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STUDIES OF OPTICAL AND MORPHOLOGICAL PROPERTIES ON THE ZnPc/Gaq3 MIXTURE THIN FILMS

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ABSTRACT

Organic photovoltaic is considered as one of the best renewable source of energy that can be used in future. A bulk heterojunction of p-type and n-type materials is reported to date that will give a better performance for organic solar cells. We report the studies on the optical and morphological properties of the thin films mixture containing p-type zinc phthalocyanine (ZnPc) and n-type tris (8-hydroxyquinoline) gallium, (Gaq3). The optical properties of the p-n mixture ZnPc/Gaq3 films will be studied via UV-visible absorption spectroscopy while the morphological properties will be investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Furthermore, the electrical characteristics of the organo-metallic hybrid solar cell based on ZnPc/Gaq3 thin film in the dark and under white light illumination will be studied using a Source-Measuring-Unit (SMU). By controlling the processing condition, the optical and morphological properties of the thin films mixture, and thus the performance of the polymer mixture based optoelectronic devices can be modified.

INTRODUCTION

In recent years organic semiconductors have drawn considerable attention due to their growing potential as active materials in electronic and optoelectronic devices such as photovoltaic devices. The organic solar cells themselves offer a lot of advantages such as providing an alternative to inorganic photovoltaic solar cells, since they can strongly absorb light and be deposited on flexible substrates at low cost. Moreover, they can be easily processed using spin-coating or evaporation technique and the vast variety of possible chemical structures and functionalities of organic materials such as organo-metallic materials, polymers, dyes, pigments and so on, make themselves to become the promising candidates in various kinds of purposes [1].

However, organic materials have a lower dielectric constant and a higher exciton binding energy the inorganic semiconductors. Therefore, the formed electrons and holes can not easily be transported due to the low mobility of charge carriers that lead to the limitation of high conversion efficiency of solar energy into electrical energy. In order to address such problems, two different materials of p-type and n-type that differ in electron donating and accepting properties have been utilized in the organic photovoltaic devices. Charges are created by photoinduced electron transfer between the two components and establish a p-n junction. To further improve the power conversion efficiencies, the electron-donor and acceptor need to be in close contact

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which is usually realized by mixing them in one single layer yielding a so-called bulk heterojunction (BHJ) structure [2-5].

In the field of research and development of low-cost solar energy converters, solar cell based on organo-metalic hybrid materials deserves a serious investigation. It is a mix of both organic and metalic materials, which combining the unique properties of organic materials with the properties of inorganic semiconductor. In addition to this, low cost synthesis, processability and versatile manufacturing of thin film devices make it attractive [6,7]. To improve the power conversion efficiency of organo-metallic hybrid solar cell, it is important to use high-mobility organic semiconductors as an active material.

Phthalocyanine (Pc) is a well-known organic semiconductor and is suitable for photovoltaic applications since it has a very high physical and chemical durability. Moreover, it offers the added advantage of a tendency to self-organize since it is a self-assembling liquid crystal developed from a common deep-blue-green pigment. Thus, its optical, electronic and photoelectronic properties are being seriously investigated [8]. Many kinds of phthalocyanines attach to various metals are applicable to different kinds of optoelectronic devices like solar cells. Among these, zinc phthalocyanine (ZnPc) ($C_{32}H_{16}N_8Zn$) which acts as an electron donor, is a promising candidate for photovoltaic applications since it is easily synthesized and environment-friendly. Moreover, the major part of incident light in the visible region can be absorbed and thus effectively leads to the photo-generation of excited carriers which are important in the photovoltaic effect [9,10]. While, gallium(iii)-8-hydroxyquinoline, (Gaq3) acts as an electron acceptor in mixing with ZnPc, forming a mixture material that can be utilized in the fabrication of solar cell. Solar energy conversion efficiencies of over 3% have been reported for solar cells made from evaporated small molecules, which based on a layered stack of phthalocyanines and C60-fullerenes [11]. Typically, the performances of optoelectronic devices can be improved by controlling the morphology of films [12] which is influenced by processing conditions like the composition, the solution concentration, type of solvent, spin coating speed and so on. Thus, the investigation of the effect of certain processing conditions on the optical and morphological properties of blend films is very important.

