Sains Malaysiana 39(4)(2010): 627–631

Effects of Annealing Temperature on the Optical Properties and Device Performance of Ag / n-Si / CuPc / Ag Solar Cell Prepared via Spin Coating Method

(Kesan Suhu Sepuh Lindap ke atas Sifat Optik dan Prestasi Peranti Sel Suria Ag / n-Si / CuPc / Ag yang disediakan Melalui Kaedah Salutan Berputar)

HANASHRIAH HASSAN*, NOOR BAA'YAH IBRAHIM
& ZAHARI IBARAHIM

ABSTRACT

Copper phthalocyanine (CuPc) thin films have been prepared using a simple spin coating method. The films were annealed at 5 different temperatures (323, 373, 473, 523 and 573 K) for one hour in air. Optical properties study using the UV-Vis spectrophotometer showed that in the range of wavelength of 300-800 nm, all of the films have identical absorption coefficient patterns and there was no systematic changes with respect to annealing temperature. The film annealed at 373 K showed the highest absorbance while the lowest absorbance was shown by the film annealed at 323 K. The results showed that the optical band gaps depended on the temperature. The film annealed at 373 K has the lowest optical energy gap. Using the five annealed films, solar cell with the configuration of Ag / n-Si / CuPc / Ag were fabricated. Under the 50 W/cm^2 light illumination, the current voltage measurements at room temperature were carried out on the device. The device which consists of film annealed at 373 K exhibited the best photovoltaic characteristics. The different annealing temperature also affect the photovoltaic behavior of the devices in a non-systematic way.

Keywords: Annealing; current-voltage; optical band gap; solar cell

ABSTRAK

Filem nipis kuprum ftalosianina (CuPc) telah disediakan melalui kaedah ringkas salutan berputar. Filem tersebut disepuh lindap pada 5 suhu yang berbeza (323, 373, 473, 523 dan 573 K) selama satu jam dalam udara. Sifat optik yang dikaji menggunakan UV-Vis spektrofotometer menunjukkan pada julat panjang gelombang 300-800 nm, semua filem mempunyai corak pekali penyerapan yang sama dan tiada perubahan sistematik terhadap suhu sepuh lindap. Filem yang disepuh lindap pada 373 K menunjukkan penyerapan tertinggi manakala penyerapan terendah ditunjukkan oleh filem yang disepuh lindap pada 323 K. Keputusan menunjukkan jurang tenaga optik adalah bergantung kepada suhu. Filem yang disepuh lindap pada suhu 373 K mempunyai jurang tenaga optik paling rendah. Menggunakan kelima-lima filem yang disepuh lindap itu, sel suria dengan konfigurasi Ag / n-Si / CuPc / Ag telah difabrikasi. Di bawah pancaran 50 W/cm^2, pengukuran arus-voltan pada suhu bilik telah dilakukan ke atas peranti. Peranti yang mengandungi filem yang disepuh lindap pada 373 K mempamerkan ciri fotovoltaik terbaik. Suhu sepuh lindap yang berbeza juga memberi kesan kepada sifat fotovoltaik peranti secara tidak sistematik.

Kata kunci: Arus-voltan; jurang tenaga optik; sepuh lindap; sel suria

INTRODUCTION

The intensive research on semiconductor heterostructures has lead to the discovery of a new class of heterostructures which involves the contact between organic and inorganic semiconductor (Chen & Shih 2006). The combination of inexpensiveness, solution processibility, easy chemical modification and strong photo-absorption coefficient of organic molecules with the high carrier mobility of inorganic material has produced new photoelectric conversion materials (El-Nahass et al. 2006; Smertenko et al. 2008). Metal phthalocyanine (i.e. copper or zinc) combine with different material such as n-type GaAs (Karimov et al. 2005), porous silicon (Levitsky 2004) and ZnO (Yuki et al. 2006) can be utilized to produce the hybrid solar cell.

