NANOSTRUCTURE FORMATION LEADING TO MODIFY THE OPTICAL ABSORPTION OF GAQ3 THIN FILMS

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ABSTRACT

This paper reports on the preparation of nanostructure along tris(8-hydroxyquinoline) gallium, Gaq3 thin film aiming at modifying its optical absorption property. The formation of nanostructure was achieved by means of thermal annealing in the temperature range from 85 ºC to 255 ºC under a flowing nitrogen gas for 10 minute. The results showed a modified optical absorption at 235 ºC to produce a broad absorption spectrum which is quite wider than that of pristine film. It was noticed from the results of x-ray diffraction, XRD and field emission scanning electron microscopy, FESEM techniques that such annealing process has led to the formation of amorphous nanorods at specific temperatures, thereby modulating the films optical absorption. The relatively decreased absorption intensity at 255 ºC was attributed to the partial crystalline formation and degraded nanostructures due to hard heating. Finally, the nanostructure growth was seen to possess a unique feature in modifying the optical behaviours of the Gaq3 thin films.

KEYWORDS: *Gaq3 Film, Optical Absorption, FESEM, Nanostructure Formation.*

INTRODUCTION

Among the organometallic compounds, tris (8-hydroxyquinoline) aluminium, Alq3 was most well known optoelectronic semiconductor that has been widely used in the fabrication of organic light emitting diodes (OLEDs) (Lian et al., 2007). Very recently, its use as buffer layer and dopant material in organic solar cells (OSCs) has also been reported (Kao, Chu, Huang, Tseng, & Chen, 2009; Vivo, Jukola, Ojala, Chukharev, & Lemmetyinen, 2008). It was seen that this has led to increase in both efficiency and stability of the devices. In addition to Alq3, tris(8-hydroxyquinoline) gallium,Gaq3 has received considerable attention thanks to the preliminary good results obtained by Wang et al. (Wang, Jiang, Zhang, & Xu, 2000), as they found Gaq3-based OLED enables to produce better performance compared to that of Alq3-based one prepared under the same condition. Since then, efforts have been made to analyze the chemical bonds, molecular geometry and electronic structure of Gaq3 (Gahungu & Zhang, 2005; Zhang & Frenking, 2004), and to investigate the influence of hydrostatic pressure on the spectroscopic behaviour of this material (Hernández & Gillin, 2009). In previous studies, we observed that Gaq3 films can attain lower optical band gap, higher electrochemical stability and smoother film formation compared to those of Alq3 (Muhammad, Abdul Hapip, & Sulaiman, 2010). Hence, modifying the photo-physical behaviours of Gaq3 is considered to be of great importance when its application in OSC and/or OLED devices is required. The optical absorption takes prominent role in the overall devices performance for OSC and/or OLED technologies. Post-deposition thermal annealing (Singh et al., 2005), in-situ controlled substrate temperature (Cho, Yu, & Perng, 2006) and the use of different substrates (Kumar, Sonia, Patel, Prakash, & Goel, 2008) are regarded to be the possible ways that are being taken by researchers to enhance the physical properties of the organic films. In this context, other research groups (Cho, et al., 2006; Yu, Cho, & Perng, 2009) utilized thermal evaporation technique under cold trap to grow crystalline Alq3 and Gaq3 nanostructures on silicon substrates at various working temperatures and pressures through a controlled amount of Ar and/or He gases. This was however resulted in the enhanced photoluminescence properties of the films, the crystallized structure might cause problems in the devices operation (Higginson, Zhang, & Papadimitrakopoulos, 1998), thereby producing undesirable light scattering or leak current (Yokoyama, Sakaguchi, Suzuki, & Adachi, 2009), especially in OLEDs application. In this work, a post-thermal annealing process upon vacuum deposited Gaq3 film is carried out under flowing of nitrogen gas for 10 minute, aiming at monitoring the nanostructure morphology and hence modifying the optical absorption of Gaq3 thin film. We found that, this method is able to produce amorphous Gaq3 nanorods, which acts as a new path for the nanostructure formation in this type of organic material on one hand and to modify the optical absorption of Gaq3 thin films on the other hand.

