ISSN (Online) 2348 – 7968 | Impact Factor (2019) – 6.248
www.ijiset.com

Chemical Bonding Composition and Humidity Sensing Properties of a-CNx Thin Films by Low-Temperature rf-PECVD Technique

Rozidawati Awang and Siti Aisyah Abd Aziz

School of Applied Physics, Universiti Kebangsaan Malaysia,
43600 UKM Bangi, Selangor, Malaysia

Abstract
Amorphous carbon nitride (a-CN_x) thin films were deposited by low temperature radio frequency plasma enhance chemical vapor deposition (RF–PECVD) technique. The effect of substrate temperatures on chemical bonding composition and its humidity sensing properties were studied. The chemical bonding composition of the a-CNx thin films was characterized using Fourier transform infrared spectroscopy (FTIR) and its sensing properties was determined using a home built humidity sensor system. All samples show the presence of C-N, C = C, C = N, C≡N, C-H and N-H / O-H bonds, which are the corresponding bonds present in a-CNx thin films. In this study, high content of C=N, C≡N, C-H and N-H bonds in a-CNx thin film increases the sensitivity of the a-CNx thin film to humidity. At the optimum substrate temperature of 100℃, the sample exhibits highest sensitivity, fast response (23 s) and fast recovery time (19 s).
Keywords: *FTIR, Relative Humidity, Resistance, Sensitivity.*

1. Introduction

Nowadays, humidity sensing measurement is important for various applications in everyday life such as for industrial process control, food storage, medicine and healthcare. Commercial humidity sensors are usually made of polymer with dye-coating techniques. Although the technique is cheap and concise, it is difficult to produce a micro-sensor on a semiconductor substrate that can operate at high temperatures [1]. To overcome this problem, researchers began to shift studies from polymer-based materials to ceramic materials [2, 3]. However, the production of ceramic materials is in the form of bulk. In order to produce small-sized humidity sensors, researchers began looking for other alternatives by producing sensors from thin films using carbon-based materials [4]. Carbon-based materials are cheap, environmentally friendly and can operate at high temperatures. Among the carbon-based materials, amorphous carbon nitride thin film (a-CN_x) attracts current researchers due to its response to humidity and its applications in the electronic field [5, 6].

Currently, most developed humidity sensors have been commercialized according to changes detected by material sensors such as resistance, capacitance, electromagnetic and gravimetry. Resistor-type humidity sensors are commonly used because they have small size and are easily produced [7]. Additionally, the advantages associated with resistance humidity sensors are having a better and faster response than other sensors of humidity. Humidity sensing characteristics such as repeatability, reliability and rapid response to relative humidity should be dedicated in producing quality and high-performance humidity sensors as well as being produced at low cost [8, 9]. The use of a-CNx material as a resistive humidity sensor is believed to produce humidity sensor devices that have good features in addition to being fit and safe to use in everyday life.

The production of carbon-based thin films are usually attained from physical vapor deposition (PVD) such as magnetron sputtering techniques [10] and chemical vapor deposition (CVD) deposition such as plasma-enhanced CVD (PECVD). In this study, PECVD technique is used to produce a-CN_x thin film because of its homogeneous deposition, high deposition rates [11] and low substrate temperatures [5]. This technique also has the advantage of producing a good film adhesion and uniform film thickness on a substrate. Besides that, it also produces flawless and hollow-free films as compared to other techniques [12]. In this study, acetylene (C_2H_2) gas is used as a hydrocarbon precursor gas because its unsaturated bonds facilitate the process of reacting with nitrogen during the deposition. The use of this gas as a precursor gas is expected to increase the content of C = N, C≡N, C-H and N-H in the deposited a-CNx thin films. The bond plays a very important role in humidity sensing properties of a-CNx thin films so it is expected that the resulting sample will have higher efficiency as humidity sensor

2. Experimental Method

In this study, the a-CNx thin films were deposited in a PECVD system and the schematic diagram is shown in Figure 1, using C_2H_2 and N_2, as precursor gas. Both gases were mixed prior to admission into deposition chamber at a fixed flow rate of C_2H_2 at 20 sccm and N_2 at 50 sccm. The films were deposited at various substrate temperatures of 80, 100, 120, 150 and 180 ℃ at RF power of 80 W for 45 min. The deposition pressure and electrode distance, were fixed at 0.8 mbar and 1 cm respectively. The chemical bonding composition was investigated by Fourier Transform Infrared (FTIR) spectroscopy. The humidity sensing properties were characterized using a home build humidity sensor system. The interdigitated silver (Ag) electrode was deposited onto the a-CN_x thin film using RF magnetron sputtering technique [5].

