PAPER–BASED ZnO, ZnO:SnO$_2$ AND SnO$_2$ ULTRAVIOLET SENSORS

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ABSTRACT

Three photoelectrical devices ZnO, ZnO:SnO$_2$ and SnO$_2$ are made on common pencil drawn circuit over a regular paper as substrate. These three sensors are well capable of detecting UV light and demonstrate features comparable to those of made with complex and expensive techniques. The responses of these sensors are different to the two UV spectra which are used as light sources. Explanation of sensors responses relates samples energy gap values with the UV wavelengths energies and intensities of the two applied UV spectra. Also the role of oxygen adsorption on the variations of samples resistances is discussed. Measurements comparing properties of the three sensors show better performance for ZnO sensor than the two other sensors; but with longer rise and fall times.

Keywords: ultraviolet sensors, ZnO, ZnO:SnO$_2$ and SnO$_2$, response time, paper, pencil**.**

I. INTRODUCTION

Many scientific research groups are trying to obtain a low-cost and large-scale mode of flexible electronics with reasonably high photo response that can be detected without complex systems. Paper-based sensors meet the criteria of low cost, simplicity, rapid fabrication and efficient production process. These sensors are a new alternative technology for fabricating portable and disposable analytical devices for many application areas (Liana, et al., 2012); moreover, they do not generate potentially negative environmental impact during processing and device fabrication.

Devices can be fabricated in minutes by using pencil-on-paper method to develop sensing platforms utilizing nothing more than common office supplies. The 4B pencil lead main component is fine graphite powders bound together by clays (4:1 graphite to clay binder ratio). Pencil traces; which can take on different shapes and patterns, can be regarded as conductive thin films made of graphite particle network on paper. Pencil traces are quite stable against moisture, chemicals and UV irradiation (Lin, et al., 2014).

Reports have mentioned the detailed mechanism of paper based light sensors work (Bao, et al., 2011, Gimenez, et.al., 2012) In this contribution a two popular oxide materials used in fabrication of UV sensors are put into action independently and mixed (they are ZnO,SnO$_2$ and ZnO: SnO$_2$). For the fabrication of a UV radiation (above 3.1 eV) sensor, ZnO and SnO$_2$ are a good candidate because of their appropriate band gaps. These wide-band gap materials are chemically and thermally more stable, which is an advantage for devices operating in hard environments (Chiou and Tang, 2004)

Our sensor uses paper as a porous matrix to hold ZnO and SnO$_2$ crystals; it has been proven that cellulose fibers effectively bind ZnO without an additional binder, which could be useful for several technological applications (Ghule, et al., 2006). Another reason in making paper a good substrate is that our powder resistivities are lower compared to paper resistivity. This implies that electric current preferentially flows on the oxide films.

In this work the results of sensor testing of three paper based UV sensors by using two different UV spectra are reported. An attempt to explain the different responses of the three devices is presented.

II. EXPERIMENTAL DETAILS

The paper used for our UV sensor devices is a regular paper of type Double A (Thailand), which is used for common daily printing. Three solvent suspensions are prepared by putting 1 g of one of the following ZnO, SnO$_2$ and ZnO:SnO$_2$ 50:50 wt.% powder mixtures into 10 mL of methanol. The suspension is dispersed using a magnetic stirrer for 10 minutes. Subsequently four drops (about 4 ml) from each suspension are deposited onto paper immediately to avoid precipitation and

