

## Photoresponse characteristics from vacuum deposited thin film of copper phthalocyanine: Dependence on grain size

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An organic photodetector (PD) is fabricated with single layer thin film of copper phthalocyanine (CuPc) on glass substrate. The thermal deposition of CuPc film on the substrate was realized under high vacuum and at different substrate temperature (room temperature, 40 °C, 70 °C, 100 °C). The comparison of photoresponse characteristics of CuPc thin film deposited under different conditions showed good improvement with increase in the substrate temperature, and the best performances being observed for the film deposited at substrate temperature of 100 °C. The thin film of CuPc characterized through X-ray diffraction (XRD) spectroscopy and atomic force microscopy (AFM) clearly indicated that with increase in substrate temperature, the grain size of CuPc film increased, which improved the crystallinity and hence the photoconductivity of the device. The CuPc thin film based PD displayed stable and reproducible photoswitching characteristics under white light irradiation, with photocurrent modulation by varying in input optical power. The highest photo to dark current ratio and responsivity of the devices was calculated to be, ca. 6.5 and 7.1 mA-W<sup>-1</sup> at low optical power, ca. 14.5 mW-cm<sup>-2</sup>.

**Key words:** Copper phthalocyanine, photodetector, photoswitching, vacuum deposition.

### 1. Introduction

In recent years, a range of organic semiconductors (OSCs) have been identified and employed to fabricate various electronic and optoelectronic devices. To fulfill the demand for low cost, flexible, wearable and miniaturized gadgets for future consumer electronic devices, extensive research focus has been paid on the synthesis and development of various OSCs. Apart from cost-effective synthesis method, these OSC offer various advantages, including easy device fabrication, low temperature processing, 3-D stacking, mechanical flexibility and tuning of molecular properties via tailoring of chemical structure [1]. Not surprisingly, wide varieties of electronic and optoelectronic devices have been fabricated by different OSCs with performances comparable or sometimes surpassing to their inorganic counterpart. The performances exhibited by the devices like, organic solar cells [2], organic thin film transistors [3–5], phototransistors [1,6,7], sensors [8,9], and memory devices [10,11] have shown great promise as potential candidate for wearable and flexible optoelectronics applications.

A photodetector (PD) is a light sensing device which employs a photosensitive layer whose con-

ductance value changes upon illumination of suitable radiation. To date, various kinds of materials have been explored which includes thin film of inorganic, organic or composite materials as the active layer [12–17]. Although, PD comprising of multilayered materials or composite semiconductor exhibited better photosensing performances compared to single layer structure, the fabrication time and cost will also be higher. On the contrary, single layer photodetector devices are preferred due to their easy fabrication method and operational flexibility. Considerable attention has been paid to apply different small organic molecules in fabrication of PD, including copper phthalocyanine, zinc phthalocyanine, pentacene and perylene derivative [18–22]. However, in most of these devices bilayers, multilayers or composite layers were deposited as active photosensitive materials which needed much complicated fabrication technique.

Herein, the single layer PD has been fabricated with vacuum deposited thin film of copper phthalocyanine (CuPc) as the photosensitive layer which exhibited modest performances under visible light illumination. Here CuPc molecule is chosen as the active compound, because, it is highly stable and optically active materials. Additionally, the absorption of CuPc in visible region would also eliminate the need of any sophisticated

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UV or IR light source for designing the PD. The deposition of thin film of CuPc was performed under high vacuum with varying substrate temperature. It was observed that with increase in the substrate temperature, the grain size of CuPc thin film also increased which enhanced the crystallinity of the film. Comparison of the PD performances of different CuPc films deposited under different substrate temperature indicated that higher the substrate temperature, better is the PD performances. The CuPc based PD exhibited best performances for the film fabricated at substrate temperature of 100 °C, demonstrating the photo to dark current ratio ( $\frac{I_L}{I_D}$ ), *ca.* 6.5 and responsivity, *ca.* 7.1 mA-W<sup>-1</sup> at incident illumination intensity of 14.5 mW-cm<sup>-2</sup>. Moreover, the PD showed reproducible photoswitching characteristics under pulsed light illumination along with excellent photocurrent modulation by the variation in the incident optical power.