EXPERIMENTAL PROCEDURES

Materials and solutions

The organo-metallic material ZnPc and Gaq3 were purchased from Sigma-Aldrich, Inc and H.W. Sands Corp respectively. The chemical structures of ZnPc and Gaq3 are shown in Figure 1. Mixture solutions with various compositions of Gaq3 component (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70% and 100% Gaq3) were prepared in chloroform at a solution concentration of 60mg/ml. These solutions were then stirred for 24 hours at room temperature.

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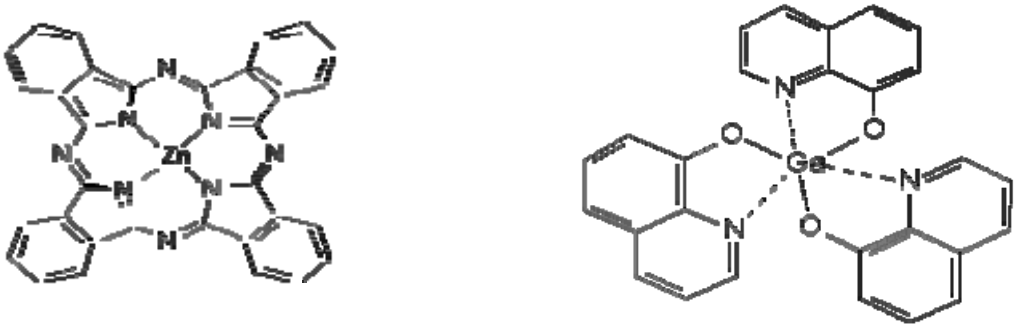
Film and device fabrication

For this research work, glass substrates were used for ultraviolet-visible (UV-Vis) absorption and atomic force microscopy (AFM) measurements. Before film deposition, all glass substrates must be properly. The mixture solutions were spin-coated onto the cleaned glass substrates at spin speed of 2000 rpm for 30 seconds using a model Laurell 400B Spin Coater to produce uniform thin films. The solar cell devices were designed in a sandwich structure of the photoactive mixture layer between an anode of indium tin oxide (ITO) and a metal cathode of aluminium (Al). For solar cell fabrication, ITO coated glass having a resistance of 30 Ω/cm^2, was used as substrate. The ITO was ultrasonically cleaned using DECON^{TM} foam solution, deionized water, acetone and isopropyl alcohol sequentially for 10 minutes, respectively. After drying using flowing nitrogen, a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Baytron P VPAI 4083 grade, HC Stark) layer was spin-coated on top of the cleaned ITO, before being annealed at 110°C on a hot plate for 30 minutes in order to reduce roughness and increase the wettability of the substrate surface. Then, the ZnPc:Gaq3 mixture solution was spin-coated on the PEDOT:PSS layer at 7000 rpm for 20 seconds. A mixture thin film (including the PEDOT:PSS layer) with thickness of ~140 nm was produced, in which its thickness was measured using Scanning Electron Microscope (SEM). Finally, aluminium layer was deposited on the mixture films under vacuum using Edward 306 Thermal Evaporator at $\sim 7\times10^{-6}$ mbar, defining an active area of $0.18cm^2$. The final solar cell construction can be written as ITO/PEDOT-PSS/ZnPc:Gaq3/Al device as shown in Figure 2.

Measurements

The optical absorption spectra of mixture thin films were measured using UV-VIS/NIR Spectrophotometer model Jasco 570 UV-VIS/NIR. The surface morphology of the films was studied using Veeco AFM D3000. The current-voltage characteristics were measured with a Keithley 2400 source measuring unit by illuminating devices through the ITO side with white light from a halogen lamp delivering a power density of 80 mW/cm^2. All measurements were carried out under ambient condition at room temperature.



1(a) 1(b)

Figure 1: The chemical structure of (a) ZnPc and (b) Gaq3.