clustering. To test the response of the paper sensors, a UV lamp of type CAMAG (Swiss made) is used to give two UV spectra as shown in Figure 1. Interdigitated graphite electrodes are drawn with a 4B pencil to achieve appropriate film area between electrodes as shown in Figure 2. Current versus voltage (I - V) measurements are performed on a sensor device under dark and UV illumination. Response time for each sample is measured in 180 seconds. A voltage 10 V is applied between the two electrodes of each sample during response time measurement. The surface morphologies of paper, drawn lines by 4B pencil and deposited layer are observed under an optical Nikon Type 120 (Japan) microscope provided with a digital camera of type DXM 1200 F. To measure the optical energy gaps of samples, dip coating method is used to deposit the materials on glass slides. Optical absorption measurements are performed with a Shimadzu UV-VIS-NIR spectrophotometer. An Ocean Optics photospectrometer of type HR4000CG-UV-NIR (Netherland) is used to specify UV lamp wavelengths and their intensities.
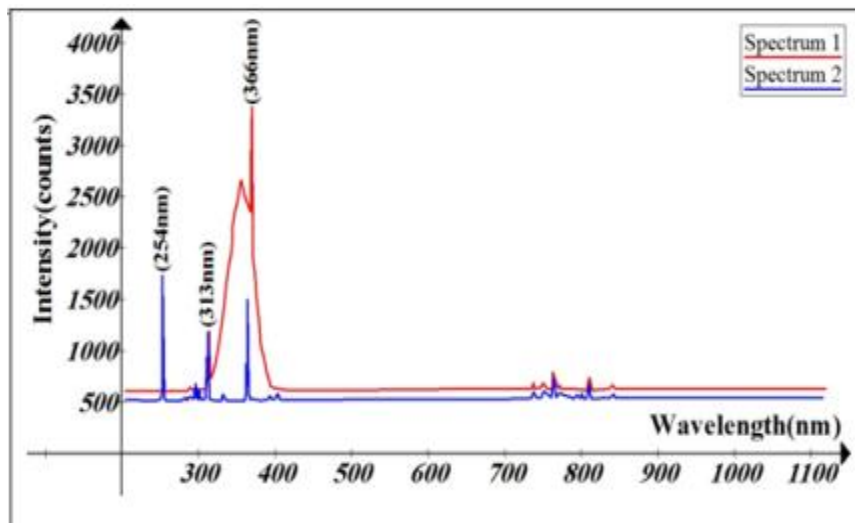

Figure 1. Spectra of two different UV sources.
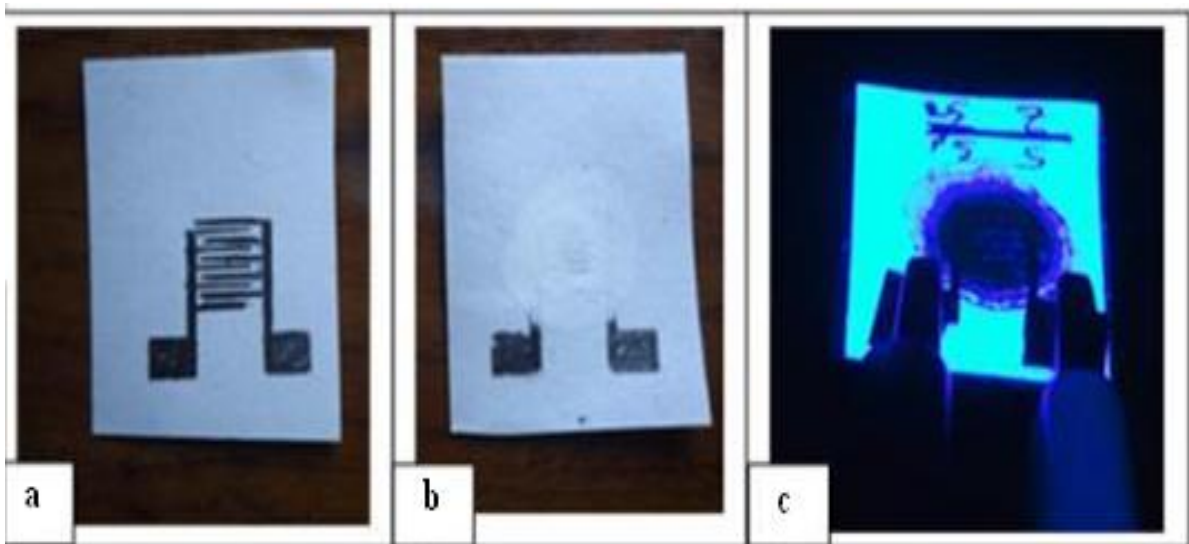
Figure 2. (a) Graphite electrodes drawn by 4B pencil on a paper substrate, (b) ZnO:SnO$_2$ sensor on a paper substrate, (c) Illustrated sample by UV ray.
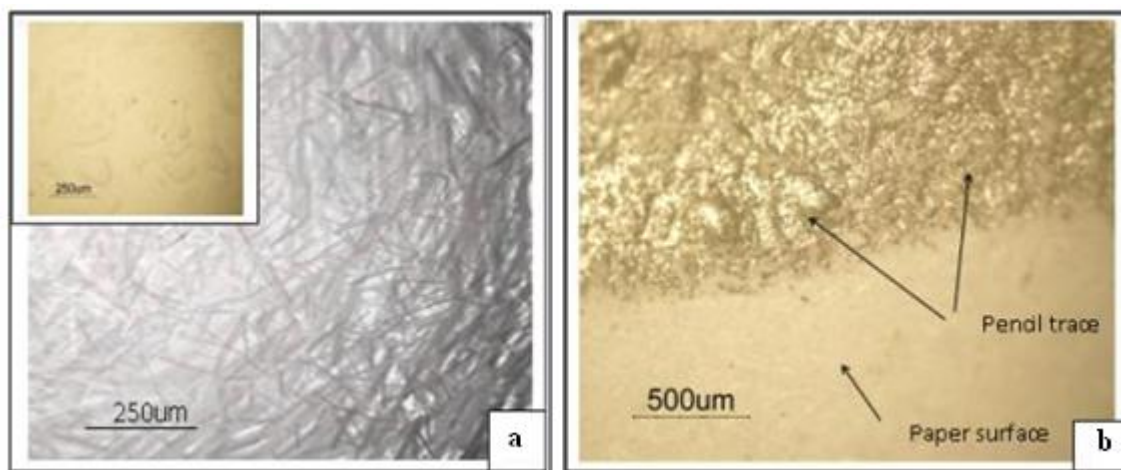
Figure 3. (a) Cellulose paper surface (the insert depicts the deposited ZnO:SnO$_2$ mixture), (b) Optical image of pencil trace.