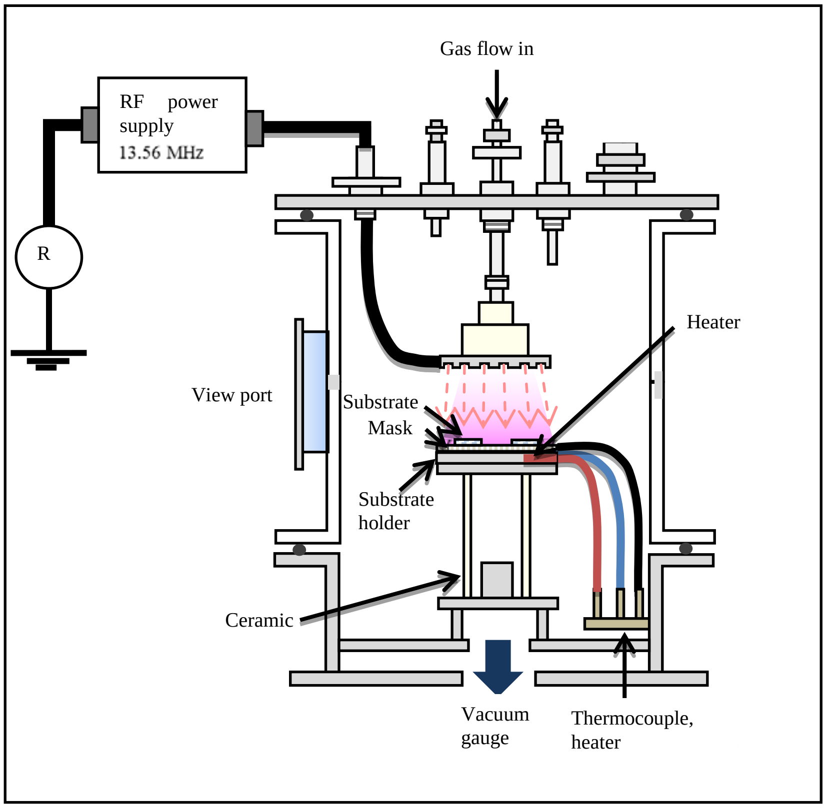


Fig. 1 Schematic diagram of deposition chamber in RF-PECVD system.

3. Results and Discussion

3.1 Chemical Bonding of a-CN_x Thin Films

Figure 2 shows the FTIR spectrum of a-CNx thin film deposited at different substrate temperatures. The vibration band at the 1350 - 1400 cm^{-1} wave number range indicates the C-N bond. While at the range of 1400 - 1500 cm^{-1} and 1500 - 1500 cm^{-1} wave numbers show the bonding modes of C=C and C=N respectively. In this study, C=C and C=N bonds are more

ISSN (Online) 2348 – 7968 | Impact Factor (2019) – 6.248

www.ijiset.com

dominant than C-N bonds. Nitrogen diffusion causes a stronger component breakdown of C=C and C=N bond which contributes to the formation of a-CN_x film. From the figure, a-CN_x thin films deposited at 100 ℃ showed the highest C-N, C=C and C=N peaks intensity compared to other samples. The formation of C=N bonds in a-CN_x thin films is due to the bombardment of N^+ ion during deposition. However, at high temperatures, the formation of N^+ ions decrease because of their tendency to form C_2N_2 molecules [13] and the effects of erosion and etching by hydrogen. Thus, in this study, it is found that the intensity of bond C=N decreases when the temperature is increased over 100 ℃.

