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Temperature dependence of performance of ZnO-based metal-semiconductor-metal ultraviolet photodetectors

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ABSTRACT

ZnO as a wide bandgap semiconductor material can be used in ultraviolet photodetection for its direct bandgap (3.37 eV) corresponding to the energy of an ultraviolet photon. Recently, ZnO based ultraviolet photodetectors have been deeply investigated, people have successfully fabricated high-performance MSM (Metal-semiconductor-metal) photodetectors and vertical-structured ultraviolet photodetectors, moreover the sensitive spectral region for detection has been extended into solar-blind spectral range. However, the temperature dependence of photodetector's performance has seldom been studied, so we fabricated high performance ZnO based MSM ultraviolet photodetectors and then the temperature dependence of performance has been investigated. We compared the photo-response measurement results at room temperature with the results measured at other higher temperatures. We found that photocurrent and responsivity decrease with temperature rising in the temperature range from room temperature to 200 °C due to bandgap shrinkage and lattice scattering. Dark current decreases with temperature for mobility decrease below 100 °C, but it increases with temperature for thermal generation above 100 °C. These are not good for the stability of devices. Decreasing the working voltage may be an option to lessen the influence of temperature, but a low signal-to-noise ratio is the cost.

1. Introduction

ZnO is a promising semiconductor material for its wide bandgap (3.37 eV) [1]. And because its direct bandgap is corresponding to the energy of an ultraviolet photon, it can be a good candidate for UV photodetectors [2]. UV photodetectors are widely used in a lot of situations, such as UV monitoring, ozone detection, flame alarm and missile warning system [3].There are many types of photodetectors like photodiode, p–i–n photodetector, MSM photodetector and Schottky photodetector. Each type has its particular advantages and disadvantages [4]. Generally speaking, photodiode has good frequency characteristics, but the photo current is usually small; p–i–n photodetector has high sensitivity and large output current and fast response, but it is not suitable for UV light due to the small penetration depth of UV light; Schottky photodetector has fairly high speed of response, but it might be difficult for some semiconductor to find the appropriate metal to realize the rectifying junction; MSM photodetector has a very large photoconductive gain thus a large responsivity, but long response time is its notable shortcoming. In recent years, MSM photodetector and Schottky photodetector have gained intensive interest for their good performance in responsivity and response time, respectively [2,5–8]. What's more, the fabrication process of ZnO based photodetectors is easy and environmental-friendly. Nowadays, researchers have taken great efforts to better the performance of UV photodetectors [9], by means of changing the structure of device, using other substrates or altering electrode material [10–13]. Actually, photodetectors with nano-structure which can bring some quantum effects are more and more popular and fascinating [14,15]. Quantum effects resulted from nano-structures include quantum size effect, ballistic transport mode, quantization of electrical conductance, electron tunneling, coulomb blockade effect, quantization of thermal conductance, universal conductance fluctuations and quantum interference phenomena including Aharonov–Bohm effects and quantum Hall effect. Some of these effects such as ballistic transport mode can be used to improve the performance of detectors. Because the size of some part of the device is shorter than the free path of electrons, electrons drift in the field between electrodes without scattering. Thus it shortens the transit time of electron and enhances the response speed of the detector. Another research trend is to shift the sensitive spectral range of UV photodetectors from near UV band to deep UV band, which includes the solar-blind spectral range [16,17].

No matter which type of UV photodetectors it is, especially the MSM photodetector, its performance is usually sensitive to environmental temperature. S. J. Young et al. have investigated the temperature dependence of Ir/n-ZnO Schottky diodes. They found the barrier height decreased as the temperature increased [18].

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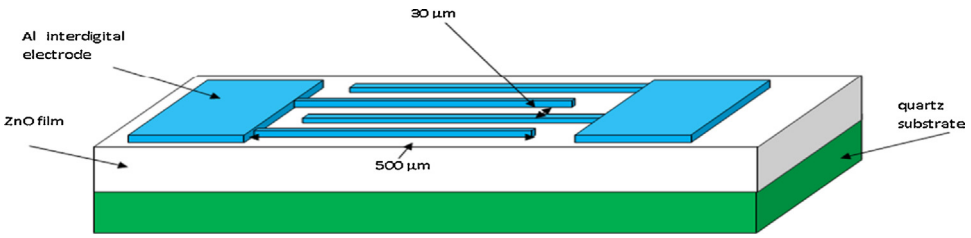

Fig. 1. Structure scheme of ZnObased MSM UV photodetector.