III. RESULTS AND DISCUSSION

Figure 3 shows optical images of paper surface, pencil line and deposited layer of ZnO:SnO$_2$ mixture, while the UV-VIS spectra of the samples are displayed in Figure 4. The top absorption peaks of ZnO, ZnO:SnO$_2$ and SnO$_2$ occurs at the wavelengths of 380 nm (3.26 eV), 365 nm (3.4 eV) and 345 nm (3.6 eV) respectively. The middle value of ZnO:SnO$_2$ energy gap between that of ZnO and SnO$_2$ was already recorded by another worker (Cha, et al., 2012).
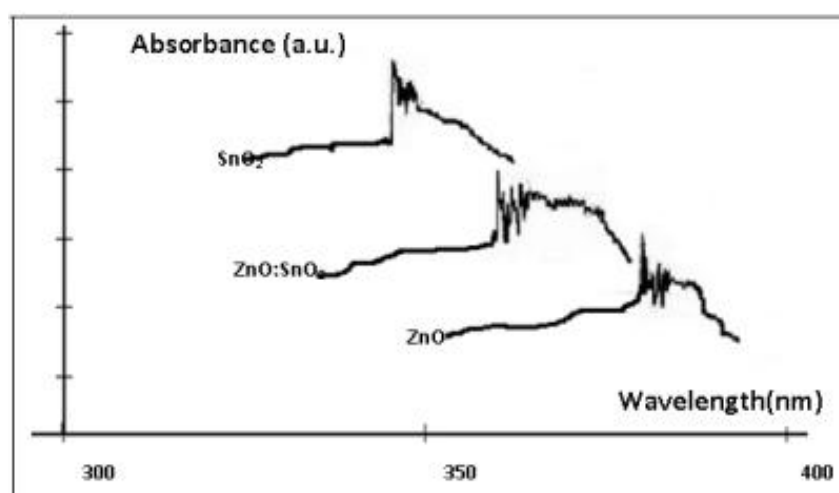
Figure 4. UV-VIS absorption spectra of pure ZnO, ZnO:SnO$_2$ and pure SnO$_2$.

