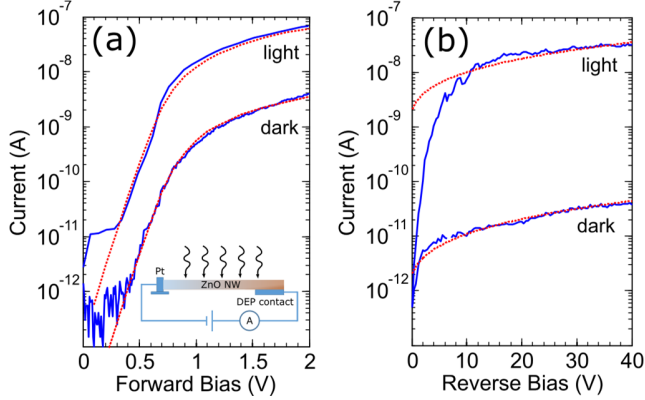


Fig. 2. (a) IV curves taken under forward bias in darkness and under illumination. Dashed lines represent the fitting curves from Eq. (1) and (2). (b) Reverse bias characteristics. Dashed lines represent the fitting at large voltages obtained from Eq. (3) and (4).

The forward current-voltage (IV) characteristic exhibits a current enhancement as the voltage increases, limited by the series resistance (R_s) at voltages above 1 V (Fig. 2(a)). The behavior is attributed to the emission of electrons from the semiconductor to the Cu electrode over the potential barrier formed by the internal band bending at the NW surface. The UV illumination of the NW (wavelength=365 nm, power density=2.3 $\mu\text{W}/\text{cm}^2$) invokes an increase of the delivered current.

Both dark and light IV curves can be conveniently fitted using

$$I = I_0 \left\{ \exp \left(\frac{q(V - IR_s)}{\eta k_B T} \right) - 1 \right\} \quad (1)$$

$$I_0 = AA^* T^2 \exp \left(-\frac{q\phi_B}{k_B T} \right) \quad (2)$$

where V is the applied voltage, T is the temperature, k_B is the Boltzmann constant, η is the ideality factor, R_s is the series resistance, ϕ_B is the barrier height, A is the contact area, and A^* is the Richardson constant, which has a value of around 32 $\text{A cm}^{-2} \text{K}^{-2}$ for n-type ZnO. Although the value of the Richardson constant is found to be lower in bulk ZnO diodes, slight deviations from the theoretical value would only produce small variations of the barrier height [10]. Eq. (1) and (2) account for both thermionic emission and tunneling transport at the metal-semiconductor junction. The expression is used to calculate the current by solving the transcendental equation for each voltage V , given a set of ϕ_B , R_s and η values as parameters. The best fitting values obtained for those parameters are shown in Table I. In darkness, the fitting yields a barrier height of 0.85 V, a value that is within the range obtained by ultraviolet

photoelectron spectroscopy for the surface band bending at the sidewalls of ZnO NWs for different oxygen coating levels [9]. Taking into account the values of the electron affinity for ZnO ($\chi_{\text{ZnO}}=4.2\text{--}4.35$ V) and the work function for Cu ($\phi_{\text{Cu}}=4.7$ V), the value seems to depart from the Schottky-Mott model for metal-semiconductor junctions. Thus, the extracted value suggests the existence of an interface charge layer, which influences the position of the Fermi level below the minimum of the conduction band. Under UV illumination, the barrier height reduces from 0.85 to 0.75 V. This lowering is the result of surface electron emission from the NW-Cu interface to the Cu electrode.

Unlike bulk photodiodes, the NW diode exhibits a series resistance significantly reduced under illumination at large forward bias thanks to the broadening of the conductive channel along the NW. Similar ideality factors are found in darkness and under illumination. The large values can be related to the interface charge layer and the inhomogeneous properties of the

TABLE I
FITTING PARAMETERS OF FORWARD CHARACTERISTICS

| | ϕ_B (V) | R_s (M Ω) | η |
|--------------|-----------------|---------------------|---------------|
| Dark | 0.85 \pm 0.03 | 300 \pm 20 | 2.7 \pm 0.1 |
| Illumination | 0.75 \pm 0.08 | 18 \pm 6 | 2.8 \pm 0.4 |

junction, including the possible existence of small air gaps at the interface caused by the Cu electrode roughness. These properties are major causes for η enhancement [11]–[13].