## 2. Materials and Methods

Copper phthalocyanine (CuPc) was purchased from Aldrich Chemicals and was used without further purification. To fabricate photodetector devices on glass substrate, the substrates were cleaned following the standard cleaning procedure. The substrates were cleaned successively with detergent, acetone, isopropyl alcohol and de-ionized water under ultrasonic bath [23]. The substrates were then dried at 90 °C for 30 minutes in ambient condition. The thin film of CuPc (70 nm) was then thermally vacuum evaporated over the glass substrate with a base pressure of  $5 \times 10^{-6}$  torr at different substrate temperature (RT, 40 °C, 70 °C, and 100 °C). Finally, gold (Au) electrode was deposited (50 nm) on top of the CuPc film under high vacuum ( $5 \times 10^{-6}$  torr) to complete the device fabrication. A shadow mask was used during Au deposition which defined the separation between the coplanar electrodes as 50  $\mu$ m. The PD devices in which CuPc film was evaporated at RT, 40 °C, 70 °C, and 100 °C will be denoted as C1, C2, C3, C4, respectively. The electrical characterization of the devices were performed by HP4145B semiconductor parameter analyzer under ambient condition. X-ray diffraction (XRD) spectra of the films were recorded with an X'pert Pro (Pananalytical) X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54$  Å). AFM measurements of CuPc thin films were done using a Nanoscope IIIa (Veeco, Digital Instruments). For measurement under white light illumination, a common incandescent lamp was used as a source

and the light was incident on the device from the top. The switching on/off of the light source was controlled by a mechanical shutter.

## 3. Results and Discussions

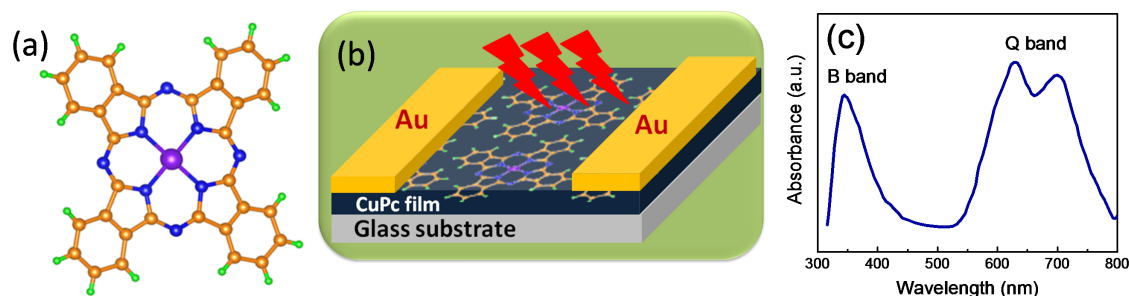
The molecular structure of the active component, *viz.*, copper phthalocyanine (CuPc) together with schematic of the photodetector device are shown in Figure 1(a) and (b), respectively. Light is directly shined from the top over CuPc film so that maximum absorption of incident illumination can take place. The UV-Vis absorption spectrum of as deposited CuPc film on glass substrate at room temperature is illustrated in Figure 1(c). The spectrum shows a peak around 342 nm (B-band), while a peak doublet is observed in the visible region. The doublet of peaks existing around 623 and 701 nm in the visible region of the spectrum (Q-bands) originates due to Davydov splitting [24], the relative intensities of which are different for different polymorph. It is well established that the  $\pi$  electron system in phthalocyanine (PC) molecules is responsible for the electronic transitions in the visible region and the molecular orbitals within these  $\pi$  electrons together with overlapping orbitals on the central metal atom gives rise to optical spectrum for PCs [25]. For the annealed CuPc film, the UV-Vis spectrum did not exhibit any significant difference, only a slight red shifts in the peak position of all bands towards higher wavelengths of the spectrum was noticed. The rigid and planar structure of the molecule (CuPc) with high absorption coefficient in the visible region might induce larger photogenerated carriers and result in high photocurrent densities in the film.