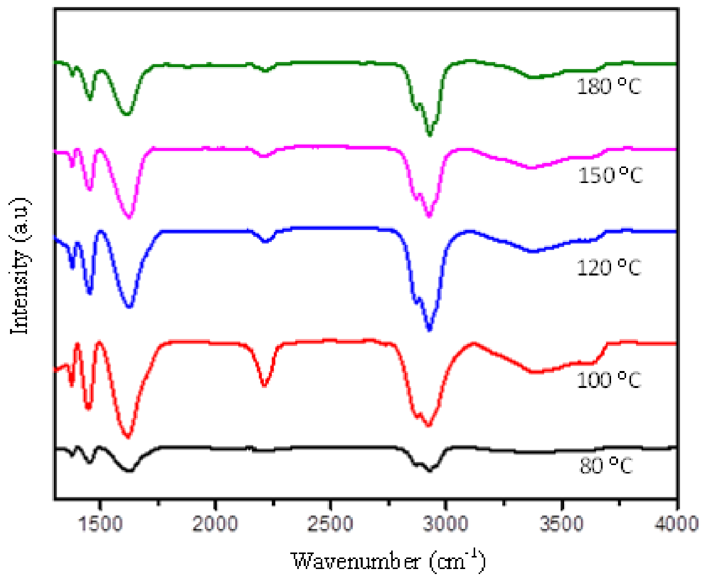


Fig. 2 FTIR spectra of a-CNx thin films at different deposition temperatures.

All samples show the presence of C-N, C = C, C = N, C≡N, C-H and N-H / O-H bonds, which are the corresponding bonds present in a-CNx thin films. Sample deposited at 100 ℃ showed that the C-N, C=N, C≡N, C=C and N-H peaks were highest compared to other samples. Transmission intensity decreases when the deposition temperature is increased above 100 ℃. This indicates that, in this study, the optimum deposition temperature of a-CNx thin film with highest C-N, C=N, C≡N, C=C and N-H bonds composition is at 100 ℃. There were significant and drastic changes in the FTIR spectrum for a-CNx thin films as the deposition temperature increased from 80 ℃ to 100 ℃. This occurs when there is a structural change due to the addition of nitrogen into the film as reported by Ferrari et al. [14].

3.2 Humidity Sensing Properties of a-CN_x Thin Films

The humidity sensor test system was used to study the sensitivity of the a-CN_x thin film sample deposited at different substrate temperatures (80, 100, 120, 150 and 180 ℃). In this study, the response of a-CN_x thin film as humidity sensor is examined in relative humidity (RH) of 9% to 89% RH. The characteristics of a-CN_x thin film such as repeatability, sensitivity, response and recovery time as well as its stability as a humidity sensor were studied.

3.2.1 Repeatability

The electrical response of a-CN_x thin film deposited at different substrate temperatures with an interval of 4 minutes is shown in Figure 3. Overall, all samples show good response and repeatability to different RH. The figure also shows the maximum and minimum resistance values that can give a sensitivity value to each sample. Generally, the sensor mechanism of a thin film a-CN_x humidity sensor involves the absorption of water molecules in the air causing a thin film resistance of a-CN_x to decrease when RH values increase.

ISSN (Online) 2348 – 7968 | Impact Factor (2019) – 6.248
www.ijiset.com

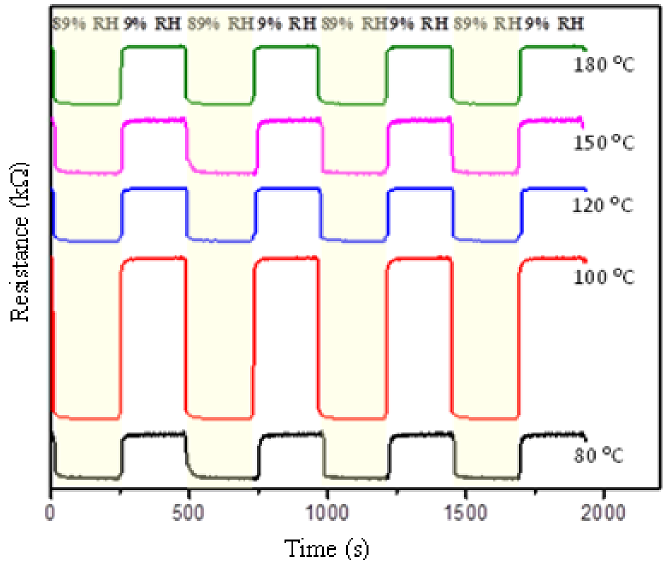


Fig. 3 Dynamic response of the a-CN_x thin film deposited at different substrate temperature to different RH level, 9-89%.

3.2.2 Sensitivity

The difference between the maximum and minimum resistance values giving different sensitivity values for each sample is tabulated in Table 1. From the table, sample deposited at substrate temperature of 100 ℃ shows the highest sensitivity of 81.3%.

Table 1: Electrical response (maximum and minimum resistance) and a-CNx humidity sensitivity at different substrate temperature.