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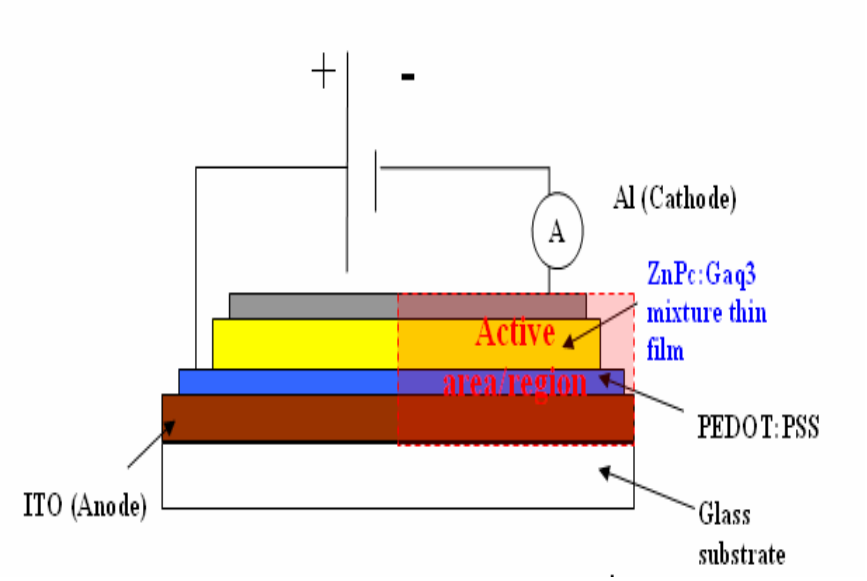
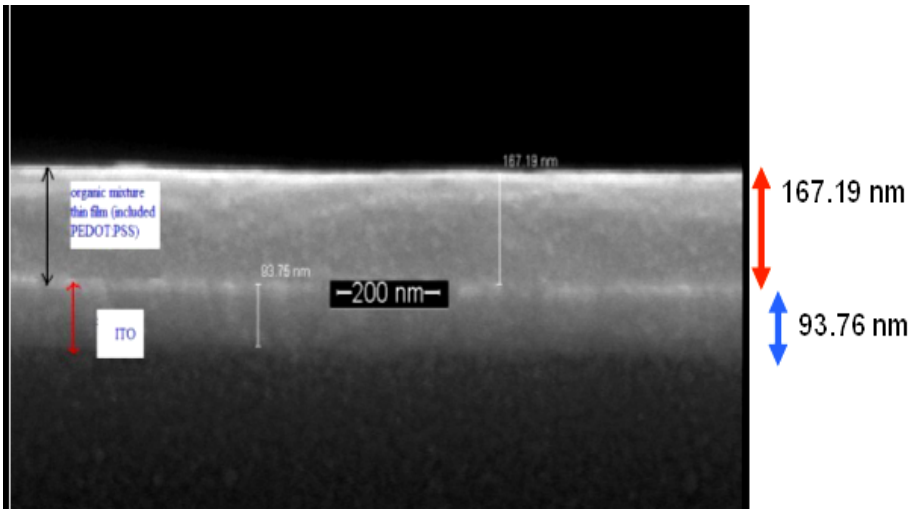


2(a)



(b)

Figure 2: (a) The solar cell construction, (b) The measurement of thin films thickness via SEM analysis

RESULTS AND DISCUSSION

UV-visible/NIR Spectrum Characterization

Figure 3 shows the effect of Gaq3 content in the ZnPc:Gaq3 mixture films. For ZnPc film, the peak wavelengths in the absorption spectrum are found at 346 nm and 692 nm, with a shoulder at around 630 nm. In the case of phthalocyanines, they possess two kinds of energy bands. One of them is called the visible absorption Q band, which arises from an allowed a_{14} (π) to e_g (π^*) transition; another one is called the ultraviolet B band, which arises from an a_{24} (π) to e_g (π^*) together with a b_{24} (n) to e_g (π^*) transition. The

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populated ground highest occupied molecular orbital (HOMO) and singlet highest occupied molecular orbital (SHOMO) levels are a_{14} (π) and a_{24} (π) and the first excited lowest unoccupied molecular orbitals (LUMO) level is e_g (π^*). The absorption peaks at 692 nm correspond to the Q band, where the one at 346 nm corresponds to the B band [13-15]. On the other hand, Gaq3 film exhibits relatively a low absorbance in Q band compared to ZnPc film. For the absorption spectra of ZnPc:Gaq3 mixture film, it shows that it is a superposition of the absorption spectra of ZnPc and Gaq3. Upon adding Gaq3 molecules into ZnPc, an absorption quenching is observed, in which the absorbance in Q band decreases. This may attribute to the formation of aggregates and complexes in mixture thin film phase that destruct the self-organized structure of the ZnPc [16].