However, nearly no literature about the temperature dependence of the performance of photoconductive MSM type UV photodetectors is published to the best of our knowledge. This article just focuses on the temperature dependence of the performance of MSM UV photodetectors. The response of UV photodetectors based on ZnO MSM structure was measured at different temperatures above room temperature. From the experimental data of our measurement, it can be concluded that the impact of temperature on the performance of ZnO based MSM UV photodetector is large and unwelcome. We'd better keep environmental temperature steady for the sake of stability of the performance of UV photodetectors, or find a tradeoff between stability of the performance and the signal-to-noise ratio.

2. Experimental

The MSM UV photodetectors used in our experiments were fabricated based on high quality ZnO thin film deposited by radio frequency magnetron sputtering on quartz substrate. The target was polycrystalline ZnO ceramic (99.99% purity), the diameter of which was 50 mm. The substrate was heated at 400 °C and a mixture of oxygen (99.999% purity) and argon gas (99.999% purity) was injected into the chamber during the growth of ZnO film. The distance between substrate and target was 70 mm. Mass flow controller showed that the flow rate of oxygen and argon were 35 sccm and 25 sccm, respectively. The gas pressure in the chamber was kept at 1.2 Pa and the RF power was 70 W. The whole deposition process lasted 90 min. In fact, 10 min pre-sputtering to remove the absorbed substance on substrate and the wall of chamber had been done before deposition. At the very beginning, the substrate was ultrasonically cleaned in acetone, ethanol, de-ionized water successively. Each cleaning step lasted 10 min.

MSM photodetector was fabricated on the basis of as-grown ZnO film. Al interdigitated electrode was evaporated on the ZnO film and the planar structure was achieved through lift-off technique in which photolithography was contained. Fig. 1 illustrates the scheme of the UV photodetector. Al can be used as good Ohmic contact with ZnO films, and interdigtated electrodes have a high efficiency to collect photo-generated carriers.

The transmittance spectrum of ZnO film was measured by a Varian UV–vis spectrophotometer (Cary 5000). The X-ray diffraction was employed to characterize the orientation of ZnO film, and the SHIMADZU XRD-7000 diffractometer was used. The scanning electron microscope (JSM-6700F) image of the ZnO film is also shown below. The current and voltage (I–V) curves of MSM UV photodetector under UV illumination and without UV illumination were measured at a temperature range from room temperature (RT) to 200 °C. A Keithley picoammeter (model 6487) and 254 nm Hg lamp (LHM 254) as light source were used. The intensity of the light source was 156.1 μW/cm^2. In order to reduce measurement error, temperature controller set the temperature from low to high sequentially. And for the sake of depressing the influence of dark current, a chopper (model SR540) and a lock-in amplifier (model SR 830) are used in photo response measurement. The measurement at each temperature set point was not taken until temperature had been steady at that set point for 5 min.

3. Results and discussion

The structural scheme of the MSM UV photodetectors based on ZnO film is shown in Fig. 1. There are 50 pairs of interdigital (IDT) electrodes in the photoconductive detector. Only two pairs of them are plotted in Fig. 1 to illustrate the size of electrodes, other pairs are omitted. The thicknesses of Al electrodes and ZnO film are about 100 nm and 400 nm, respectively. And all electrode fingers are 500 μm long and 15 μm wide, the spacing between the two neighboring fingers is 30 μm. There is a total photosensitive area of 1.24×10^{-2} cm^2 for the detector. As a basic rule, the spacing between electrode fingers is an important structural parameter of the MSM photodetector. The transit time of photo-generated carriers moving from one finger to the other finger is determined by it. Given the same voltage, the transit time diminishes when the electrode gap is shortened, so does the response time. But considering the tradeoff between the precision of lithography and the response time, 30 μm was chosen in our experiments.

