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Effect of Radio Frequency Power on a-CN_x Film Properties and Its Performance as Humidity Sensors

(Kesan Kuasa Frekuensi Radio terhadap Sifat Filem Nipis a-CN_x dan Prestasinya sebagai Pengesan Kelembapan)

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ABSTRACT

A series of amorphous carbon nitride (a-CN_x) thin films were deposited on silicon (111) substrates using a home-built radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) system. The a-CN_x thin films were deposited from a mixture of a fixed flow-rate of ethane (C_2H_6, 20 sccm) and nitrogen (N_2, 47 sccm) gases with varying RF power. A higher ratio of C to H (C to H ratio is 1:3) atoms in C_2H_6 as compared to the ratio in methane (CH_4) gas (C to H ratio is 1:4) is expected to produce an interesting effect to the film properties as humidity sensor. The characterization techniques used to determine the morphology and chemical bonding of the thin films are field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR), respectively. The variation of morphology and the existence of nitrile band in these samples are correlated with the electrical properties of a-CN_x thin films. Using humidity sensing system, the sensing performance of the samples was examined. It was found that the response of sensors towards the percentage of relative humidity (% RH) change is good resistive responses and good repeatability. The sensitivity of the prepared a-CN_x thin films is significantly higher (up to 79%) as compared to previous studies using CH_4 or acetylene as precursor gas. Based on these results, the properties and the sensitivity of the a-CN_x thin films towards humidity can be tailored by using an appropriate precursor gases and deposition parameters.

Keyword: Chemical bonding; electrical properties; nitrile band; PECVD

ABSTRAK

Satu siri filem nipis nitrida karbon amorfus (a-CN_x) telah dimendapkan di atas substrat silikon (111) menggunakan sistem pemendapan wap kimia secara peningkatan plasma berfrekuensi radio (RF-PECVD) yang dibangunkan sendiri. Filem nipis a-CN_x ini dimendapkan daripada campuran gas etana (C_2H_6, 20 sccm) dan nitrogen (N_2, 47 sccm) pada kadar aliran gas malar dengan ubahan kuasa RF. Nisbah atom C terhadap atom H yang lebih tinggi dalam (C_2H_6, nisbah C kepada H ialah 1:3) berbanding nisbah tersebut untuk gas metana (CH_4, nisbah C kepada H ialah 1:4) dijangka memberi kesan yang lebih baik kepada sifat filem nipis a-CN_x sebagai pengesan kelembapan. Teknik pencirian yang telah digunakan untuk menentukan morfologi dan ikatan kimia filem nipis a-CN_x masing-masing ialah mikroskop imbasan elektron pancaran medan (FESEM) dan spektroskopi transformasi Fourier inframerah (FTIR). Perubahan morfologi permukaan dan kewujudan kumpulan berfungsi ikatan nitril di dalam sampel filem nipis ini dikaitkan dengan sifat elektriknya. Prestasi sampel sebagai pengesan kelembapan diuji dengan menggunakan sistem pengesan kelembapan. Pengujian tersebut menunjukkan tindak balas yang jelas iaitu berlaku perubahan rintangan sampel dan kebolehulangan pengesanan oleh sampel dalam peratus kelembapan relatif (% RH) yang berbeza. Kepekaan filem nipis a-CN_x yang disediakan dalam kajian ini terhadap kelembapan adalah lebih tinggi (sehingga 79%) berbanding kepekaannya dalam kajian sebelum ini yang menggunakan gas CH_4 atau asetilena sebagai gas pelopor. Berdasarkan keputusan ini, sifat dan kepekaan pengesanan kelembapan filem nipis a-CN_x boleh diubah suai dengan menggunakan gas pelopor dan parameter pemendapan yang tertentu.