Moreover, the charge transfer between the donor ZnPc organic semiconductor and the acceptor Gaq3 molecules may also contribute to the absorption quenching since ZnPc can donate an electron and Gaq3 can accept an electron [17]. The variation of the maximum absorbance, $(abs)_{max}$ with Gaq3 content in ZnPc:Gaq3 mixture films is shown in Figure 3(b). Upon adding Gaq3 into the ZnPc, the value of maximum absorbance decreases. However, upon adding more than 50 % of Gaq3 into the mixture film, the maximum absorbance is almost constant and the absorption spectrum is become similar to the Gaq3. This suggests that the existence of Gaq3 at higher composition in the mixture film does not have further significant effect on the absorbance of the film. This may be due to unavailability of free space in the ZnPc to accommodate the additional Gaq3 molecules.

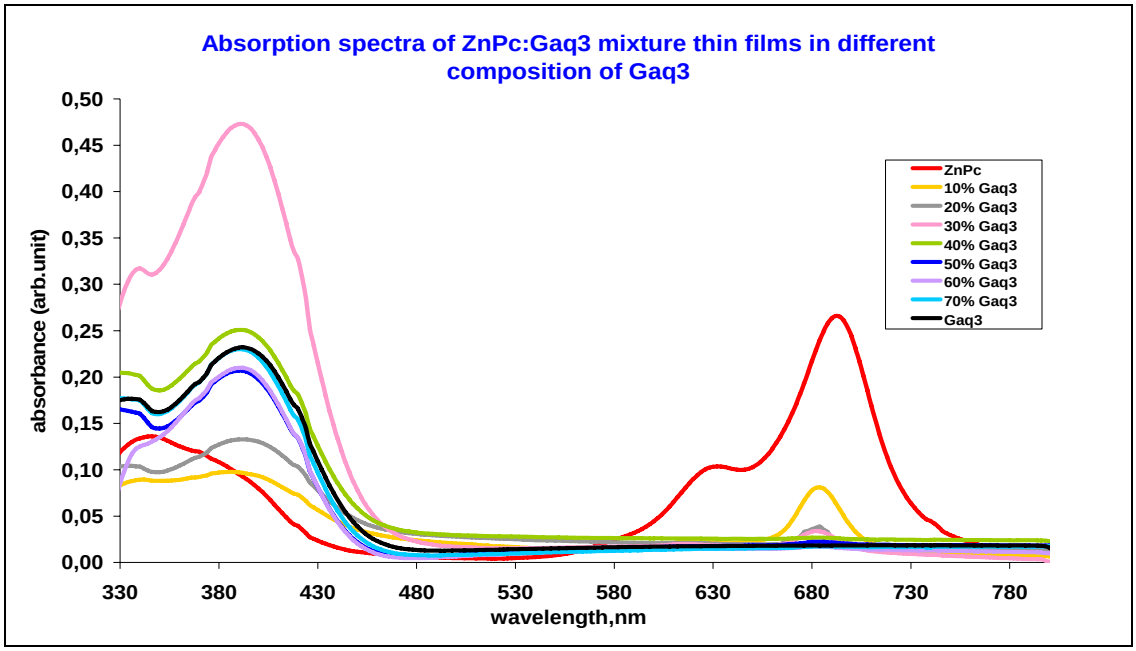

Figure 3(a): Absorption spectra of ZnPc:Gaq3 mixture thin films in different composition of Gaq3.