The transmittance spectrum of ZnO film is shown in Fig. 2. Strong absorption of UV light from 200 nm to 380 nm is observed, and on the contrary, transmittance of visible light from 400 nm to 760 nm is nearly all above 80%. This indicates high UV-to-visible rejection ratio of our photodetectors based on the as-grown ZnO film. Fig. 3 shows the XRD measurement result of the ZnO film, the diffraction peak of (0 0 2) is so evident that it means a good c-axis orientation of the ZnO film. In order to characterize the microscopic morphology of the film, SEM was deployed. From the SEM image of Fig. 4, we can attain the average grain size of ZnO film, it is almost 40 nm.

The I–V curves measured at different temperatures are shown in Fig. 5. The voltage source scanned from 0 V to 10 V with a step of

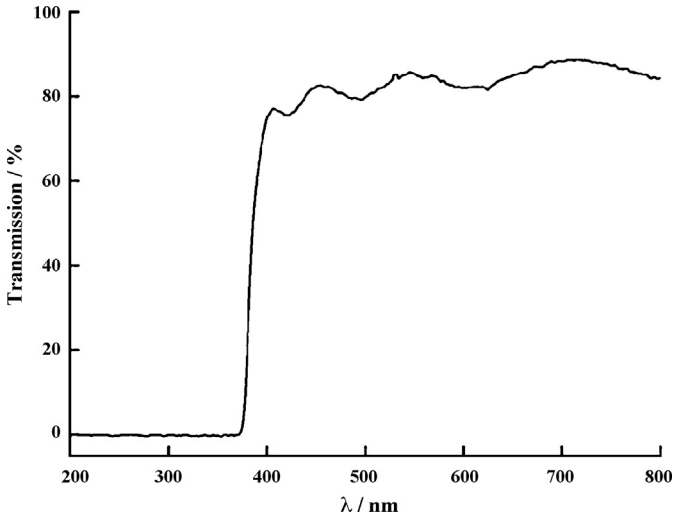

Fig. 2. Transmittance spectrum of ZnO film.

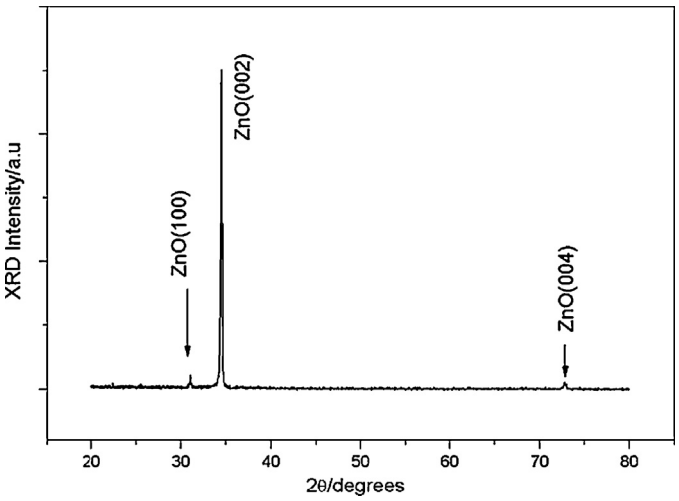

Fig. 3. XRD measurement results of ZnO film.

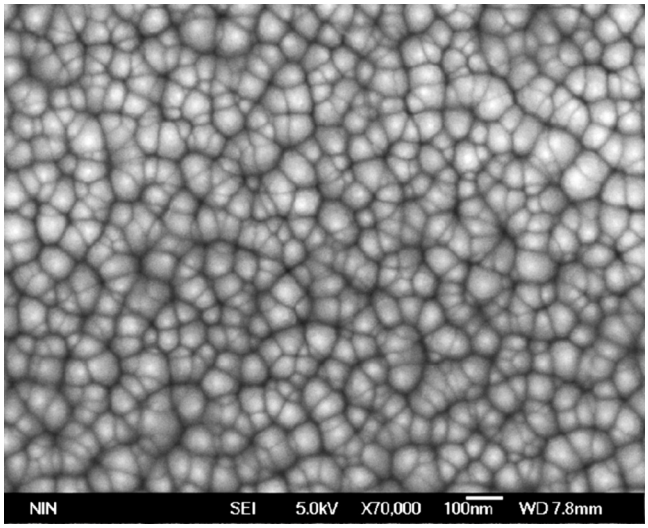

Fig. 4. SEM image of ZnO films.