At 1 V reverse bias, the dark current is 2.5 pA, a value significantly lower than those found in previous works [5], [6]. In addition, the device exhibits a current as low as 40 pA at 40 V (Fig. 2(b)), which is, up to our knowledge, the largest reverse operation voltage ever reported for a ZnO NW Schottky barrier diode. At large reverse voltages, the characteristic follows the relationship extracted from the barrier height lowering:

$$I = AA^* T^2 \exp \left(-\frac{q(\phi_B - \sqrt{qE_m/4\pi\epsilon_s})}{k_B T} \right) \quad (3)$$

where E_m is defined as

$$E_m = \sqrt{\frac{2qN_D}{\epsilon_s}} \left(V_R + \psi_{bi} - \frac{k_B T}{q} \right), \quad (4)$$

V_R is the reverse voltage, ψ_{bi} is the built-in voltage, N_D is the donor concentration, and ϵ_s is the dielectric constant of ZnO ($8.0\epsilon_0$). Approximating ψ_{bi} by the barrier height value obtained in the fitting of the forward characteristic (0.85 eV), and assuming the same value for ϕ_B , it is possible to calculate the donor concentration in the NW from the reverse characteristic at large voltages. The value obtained is $(8.0 \pm 0.5) \times 10^{16} \text{ cm}^{-3}$, which suggests that the main contribution to the current is thermionic emission rather than field effect transport, since the tunneling energy, $E_{00}=3.4$ meV, is smaller than the thermal energy $k_B T$ [12].

The current values under illumination are much larger than the values expected from a device with an external quantum efficiency of 100%. To deepen into the origin of the gain, the current under illumination is fitted at large voltages using (3) and (4), leaving the barrier height as a fitting parameter and using the doping level extracted in darkness as a constant. The

best fitting value is 0.64 ± 0.01 V. The photogenerated holes are, in this case, electrostatically attracted towards the surface, contributing to reduce more the potential barrier than at forward bias. The currents at low reverse voltages cannot be properly

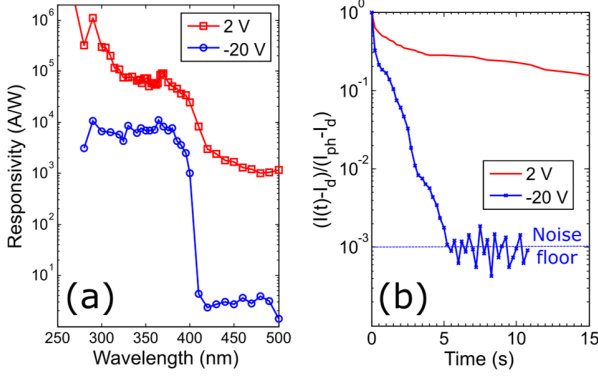


Fig. 3. (a) Spectral responses measured at 2 V and -20 V. (b) Relative decay curves measured after continuous illumination at 365 nm for 1 min. Optical power = $2.3 \mu\text{W}/\text{cm}^2$.

fitted assuming a constant ϕ_B in Eq. (3) and (4). The curvature in that range might be influenced by the increasing drift of holes towards the interface as the reverse bias increases.

The spectral response of the devices is measured at 2 V and -20 V (Fig. 3(a)). The responsivity is calculated from the difference between the current under illumination and the dark current, after dividing it by the optical power density of the system and the NW in-plane area exposed to the light. The responsivity at 2 V is higher than that obtained at -20 V. At 365 nm, the values are 7.8×10^4 A/W, at 2 V, and 1.1×10^4 A/W, at -20 V. At 2 V, the current is limited by the series resistance introduced by the NW. As this resistance is mainly affected by the conductivity of the NW, the broadening of the conductive volume under illumination produces a significant increase of the response, similar to that found in photoconductors. This mechanism involves the entire volume of the NW.

The UV/visible contrast, i.e. the ratio between the responsivities obtained below and above the response cut-off, is between 10 and 100, at 2 V, and about 5×10^3 at -20 V. The response of the device at the longest wavelengths is related to the photoemission of electrons from the interface traps. This process seems to be more effectively driven by electrostatic forces under forward bias than under reverse bias, justifying the behavior of the UV/visible contrast.

The device reset times in both operation modes also show some interesting differences. Figure 3(b) represents the $(I(t) - I_d)/(I_{ph} - I_d)$ function, where I_d is the dark current, I_{ph} is the current under illumination, and $I(t)$ is the time-dependent current after illumination. At forward bias, the device shows a slow recovery process due to the persistent photoconductivity. As the conduction in this operation mode is limited by the series resistance, device recovery takes place through the filling of surface states, not only at the metal-semiconductor interface, but also on the rest of the NW surface. At 2 V, the reset time, defined as the time needed to obtain a $1/e$ signal reduction, is found to be 2 s. Under reverse bias, the

response shows a signal attenuation of three orders of magnitude in about 5 seconds, before reaching the noise floor of the experimental setup. A reset time of 0.2 s is obtained at -20 V. We hypothesize that, since the series resistance has weak influence on the reverse characteristics, the filling of the interface states is the most relevant process to restore the dark current level.

IV. CONCLUSION

The paper describes the method to obtain Schottky barrier photodiodes from the DEP assembly of a ZnO NW on a Cu electrode. The characterization results show that those contacts can produce devices with low leakage currents at very high reverse voltages, enabling the enhancement of the collection efficiency along the NW.

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