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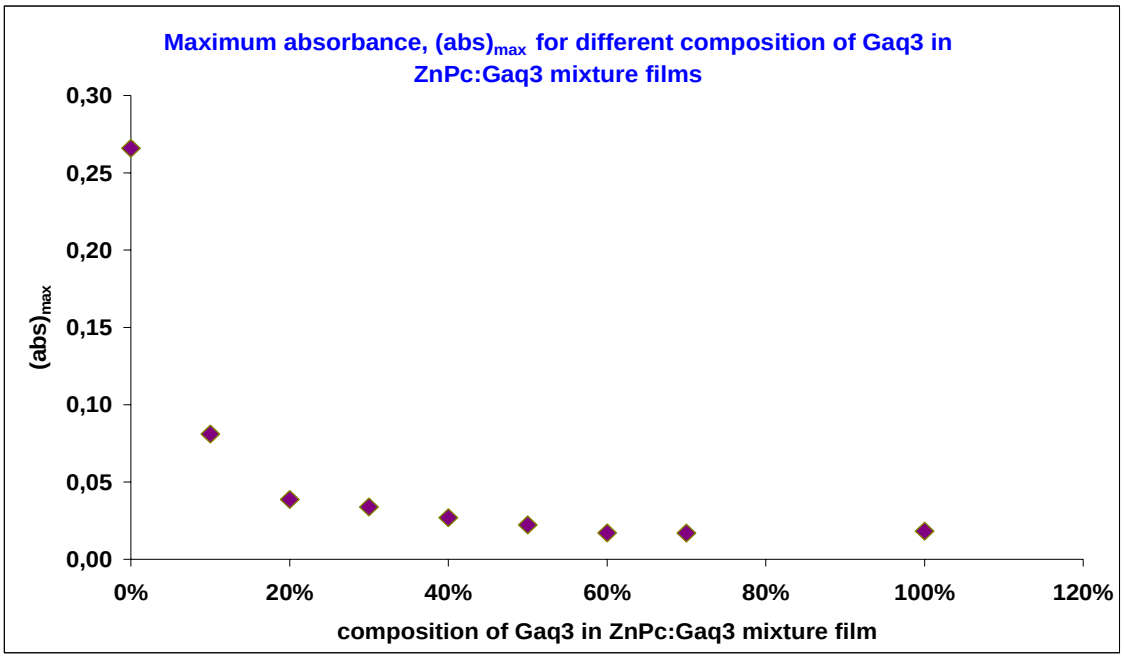

Figure 3(b): Maximum absorbance, $(abs)_{max}$ for different composition of Gaq3 in mixture films.

Atomic Force Microscopy (AFM) characterization

The surface morphology of AFM images of ZnPc:Gaq3 mixture films with different composition of Gaq3 are shown in Figure 4. As the composition of Gaq3 increases, the surface of the mixture film becomes rougher and its surface mean roughness increases. For the ZnPc film, it shows a relatively smooth surface and its surface mean roughness (rms) is 2.590 nm. For ZnPc:Gaq3 mixture film with 10% Gaq3 in film, its surface morphology is slightly coarser than the ZnPc film with an rms about 4.323 nm. This may attribute to the formation of Gaq3 domains in mixture film that gives rise to the phase segregation. Therefore, the film morphology of the ZnPc:Gaq3 mixture films are strongly dependent on the mixture composition [18].