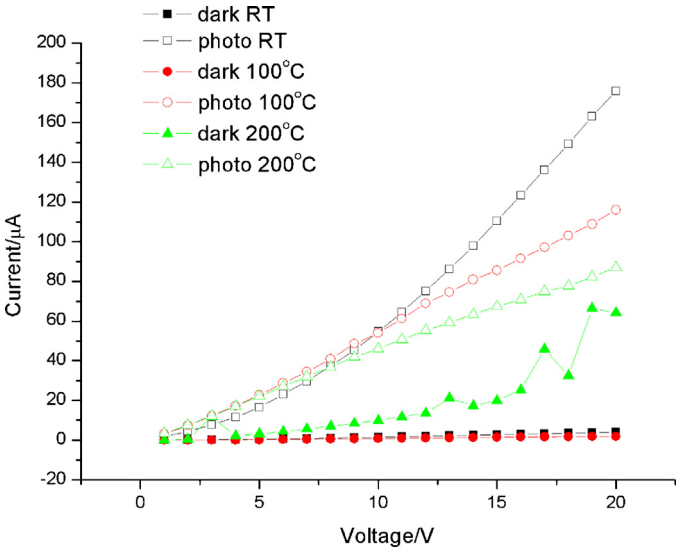

Fig. 5. *I–V* curves measured at RT (Room Temperature),100 °C, 200 °C, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

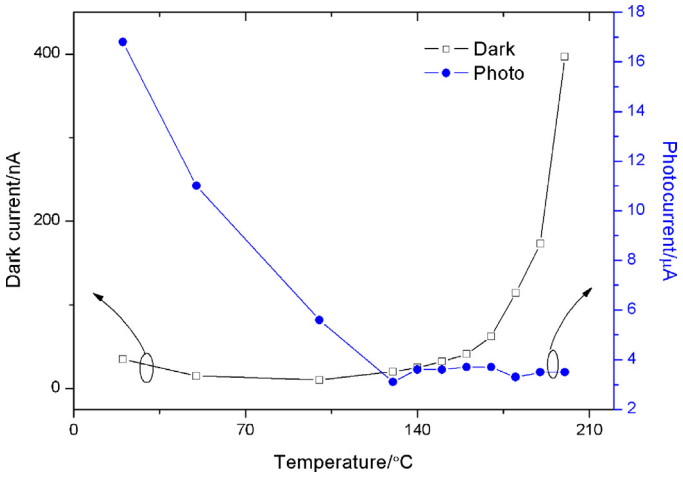

Fig. 6. Dark current and photocurrent at different temperatures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

1 V. From the results it can be seen that at room temperature (RT) and 100 °C, the dark currents of detector are small and show nearly good linearity. However when temperature went up to 200 °C, dark current began to increase sharply with voltage rising, and it would not be precisely linear to the voltage any more. This phenomenon may be caused by the carriers generation related to electrons bumping with thermal energy and the oxygen desorption [10,19]. At higher temperature, more oxygen atoms leave the absorbing sites which are often at the surface or on the grain boundary, and every oxygen atom releases two electrons while this happens. Since more carriers generated at high temperature and lattice vibration is enhanced, the scattering to the charge carriers is stronger. The threshold voltage beyond which the carrier mobility starts to decrease is lowered. Then nonlinearity of the relations between carrier velocity and electric field occurs above the threshold voltage, that is to say the *I–V* curve may deviate Ohm's law. Moreover, we can get information from the figure that dark current at 200 °C is larger than those at 100 °C and room temperature, however photocurrent at 200 °C is smaller than that at 100 °C and photocurrent at room temperature is largest of the three. That indicates a rule that dark current increases with temperature rising and photocurrent represents an opposite variation. More measuring points in Fig. 6 give a further and more convincing evidence for this conclusion. The reason for the increase of dark current with temperature rising may be that more electrons are bumped to conduction energy band by thermal energy when temperature goes up. However the temperature dependence of photocurrent is a little more complicated. It is concerned with the enhanced lattice scattering and the shrinkage of bandgap with increasing temperature. The typical relation between bandgap of ZnO and temperature is shown Fig. 7, it has been demonstrated both theoretically and experimentally [20]. The bandgap of ZnO decreases by 65.7 meV when temperature changes from 20 °C to 200 °C according to Fig. 7. Thus if bandgap decreases with temperature going up, then response peak of the detector, which is determined by the bandgap according to Eq. (1), also changes towards long wavelength direction. The responsivity of detector to the 254 nm mercury lamp decreases as well. So it reflects that photocurrent diminishes with increased temperature. The explanation is further supported by Fig. 8 which shows the variation of responsivity spectrum with temperature changing.