Kata kunci: Ikatan kimia; jalur nitril; PECVD; sifat elektrik

INTRODUCTION

Amorphous carbon nitride (a-CN^x) thin films have been extensively developed owing to its unique combination of electrical, optical and mechanical properties (Abd El-kader et al. 2012; Sekhar et al. 2014; Zheng et al. 2014). Among these properties, the electrical property is seen to be of significant interest and therefore have been widely investigated. It has been reported that a-CN^x thin films exhibit an improvement on the electrical properties due to the formation of sp^2-clusters and are responsible for the enhancement of conductivity of the a-CN^x thin films (Sekhar et al. 2014). The formation of sp^2-clusters is induced by the nitrogen incorporation in the a-CN^x thin films (Ferrari et al. 2003). Various techniques have been reported to produce carbon based thin films such as thermal chemical vapor deposition (T-CVD) (Shaharin et al. 2014) and plasma enhanced chemical vapor deposition PECVD (Awang & Rahman 2008). In the CVD growth, the gas used as precursor is one of the major issues. In the previous work, the performance of a-CN^x thin films as a humidity

sensor, produced from methane, (CH_4) as a precursor gas was carried out (Aziz et al. 2015). Continuation of the work, the sensitivity a-CN_x thin films as a humidity sensor, produced from ethane (C_2H_6) gas is studied. Higher C to H ratio in C_2H_6 gas is expected to induce the nitrogen incorporations in the films (Othman et al. 2014) and promote the formation of paracyanogen (C=N) and nitrile (C≡N) bands (Othman et al. 2013). Higher content of these bands can enhance the humidity sensing property of a-CN_x thin films (Lee & Lee 2015). This work reports on the properties of a-CN_x thin films deposited using C_2H_6 and N_2 by RF-PECVD technique with varying RF power. The influence of RF power on the morphology, chemical bonding and the humidity sensing properties of the films are described.

Materials and Methods

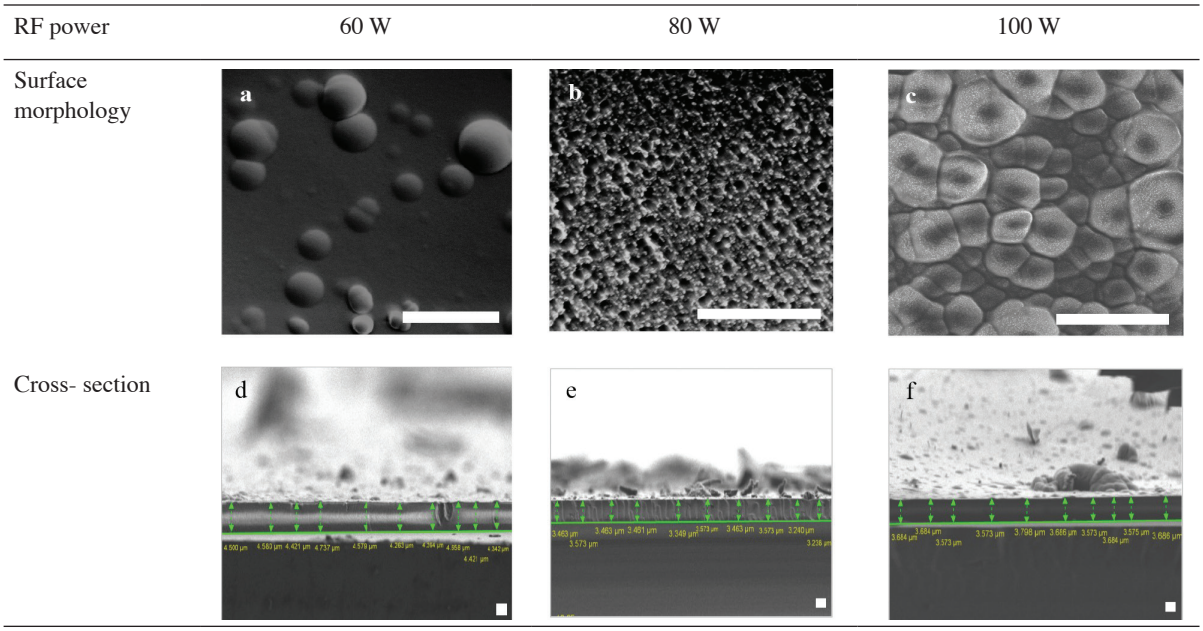
The a-CN_x thin films were prepared by RF-PECVD technique at different RF power of 60, 70, 80, 90 and 100 W. The a-CN_x thin films were deposited from the dissociation of a mixture of precursor gases C_2H_6 (20 sccm) and N_2 (47 sccm) onto p-type (111) silicon and quartz substrates. The films were deposited for 90 min. Some other parameters such as electrode distance, deposition pressure and temperature were fixed at 1 cm, 0.8 mbar and 100ºC, respectively. Pre-deposition process by means of a hydrogen plasma treatment was performed to remove unwanted impurities on the substrate surface along with improving the adhesive of deposited CN layers onto the substrate. The morphology and cross section images of the deposited a-CN^x thin films were captured by field emission scanning electron microscopy (FESEM). The film thickness was determined from the cross section images and the deposition rate of the a-CN^x thin films were deduced from the average film thickness over the deposition time. The chemical bonds were characterized by Fourier transform infrared spectroscopy (FTIR). The interdigitated electrode was then deposited onto the films using RF magnetron sputtering technique to study the variation of resistance response as a function of relative humidity (RH) and time using a home-built humidity sensing system. The interdigitated electrode was deposited to enhance the absorption and desorption response of the samples (Aziz et al. 2015). The home-built humidity sensing system consists of both moisturizing and drying in alternate time-setting of 4 min. The sensitivity, *S* of the samples in response to humidity is calculated using the equation (Chu et al. 2013) as follows;

