Thickness-dependent sensitivity of Copper Phthalocyanine chemiresistive Nitrogen Dioxide sensors

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Abstract— **Chemiresistors of varying Copper Phthalocyanine sensing layer thickness, from 10 to 350 nm, have been fabricated and tested for sensing to sub-ppm levels of Nitrogen Dioxide. The results obtained were analyzed and the kinetics was shown to correlate well with first order kinetics, rather than with Elovich model. In explaining the sensitivity trend to thickness variation, gas diffusion into the layer was found to play a role and should be taken into consideration.**

Keywords— *thickness; gas sensor; metal phthalocyanine; nitrogen dioxide*

I. INTRODUCTION

Gas sensors have been researched upon for decades, for health and safety purposes such as in industries, cars and in households[1]. Especially in recent years, the use of sensors have been extended to include personal use such as lifestyle and outdoor air monitoring. As such, there is a need for cheap, miniaturized sensors that are fast and sensitive to the target gas analyte(s)[1].

As compared to Metal Oxides that are typically used for resistive-based gas sensing, Metal Phthalocyanine (MPc) is a class of organometallic materials that have exhibited room temperature sensing which thus, reduces the power consumption and need for implementation of a heater[2]. This class of materials consists of a metal center coordinated to the Pc macrocycle which allows side group substitutions, thereby changing its sensing properties as compared to its parent MPc. This translates to a possibility of improving the selectivity of the resultant sensing layer, as well as utilizing it to differentiate gases when used in combination in a sensor array. MPc, such as Copper Phthalocyanine (CuPc), has been shown to display sensitivity to Nitrogen Dioxide (NO_2), one of the indicators for outdoor air quality[3]. To improve the gas sensitivity of MPc, several approaches have been studied, such as examining the thermal and deposition effects, using composite materials and modulating the sensing layer thickness. In particular to research efforts on sensing layer thickness, Langmuir-Blodgett (LB) monolayer(s) based on soluble MPc, as well as thickness in the range of hundreds of nm to microns of MPc have been studied. While LB monolayers have shown that a thin sensing layer would demonstrate higher gas sensitivity [4], there are challenges to solve for large-scale production and thermal lifetime issues[5]. In comparison, the thickness effect on gas sensitivity of thinner sensing layers of vacuum deposited MPc layers have not been explored nor reported. Therefore, in this work, CuPc layer thickness was varied from 10 to 350 nm and the gas sensitivity towards sub-ppm levels of NO_2 was measured based on a chemiresistor layout.

II. EXPERIMENTAL

Sublimed-grade CuPc was purchased from Sigma Aldrich, with a purity of 99% and thermally evaporated using Lesker tool onto chemiresistor with Platinum interdigitated electrodes (IDEs). A quartz crystal microbalance sensing chip in the Lesker tool helped to achieve the desired thickness of 10, 30, 60, 120 and 350 nm CuPc layers on the chemiresistor, which consisted of 14 IDE fingers, with a channel length of 10 μm. The gas measurement of the respective devices to varying concentrations of NO_2 was done at room temperature with an applied bias voltage of 5 V. 3 cycles of 7 different NO_2 concentrations were used, namely 50, 60, 80, 100, 120, 200 and 500 ppb in synthetic dry air of 20% oxygen (O_2). The NO_2 dosing was limited to one minute, while recovery in 20% O_2 synthetic dry air was done in two minutes between each NO_2 concentration. The gas measuring system was controlled using Labview and gas concentration was achieved using Mass Flow Controllers. To analyze the results and obtain the sensitivity of the respective devices to NO_2, the second cycle was normalized by dividing measured current at time t (I_t) over first current of the second cycle (I_0'), i.e. (I_t/I_0') to obtain I_N. The normalized response of the device to each concentration was then calculated by ($I_{N.gas} - I_{N.0}$), where $I_{N,0}$ and $I_{N.gas}$ are the normalised measured current before and after each concentration accordingly. The gradient of the response against NO_2 concentration plot yielded the sensitivity of the device.

The thin film layers were also deposited on cleaned, blank oxidized silicon substrates for characterization on a surface profiler after each deposition to determine the thickness and X-ray Diffraction (XRD) was used to investigate the film crystallinity. Scanning Electron Microscope (SEM) was done on the devices to obtain morphology information.

III. RESULTS AND DISCUSSION

A. Layer characterisation

Crystallinity is observed for all thicknesses of CuPc used in this work, as shown in Fig. 1. A single peak at 2θ = 7.25° for the

various thickness is obtained, which corresponds to (1 1 0) diffraction plane of the metastable α-phase CuPc, with a interplanar distance of 12.2 Ă[6]. It is noted that the peak intensity increases with the layer thickness. In similar fashion, as the layer thickness increases, the peak obtained is sharper than its thinner counterparts. While the increase in peak intensity could be directly proportionate to the thickness, a narrower peak with greater thickness could be due to increasing crystallite size, in accordance to the Scherrer equation [7]. The calculated crystallite size is shown in Table 1.