MATERIALS AND METHODS

Tris (8-hydroxyquinolinate) gallium, Gaq3 was purchased from Sigma-Aldrich Company (Malaysia branch) in powder form and used as received. The chemical structure of Gaq3 having molecular formula of $Ga(C_9H_6NO)_3$ is shown in Figure 1. Its molecule consists of three ligands each with a phenoxide and pirydyl side group. Films of Gaq3 were thermally evaporated onto pre-cleaned quartz substrates by a home-made thermal evaporator under a pressure of about 10^{-4} mbar. The quartz slides were cleaned ultrasonically with Deacon® Neutracon foam solution for 15 minutes followed by rinsing in acetone, ethanol and distilled water for 10 minute in ultrasonic bath, respectively. Finally, the quartz slides were dried thoroughly by blowing the nitrogen gas.

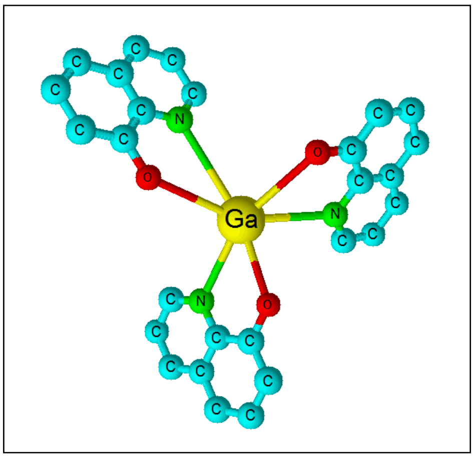

Figure (1): Three dimensional view of chemical structure of Gaq3 molecule (Muhammad, et al., 2010).

The vacuum deposited Gaq3 films of thickness ~764 nm were post annealed under a flowing nitrogen gas atmosphere using a barrel furnace. The thermal annealing process was set for 10 minute at the temperature of 85 °C, 160 °C, 235 °C and 255 °C. The optical absorption and transmission spectra of the as-deposited and annealed films were performed at room temperature using a Jasco V-570 UV-Vis-NIR spectrophotometer in the wavelength range from 200 to 2500 nm. The thicknesses of the films before and after annealing process were estimated from their transmittance spectra using envelope method described else where (Muhammad, et al., 2010). KLA Tensor P-6 surface profilometer instrument was also utilized for further confirmation of the films thickness by scratching each film at three different regions across its surface, then taking the average of the measurements. The absorption coefficient (α) of the films was calculated by using the relation $\alpha = 2.303 A/t$ where, A is the absorbance of the film and t its thickness. This relation can also be used to determine the absorption coefficient of solutions. X-ray diffractometer (Bruker AXS) using Cu K_α radiation of wavelength λ = 1.5406 A° as a source was used to measure the XRD patterns to confirm the structural nature of the films. To visualize the morphology and structural distribution of the thin films after thermally annealing, low dimensional images have been captured by the field emission scanning electronic microscopy technique (FESEM, Quanta 200F). All the tests and instrumentation have been carried out at the low dimensional materials research centre, department of Physics, faculty of science, university of Malaya, Malaysia.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the pristine and annealed films in the temperature range from 85 °C to 255 °C under nitrogen gas for 10 minute. Two peaks are seen for the pristine film, the first peak is in close proximity to the visible range at photon energy of 3.14 eV, while the second peak is located in the ultraviolet region with relatively broad and intense at energy of about 4.67 eV. These peaks have been assigned to the presence of optoelectronic transitions from $\pi \rightarrow \pi^*$ and $4p \rightarrow \pi^*$ orbital energy bands, respectively (Muhammad, et al., 2010). Upon thermally annealing, the visible absorption band rises whilst the ultraviolet, UV band falls to lower intensity. This feature continues to appear in the films annealed from 85 ºC to 160 ºC. However, at higher annealing temperature of 235 ºC, the absorption spectrum has become broader covering from the whole UV range till some parts of the visible region. The decrease in the absorption peak intensity in the UV regions was also observed for Alq3 films by Djurišiċ et al. (Djurišić, Lau, Lam, & Chan, 2004) with no given attribution when the films exposed to atmosphere, but Credo et al. (Credo, Winn, & Buratto, 2001) ascribed the behaviour to the change in chemical nature of the Alq3 films. In our work, Gaq3 films were annealed under nitrogen gas, so the influence of atmospheric exposure can be cancelled out. Referring to the absorption response of Gaq3 films, we may expect the occurrence of morphological and/or conformational changes upon our films in the temperature range from 85 to 235 ºC under the influence of nitrogen gas, as we will see later that morphological change has led to the formation of amorphous Gaq3 nanorods. Reasonably, it is such nanostructure formation and conformational change that are responsible for the optical modification of the films. This can be understood as, within the broad distribution of molecular packings, favourable $\pi - \pi$ overlaps between facing ligands may occur (Brinkmann et al., 2000), thereby involving interaction and energy exchanges at molecular level which have consequences on the spectral properties of the molecules (Auzel, Baldacchini, Baldacchini, Chiacchiaretta, & Balaji Pode, 2006).