Figure 5 illustrates the current as a function to applied voltage. Some notes can be drawn from the curves in this figure, namely (a) the ZnO sample has highest dark current, (b) the ZnO sample has highest photocurrent produced by illumination with spectrum 1, (c) all samples have photocurrent values (when the 2nd UV illumination is switched on) less than that produced from illumination with second one, and (d) the SnO$_2$ sample has approximately the same photocurrent value when illuminated with the two UV lamps. In order to obtain the relative response after illumination with the two UV spectra for each sample; the resistance relative change (R%) is calculated for each sample. R% values are listed in Table I. For ZnO and ZnO:SnO$_2$ samples, the maximum R% changes are recorded when spectrum 1 is applied. But for SnO$_2$ sample the maximum R% change is recorded when spectrum 2 is applied. There are two ways to understand the behavior of I-V curves in Figure 5 and the variation of R% in Table I. In the first method, one relates sample energy gap values with the UV wavelengths, energies and intensities of the two applied UV spectra. In the second, one investigates the effect of oxygen adsorption on the sample resistance.

The energy gap of SnO2 sample is 3.6 eV, so the UV energies greater than this value will be able to create electron-hole pairs. Electron-hole pairs numbers depend on applied spectrum intensity. There are two active wavelengths in

spectrum2: 254nm and 313nm, both with relatively high intensities; on the other hand, in spectrum1 there is an active wavelenths coexistence around 366 nm which have intensities approximately comparable to that of active wavelengths in spectrum2. Considering that photocurrent depends on intensity (among others), and the intensities of active wavelengths of the two applied UV spectums are approximately equal the result is the same photocurrent for two spectra as Figure 5c shows. All wavelengths in spectrum2 are active in the ZnO:SnO$_2$ sample because it has a 3.4 eV energy gap; but the intensities of active wavelengths in spectrum1 are higher, resulting in greater photocurrent under spectrum1 illumination, as can be seen in Figure 5b. Considering that the ZnO sample has an energy gap equal to 3.26 eV, the active wavelengths with high intensity in spectrum1 have higher intensities than that of spectrum1, consequently the ZnO sample has maximum photocurrent and has larger photocurrent when illuminated with spectrum1.

Table I. Sample resistances and   R % for the two spectra. Applied voltage is 10 volt.

Sample type	$R_{(dark)}(M\Omega)$	R%$_{(spectrum1)}$	R%$_{(spectrum2)}$
ZnO	1.87	23.53	10.7
ZnO:SnO$_2$	9.18	12.2	6.97
SnO$_2$	9.51	8.622	10.2

The important difference between ZnO and SnO$_2$ (both of them are n-type semiconductors (Smart and Moore, 2005) may come from the natural n-type doping that makes ZnO highly conductive, see table1. Also; the difference might be due to the ZnO oxidation that depletes doping at the surface (SP,et al., 2009). Hasan, et al (2012) explained the mechanism of increasing ZnO response (deposited by screen print method on paper) to UV illumination. Under dark there is a low conductivity depletion layer near the surface, free electrons in this layer are captured by adsorbed oxygen molecules, making negatively charged oxygen ions at the surface. Under light illumination photon-generated holes accumulate at the surface, partly neutralizing negatively-charged absorbed oxygen species, which reduces the surface potential, leading to a reduction of the depletion width and increased photocurrent. As a result additional source of free electrons adds to the photocurrent. Electron trapping associated with oxygen adsorption was described by Bao, et al. (2011) as follows

$$O_2(g) + e^- \quad O^{-2}(ad), \tag{1}$$

$$h^+ + O^{-2}(ad) \quad O_2(g). \tag{2}$$

On the other hand, Chowdhuri, et al. (2008) confirmed that the presence of adsorbed oxygen on SnO$_2$ film surface acts as trap centers of charge carriers and becomes O^{-2} after capturing an electron (the same function inside ZnO surface); however, the enhanced oxygen activity on SnO$_2$ film surface is triggered at ~ 130°C, and there is no resistance decrease with increasing temperature within the temperature range 130–180°C. To investigate the existence of this behavior for our ZnO, its resistance variation with temperature was observed, and the result is shown in Figure 6. Examination of Figure 6 improves the decreasing of resistance with temperature without any plateau (like that of SnO$_2$) i.e. there is no unusual oxygen behavior during any temperature period from the normal decrease of ZnO resistance with temperature. Consequently it can be deduced that there are no additional free carriers due to O$_2$ desorption when SnO$_2$ is illuminated with UV rays (as is the case with ZnO). This inference, in addition to the effect of the parameters discussed above, explains the relative high SnO$_2$ resistance after UV illumination compared to that of ZnO.