$$\lambda_{peak}(nm) = \frac{1240}{E_g(eV)} \quad (1)$$

Responsivity is an important and widely accepted parameter to weigh the performance of photoconductive detector, which is

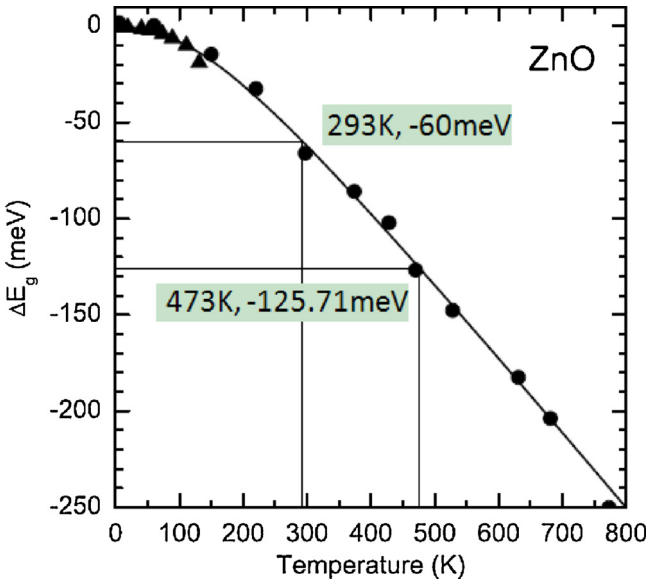

Fig. 7. Relations between bandgap of ZnO and temperature.

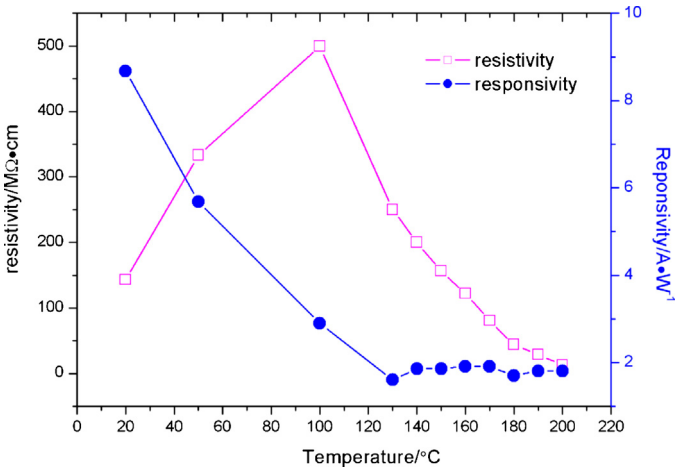

Fig. 9. Temperature dependent responsivity and resistivity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

defined by the dark current (I_D), photocurrent (I_P) and the input radiation power (P_{in}) as follow

$$R = \frac{I_P - I_D}{P_{in}} \quad (2)$$

The responsivity spectra, which are the relations between responsivity and wavelength of incident light, at different temperatures, are given in Fig. 8. The current data used to calculate responsivity are all measured at 5 V, which is almost a standard voltage recognized by many photodetector researchers. A red-shift of response peak can be easily observed in Fig. 8. As we know, response peak is correlated with bandgap of the active layer through Eq. (1). So we can indicate that bandgap of ZnO at 200 °C is smaller than that at 20 °C. It is in accordance with ZnO bandgap dependence on temperature. As a whole, we think that the red-shift of response peak resulted from bandgap shrinkage.