The phthalocyanine was chosen in this research because it is more compatible with any flexible substrate and offers low cost solar cell production (Prabakaran et al. 2008; Yakuphanoglu et al. 2008). There are two general forms of phthalocyanines, which are metal free phthalocyanine (H_2Pc) and various metal substituted forms phthalocyanines (Pcs). Metal free Pcs contains two hydrogen atoms in the centre of molecule while the various metal Pcs occur when the hydrogen atoms are replaced by a single metal atom (Abraham & Menon 2005). One of the metal phthalocyanines is copper phthalocyanine (CuPc), which is a p-type semiconductor and has the advantage of being sufficiently stable towards chemicals and heat treatment (Ambily & Menon 1999; Shaji et al. 2002). Copper phthalocyanine is a good light absorber in the UV-Vis region and also can absorb light on either side of blue green region in the spectrum (Inigo et. al. 1997; Sharma et al. 2006). In this paper, we report on the effect of annealing temperature on the optical properties of CuPc thin films prepared by a spin coating technique. Using the same films, heterostructures solar cell with the configuration of Ag / n-Si / CuPc / Ag were prepared and characterized.

MATERIALS AND METHODS

The CuPc powder obtained from Sigma Inc. was dissolved in 5 mL toluene to obtain the solvent concentration of 0.02 mM. The solution was stirred for 24 h to ensure that the CuPc powder was fully dissolved. For the optical measurement, CuPc was deposited onto the glass substrates by spin coating technique with the spinning rate of 3000 rpm for 30 seconds. The films were annealed at five different annealing temperatures i.e. 323, 373, 473, 523 and 573 K for one hour in air. The optical absorption and transmission spectra of the films were measured using UV-Vis Spectrophotometer Lambda 900 Perkin Elmer in the wavelength of 300 – 800 nm. The solar cell devices were fabricated on n-type silicon substrates that had been cut into 2 cm × 2 cm × 0.76 cm. The cleaning process of the silicon substrates was done using an ultrasonic cleaner by immersing the substrates in the methanol followed by isopropyl alcohol and distilled water for 15 minutes. The cleaned substrates were dried well using nitrogen gas before the coating process. For the junction preparation, similar coating and annealing process as mentioned for the CuPc on the glass substrate was applied. Besides to crystalline the films, the annealing process was also to gain better diffusion between CuPc and silicon. Silver electrodes (work function ~ 4.7 eV) were pasted on top and bottom of the samples. The structure of the device is shown in Figure 1. It has already been proven that, unlike the inorganic cells, the organic inorganic hybrid cells do not require a built-in-electrostatic potential for charge separation. Consequently, the electrode work function is independent of V_{oc} value (Levitsky 2004). The current-voltage measurement was carried out by the I-V set model Keithley 206 under 50 W/cm^2 light illumination.

RESULTS AND DISCUSSION

Figure 2 shows the spectrum of absorption coefficient versus wavelength for all of the films. It can be seen that all films showed identical absorption coefficient patterns and there were no systematic changes with respect to the annealing temperature. The film annealed at 323 K exhibited the lowest absorbance while the CuPc film annealed at 373 K showed the highest absorbance. This could be due to the different percentage loss of the unstable morphology layer on the CuPc film during the annealing process. Hoshi et al. (1990) reported that the unstable morphology layer may exist on the CuPc film and only can be rid off by heat treatment. The Q-band was obtained in the region 550 to 800 nm while the B-band is in the region 300 to 400 nm. The Q-band showed two shoulder peaks while the B-band has only one. This is in a good agreement with the results obtained by other researchers (Ambily & Menon 1999; Farag 2007). The Q-band corresponds to the excitation between the ground state π (HOMO) to the π* (LUMO) (El-Nahass & Yaghmour 2008). The optical band gap values were obtained from the analysis of the absorption spectrum in the high energy region.

The one electron theory was applied to obtain the information about the direct or indirect inter-band transition of the CuPc films. In the both regions, the absorption coefficient and the incident photon energy can be related as $\alpha h\nu = B\,(h\nu - E_g)^{\,m}$ where $h\nu$ indicates the energy of incident photon, E_g is the value of the optical band gap, m and B are constant (Bardeen et al. 1965; Farag 2007). In order to obtain the m value, the graph of $(\alpha h\nu)^{1/m}$ versus $h\nu$ for the region near absorption edge of Q and B bands has been plotted for m = 2, 2/3, ½, and 1/3. The m value was selected from the graph that gave the best line fit (El-Nahass & Yaghmour 2008). For our case, the best line fit was given by m = 2. By extrapolating the graph to $(\alpha h\nu)^{1/2} = 0$ the optical band gaps (Figure 3)

