Slow-rise and fast-drop current feature of ultraviolet response spectra for ZnO-nanowire film modulated by water molecules*

Ren Shou-Tian(任守田), Wang Qiang(王 强),
Zhao Feng (赵 锋), and Qu Shi-Liang(曲士良)†

Department of Optoelectronic Science, Harbin Institute of Technology at Weihai, Weihai 264209, *China*

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This study describes the fabrication of ZnO-nanowire films by electro-chemical anodization of Zn foil. The ZnO films are characterized by field emission scanning electron microscopy, X-ray diffraction patterns, and transmission electron microscopy, respectively. The ultraviolet (UV) photo-response properties of the surface-contacted ZnO film are studied through the current evolution processes under different relative humidities. Unlike the usually observed current spectra of the ZnO films, the drop time is shorter than the rise time. The photo-conductivity gain G and the response time τ are both increased with the increase of the applied bias. The photo-conductivity gain G is lowered with the increase of the environmental humidity, while the response time τ is increased. These results can be explained by considering three different surface processes: 1) the electron–hole (e–p) pair generation by the UV light illumination, 2) the following surface O_2^- species desorption, and 3) the photo-catalytic hydrolysis of water molecules adsorbed on the ZnO surface. The slow-rise and fast-drop current feature is suggested to originate from the sponge-like structure of the ZnO nanowires.

Keywords: electro-chemical anodization, ZnO nanowires, ultraviolet detector

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1. Introduction

Due to its wide and direct bandgap (3.37 eV), large excition binding energy (60 meV), and simple growth technology, zinc oxide (ZnO) has become the most popular semiconductor material. Many methods have been used to produce ZnO nanomaterials, among which the vapor-phase methods require strict experimental conditions, such as high temperature (400–1400 °C) and low pressure;[1] the hydrothermal method can be applied at low temperature (< 200 °C), however a long reaction time is usually required.[2] Thus, it is still a challenging task to fabricate large area ZnO-nanowire arrays at room temperature. In contrast to the above methods, the electro-chemical anodization is a simple but powerful method used to fabricate oxide films on certain metal substrates. Since the self-ordered porous oxide films on aluminum are formed by the anodization treatment,[3,4] many groups have focused on anodization for the formation of nanostructure metal oxides, such as nanotubular TiO_2 films, which have been used in dye sensitized solar cells.[5] However, reports on the formation of one-dimensional (1D) ZnO films via the anodization method are rarely found despite the pioneering works of Kim, Wu, and Hu *et al.*[6−8]

Due to their wide bandgap structures, ZnO nanomaterials are used to fabricate ultraviolet (UV) detectors, but some drawbacks, such as the persistent photoconductivity (PPC), need to be overcome.[9,10] PPC is the persistence of a high conductance state for a long time after the light is off. The PPC phenomenon lowers the sensitivity and the response speed of ZnO-based UV detectors, which hinders their application. To improve the response speed of ZnO-based UV detectors, the PPC must be eliminated, or at least the persisting time should be shortened.

In this article, we synthesize ZnO-nanowire film

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†Corresponding author. E-mail: slqu1@yahoo.com.cn

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by using the anodization process. The UV response of the ZnO film is measured at different biases and different humidities. It shows a slow-rise and fast-drop current feature, which is different from the previously reported results, especially for those named as PPC. The combinative effects of the desorption of O_2 species and the photo-electrolysis of water molecules are employed to explain the observed ultraviolet sensitive electronic transport properties modulated by the water molecular coverage.

2. Experimental details

The growth of ZnO nanowires films was carried out at room temperature in a home-made electrochemical cell according to the methods of Hu *et al.*[8] A zinc foil (99.999% purity, sonicated in ethanol for 10 min) was used as the anode (surface area 6 cm^2), and a graphite plate acted as the counter electrode. Before the anodization, the zinc foil was electro-polished in a 3 : 7 solution of phosphoric acid and ethanol at 20 V direct-current (DC) voltage with strong stirring for 10 min. The electrolyte was a freshly prepared $KHCO_3$ aqueous solution (20 mmol/L). The distance between the two electrodes was 10 cm. The anodization process was carried out using a 10 V DC voltage source. After anodizing for a certain time, the foil was taken out from the solution immediately, washed with distilled water, and then annealed at 250 °C in air for 60 min.