The morphological differences of CuPc films deposited at various substrate temperature was analyzed by tapping mode atomic force microscope (AFM). The AFM images of four samples are shown in Figure 2. Figure 2(a) indicated the presence of smaller crystallites for the CuPc sample deposited at room temperature (27 °C). However, as the substrate temperature is increased, the CuPc crystals grew in size as seen from the images 2 (b–d). Additionally, the CuPc crystals deposited at lower temperature (40 °C) is little less ordered, which started to become more ordered at higher temperatures (70 °C, 100 °C).

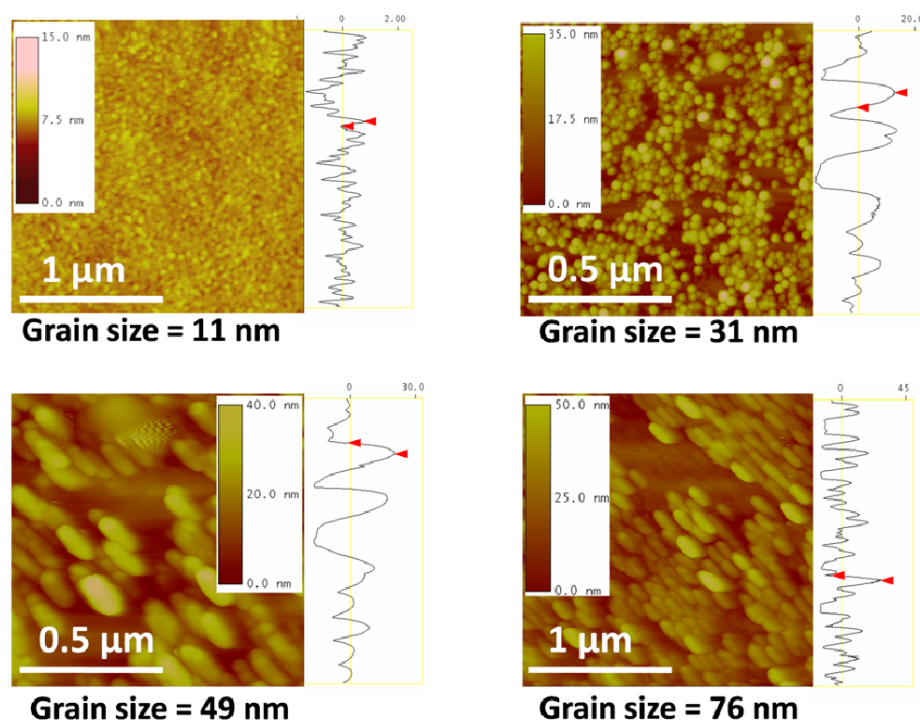
As calculated from the line profiles, the height of grains from the valley for CuPc crystals were 1 nm at 27 °C, 10 nm at 40 °C, 17 nm at 70 °C, and 26 nm at 100 °C. The corresponding grain sizes (average) were calculated to be 11, 31, 49 and

76 nm, respectively. All these results confirmed the growth of ordered CuPc crystals as a function of the substrate temperature, which could further

increase the mobility of CuPc thin film for any optoelectronics applications.



**Figure 1.** (a) Chemical structure of copper phthalocyanine (CuPc) molecule and (b) schematic of CuPc based photodetector device. (c) UV-Vis absorption spectrum of CuPc thin film deposited on glass substrate at RT.