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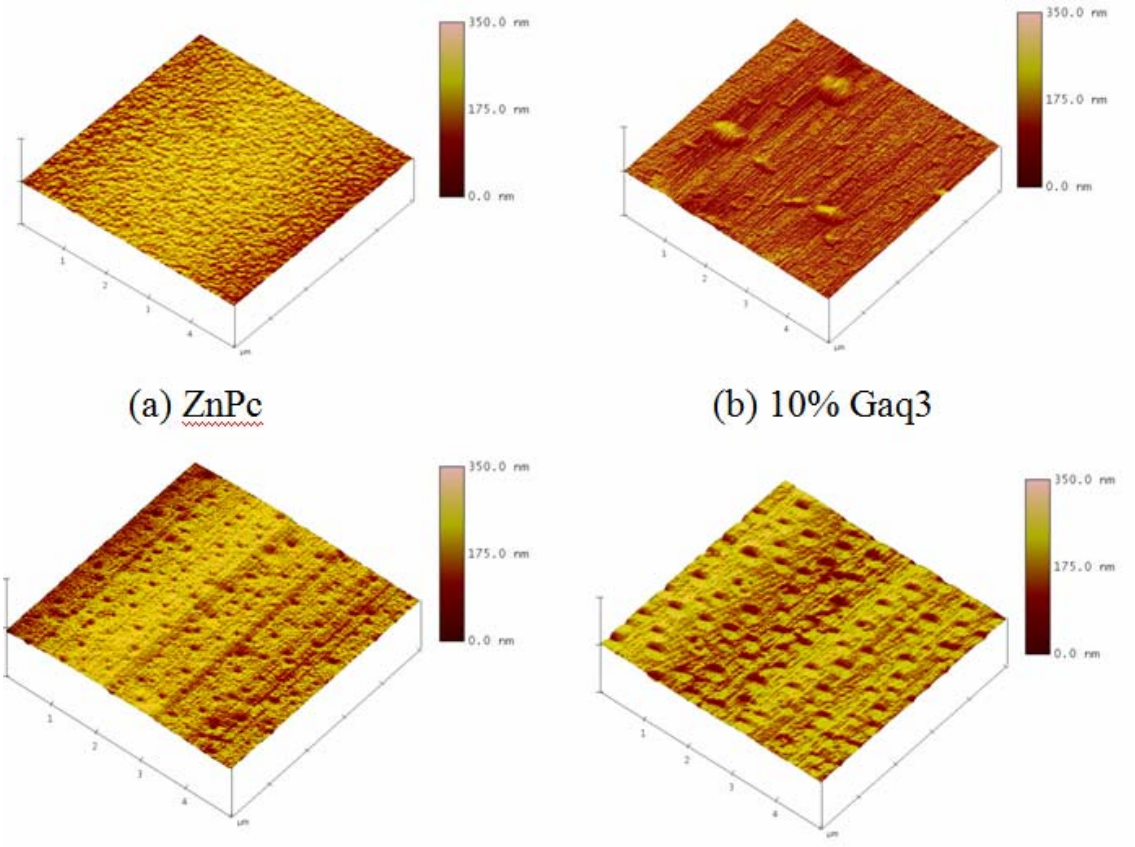

Figure 4: The AFM images of ZnPc:Gaq3 mixture thin films

Current-Voltage Characteristics

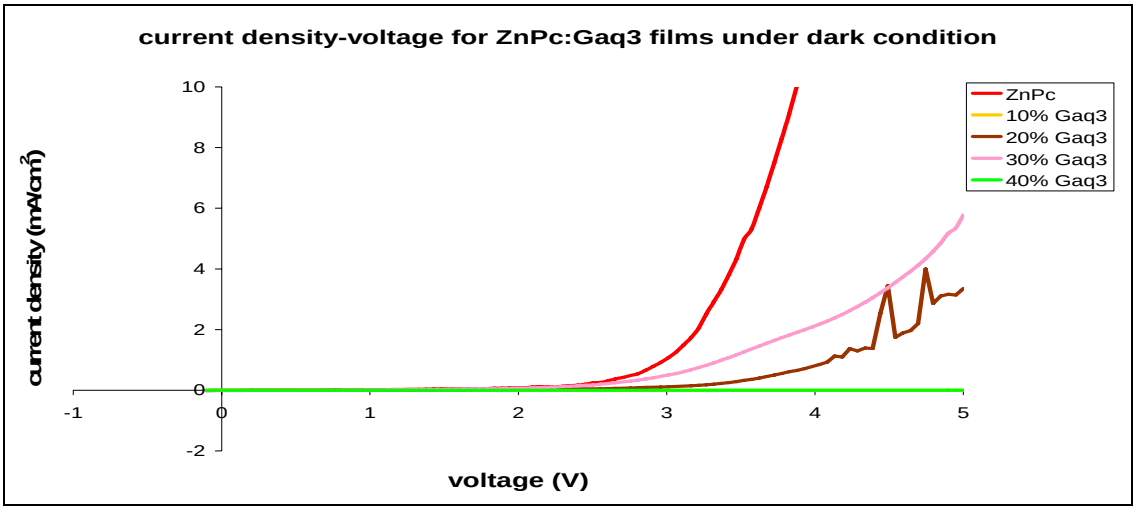

Figure 5(a): The current density-voltage curve of the ITO/ZnPc:Gaq3/Al solar cell in the dark.