In the anodization process, hydrogen gas was produced at the cathode via hydrogen ions capturing the electrons. At the anode, $Zn(OH)_4^{-2}$ ions were formed. During the electrochemical etching process, the uneven zinc surface led to a non-uniform electric field distribution and the formation of many hot spots. The negatively charged $Zn(OH)_4^{-2}$ congregated at the hot spots, and thus the nanowires were formed. After annealing in air, the surface layer containing the zinc hydroxide was decomposed into the as-prepared ZnO nanowire.

Surface morphologies and structural features of the ZnO film were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) patterns, and transmission electron microscopy (TEM) respectively. The standard electrical measurement setup was used to obtain current evolution spectra by adjusting the cyclic on/off states of the UV light (365 nm). A 6 W xenon arc lamp light source was used for the UV photo-response measurements. Different humidity sources were obtained by employing the several saturated salt solutions described in our previous paper.[11]

3. Results and discussion

3.1. Characterization of the sample

After anodization and annealing, the zinc foil is covered with a layer of white product. SEM, TEM, and XRD characterizations are used to investigate the surface morphologies and the structural features of the sample, as shown in Fig. 1. ZnO nanowires with a uniform diameter of about 150 nm and sharpened tips are found. The lengths of the nanowires are tens of microns, which can be controlled by the reaction time. As shown in Figs. 1(a) and 1(b), the tips of the ZnO nanowires usually converge together and present a honeycomb-like pattern, which may be caused by the capillary force between adjacent ZnO nanowires during the drying process. The SEM picture of one sonically dispersed nanowire is shown in Fig. 1(c), where we can see that many nano-crevices exist on the interface of the nanowire, which may be very helpful for surface oxygen and water adsorption. The XRD is used to analyze the structure of the ZnO-nanowire film (Fig. 1(d)). In addition to the sharp zinc peaks assigned to the metal zinc foil (JCPDS 04-0831), several broadened diffraction peaks corresponding very well to that of the hexagonal wurtzite ZnO (JCPDS 36-1451) are found and identified to be associated with (100), (002), (102), (110), (103), and (112) lattice planes, suggesting that the white product consists of polycrystalline ZnO nanoparticles arranged in a wire-like structure. The sponge-like structure is observed in the TEM characterization (Fig. 1(e)) of the ZnO naowire, which is actually composed of nanoparticles. The sponge-like structure may be the key reason for high oxygen and water adsorption ability, as shown in the following discussion. The high-resolution TEM (the inset of Fig. 1(e)) further confirms the polycrystalline nature of the ZnO nanowires with the preferential orientation along [100], which is consistent with the XRD results in Fig. 1(d) and the selected area electron diffraction (SAED) pattern in Fig. 1(f). The spotty ring pattern shows six diffraction rings corresponding to (100), (002), (102), (110), (103), and (112) lattice planes of ZnO.