$$S = \frac{R_h - R_o}{R_o} \times 100\% \quad (1)$$

where R_h refers to the resistance at certain humidity (in this work, 85% RH) and R_o represents the original resistance of the sensors in air of 9% RH.

Results and Discussion

The micrograph images of a-CN_x thin films captured using FESEM are shown in Figure 1. Surface morphology is shown in Figure 1(a) - 1(c)) and their corresponding cross sections is in Figure 1(d) - 1(f)). The effects of RF power on the morphology and the average thickness of the deposited a-CN_x thin films were studied. The FESEM image shows that the round structures with different diameters were produced and dispersed unevenly on the film surface



The scale bar shown for 2 µm

FIGURE 1. FESEM morphology images (a-c) and cross sections (d-f) of a-CN_x deposited at 60 W, 80 W and100 W

deposited at lowest RF power of 60 W. However, the film produced at RF power of 80 W showed voids structure appeared uniformly on the film surface. The structure of voids can be regarded as the sites that enhanced the adsorption of water vapour molecules. At high RF power of 100 W, the morphology of the film appears to be dense with multi-shaped grains with clear grain boundaries. The film thickness of the a-CN_x thin films was detected from the cross section images. The thickness of the films decreased as the RF power was increased from 60 to 100 W. Figure 2 shows the relationship between the deposition rates of a-CN_x thin films as a function of RF power. This result was expected because the plasma particles gain more energy with the higher RF power, which can bombard onto the film surface and increases the amount of physical etching followed by the changes of film morphology. Increased in RF power will enhances a structural modification by a high energetic ions (Haviar et al. 2014; Tien et al. 2015). The enhancement of bombarded ions by the precursor gases creating high plasma consequently lead to a higher suppression of the growth film. Compared to our previous work using CH_4 gas, thin films deposited using C_2H_6 in this work showed higher deposition rate. This result is not in agreement with other work (Othman et al. 2013) which used relatively low RF power density (1.2 W/cm3). Using the C_2H_6 the dissociation of precursor gases had to undergo an additional step to form the CH_3 radical step (Haviar et al. 2014). Thus, the growth rate of films prepared from the C_2H_6 mixture is lower than CH4 mixture. The reactions are as follows (Legrand et al. 1999):

$$CH_4 \xrightarrow{N_2} CH_3$$

$$C_2H_6 \xrightarrow{N_2} C_2H_5 \xrightarrow{H_2} 2CH_3$$

Higher power density (more than 1.2 W/cm^3) used in this work may results in complete dissociation of the precursor gas with more production of CH_3 radicals resulting higher deposition rate using C_2H_6 mixture.