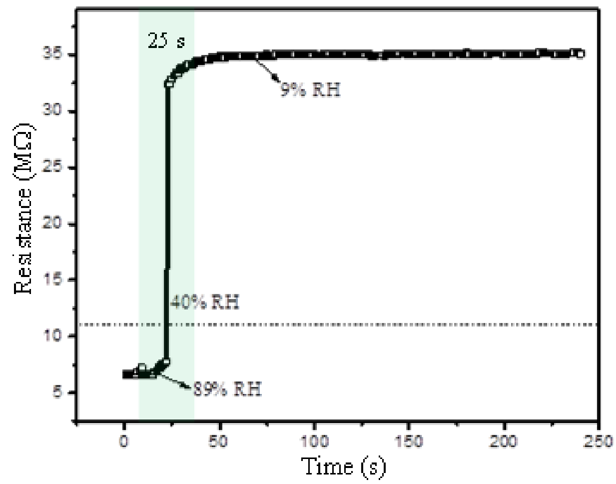
Substrate temperature (°C)	*Resistance (dry), R_o (MΩ±0.01)*	*Resistance (humid), R_h (MΩ±0.01)*	*Sensitivity, S (%)* $S = \frac{R_h - R_o}{R_o}$
80	6.78	14.48	53.17
100	6.55	35.10	81.33
120	6.44	15.82	59.26
150	6.76	16.44	58.85
180	6.43	16.67	61.46

3.2.3 Response and recovery times

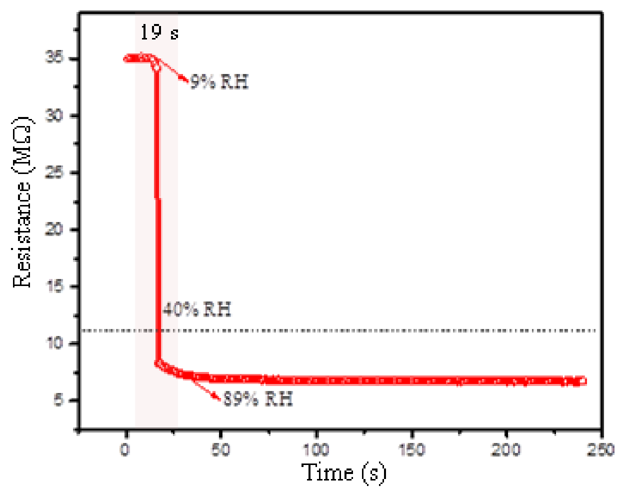
Figure 4 (a) shows the response time (τ response) and (b) the recovery time (τ recovery) measured by the sample deposited at the substrate temperature of 100 ℃. Response and recovery time is measured for 240 s (4 minutes). From the figure, the response time is 23 s while recovery time is 19 s. The durations were considered as fast response and fast recovery time.

ISSN (Online) 2348 – 7968 | Impact Factor (2019) – 6.248

www.ijiset.com



(a)



(b)

Fig. 4 (a) Response (drying process) and (b) recovery times (moisturizing process) of the a-CNx as a function of relative humidity (9-89% RH).

3.2.4 Stability

Short-term stability test of a-CN_x thin film as a humidity sensor were done on samples deposited at substrate temperature of 100 ℃ and is shown in Figure 5. Based on the figure, the change of resistance was observed for 40 min under different humidity conditions repeatedly every 5 minutes. As seen, resistance of the sensor is almost unchanged in the measurement process. This condition proves that an a-CN_x as humidity sensor has excellent short-term stability.