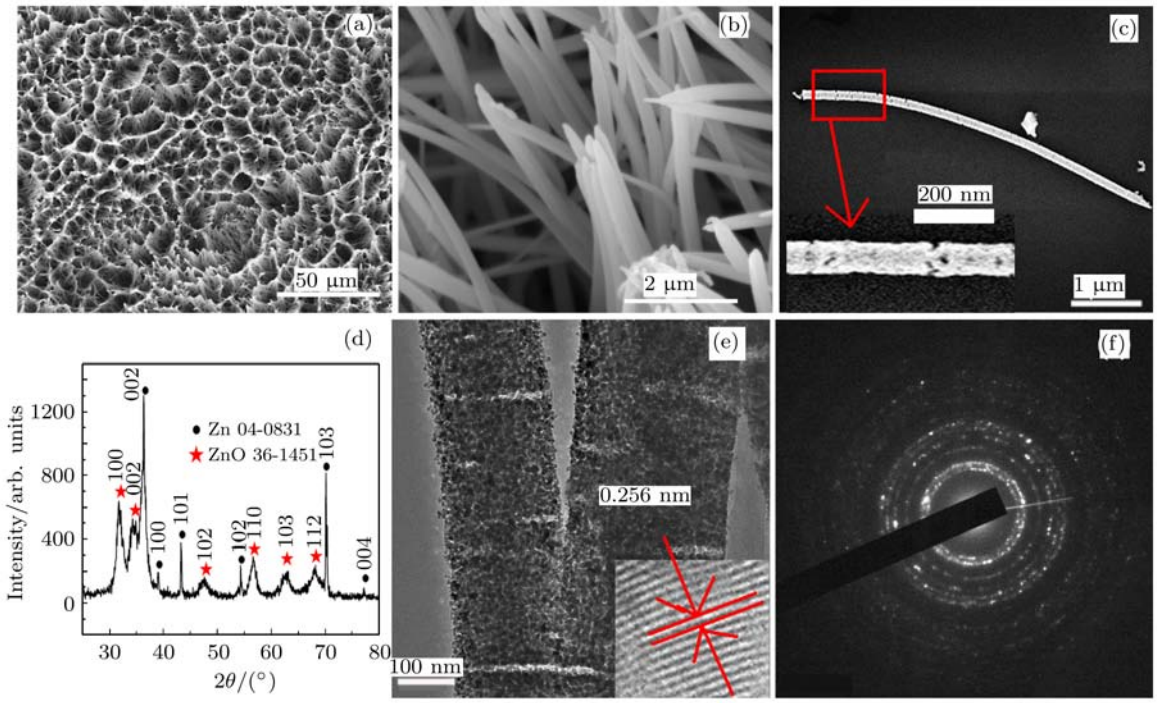


Fig. 1. (colour online) Morphologies and microstructures of ZnO nanowires. (a), (b), and (c) SEM images with different magnifications. (d) XRD pattern. (e) TEM image of a single ZnO nanowire, the inset is an HRTEM image of the ZnO nanowire. (f) SAED pattern of a single nanowire.

3.2. Current feature for UV response: slow-rise and fast-drop

The schematic circuit for measuring the UV response of the ZnO film is shown in the left of Fig. 2(a). Cu leads are connected with the ZnO-nanowire film with conductive silver paste. The electron conduction route follows the way from one electrode (silver paste) to the underneath ZnO nanowires then to the Zn metal and then back to the ZnO nanowires underneath the other electrode and then to the other electrode, which is indicated by the red dotted line. As the ZnO nanowires naturally grow on the Zn foil, the ZnO–Zn contact can be considered to be an Ohmic contact, which is consistent with the results in the literature.[12] So the electronic transport route is simplified, which now is an electrode to ZnO nanowires and then to the other electrode (shown in the right of Fig. 2(a)). The electrode–ZnO nanowires–electrode circuit can be regarded as two back-to-back metal-semiconductor (MS) junctions,[13–16] and it shows a nonlinear I–V character, indicating that the transport properties are dominated by the reversely biased barrier. A detailed discussion will be provided in a separate article to analyse the electronic transport properties.

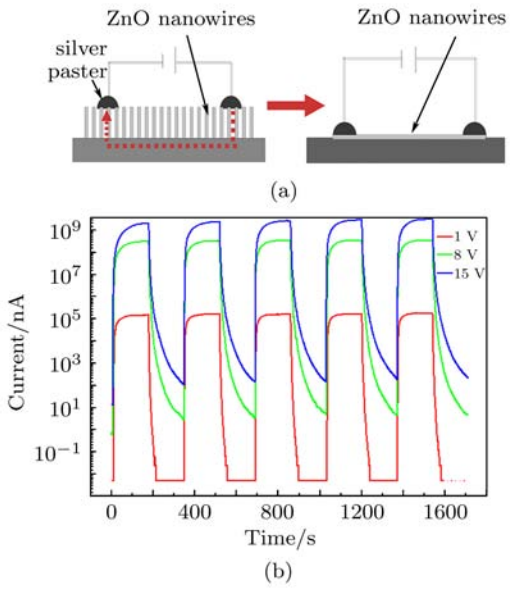


Fig. 2. (colour online) (a) Schematic circuit for measuring UV and humidity responses of ZnO film, and the simplified equivalent circuit. (b) UV photo-response at different biases.