On the other hand, annealing at higher temperature of 255 ºC, caused the broad band to fall to lower absorption intensity and the absorption edge slightly shifted towards the UV region in comparison to that of the pristine film. This behaviour is consistent with the results obtained by Credo et al (Credo, et al., 2001) for the Alq3 films (counterpart of Gaq3) annealed above glass transition temperature (T_g = 172 ºC for Alq3). It was reported that glass transition temperature, T_g of Alq3 is at 172 ºC, and upon annealing Alq3 film above T_g the crystalline region in the films would be formed (Credo, et al., 2001). This crystalline formation was seen for our Gaq3 films annealed at 225 ºC.

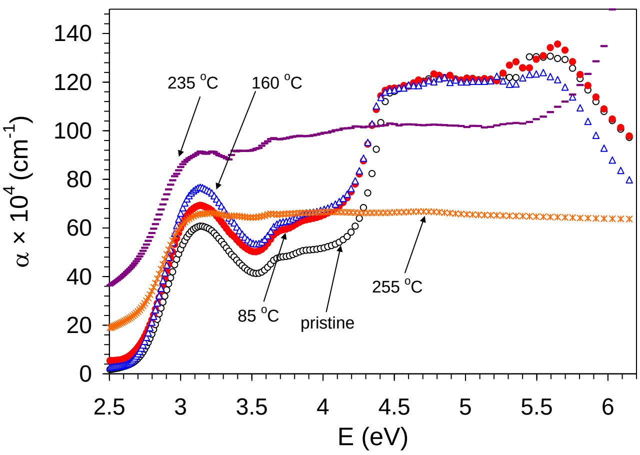

Figure (2): Absorption spectra of the pristine and thermally annealed films of Gaq3.

Figure 3 shows the XRD patterns recorded for the films that demonstrated the merged and broadened absorption spectrum, i.e., annealed films at 235 and 255 ºC, respectively. The crystalline portion was found to appear only for the films annealed at 255 ºC with its intense diffraction peak at angle of 2θ = 15.9º, which corresponds to a periodicity of about d = 0.557 nm. This can be considered to be one of the reasons for the decrease in the intensity of the absorption spectra shown in Fig. 2.

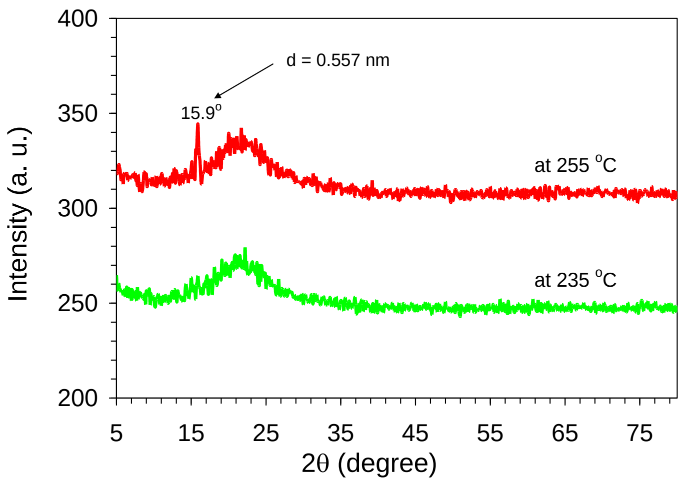

Figure (3): The XRD patterns for the Gaq3 films annealed at 235 and 255 ºC.