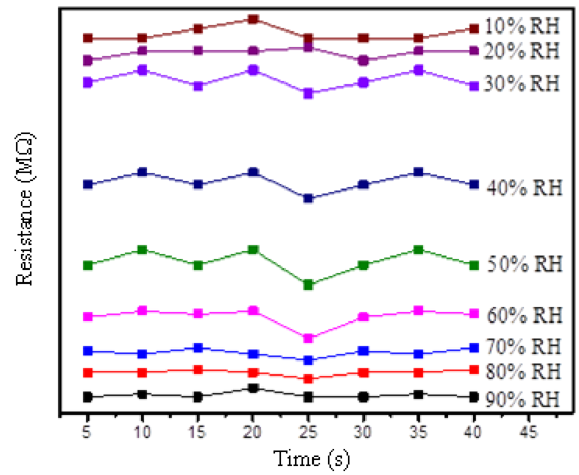
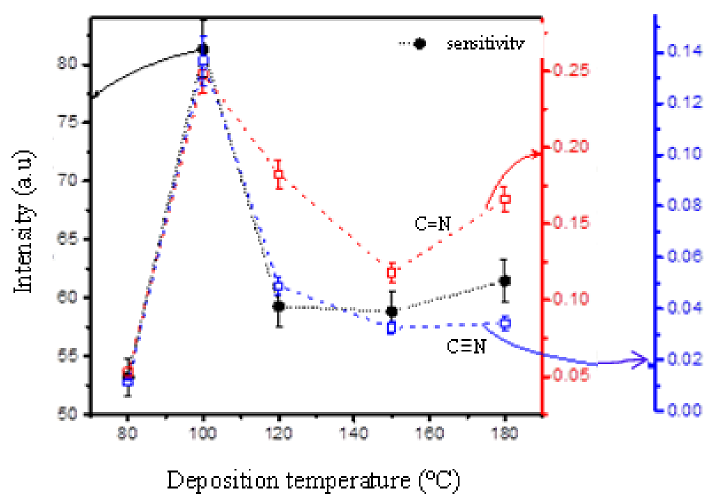


Fig. 5 Short-term stability of a-CNx thin film at different RH on samples deposited at substrate temperature of 100 ℃.

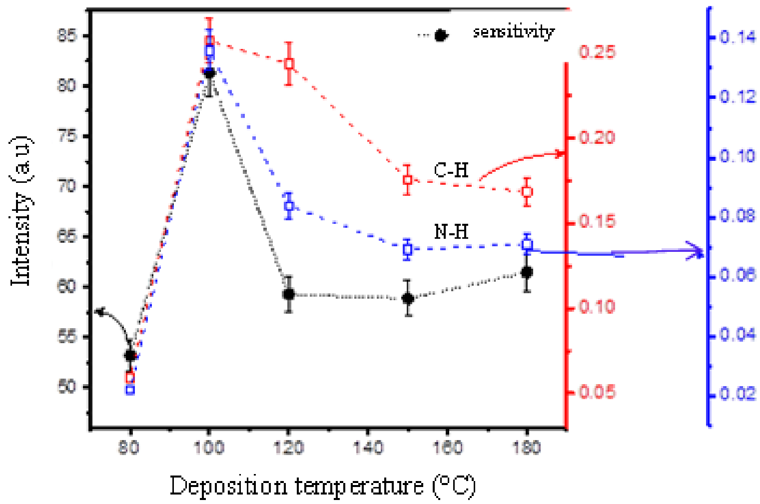
3.3 Influence of Chemical Bonding Composition on Humidity Sensing Properties

Figure 6 shows the sensitivity of the sample with the C=N, C≡N, C-H and N-H bonds content in the samples deposited at different substrate temperatures. Based on the figure, the sensitivity of the samples to the humidity depends on the content of C=N, C≡N, C-H and N-H bonds. The content of these bonds contributes to the sensitivity of the sample as a humidity sensor. However C-H bonds have less influence on sensitivity than other bonds. In this study, the sample deposited at substrate temperature of 100 ℃ is optimum in terms of sensitivity as humidity sensor with highest C=N, C≡N, C-H and N-H bonds content in the sample.



(a)

ISSN (Online) 2348 – 7968 | Impact Factor (2019) – 6.248
www.ijiset.com



(b)

Fig. 5 The correlation between a-CNx thin film sensitivity with the intensity of (a) C = N and C≡N bond, and (b) C-H and N-H bond

4. Conclusions

The a-CN_x thin film has been successfully deposited at different substrate temperature using hydrocarbon precursor of C_2H_2 and N_2. All samples show the presence of C-N, C=C, C = N, C≡N, C-H and N-H / O-H bonds, which are the corresponding bonds present in a-CNx thin films. The sample deposited at 100 ℃ has highest content of C=N, C≡N, C-H and N-H bond with the highest sensitivity to humidity of 81% accompanied by fast response and recovery time. From this study, it shows that the C=N, C≡N, C-H and N-H bonds play an important role in improving the performance of a-CN_x thin films as a humidity sensor. In addition, these factors also play a role in enhancing resistance response and shortening both response time and recovery of sensor humidity device.

Acknowledgments

This research was funded by FRGS/2/2013/SG02/UKM/02/1 and FRGS/1/2018/STG02/UKM/02/6 from the Ministry of Higher Education (Kementerian Pendidikan Malaysia, KPM), Malaysia. The authors would like to thank the School of Applied Physics and the Center for Research and Instrumentation Management (CRIM), Universiti Kebangsaan Malaysia for the facilities provided.