P_{in} is the effective optical power of input UV radiation. And it is the product of radiation intensity of UV light source and photosensitive area of the detector. From Fig. 8 it is apparent that

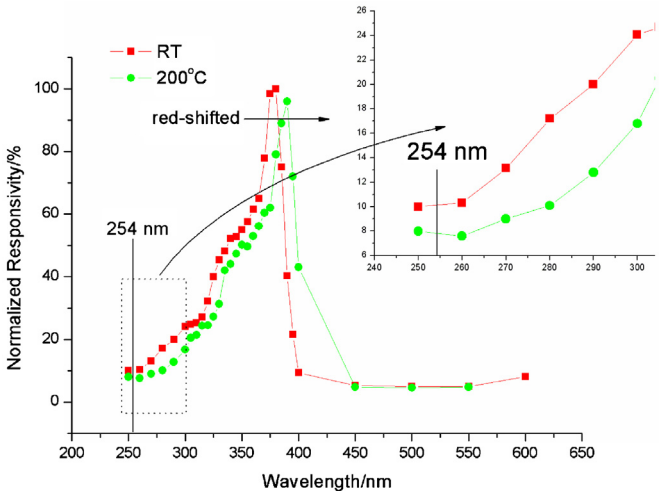

Fig. 8. Responsivity spectra at different temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

responsivity is dependent with temperature and the response peak is red-shifted as temperature changes from room temperature to 200 °C. At 254 nm, the responsivity decreases due to the red-shift. It results decrease of photocurrent with temperature rising. Actually, similar phenomenon has been found in infrared photoconductive detectors based on PbS and some other narrow gap materials [21]. The responsivity is found to be directly proportional to the square root of the ratio of the absorption coefficient to the thermal generation rate, and the ratio decreases with temperature increasing. Although the dark current variation with temperature has been given in Fig. 6, we also give the temperature dependent resistivity of ZnO to make our conclusion more convincing. It is shown with the temperature dependent responsivities in Fig. 9. As we know, conductance which is the reciprocal of resistance represents both impacts of density and mobility of charge carriers. Actually there are two mechanisms in the temperature dependence of the conductance of ZnO based MSM detectors. One is that as temperature goes up, more and more charge carriers generated by thermal generation and released by desorbed oxygen atoms emerge in the film, and then it results in an increase of the conductance of the detector. The other is that the carrier mobility decreases when temperature increases, because the scattering of crystal lattice enhances, then the conductance will decrease. Obviously, the two mechanisms have opposite effects on the conductance of the detectors. As shown in Fig. 9, when temperature is below 100 °C, thermal generation is not so violent, and mobility decrease with increased temperature plays major role in resistivity determination. Thus resistivity increases with temperature rising. However, when temperature goes up above 100 °C, the more violently increased thermal generation becomes more influential and its effect exceeds the effect of mobility decrease. Then resistivity decreases with temperature rising. In Fig. 9, it can also be easily found that the curve of responsivity shows a downward tendency with temperature rising. This is mainly caused by the decrease of photocurrent, due to bandgap shrinkage and lattice scattering. Anyway, the increase of dark current and the decrease of responsivity are quite unwelcome and harmful to photodetectors. So we should take measures to get rid of them or to minimize the influence as possible as we can. The charge carriers generated by thermal generation and released by desorbed oxygen are responsible for the increase of the current. Moreover, from the results it can be concluded that responsivity of ZnO photodetector decreases with temperature.