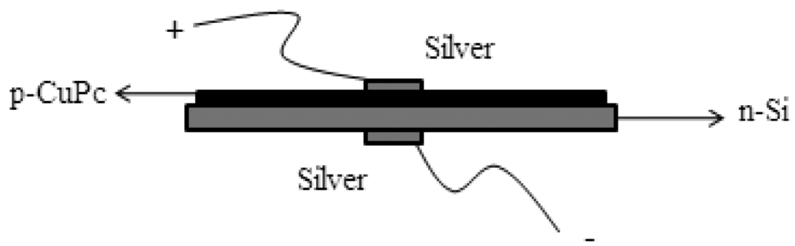

FIGURE 1. Heterostructures device Ag / CuPc / n-Si / Ag

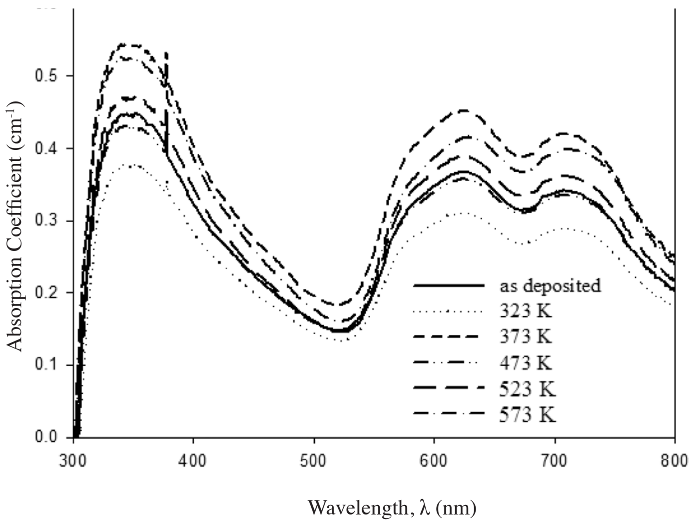

FIGURE 2. Absorption coefficient spectrum of as deposited CuPc films and CuPc films annealed at 323 K, 373 K, 473 K, 523 K and 573 K for one hour in air

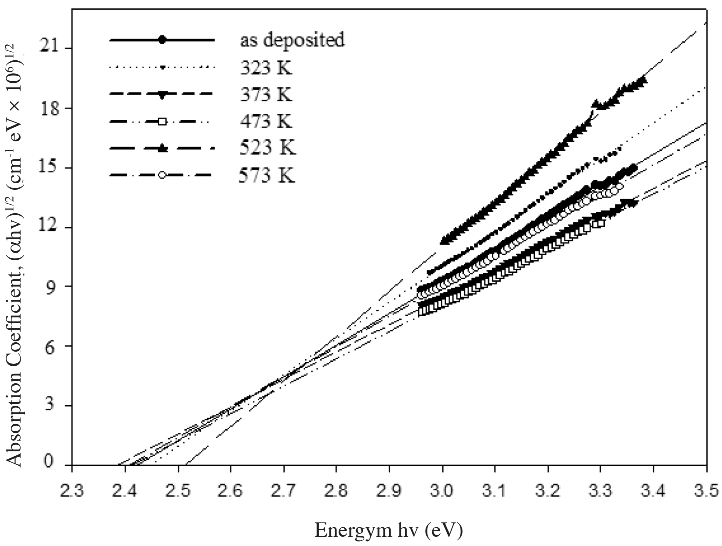

FIGURE 3. Plot of $(\alpha h\nu)^{1/2}$ against hν

were obtained. Our results showed that the optical band gaps were dependent on annealing temperature. However, the changes are in non-systematic order as the annealing temperature was increased. The highest optical band gap was obtained from the sample annealed at 523 K while the lowest value was from the sample annealed at 373 K as shown in Table 1.