References

[1] S. Lee, “Synthesis and characterization of carbon nitride films for micro humidity sensors”. Sensors, 8, 2008, pp. 1508–1518.
[2] H. Chen, Q. Xue, M. Ma and X. Zhou, “Chemical Capacitive humidity sensor based on amorphous carbon film/n- Si heterojunctions”, Sensors & Actuators: B. Chemical 150(1), 2010, pp. 487–489.
[3] A. Tripathy, S. Pramanik, J. Cho, J. Santhosh, and N.A.A. Osman, “Role of morphological structure, doping, and coating of different materials in the sensing characteristics of humidity sensors”, Sensors (Switzerland) 14(9), 2014, pp. 16343–16422.
[4] Z. Zhao, X. Liu, , W. Chen, and T. Li, “Physical Carbon nanotubes humidity sensor based on high testing frequencies”, Sensors & Actuators: A. Physical 168(1): 2011, pp. 10–13.
[5] S.A.A. Aziz, N. Purhanudin, and R. Awang, “Chemical bonding and humidity sensing properties of amorphous carbon nitride (a-CNx) by acetylene gas”, AIP Conference Proceedings 1838(1), 2017, pp. 20010.
[6] P. Chen, H. Wang, H. Liu, Z. Ni, J. Li, Y. Zhou, and F. Dong, “Directional electron delivery and enhanced reactants activation enable efficient photocatalytic air purification on amorphous carbon nitride co-functionalized with O/La”, Applied Catalysis B: Environmental, Volume 242, 2019, pp. 19-30.

[7] E. Mikmeková, J. Polˇ, and O. Caha, “Humidity resistant hydrogenated carbon nitride films”, Applied Surface Science, 275, 2013, pp. 7-13.

[8] J. Chu, X.Peng, P. Feng, Y. Sheng, and J. Zhang, “Study of humidity sensors based on nanostructured carbon films produced by physical vapor deposition”, Sensors and Actuators, B: Chemical, 178, 2013, pp. 508-513.

[9] S. Lee, “Synthesis and characterization of carbon nitride films for micro humidity sensors”, Sensors, 8, 2008, pp. 1508-1518.

[10] H.-M. Wang, Y.-F. Li, H.-L. Shen, , Z.-H. Zhai, J.-Y. Chen, J.-L. Yang, and Y. Yang, “Effect of Nitrogen Gas Flow Rate on Properties of Diamond Like Carbon Films Prepared by Magnetron Sputtering”. Guangzi Xuebao/Acta Photonica Sinica, Volume 48, Issue 4, 2019, pp 0416003.

[11] G. Lee, D.K. Sohn, S.H. Seok, and H.S Ko, “The effect of hole density variation in the PECVD reactor showerhead on the deposition of amorphous carbon layer”, Vacuum, Volume 163, 2019, pp. 37-44.

[12] R. Ritikos, C.C. Siong, S.M. Ab Gani, M.R. Muhamad, and S.A. Rahman, “Effect of annealing on the optical and chemical bonding properties of hydrogenated amorphous carbon and hydrogenated amorphous carbon nitride thin films”, Japanese Journal of Applied Physics 48(10), 2009, pp. 101301.

[13] C.-Y. Hsu, and F.C.-N. Hong, “The effect of substrate temperature on the growth of CNx films with beta-C3N4-like microcrystallites by an inductively coupled plasma (ICP) sputtering method”, Diamond and Related Materials 8(7), 1999, pp. 1315-1323.

[14] A.C. Ferrari, S.E. Rodil, and J. Robertson, “Interpretation of infrared and Raman spectra of amorphous carbon nitrides”, Physical Review B 67(15), 2003, pp. 155306.

Rozidawati Awang List of degrees: PhD (2009), MSc (2000), BSc. (1997); places of employ: KYPM, Bangi, as a lecturer (2000-2002) and UKM, Bangi as a Senior Lecturer (2002-now); Research output: Citations 97, h-index 6, number of papers 37; current research interests: Carbon based thin films and nanotechnology; a life member of Malaysian Solid State Science and Technology Society (MASS).

Siti Aisyah Abd Aziz List of degrees: MSc (2018), BSc. (2015); place of employ: MRSM, as teacher (2018-now).