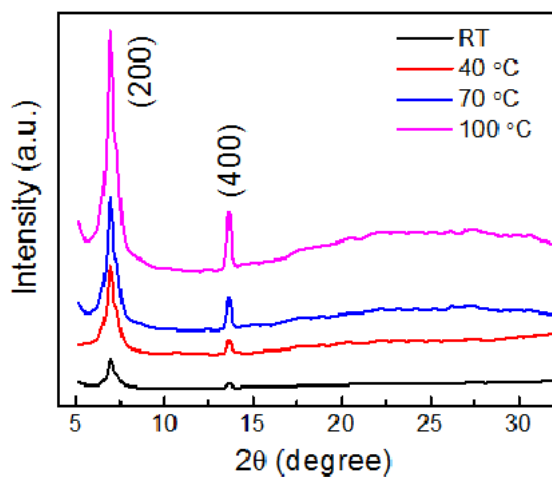


**Figure 2.** (a) Tapping mode Atomic force microscope (AFM) images of CuPc thin film deposited at (a) room temperature (27 °C), (b) 40 °C (c) 70 °C and (d) 100 °C on glass substrate. Line profile of each of the image is also shown at the right side.

To determine the crystallinity and phase purity of thermally deposited CuPc film under different temperatures, XRD spectra of the samples were recorded. Figure 3 shows the XRD spectra of CuPc films on glass at different substrate temperatures. The background scattering arising due to glass substrate has been subtracted. Although, the spectra at different temperatures looks similar, the intensity of prominent peaks increased with in-

crease in temperature. The sharp peak observed at  $2\theta = 6.9^\circ$  in the XRD pattern of annealed CuPc film indicated the appearance of crystalline phase of the molecule. As the substrate temperature is increased, the grain size of CuPc also increases, as a result of which the crystallization of CuPc films increases. This observation is in line with the morphological changes of the film observed in AFM images. The characteristics peak at  $2\theta = 6.9^\circ$

and  $13.7^\circ$  can be indexed respectively to (200) and (400) lattice planes and describes the  $\alpha$ -phase of CuPc. This result is well consistent with earlier published reports [26].



**Figure 3.** XRD spectra of CuPc thin film deposited at various substrate temperatures.

The electrical transport characteristics of the devices in the dark and under illumination were measured by sweeping the bias from +30 V to -30 V at a step of 0.2 V. Figure 4(a) and (b) shows respectively the photoresponsive current-voltage ( $I$ - $V$ ) characteristics of CuPc thin films deposited at room temperature and at 100 °C substrate temperature. The results show that under white light illumination, the current increased appreciably to the value which is much higher compared to that in the dark. Also, the linear behavior of the  $I$ - $V$  curves indicated the ohmic contact between organic (CuPc) thin film and metal (Au) electrodes. It is noteworthy that the dark and photocurrent level in case of CuPc film deposited at high temperature is significantly higher compared to the film deposited at RT (Figure 4(b)).

This might be due to the fact that larger grain size of the molecule deposited at 100 °C increased the crystallinity of the CuPc film, which in turn, contributed to the enhanced conductivity of the device. When visible light is incident on the material, bound electron-hole pairs (excitons) are generated, which ultimately dissociated into free charge carriers, with electrons in the lowest unoccupied molecular orbital (LUMO) and holes in the highest occupied molecular orbital (HOMO) of CuPc. These additional photo injected charge carriers increased the bulk conductivity of the devices.