Figure 4 shows the images of field emission scanning electron microscopy (FESEM) captured for the Gaq3 films annealed at temperatures 235 and 255 ºC. The surface morphology is seen strongly being affected by the temperatures, where 235 ºC is the most appropriate annealing temperatures for the clear formation of nanorods from the film. This growth of nanorods can be interpreted by means of molecular migration (Kumar, et al., 2008), as the Gaq3 molecules migrate and pile up by acquiring enough thermal energy from the appropriate heat treatment. It was observed that at 235 ºC, the conformational change towards amorphous nanorod formation was responsible for the optical absorption to show a broad spectrum. However, upon hard heating and annealing at higher temperature of 255 ºC, Gaq3 rods are no longer fortified, they were degraded and cross linked along with the formation of crystalline portion in the film, as it was discussed before. This nano-surface degradation of the film has led to considerable drop in the optical absorption spectra of Gaq3 films (see Fig. 2).

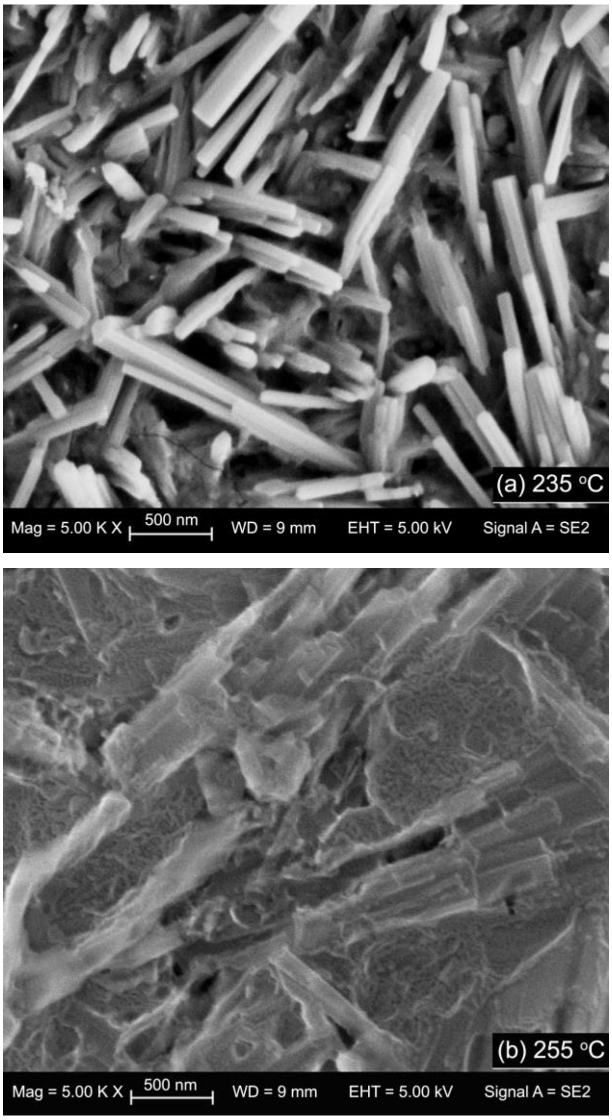

Figure (4): FESEM pictures of annealed Gaq3 films at (a) 235 ^{o}C and (b) 255 ^{o}C.

CONCLUSIONS

The optical absorption properties of Gaq3 thin film was modified by means of nanostructure formation under the influence of thermal annealing in the temperature range from 85 ^{o}C to 255 ^{o}C. The results showed significant enhancement in the absorption behaviour of the films at 235 ^{o}C and 255 ^{o}C that could be of practical interest for OLED and/or OSC devices fabrication. This improvement was ascribed to the formation of Gaq3 nanostructures upon annealing. It was seen that at high annealing temperature of 255 ^{o}C, the film demonstrated relatively lower absorption intensity. This was attributed to the formation of partial crystallinity, cross linking and degradation of the Gaq3 nanorods, as they were asserted by XRD and FESEM techniques. We conclude that, Gaq3 can be a promising material to be applied in both of the OLED and OSC devices upon controlling its nanostructure morphology through annealing process. Further works can be suggested to be done by annealing Gaq3 films within different time intervals and exploiting them in the organic electronics technology.