The current-voltage measurements were carried out under illumination of 50 W/cm^2. The photons with low wavelength (below 400 nm) are absorbed by the n-Si. The electrons which gain enough energy will be excited from the valence band to conduction band and subsequently collected by bottom electrode (silver). The holes in the valence band of n-Si diffused towards the CuPc and finally collected by the top electrode (silver). The photons above 400 nm were absorbed by the CuPc film and excitons were created. These excitons dissociate into free carriers

TABLE 1. The optical band gap, E_{opt} values for the CuPc films prepared by spin coating technique

Annealing temperature / K	Optical band gap, E_{opt} (± 0.02) / eV
As deposited	2.42
323	2.45
373	2.38
473	2.41
523	2.51
573	2.41

due to the heterojunction (Sharma et al. 2006). In order to study the film optimum annealing temperature for the hybrid cell, the current voltage measurements under 50 W/

cm^2 light illumination were carried out on five different devices which contain the as deposited CuPc and CuPc annealed at different temperature (323 K to 573 K). The measurements were done at room temperature between 0 and 1V. Table 2 shows the results while Figure 4 shows the photovoltaic behavior of the cell under light illumination. The results show that different annealing temperature affect the photovoltaic behavior but in a non-systematic way. The highest J_{sc} and V_{oc} values were obtained from the device with film annealed at 373 K. This could be due to the lowest optical band gap value of the CuPc annealed at this temperature.

TABLE 2. The Short circuit current density, J_{sc} and open circuit voltage, V_{oc} for the solar cell heterostructures devices annealed at various temperatures

Annealing temperature / K	Short circuit current density, J_{sc} ± 0.01 / (μA cm^{-2})	Open circuit voltage V_{oc} ± 0.01 / Volt
As deposited	0.26	0.21
323	5.50	0.26
373	7.50	0.33
473	0.80	0.16
523	0.06	0.11
573	3.50	0.13

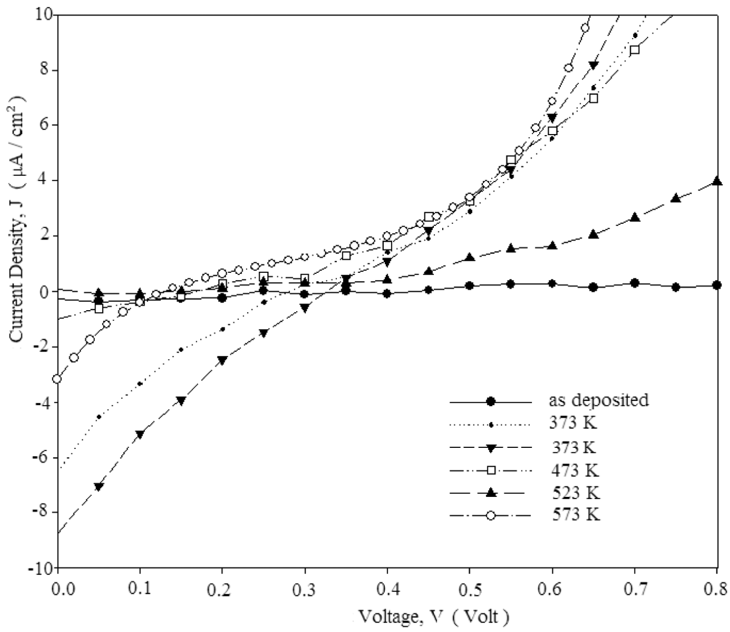

FIGURE 4. I-V Characteristics of CuPc heterostructures devices annealed at five different annealing temperatures. The measurement was made under 50 W / cm^2 light illumination

CONCLUSION

CuPc films have been successfully prepared by a simple method spin coating. The optical properties of the films were affected by the annealing process. The film annealed at 373 K has the lowest optical energy gap. Using the same films, heterojunction solar cells with configuration of Ag / n-Si / CuPc / Ag were built and it was found that the annealing temperature also affect the device performance. The device consists of a film annealed at 373 K gave the highest J_{sc} and V_{oc} values. However, few modifications should be done in order to further enhance the electrical properties of the CuPc solar cell device. The electrode design and deposition of buffer layer such as poly (3,4-ethylenedioxythiophene) PEDOT on top of film surface should also be considered in the fabrication.