Figure 5(a) illustrates the time resolved photo-

switching characteristics of different PD under fixed bias (30 V) when incident light ( $9.2 \text{ mW}\cdot\text{cm}^{-2}$ ) is applied in pulsed form. The photoresponse of C1 device is much less compared to other devices. Another thing is that a remanent photoconductivity was observed for the device, which is usual phenomena for a single layer organic PD device. This transient phenomenon can be ascribed to the interfacial charging at metal/semiconductor junction as well as trap-induced space charges [27]. The photo to dark current ratio ( $\frac{I_L}{I_D}$ ), which is one of the figure of merit of a PD, increased from C1 to C4 device, as depicted in Figure 5(a). Also, the dark current of the PD increased gradually from C1 to C4 device. This might be due to the fact that with increase in substrate temperature during the film deposition, the grain size of CuPc increased which increased the crystallinity of the active material. This, in turn, enhanced the overall conductivity of the device. The maximum response and hence the maximum  $\frac{I_L}{I_D}$  was observed for the C4 device. The better crystallinity due to the presence of larger grain sizes of CuPc film in C4 device reduces the number of traps and defects which might contribute to the reduction in recombination of charge carriers. As a result, the photocurrent, and hence the ratio  $\frac{I_L}{I_D}$  showed increment from C1 to C4 device. The effect of incident illumination of varying intensities on the PD is also studied and a typical result for C4 device is presented in Fig. 5(b). The voltage bias between the electrodes were kept fixed at 30 V and the current was measured as a function of time. With increase in optical intensity in pulsed form, the photo current of the device also increased accordingly, which is due to the generation of more photocarriers at higher optical power. With the dark current remaining almost the same, this increased photocurrent with higher optical power results in higher photosensitivity and greater photo to dark current ratio.

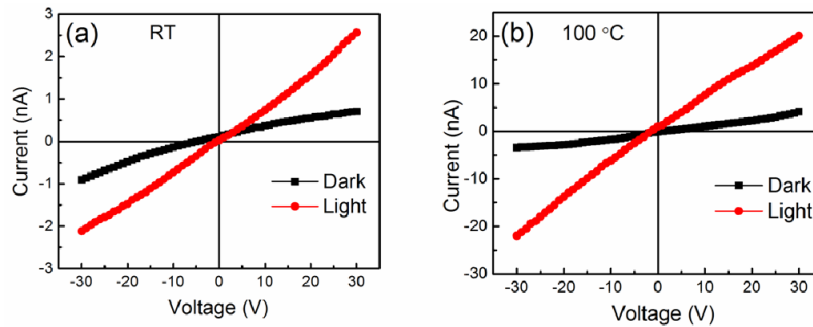
Photoresponsivity ( $R$ ) is the most important attribute for a photodetector, which is defined as follows:

$$R = \frac{I_L - I_D}{P_{in} \times A}$$

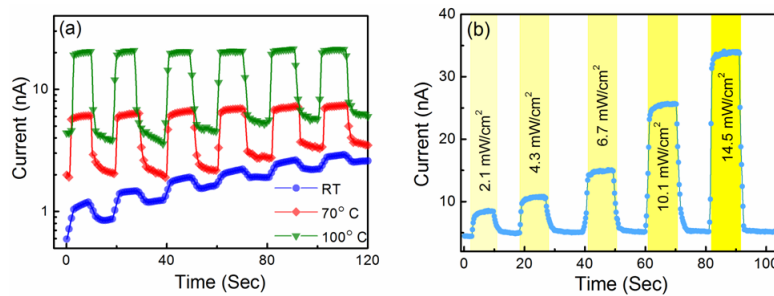
where,  $I_D$  is the dark current,  $I_L$  is the current with light illumination,  $P_{in}$  is the input light power and  $A$  is the active area of the PD. The maximum  $R$  value in the present CuPc based photodetector (C4 device) was estimated to be *ca.*  $7.1 \text{ mA}\cdot\text{W}^{-1}$  at bias voltage of 30 V at an incident light power of  $14.5 \text{ mW}\cdot\text{cm}^{-2}$ . A summarized result which shows the variation of  $R$  and  $\frac{I_L}{I_D}$  of

CuPc PD (C4 device) with incident illumination is presented in Figure 6(a). Both  $R$  and  $\frac{I_L}{I_D}$  were found to rise with rise in input optical power. The maximum value of  $\frac{I_L}{I_D}$  obtained within the measurement range was equal to 6.5 at input optical power of  $14.5 \text{ mW}\cdot\text{cm}^{-2}$ . These results further suggests that input illumination intensity could be an effective parameter to modulate the photo-