Now we investigate the evolution process of the photocurrent at the on/off state of the UV light. To investigate the current evolution feature, the UV photo-responses with five on/off cycles are recorded at the biases of 1 V, 8 V, and 15 V respectively (Fig. 2(b)). Two obvious results can be obtained: 1) the rise time is longer than the drop time for all three

different biases, which is distinctly different from that in the previous reports, especially for the PPC phenomenon; 2) both the rise and the drop time are elongated with the increase of the applied voltage. The rise (drop) time is defined as the time to reach 90% of the current variation after turning on (off) the UV light. For different voltages and cycles, the current rise and drop time obtained from Fig. 2(b) is listed in Table 1. Two results can be obtained from Table 1: 1) at different bias, the drop time is always shorter than the rise time; (b) with the increase of the recording cycles, the rise and the drop time is gradually shortened and then stabilized for all biases, indicating that the modulation of the barrier height of the reverse junction by UV is stabilized.

In order to explain the above voltage-related on/off current evolution spectra, two questions need to be answered: 1) what are the underlying mechanisms for the rise and the drop processes; 2) how do these mechanisms contribute to the carrier transport with the increase of the applied voltage on the back-to-back MS junctions.

We analyze the current evolution spectra and extract the characteristic time constants, which is helpful to understand the mechanism of the current evolution. We can fit the current rise process with a sum of two exponential functions

$$I_{\rm rise} = I_{01} + A_1\left(1 - {\rm e}^{-t/\tau_1}\right) + B_1\left(1 - {\rm e}^{-t/\tau_2}\right), \quad (1)$$

where τ_1 and τ_2 are the characteristic time constants, which correspond to two different physical processes (a quick one and a slow one) contributing to the overall UV response process, A_1 and A_2 are the amplitudes of the two processes, respectively. The ratio A_1/A_2 can be used to explain which physical process plays the key role in the whole UV response process.

For the fitting of the current drop process of the ZnO sample, a solo-exponential equation can be used, which is expressed as

$$I_{\rm drop} = I_{02} + A_2\,{\rm e}^{-t/\tau'}, \quad (2)$$

where τ' is the characteristic time constant, which can indicate the response speed of the drop process, and A_2 is the amplitude of the drop process. This fitting works well for all three different voltages, while different parameters are selected for optimum fittings. The typical fitting curves at 8 V for the rise and the drop processes are shown in Figs. 3(a) and 3(b), respectively. The fitting parameters for different biases are listed in Table 2. The following results can be obtained from these fittings: 1) the slow rise component is comparatively enhanced with the increase of the voltage, as shown by the decreased A_1/B_1; 2) the characteristic time constant of the quick component τ_1 is rather stable with the increase of the bias, while that of the slow component τ_2 is increased; 3) the drop time constant τ' is increased with the increase of the bias.

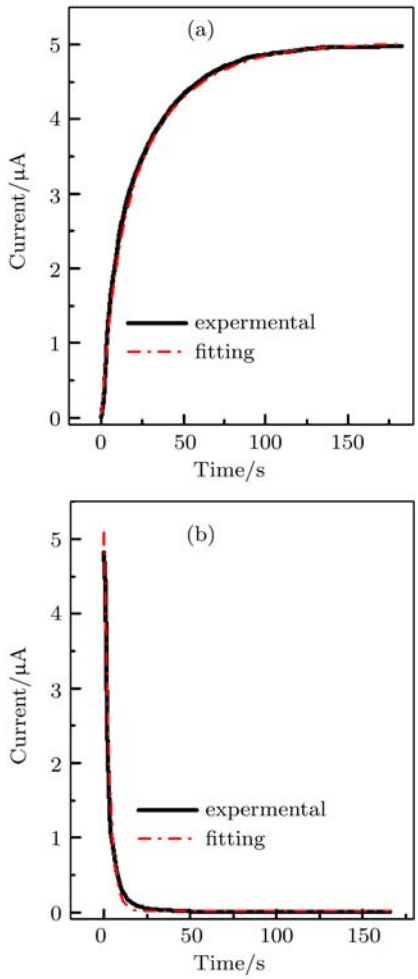


Fig. 3. (colour online) Fitting curves of photo-responses of ZnO-nanowire film at 8 V bias for (a) rise and (b) drop processes.

To explain the photo-response process, the schematic diagrams of the overall photo-initiated chemical-physical reactions are shown in Fig. 4. In the dark, oxygen and water molecules are absorbed on the ZnO interface (Fig. 4(a)). For the current rise process with the UV light on, the quick process is the uneqilibrium electron–hole (e–p) pair generation induced by the incident photons, which initiates the surface O_2^- species desorption (lowering the barrier height for the reversely biased MS junction), as shown in Fig. 4(b). However, we should always bear in mind that

Table 1. Rise (TR) and drop (TD) times in the unit of second at different biases for five cycles.