In looking at the morphology investigated through SEM, as shown in Fig. 2, the particle size and roughness grew with the increase in CuPc layer thickness. This is also in agreement with the XRD results, where the crystallite size is bigger with thicker layers.
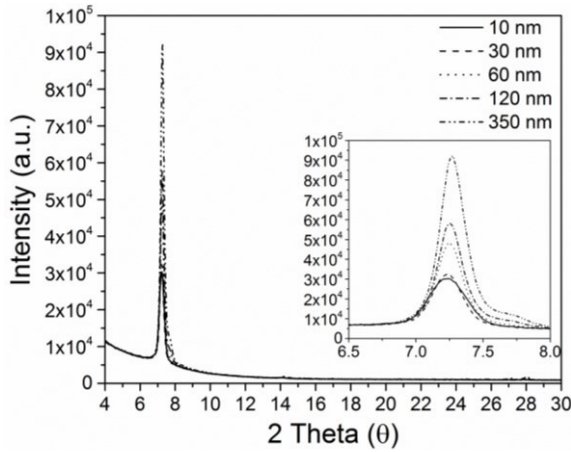

Fig. 1. XRD patterns of CuPc of varying thickness, from 10 to 350 nm, from 2 Theta values of 4° to 20°. The inset shows the XRD patterns between 6.5° to 8°.
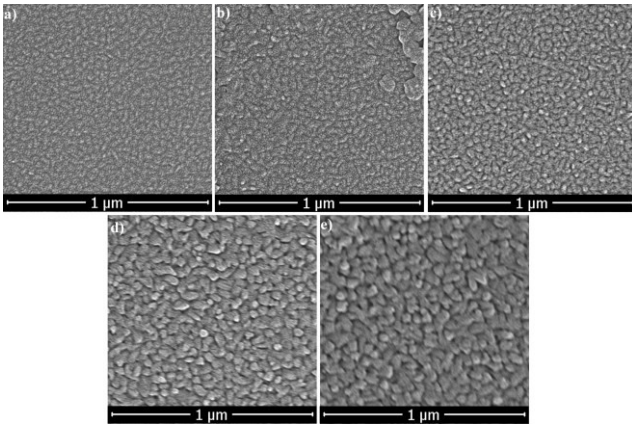

Fig. 2. SEM images of CuPc layers with (a) 10 nm, (b) 30 nm, (c) 60 nm, (d) 120 nm and (e) 350 nm thickness on the chemiresistor device. The image is taken at the edge of the Platinum interdigitated electrode finger.

TABLE I.   CRYSTALLITE SIZE OF THE FILMS AS CALCULATED BASED ON SCHERRER EQUATION

CuPc thickness (nm)	10	30	60	120	350
Crystallite size (nm)	21.6	26.7	30.3	32.4	37.8

B. Device performance to NO$_2$ dosing

The current obtained from the second cycle of NO$_2$ dosing is normalized and shown in Fig. 3 for the respective CuPc devices. As CuPc is a p-type semiconductor, exposure to oxidizing gas NO$_2$ will create more holes and improve the layer conductivity and subsequently, the measured current, as displayed in Fig. 3. Also, it is noted that there is a baseline shift for the all of the devices. However, in comparing the desorption of NO$_2$ of 10 nm CuPc device with 350 nm CuPc device, 10 nm CuPc device demonstrates faster desorption, as seen from the steeper slope in the recovery phase. Additionally, full recovery may be expected from 10 nm CuPc device when exposed to low NO$_2$ concentrations, up to 80 ppb at room temperature, as depicted in Fig. 3.

The sensitivity of the devices are then obtained as described in the experimental section and shown in Fig. 4, where the device with the thinnest CuPc layer showed the highest sensitivity and vice versa, the device with the thickest CuPc layer showed the lowest sensitivity. To explain the improvement seen in Fig. 4 with the thickness effect, it is important to relate the kinetics effect with gas sensing.

Prior works done to understand kinetics of MPc had employed the Elovich equation (1), where θ here refers to the amount of adsorbed gas during time t, while α is the initial sorption rate and β is the desorption constant [8, 9].

$$\frac{d\theta}{dt} = \alpha \exp(-\beta\theta) \tag{1}$$

Simplification of the (1) has been done by assuming a proportional conductivity change with the surface coverage and subsequently, linearity should be observed for a plot of current change (ΔI) against log (t) [9, 10]. The results obtained in this work has been analyzed based on this model and shown in Fig.5(top), for exposure to 50 ppb of NO$_2$, which is the lowest NO$_2$ concentrated tested in each cycle. The expected linearity from Elovich model is not seen in the results presented in this work, even for the lowest concentration tested. Hence, due to the lack of linearity, this model is not suitable to explain the kinetics observed.
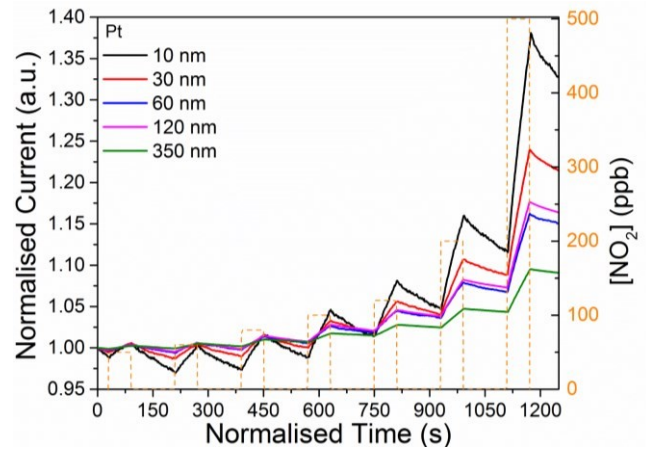