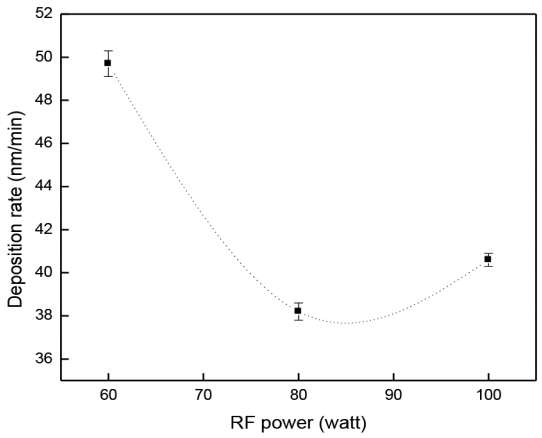


FIGURE 2. Deposition rate variation with RF power for a-CN_x thin films

The FTIR spectra in Figure 3(a) showed the existence of C-N (sp^3), C=N (sp^2), C≡N (sp^1), C-H and N-H/O-H bonds within a scanning range from 1000 to 4000 cm^{-1} as expected in a-CN_x thin films. In accordance with previous studies, the peaks correspond to the formation of single, double and triple CN bonds at wavenumbers of 1100, 1642 and 2333 cm^{-1}, respectively (Legrand et al. 1999; Othman et al. 2014; Tien et al. 2015), together with the C-H and OH bonds within the region of 2800-3000 and 3200-3500 cm^{-1}, respectively. As the presence of the C=N and C≡N bonds in a-CN_x thin films are preferential in detecting moisture for humidity sensor, the discussion of the infrared transmission spectra focuses on C=N and C≡N peaks. From Figure 3(a), the intensity of the peak for C=N increases as the deposition power increased from 60 to 80 W. The intensity of the peak appears to be slightly reduced and constant when the RF power was applied for more than 80 W. The intensity of C≡N peaks in Figure 3(b), shows that the intensity of the peak is maximum at RF power of 80 W. The FTIR spectra of a-CN_x films studied in this work showed that 80 W is the optimum RF power in inducing the formation C=N and C≡N bonds.

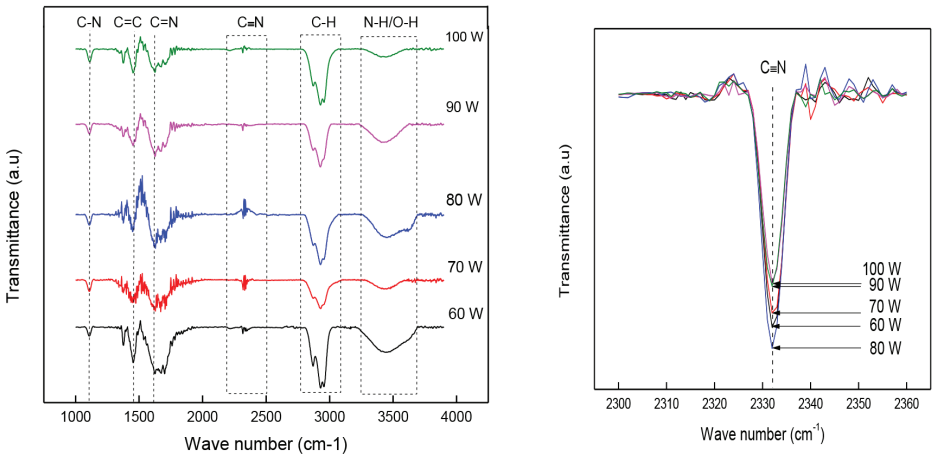


FIGURE 3. (a) Variation in FTIR transmittance spectra for films deposited as a function of RF power, (b) spectra of a specific region near 2330 cm^{-1} for the formation of triple bond (C≡N)