Although oxygen desorption does not play a so important role in oxide semiconductor films as in oxide semiconductor

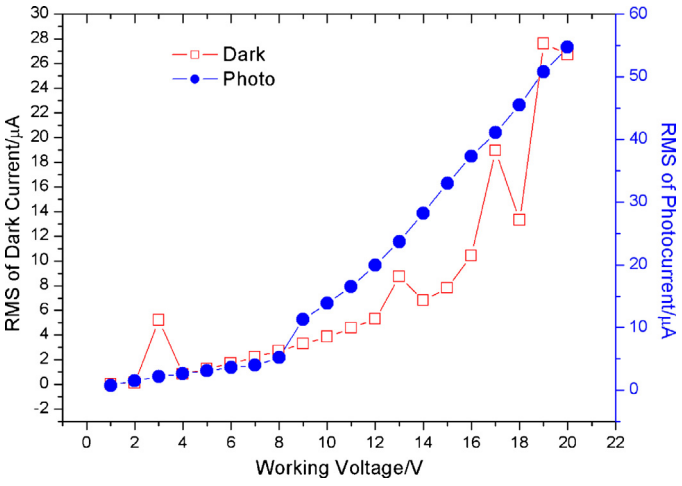

Fig. 10. Relations between the RMSs of dark current and photocurrent at different temperatures and working voltage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

nano-structures such as nanowires and nanotubes, because the latter ones have a large surface-to-volume ratio [22], carriers released by desorbed oxygen in semiconductor films still has an unexpected impact on dark current and photocurrent of photodetectors. Besides, densities of doping impurities and defects, and oxygen gas pressure in the ambient also have impacts on the conductivity of ZnO photodetector. Mass charge carriers from ionized impurities and defects can increase the conductivity. Nevertheless, ionized impurities and defects can scatter the charge carriers when they are transferring in the electric field, thus it reduce the conductivity. Oxygen gas pressure in the ambient can influence the conductivity through oxygen adsorption and desorption process. So keeping the temperature in a small range may lower the unexpected effect. Therefore a thermostat may be needed or temperature compensation circuitry may be another good choice. Keeping the oxygen gas pressure fixed is helpful to remove the erroneous response of the photodetector to oxygen gas pressure changing. In our experiments we found that if the working voltage increased, then the vibration of dark current and photocurrent both would be more violent. It can be easily seen from Fig. 10, the RMSs (Root mean square) of dark current and photocurrent at different temperatures both show apparent augmentation as working voltage rises. They are defined as Eq. (3-1) and Eq. (3-2), respectively.

$$RMS(I_P) = \left[\frac{I_P^2(RT) + I_P^2(50^\circ C) + I_P^2(100^\circ C) + I_P^2(150^\circ C) + I_P^2(200^\circ C)}{5}\right]^{1/2} \quad (3\text{-}1)$$

$$RMS(I_D) = \left[\frac{I_D^2(RT) + I_D^2(50^\circ C) + I_D^2(100^\circ C) + I_D^2(150^\circ C) + I_D^2(200^\circ C)}{5}\right]^{1/2} \quad (3\text{-}2)$$

Here we take the root mean squares of dark current and photocurrent to measure the changing range the currents variation with temperature. From Fig. 10, it appears that reducing the working voltage is helpful to restrain the unfavorable effect. But signal-to-noise ratio would be depressed at the same time when the working voltage falls [23]. There might be a tradeoff between restraining the unwelcome effect and keeping the signal-to-noise ratio high enough.

4. Conclusions

High performance ZnO based MSM UV photodetectors have been prepared. As we know, if UV photodetectors are used for free space communication, fire detection and missile alarm, a good temperature stability of the detectors is necessary for the sake of avoiding erroneous response and strengthening capability of resistance to environmental interference. So the temperature dependence of dark current, photocurrent and responsivity of photodetectors were required to be studied and deeply understood. We measured the *I–V* curves in a temperature range form room temperature (RT) to 200 °C. And the temperature dependence of performance of the ZnO photodetectors has been analyzed and discussed. Bandgap shrinkage, lattice scattering, thermal generation and oxygen desorption play important roles in determining the performance of oxide semiconductor based photodetectors at different temperatures. The decrease of responsivity and increase of dark current are harmful to the applications of UV photodetectors, and reducing the working voltage seems to be helpful in weakening the bad influence of the unfavorable effect.

Acknowledgments

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