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دروستكردنى پێكهاتەى نانۆيي دەبێتە هۆي گۆڕينى هەڵمژينى ڕووناكي لە چينە تەنكەكانى مادەى Gaq3 پوختە

ئەم توێژينەوەيە تەرخانكراوە بۆ ئاماژەكردن بە دروستكردنى پێكهاتەى نانۆيي لە چينە تەنكەكانى مادەى tris (8-hydroxyquinoline) gallium ، ئەمەش بە مەبەستى گۆڕانكاريكردن لە سيفەتي هەڵمژينى ڕوناكى مادەى ناوبراودا. دروستكردنى پێكهاتەى نانۆيي ئەنجامدرا لە ڕێگەى كردارى كوتاندنەوە بە گەرمي لە پلەي گەرمي نێوان 85 س^0 بۆ 225 س^0 پلەي سەدي لەژێر كاريگەرى تێپەڕاندنى گازى نايترۆجين بۆ ماوەى 10 خولەك. ئەنجامەكان دەريانخست هەڵمژينى ڕووناكي بۆ فيلمەكان لە پلەى گەرمي 235 س^0 گۆڕانكارييەكي بەرچاوى بەسەرهاتووە ، ئەويش بە دروستكردنى شەبەنگێكى فراوانى هەڵمژين بە بەراورد لەگەڵ ئەوەى فيلمە سەرەتاييەكان (گەرم نەكراوەكان) بەپشت بەستن بە ئەنجامەكانى هەردوو تەكنيكي (XRD) و (FSEM) تێبينى كرا كە ئەم پرۆسەى گەرمكردنە بووەتە هۆى دروستكردنى تووڵى نانۆيي نابلورى لە پلە گەرمييە دياريكراوەكاندا ، وە لە ئەنجامدا سيفەتي هەڵمژينى ڕووناكى گۆڕانى بەسەرداهاتووە. هۆكاري تاڕادەيەك كەمبوونەوە لە پلەى هەڵمژينى ڕووناكيدا لەپلەى گەرمي 255 س^0 گەڕێندرايەوە بۆ دروستبوونى پێكهاتەى نيمچە بلورى و بەسەريەكدا تێكشكانى تووڵە نانۆييەكان بەهۆي ئەم پلە گەرمييە بەرزەوە. لە كۆتاييدا دەركەوت كە دروستبوونى پێكهاتەى نانۆيي كاريگەرى بەرچاوى هەيە لە گۆڕينى سيفەتە ڕووناكييەكانى مادەى Gaq3 .

بناء البنية النانوية تؤدي إلى تغيير في الأمتصاصية البصرية للأغشية الرقيقة Gaq3

الملخص

هذا البحث تقريرا عن إنتاج البنية النانوية على طول الأغشية الرقيقة لمادة tris (8-hydroxyquinoline) galliumتهدف الى تغيير خاصيتها الأمتصاصية البصرية. لقد تم تحقيق تشكيل البنية النانوية بواصطة التلدين الحراري في نطاق درجات الحرارة من 85 درجة مئوية إلى 255 درجة مئوية وذلك تحت تأثير مرور الغاز النيتروجين لمدة 10 دقيقة. أظهرت من خلال النتائج بأن هناك وجود تغيير كبير في الأمتصاصية عند الدرجة الحرارة 235 م^0 لتوليد طيف ذو واسع الامتصاص حيث هو أوسع تماما مقارنة بما كان في الأغشية الغير متأثرة. ولاحظ من النتائج المحصولة في التقنيات XRD و FESEM بأن هذه العملية الحرارية أدت إلى تشكيل قضيب نانوي غير متبلور في درجات حرارة معينة، وبالتالي إن هذه أدت إلى تغيير الأمتصاصية البصرية للأغشية الرقيقة. إن الأنخفاض في الأمتصاصية نسبياً عند الدرجة الحرارة 255 م^0 أرجعت الى حدوث التحطيم على الأقضاب النانوي و إنتاج مناطق شبه متبلورة بسبب تأثير هذه الدرجة الحرارة العالية. وأخيرا، أوضحت بأن نمو البنية النانوية له ميزة فريدة من نوعها في تغيير السلوكيات البصرية للأغشية الرقيقة Gaq3.