Bias/V	Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD
1	45	4.5	37	4.5	30	5	30	5.5	30	5.5
8	67	7	57	8.5	49	8	50	9	50	9
15	100	8.5	78	9	69	9.5	70	9.5	67	9.5

Table 2. Optimized fitting parameters selected for fittings at different biases.

Voltage/V	A_1/nA	B_1/nA	A_1/B_1	τ_1/s	τ_2/s	τ'/s
1	140.2	44.4	3.18	8.1	30.1	1.5
8	1974	3041	0.65	8.1	35.1	2.9
15	3677	8340	0.44	8.4	50.5	3.2

without lowering the contact barrier height, no apparent current increase can be detected, even though the conductivity of the ZnO film is greatly enhanced by the e–p pair generation, as the current transport is dominated by the reverse-biased MS junction. So the above mentioned photon-induced e–p pair generation and surface O_2^- species desorption process should be combined as one with an effective quick response time. Then the slow response path must be identified.

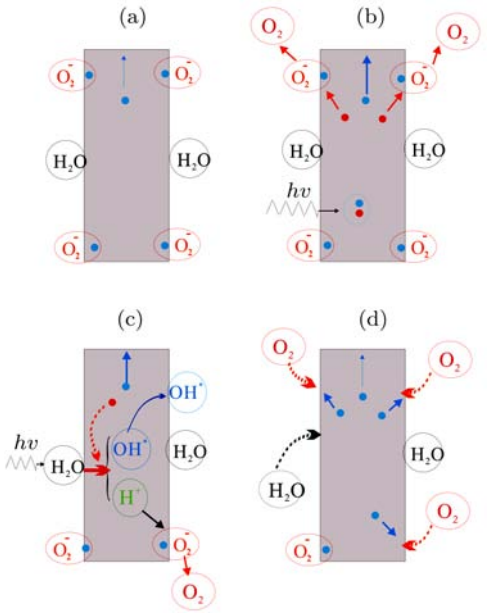


Fig. 4. (colour online) Schematic photo-initiated chemical-physical reactions for the photo response of ZnO-nanowire film: (a) in dark, (b) oxygen desorption process, (c) photo-electrolysis process, and (d) re-adsorption of oxygen and water molecules when UV light is off. Blue and orange dots represent electrons and holes, respectively.

Except for the well-known oxygen molecules, water molecules are another major absorbent species on the ZnO interface, as our measurement is performed in air. The interaction of water molecules with ZnO is a complicated process, especially when the influence of the UV light illumination is considered. Fujishima and Honda showed that water could be efficiently photo-electrolyzed at titanium dioxide (TiO_2) electrodes under UV light illumination, and ZnO was also suggested as a promising replacement of TiO_2.[17] The photo-electrolysis process is employed here to interpret the slow current rise component.

As the most popular photocatalyst, TiO_2 is believed to have microsized photoelectrochemical cells with both the anode and the cathode existing in the same grain.[18] The ZnO nanowires are composed of many nanoparticles, they can also be treated as many microsized photoelectrochemical cells under UV illumination in air. The photo-electrolysis of water molecules on the ZnO interface includes three processes: 1) e–p pair generation caused by the UV light illumination, 2) anodic oxidation, and 3) cathodic reduction.

Under UV light illumination, the surface O_2^- species desorption occurs via reacting with the photon-induced holes, and the photo-current rapidly increases, which is the rapid process mentioned above. Simultaneously, the absorbed water molecules are electrolyzed. At the anode, the water molecules react with the light-induced holes, and hydrogen peroxide is formed[19]

$$(2H_2O)_l + (2h^*)_s \rightarrow (H_2O_2)_l + (2H^+)_l, \qquad (3)$$

where subscripts l and s indicate the liquid and the solid phases, respectively. Another possible reaction process realized at the photoanode is the formation of OH^* radicals and H^+ ions[19]

$$(H_2O)_l + (h^\bullet)_s \rightarrow (OH^*)_l + (H^+)_l. \qquad (4)$$

At the cathode, the chemically absorbed O_2^- species react with the H^+ ions, forming hydroperoxide radicals HO_2^*[19]

$$O_2^- + H^+ \rightarrow HO_2^*. \qquad (5)$$

In comparison with the initial surface barrier without water participation, the O_2^- species desorption during the photo-electrolysis process will further lower the reverse junction barrier height, and bigger photocurrents can be obtained (Fig. 4(c)). When the UV light is off, oxygen and water molecules are re-absorbed on the ZnO interface (Fig. 4(d)).

