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Optical and morphological modifications in post-thermally treated tris(8-hydroxyquinoline) gallium films deposited on quartz substrates

Fahmi Fariq Muhammad* , Khaulah Sulaiman

^a Department of Physics, Faculty of Science & Health, Koya University, Koya, Kurdistan Region, Iraq ^b Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

- \bullet Post-thermal treatment under N₂ gas produced amorphous nanorod in Gaq3 film.
- The optical response of Gaq3 film was
tuned through morphological morphological modification.
- Luminescence was increased to five times stronger than that of pristine Gaq3.

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1. Introduction

It is well known that tris (8-hydroxyquinoline) aluminium (Alq3) metal can be a viable candidate for the application in organic light emitting diodes (OLED)s $[1-5]$ $[1-5]$. It has been noticed that the utilization of Alq3 as buffer layer and dopant material in the organic solar cells (OSCs) acted upon increasing the efficiency and stability of the devices [\[6,7\].](#page--1-0) In addition to Alq3, tris(8-hydroxyquinoline)

Corresponding author. Tel.: $+964$ 7701935331. E-mail address: fahmi982@gmail.com (F.F. Muhammad).

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GRAPHICAL ABSTRACT

ABSTRACT

This work reports the optical and morphological modifications in vacuum deposited Gaq3 films upon thermal annealing. The annealing process has been carried out under flowing nitrogen gas for 10 min. It was noticed from the results that at 235 \degree C a broad absorption spectrum and increased photoluminescence to five times stronger than that of pristine film was achieved. Scanning electron microscopy and X-ray diffraction techniques ascertained morphological changes towards the formation of amorphous nanorods. The improvement in optical properties of Gaq3 films was found to be resulted from this morphological modification. The nanostructure formation was seen to be a viable method to enhance the morpho-optical properties of Gaq3 films, making Gaq3 a promising candidate for the application in organic electronics technology.

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gallium (Gaq3) received considerable attention thanks to the preliminary good results obtained by Wang et al. [\[8\]](#page--1-0), in which Gaq3 based OLED demonstrated an improved performance over that of the Alq3-based one. Interestingly, theoretical studies have been carried out to analyse the chemical bonds, molecular geometry and electronic structure of Gaq3 [\[9,10\]](#page--1-0) on one hand, and practical investigations addressing the impact of hydrostatic pressure on the spectroscopic behaviour of Gaq3 films has been reported on the other hand [\[11\]](#page--1-0). It was realized that Gaq3 can have a lower optical band gap, higher electrochemical stability and smoother film for-mation compared to those of Alq3 [\[12\]](#page--1-0). Comprehensive understanding of the properties of Gaq3 films is crucial prior to its

application in OSC and/or OLED technologies. For instance, the optical absorption and photoluminescence behaviours of thin films are two major properties playing effective role in defining the overall performance of OSC and OLED devices. Various methodologies were undertaken by researchers to enhance the physical properties of organic thin films. Among them are post-thermal annealing [\[13\]](#page--1-0), in-situ controlled substrate temperature [\[14\]](#page--1-0) and the use of different substrates $[15]$. In these contexts, other research groups [\[14,16\]](#page--1-0) 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 for the films, the crystallized structure might cause problems in the OLED application [\[17\]](#page--1-0) thereby producing undesirable light scattering or leak currents [\[18\]](#page--1-0). In this research work, a post-thermal annealing process under nitrogen gas is carried out aiming at investigating the optical and morphological properties of vacuum deposited Gaq3 films on quartz substrates. It was observed that this method is capable of modulating the optical behaviour and produce amorphous nanorod structure along the surface of the Gaq3 films. This technique can be a viable strategy to improve the optical and morphological properties of Gaq3 films.

2. Materials and methods

Tris (8-hydroxyquinolinate) gallium (Gaq3) was purchased from Sigma-Aldrich in powder form and used as received without further purification. Fig. 1 shows the structure of Gaq3 with molecular formula $Ga(C_9H_6NO)_3$. Its molecules comprise of three ligands, where each ligand includes a phenoxide and pyridyl side group. Films of Gaq3 were thermally evaporated onto the precleaned 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 min followed by rinsing in acetone, ethanol and distilled water for 10 min in ultrasonic bath, respectively. Finally, the quartz slides were dried thoroughly by blowing the nitrogen gas.

The vacuum deposited Gaq3 films were post-thermally annealed under the flowing nitrogen gas using a barrel furnace as shown in Fig. 2. The thickness of the films was measured by using envelope method [\[12\]](#page--1-0) and a KLA Tensor P-6 surface profilometer instrument. The thermal annealing process was set for 10 min at

Fig. 1. The chemical structure of Gaq3 molecule.

Fig. 2. The barrel furnace instrument.

the temperatures 85 °C, 160 °C, 235 °C and 255 °C. The optical absorption for the as-deposited and annealed films was performed using a Jasco V-570 UV-Vis-NIR spectrophotometer in the wavelength range from 200 to 2500 nm. Photoluminescence spectra for the films were carried out at room temperature using a LS50B PERKIN ELMER luminescence spectrometer in the wavelength range from 200 nm to 800 nm. X-ray diffractometer (Bruker AXS), using Cu K_a radiation of wavelength $\lambda = 1.5406$ Å as a source, was used to measure the XRD patterns confirming the structural nature of the investigated films. Field emission scanning electronic microscopy technique (FESEM, Quanta 200F) was utilized to image the morphology of the films before and after annealing process.

3. Results and discussion

The absorption coefficient (α) of the films was calculated by using the relation $\alpha = 2.3.03A/t$ where A is the absorbance of the film and t its thickness. Fig. 3 shows the absorption coefficient of the pristine and annealed films in the temperature range from 85 to 255 \degree C. Two pronounced peaks was found for the pristine film at the photon energies of 3.14 eV and 4.67 eV, which can be attributed

Fig. 3. Absorption coefficient of the pristine and thermally annealed films of Gaq3.

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