Table II. Rise and fall times under two different UV spectra.

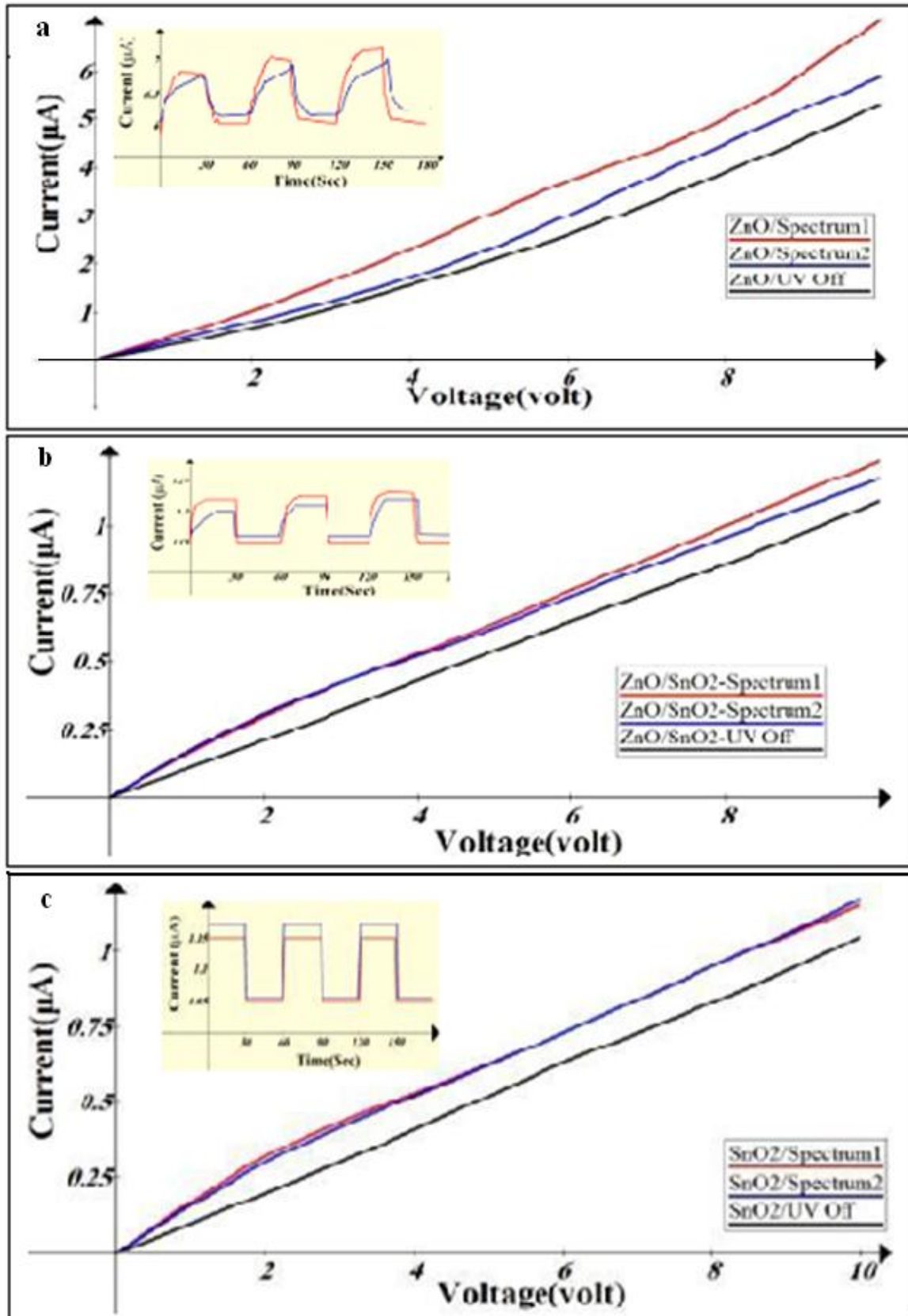| Sample type	Spectrum1		Spectrum2	
	Rise Time (s)	Fall Time (s)	Rise Time (s)	Fall Time (s)
ZnO	14	5	10	10
ZnO:SnO$_2$	5	3	7	3
SnO$_2$	1	1	1	2