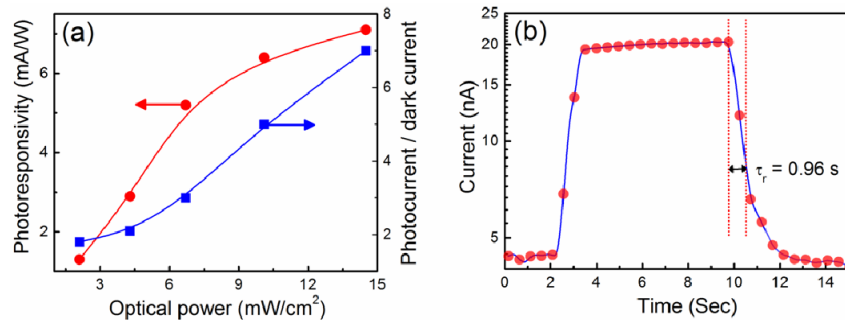
carriers in the devices and to precisely tune the performance of the PD for photosensing, optical switching, and signal amplification. The performances of the PD device in the present case can be considered to be quite impressive, keeping in view the device simplicity and without the requirement of any additional layer/component.



**Figure 4.** Photoreponsive current-voltage characteristics of CuPc based PD for (a) C1 ( $27^\circ\text{C}$ ) and (b) C4 devices ( $100^\circ\text{C}$ ) at light intensity =  $9.2 \text{ mW}\cdot\text{cm}^{-2}$ .



**Figure 5.** (a) Reversible photoswitching of CuPc films deposited at different substrate temperature under pulsed light ( $9.2 \text{ mW}\cdot\text{cm}^{-2}$ ) and fixed bias (30 V). (d) Photoresponse of CuPc PD (C4) under varying input optical power (bias voltage = 30 V).



**Figure 6.** (a) Dependence of photo to dark current ratio and photoresponsivity of CuPc PD (C4) with input optical power. (b) Transient behavior of photocurrent and measured relaxation time of C4 device.

To measure the decay time or the relaxation time ( $\tau_r$ ) of the PD device (C4), the exposed light, which was shined on the sample externally, is switched off from the point of photocurrent sat-

uration. The current did not returned to the base value sharply, rather, a slow decline for the PD device appears (compared to the rising process) followed by a persistence in the photoconductive-

ity. The summarized result is presented in Figure 6(b). Typical relaxation time (photocurrent decreased by more than 37% of the saturation value) for decreasing photocurrent was measured to be  $\tau_r = 0.96$  sec. Often, the persistent photoconductivity in organic PD or photosensor device is attributed to the slow nature of recombination of charge carriers, which is limited by the poor recombination cross section of the trapped holes within the active semiconductor in presence of the field [28].

#### 4. Conclusions

In conclusion, a high performance photodetector has been fabricated from thin film of copper phthalocyanine on glass substrate. The vacuum deposited thin film of CuPc showed increase in grain size with increase in substrate temperature as confirmed from the atomic force microscope image and x-ray diffraction (XRD) spectra. The CuPc thin film exhibited good photoresponse characteristics under white light illumination which showed further improvement for the film deposited at higher substrate temperature. The best photoresponse performances being observed for the CuPc film deposited at substrate temperature of 100 °C with photo to dark current ratio, *ca.* 6.5, and responsivity, *ca.* 7.1 mA-W<sup>-1</sup> at optical power of 14.5 mW-cm<sup>-2</sup>. The CuPc photodetector displayed stable and reproducible photoswitching characteristics and photocurrent modulation of devices' could precisely be tuned by controlling the input optical power.