Figure 4 shows the result of humidity sensor tests for a-CN_x thin film deposited at 60, 70, 80, 90 and 100 W. During the drying process (low %RH, labelled as RH↓), water vapor were removed from the chamber. For moisturizing process (high %RH, labelled as RH), water vapor is channelled to the chamber, thus increasing the moisture level in the chamber. The resistance of the sample was reduced to minimum which changes the electrical response from an insulating material (high resistance) to a conductive material (low resistance). Each sample had shown the repeatability of electrical response to the change of different relative humidity (%RH) with time interval of 4 min. However, all samples showed a small delayed response to high %RH after a few cycles except for sample deposited at 80 W. Table 1 shows the values of maximum and minimum resistance and the calculated sensitivity of the sample responses to the %RH. It is seen that all samples showed similar sensitivity towards the different relative humidity with slightly higher sensitivity captured by sample deposited at RF power of 80 W. The humidity sensor tests for a-CN_x thin film in this work demonstrates that sample deposited at RF power of 80 W show best resistive responses compared to other samples with no delay response and highest sensitivity. In this study, the a-CN_x thin films produced from ethane showed significantly better performance as humidity sensor as compared to previous studies using methane (Aziz et al. 2015) and acetylene (Abd Aziz & Awang 2017) as precursor gas. Higher C to H ratio in C_2H_6 gas may induce the nitrogen incorporations in the films and promote the formation of paracyanogen (C=N) and nitrile (C≡N) bands hence contributing to a higher sensitivity with respect to the humidity sensing property of a-CN_x films.

Conclusion

The a-CN_x thin films were successfully prepared by RF-PECVD technique using ethane (C_2H_6) and nitrogen (N_2) as precursor gases. The effects of the deposition RF power on morphology, chemical bonding properties and humidity sensing properties in a-CN_x thin-films were investigated. It was determined that thin films deposited using ethane in this work results in higher deposition rate, imitating a good resistive responses to different relative humidity with higher sensitivity as compared to a-CN_x thin films prepared using methane. Sample prepared at RF power of 80 W showed porous and spongy like microstructure with the most abundant contents of C=N and C≡N. The sample portrays no delay response in humidity sensor tests and gives the highest performance in percentage sensitivity of

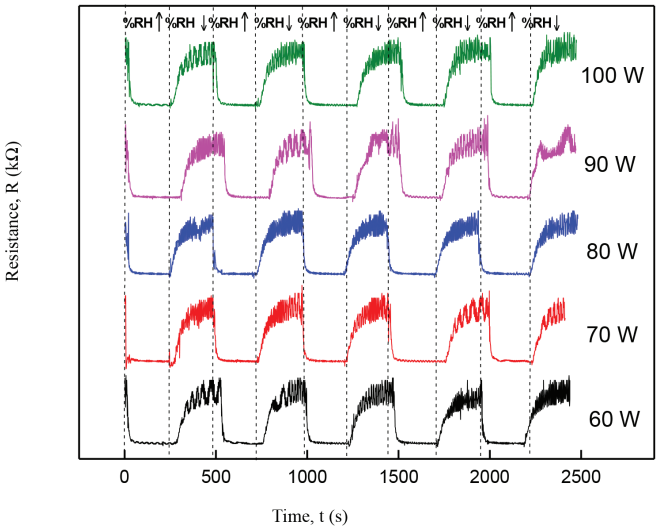


FIGURE 4. Dynamic response of the a-CN^x thin films deposited at different RF power to different RH levels, 4-87%

TABLE 1. Maximum and minimum resistance and sensitivity of a-CN^x thin films at different RF power

RF power (W)	Resistance (dry), R_o (kΩ ± 0.01)	Resistance (humid), R_h (kΩ ± 0.01)	Sensitivity, S (%)
60	22.28	5.14	76
70	22.22	5.33	76
80	24.86	5.23	79
90	23.32	5.31	77
100	21.18	5.28	75

79%. The optimal RF power on depositing the a-CN_x thin film is 80W which correlates with the best performance of a good humidity sensing material.

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