ACKNOWLEDGEMENTS

This work was supported by the research grant FRGS-0010-2006 from the Ministry of Higher Education. Hanashriah Hassan would like to thank the Malaysian Ministry of Science, Technology and Innovation for the NSF Scholarship.

REFERENCES

Abraham, C.V. & Menon, C.S. 2005. Electrical conductivity studied of mixed phthalocyanine thin films. *Central European Journal of Physics* 3(1): 8-14.

Ambily, S. & Menon, C.S. 1999. The effect of growth parameters on the electrical, optical and structural properties of copper phthalocyanine thin films. *Thin Solid Films* 347: 284-288.

Bardeen, J., Blatt, F.J. & Hall, L.H. 1965. Indirect transitions from the valence to the conduction bands. *Proceeding of Conference on Photoconductivity*: 149-154.

Chen, C.H. & Shih, I. 2006. Hybrid organic on inorganic semiconductor heterojunction. *J Mater Sci: Mater Electron* 17: 1047-1053.

El-Nahass, M.M., Farid, A.M., Farag, A.A.M. & Ali, H.A.M. 2006. Carrier transport mechanisms and photovoltaic characteristics of p-H_2Pc / n-Si heterojunction. *Vacuum* 81: 8-12.

El-Nahass, M.M. & Yaghmour, S. 2008. Effect of annealing temperature on the optical properties of thermally evaporated tin phthalocyanine thin films. *Applied Surface Science* 255: 1631-1636.

Farag, A.A.M. 2007. Optical absorption studies of copper phthalocyanine thin films. *Optics & laser Technology* 39: 782-732.

Hoshi, H., Dann, A. & Maruyama, Y. 1990. The structure and properties of phthalocyanine films grown by the molecular beam epitaxy technique. II. Ultraviolet visible spectroscopic study. *Journal of Applied Physics* 67: 1845-1849.

Inigo, A.R., Xavier, F.P. & Goldsmith, G.J. 1997. Copper Phthalocyanine as an efficient dopant in development of solar cells. *Materials Research Bulletin* 32(5): 539.

Karimov, Kh. S., Ahmed, M.M., Moiz, S.A. & Fedorov, M.I. 2005. Temperature dependant properties of organic-on-inorganic Ag /p-CuPc / n-GaAs / Ag Photoelectric Cell. *Solar Energy Materials and Solar Cell* 87: 61-75.

Levitsky, I.A. 2004. Hybrid Solar Cells based on porous Si and copper phthalocyanine derivatives. *Applied Physics Letter* 85(25): 6245-6247.

Prabakaran, R., Fortunato, E., Martins, R. & Ferreira, I. 2008. Fabrication and characterization of Hybrid Solar Cells based on copper phthalocyanine/porous silicon. *Journal of Non-Crystalline Solids* 354: 2892-2896.

Shaji, V., Mercy, I., Mathew, E.J. & Menon, C.S. 2002. Determination of energy gap of thin films of cadmium sulphide, copper phthalocyanine and hybrid cadmium sulphide/copper phthalocyanine from its optical studies. *Materials Letters* 56: 1078-1083.

Sharma, G.D., Raj Kumar, Shailendra Kumar Sharma & Roy, M.S. 2006. *Solar Energy Materials and Solar Cell* 90: 933-943.

Smertenko, P.S., Kostylev, V.P., Kislyuk. V.V., Syngaevsky, A.F., Zynio, S.A. & Dimitriev, O.P. 2008. Photovoltaic cells based on Cadmium sulphide-phthalocyanine heterojunction. *Solar Energy Materials and Solar Cells* 92: 976-979.

Yakuphanoglu, F., Kandaz, M. & Senkal, B.F. 2008. Current-Voltage and Capacitance Voltage Characteristics of Al / p-type silicon/organic semiconductor based on phthalocyanine rectifier contact. *Thin Solid Films* 516: 8793-8796.

Yuki, Y., Makoto, M., Senku, T., Ichiro, H., Yasuhisa, F. & Katsumi, Y. 2006. Photovoltaic Properties and inner electric field of ZnO/Zn-phthalocyanine hybrid solar cells. *Synthetic Metals* 156: 1213-1217.

School of Applied Phyics
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia

*Corresponding author; email: baayah@ukm.my

Received: 14 August 2009
Accepted: 5 November 2009