Figure 5. The current vs. applied voltage under three conditions: (a) dark, (b) UV illumination, (c) two spectra

Table II shows rise and fall times under two different UV spectra, and the differences among sample rise and fall times can be seen when UV spectrum1 is illuminated. The same can be seen for spectrum2. There is an exception for SnO_2 and ZnO samples under illumination of spectrum1 and 2 respectively, where rise time is equal to fall time. For ZnO and $ZnO:SnO_2$ samples; once the spectrum1 exposure is turned on, it takes some time to generate electron-hole pairs. This long response time indicates that there are other reactions involved in these sensors. O_2 desorption after electron-hole pairs generation (UV illumination is turned on) may takes longer time than that of its absorption after UV source is turned off. As it previously stated; there is no active O_2 absorption and desorption at room temperature (the temperature of UV illumination) with SnO_2 sample. So there is no effect of these phenomena on rise and fall time of SnO_2 sensor. Illumination ZnO sample with spectrum2 produces less electron-hole pairs due to its lower intensity compared with that of spectrum1 (see Figure 5a). As a result, the effect of O_2 absorption and desorption becomes lower. Approximately the middle rise and fall times of $ZnO:SnO_2$ confirms the role of O_2 absorption and desorption in response times of both ZnO and SnO_2. Finally it is worth noting that the photocurrent values in this work are in the microampere scale compared with other workers (Gimenez , et al., 2011) who deposited ZnO on paper and glass; their experimental photocurrent is in the nanoampere scale. This merit in this work comes from using a very fine distance between electrodes, as seen in Figure 2a.
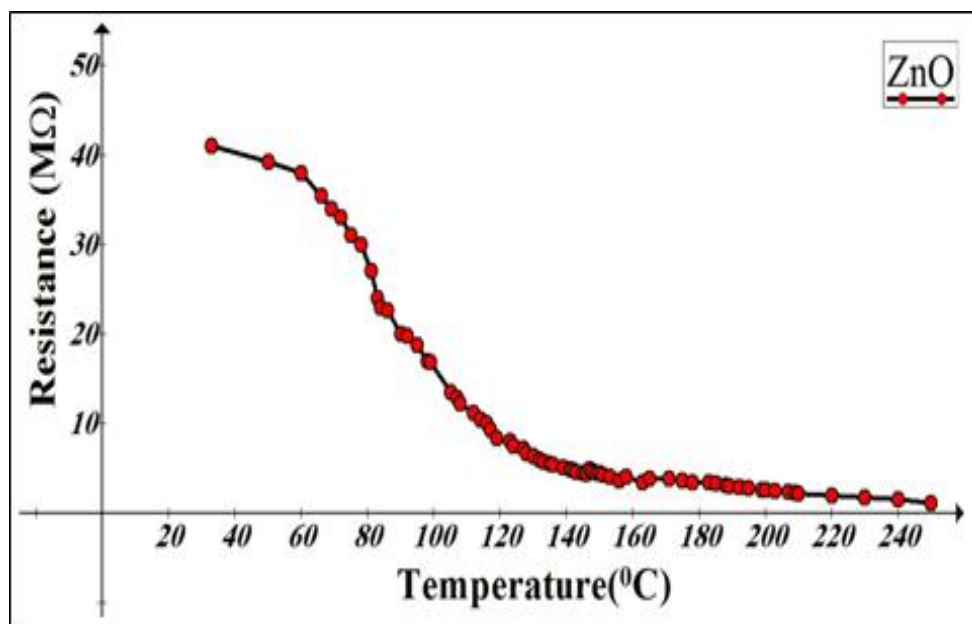

Figure 6. ZnO resistance variation with temperature.

CONCLUSIONS

Measurements comparing properties of $ZnO, ZnO:SnO_2$ and SnO_2 films on paper show better performance of ZnO than other two powders due to its higher dark current, higher photocurrent and maximum R%. Paper is a good substrate to fabricate $ZnO, ZnO:SnO_2$ and SnO_2 sensors with appropriate properties to be used in UV sensing applications. Moreover, O_2 adsorption-desorption processes play an essential role in resistance changes of UV sensors.

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