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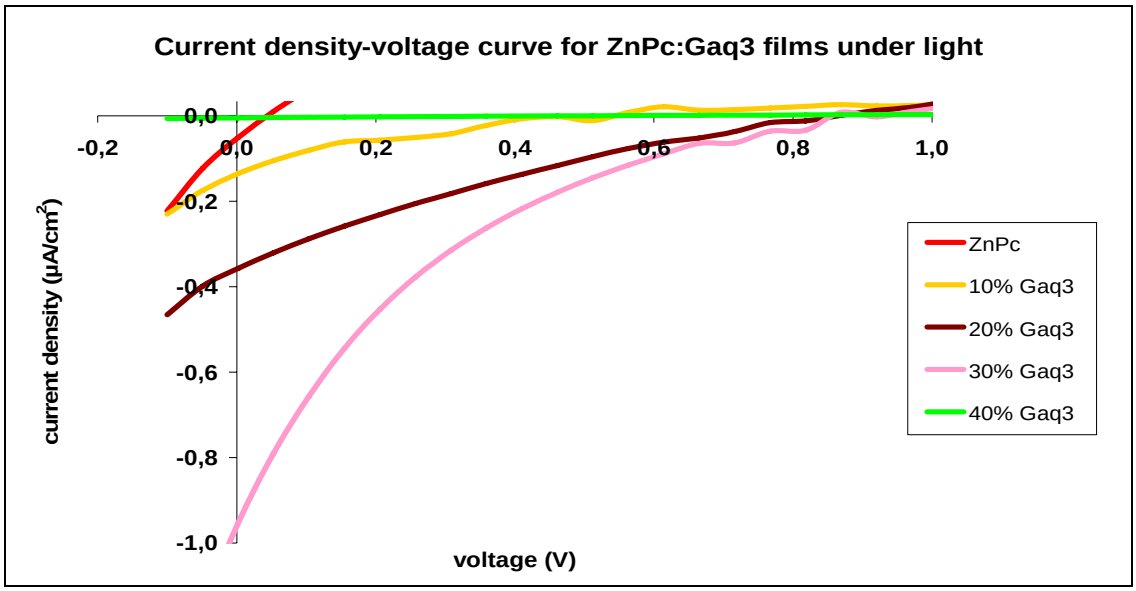

Figure 5(b): The current density-voltage curve of the ITO/ZnPc:Gaq3/Al solar cell under illumination.

Figure 5(a) and (b) show the current density-voltage curves of the the ITO/ZnPc:Gaq3/Al solar cell with different composition of Gaq3 in the dark and under white light illumination. In the dark, ZnPc device shows the highest curve slope, indicates that it a good conductivity. For solar cell, the forth quadrant of the I-V curve is mainly investigated as shown in Figure 5(b). Under light illumination, two important parameters are obtained, which are the x- and y-intercept of the curve. One is the open-circuit voltage V_{oc} (x-intercept), and the other is the short-circuit current density J_{sc} (y-intercept). The shape of the I-V curves is similar for the composition from ZnPc to 30% Gaq3, showing a gradual increase in both short-circuit current density J_{sc} and open-circuit voltage V_{oc} with increasing Gaq3 content [19]. At higher composition of Gaq3, the J_{sc} decreases significantly whereas the V_{oc} continues to increase up to 30% Gaq3. Thus, we found that the optimum content of Gaq3 is 30% with V_{oc} of 0.87V, J_{sc} of 0.95μA/cm^2, and a fill factor of 0.12.

CONCLUSION

The effect of mixture composition on the optical and structural properties for solar cells with thin films mixture of ZnPc and Gaq3 has been studied. The addition of Gaq3 into ZnPc has reduced the optical absorbance due to the formation of aggregates in mixture thin film. However, the mean surface roughness of the mixture films increase with higher composition of Gaq3 in films, indicating the occurrence of phase segregation. The highest solar cell performance is achieved for film mixture with 30% Gaq3. Further addition of Gaq3 (above 30% Gaq3) significantly reduces the fill factor and solar cell performances. Therefore, it can be concluded that the 30% Gaq3 is the most optimum mixture composition in enhancing the solar cell performances.

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