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#### References

- [1] C. Wang, X. Zhang, and W. Hu, Chem. Soc. Rev., 49, 653–670 (2020).
- [2] A M Ali, D A Said, M Khayyat, M Boustimi, and R Seoudi, Results in Phys., 16, 102819 (8 pages) (2020).
- [3] J Jang, S Nam, K Im, J Hur, S N Cha, J Kim, H B Son, H Suh, M A Loth, J E Anthony, J Park, C E Park, J M Kim, and K Kim, Adv. Funct. Mater., 22, 1005–1014 (2012).
- [4] L Jiang, J Liu, X Lu, L Fu, Y Shi, J Zhang, X Zhang, H Geng, Y Hu, H Dong, L Jiang, J Yu, and W Hu, J. Mater. Chem. C, 6, 2419–2423 (2018).
- [5] B Mukherjee and M Mukherjee, Langmuir, 27, 11246–11250 (2011).
- [6] B Mukherjee, K Sim, T J Shin, J Lee, M Mukherjee, M Ree, and S Pyo, J. Mater. Chem., 22, 3192–3200 (2012).
- [7] X Huang, D Ji, H Fuchs, W Hu, and T Li, Chem Photo Chem., 4, 9–38 (2020).
- [8] M C McAlpine, H Ahmad, D Wang, and J R Heath, Nat. Mater., 6, 379–384 (2007).
- [9] Z Hussain, R Ojha, L L Martin, A M Bond, R Ramanathan, and V Bansal, Emergent Mater., 2, 35–44 (2019).
- [10] B Mukherjee, J. Electron. Mater., 48, 2131–2136 (2019).
- [11] B Cho, S Song, Y Ji, T W Kim, and T Lee, Adv. Funct. Mater., 21, 2806–2829 (2011).
- [12] Z Zhan, J An, Y Wei, V T Tran, and H Du, Nanoscale, 9, 965–993 (2017).
- [13] N O Weiss and X Duan, NPG Asia Mater., 5, e74 (2013).
- [14] Z Liu, G Chen, B Liang, G Yu, H Huang, D Chen, and G Z Shen, Opt. Exp., 21, 7799–7810 (2013).
- [15] T K An, C E Park, and D S Chuang, Appl. Phys. Lett., 102, 193306 (2013).
- [16] X Wang, W Song, B Liu, G Chen, D Chen, C Zhou, and G Z Shen, Adv. Funct. Mater., 9, 1202–1209 (2013).
- [17] S Dhara and P K Giri, J. Appl. Phys., 111, 044320 (2012).
- [18] T Pal, D Joung, S Ghosh, A Chunder, L Zhai, and S I Khondaker, J. Mater. Res., 33, 3999–4006 (2018).
- [19] G Wei, Z Lu, Y Cai, and C Sui, Mater. Lett., 201, 137–139 (2017).
- [20] S Doring, T Otto, M Cehovski, O Charfi, R Caspary, W Kowalsky, and T Rabe, Phys. Stat. Sol. A, 213, 2387–2391 (2016).
- [21] T Morimune, H Kajii, and Y Ohmori, IEEE Photon. Technol. Lett. 18, 2662 (2006).
- [22] T Hamid, S D Yambem, and A K Pandey, Synth. Met., 256, 116117–116122 (2019).
- [23] H Wang, Y Rahaq, and V Kumar, Sci. Rep., 6, 29567 (2016).
- [24] E A Lucia and F D Verderame, J. Chem. Phys., 48, 2674–2681 (1968).
- [25] M J Stillman and T N Nyokong, Phthalocyanines: Properties and Applications, Vol. 1, VCH, New York, p. 133 (1989).
- [26] M D Pirriera, J Puigdollers, C Voz, M Stella, J Bertomeu, and R Alcubilla, J. Phys. D: Appl. Phys., 42, 145102 (5 pages) (2009).
- [27] L Hu, X Liu, S Dagleish, M M Matsushita, H Yoshikawa, and K Awaga, J. Mater. Chem. C, 3, 5122–5135 (2015).
- [28] S Dutta and K S Narayan, Adv. Mater., 16, 2151 (2004).