Fig. 3. Normalised current of CuPc chemiresistors of varying thickness to NO$_2$ dosing. The time has been normalised to indicate the start of the second cycle.
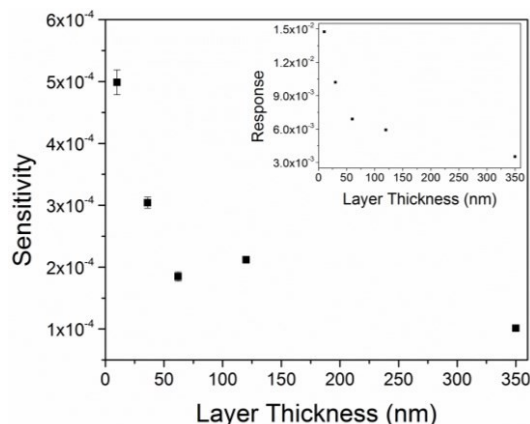
Fig. 4. Sensitivity of CuPc devices against thickness of the CuPc layer. The inset shows the normalised response of the respective layers to exposure of 50 ppb of NO_2
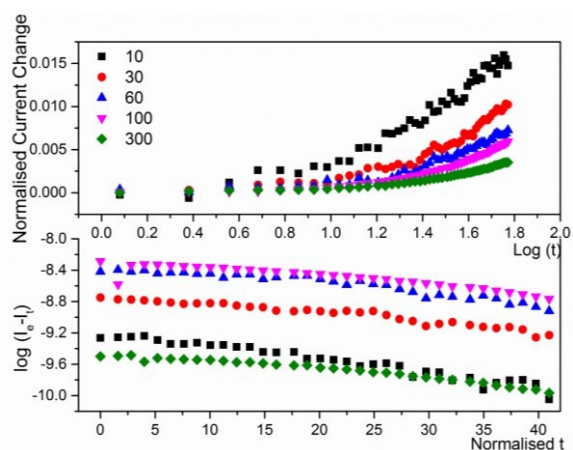

Fig. 5. (top) Elovich plot and (bottom) first order kinetic plot for various CuPc thickness (unit: nm) with exposure to 50 ppb of NO_2. Both plots share the same legend for the various CuPc thickness. Here, normalised t was taken as the time from which the respective CuPc devices are exposed to 50 ppb of NO_2.

An alternative model is the pseudo first order kinetics, which has been described elsewhere [9, 11]. In this model, a linear relationship is expected between time and the measured current, as the taken up rate of adsorption sites is proposed to be proportional to the number of free sites on the layer and measured current is assumed to correspond with the amount of gas adsorbed [9, 11]. In similar fashion, results obtained for 50 ppb NO_2 have been analyzed using this model to show a linear relationship (Fig. 5, bottom) between measured current and time, in accordance to the first order kinetics.

While the kinetics of the reaction was found to correspond to first order kinetics model, describing the current change with NO_2 exposure with only surface adsorption is insufficient in representing the NO_2 interaction with CuPc devices and it may be necessary to include the role of gas diffusion. Therefore, with reference to model derived by Sakai et al on gas response based on Knudsen diffusion and first order surface reaction [12], the response (R) is taken to be influenced by the rate constant (k), Knudsen diffusion coefficient (D) and thickness (T) in the relationship $R \propto \tanh[T\sqrt{(k/D)}]/[T\sqrt{(k/D)}]$. As such, as the layer thickness increases, the response and hence sensitivity of the

layer is expected to plateau, as seen in Fig.4. In another case, the normalized response of the different devices to 50 ppb of NO_2 (inset of Fig.4) displayed similar downward trend to sensitivity and work shown in previous work [11]. Within the same time frame, the lower response shown for thicker layers can be attributed to the additional diffusion of gas through the thick layer which led to a smaller response than in a thinner layer. It should be noted that while D is affected by the particle size, a larger effect from the thickness variation is seen in this work.

IV. CONCLUSION

CuPc devices with thickness ranging from 10 to 350 nm have been fabricated and comparison on the sensitivity to sub-ppm levels of NO_2 showed that lower sensing layer thickness has higher sensitivity. Attempts have been made to correlate to kinetic models and it was found that a first order kinetics model may be more appropriate than Elovich model. In describing the thickness effect, Knudsen diffusion effect was taken into consideration and shown to correlate with the results shown.

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