The photo-electrolysis is a multi-step slow process. As can be seen from Table 2, at a low bias (1 V), the higher ratio A_1/B_1 means that the fast process dominates the UV response process. As bias V increases, ratio A_1/B_1 is decreased, and the slow rise time constant τ_2 is increased, which means that the slow photocatalytic hydrolysis process is becoming more and more important. At different bias V, τ_1 of the fast process is almost the same, indicating a consistent surface O_2^- species desorption mechanism independent of the bias. From a combinative point of view, at the higher bias, less O_2^- on the ZnO interface means that it takes a longer time to reach the O_2 equilibrium state between the ZnO interface and the surrounding environment, which can explain the larger drop time constant at the higher bias.

The shorter drop time is really an interesting phenomenon, and as far as we know, none of the models from the previous publications can be used to explain it. When the UV light is off, excessive electrons need to be recombined with holes or trapped by the surface adsorbent O_2. As we have discussed above in Eqs. (3) and (4), the holes are sacrificed by successive processes of O_2^- desorption and photocatalytic hydrolysis, so excessive electrons can only be trapped by O_2. The only presumable explanation is that the sponge-like structure of the as-prepared ZnO nanowires can enhance the absorption ability of gas molecules, while it is not conducive to the desorption process. Put simply, the slow-rise and fast-drop current feature originates from the special sponge-like structure.

To further confirm the influence of the surface adsorbed water molecules on the UV photo-response of the ZnO-nanowire film, the UV responses of the ZnO film at different humidities are performed at the same bias of 8 V, as shown in Fig. 5. As the relative humidity (RH) increases from 35.0%, 52.9% to 93.6%, the on/off current ratio is decreased from 3060, 60 to 3, indicating a great drop of the photo-conductivity gain. As the humidity increases, the rise time is increased from 8.5 s, 88 s to 159 s, while the drop time is greatly increased from 8.5 s to 37.3 s with a singular drop to 5.3 s at the RH of 52.9%.

As we know, at high humidity, water molecules occupy the active surface sites previously situated by O_2^- species, which is plausibly due to the ionization of water, resulting in the release of the free electrons. This process lowers the surface potential of the ZnO surface, and the conductivity of the ZnO system in the dark will also be enhanced. Less O_2^- on the ZnO interface leads to a weaker photo-response. At the same time, in higher humidity environments, the slow process is significantly enhanced due to the larger water molecules coverage, which is consistent with the experimental results. The two aspects mentioned above can explain the longer rise time and the weaker photo-conductivity gain at high humidity.

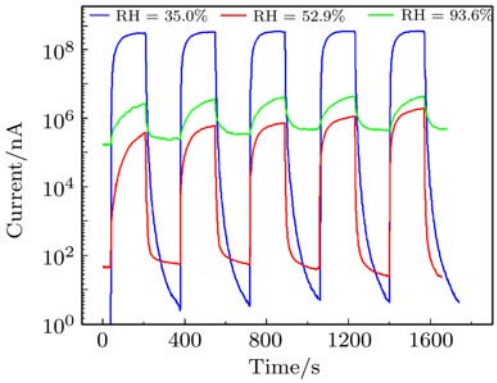


Fig. 5. (colour online) Photo-responses of ZnO nanowires film at different relative humidities.

4. Conclusion

In summary, ZnO nanowire films are fabricated by using a simple electro-chemical anodization method. The UV light response of the surface-contacted ZnO film is studied through the current evolution process with the UV light illumination turned on/off under different humidities. For our ZnO films, the drop time is shorter than the rise time, which is different from that in the usually observed current spectra of the ZnO films. As the applied bias V increases, the photo-conductivity gain G and the response time τ both increase. The higher environmental humidity leads to a lower photo-conductivity gain and a longer response time. The surface O_2^- species desorption and the photo-catalytic hydrolysis play key roles for the UV response of the ZnO films. The anodizing method provides a simple but powerful way to fabricate low-cost UV detectors.

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