

Raman spectra characteristics of Carbon Doped Film from Ethanol Precursor and Nitrogen Doping

Ishak Annuar¹, Mazlina Mansor Hassan¹, Noor Azland Jainudin¹, M. Rusop²
¹(UiTM Sarawak Kampus Kota Samarahan Jalan Meranek, Sarawak, Malaysia)
²(NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia)

ABSTRACT: The nitrogen doped carbon (a-C:N) films were successfully prepared from vaporized ethanol and nitrogen gas as material sources. The a-C:N films obtained from ethanol precursor were analyzed by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). Positive bias voltage (0 to +50V) at 500°C were used for determine the structural properties. It was found that the carbon film were amorphous in nature. The negative bias gives significant effect to change the structural properties.

KEYWORDS - Renewable carbon precursor, Doping, Deposition, Ethanol

I. INTRODUCTION

Nitrogenated carbon (a-C:N) film has been widely investigated in the past decade with various methods and precursors. It was understood that by any method of synthesis, deposition condition or even precursor use, the undoped carbon thin film are weakly p-type and high density of intrinsic defects in nature [1-4]. Doping mechanism is known the best way for successfully changing its electrical properties from different types of dopants such as nitrogen, phosphorous, iodine or boron and showed an increase in conductivity and decrease in resistivity. It was reported that deposition parameters affect the formation of crystalline phase and amorphous structure of a-C:N thin films due to the incorporation of nitrogen (N) which can be observed with the change of in the ratio of tetrahedral bonded carbon (sp^3 -C) to trihedral bonded carbon (sp^2 -C) in the carbon films. In fact, nitrogen incorporation in amorphous carbon films is a complex procedure and the chemistry of an N atom in a-C depends heavily on its local environment. There are many possibly bonding configurations in the carbon network, including the sp^3 and sp^2 substitutional sites (doping sites) and other configurations such as pyridine, pyrrole, and nitrile (non-doping sites) [1-3].

Beside of boron as previously discussed, nitrogen can be used as a dopant for p-type a-C thin film prepared from different techniques and precursors [4-6] and therefore it is believed that a-C:N film can be deposited with this technique and palm oil precursor which has been rarely reported by other groups. Since the microstructure of a-C thin films is strongly dependent on the deposition conditions, method and precursor, it is important to analyze the a-C:N prepared by different positive bias voltages (+10 V to +50 V). The objectives of the studies are to investigate the effect of positive bias voltage on the Raman properties of a-C:N films prepared by custom-made-CVD using ethanol as a precursor.

II. METHODOLOGY

A preparation method use for synthesize ethanol and the cleaning process for glass and silicon substrates has been previously reported elsewhere [4,5]. The ethanol is heated at 100°C by hot platter heater. The vapor of ethanol, and argon were flowed at 100 mL/min, 150 mL/min, respectively. The argon gas was used as a carrier of deposition particle and as a medium to dispose contaminated particles outside the chamber. Positive bias voltages (0 to +50V) at 500°C were used for investigated. The samples were characterized by Raman spectroscopy and Fourier transforms infrared spectroscopy for structural properties, respectively.

III. RESULT AND DISCUSSION

The Raman scattering spectra of a-C:N film deposited at different positive bias (Fig. 1) show similar structure, which might be indicated similar sp^3/sp^2 composition [3]. Characteristics parameters of Raman spectra, including position of G peak, full width at half maximum (FWHM) of G peak, and $I(D)/I(G)$ (intensity ration of D peak and G peak), are calculated by fitting two Lorentzian peaks to the spectra Raman spectra as

Raman spectra characteristics of Carbon Doped Film from Ethanol Precursor and Nitrogen Doping

shown in Table 1. Here Pos G representing position of G peak, Width (G) is the FWHM of G peak, and $I(D)/I(G)$ is intensity ratio of the D peaks and G peak. The position, the FWHM and the integrated intensity ratio ($I(D)/I(G)$), can be used as indicators of carbon bond arrangement. The G and D bands observed from 0 to +50 V are relatively broad indicating that the crystallite size of the carbon in the a-C:N is small as reported in . The peak around 1550 cm^{-1} shows the amorphous nature of the a-C films and therefore the a-C:N films deposited by this technique using palm oil precursor are also amorphous film [3,8].

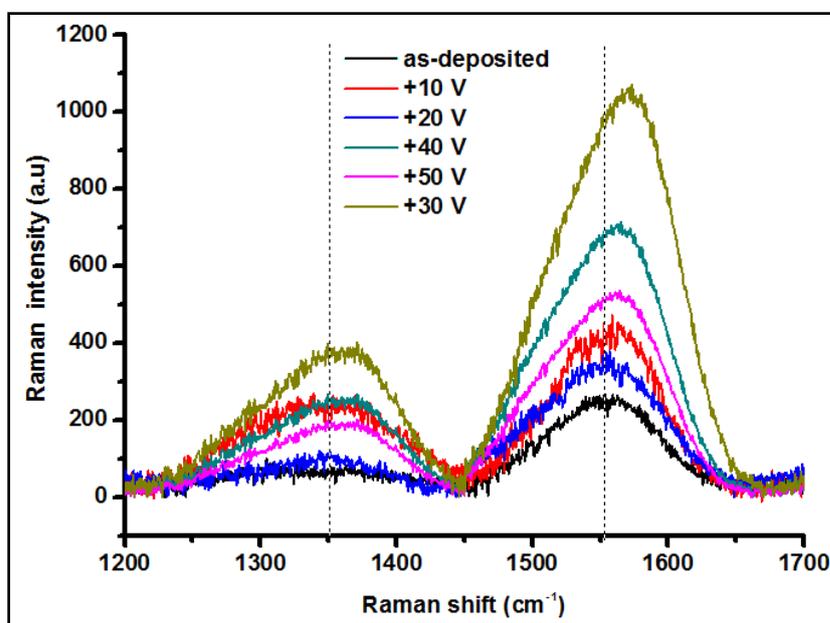


Fig. 1. The Raman spectra of a-C:N films at difference positive bias voltages

At no bias applied (0 V), the D band position is low compared to a-C:N film deposited with positive bias voltage. The D band of a-C:N film is gradually increase until +30 V and decrease thereafter. Thus, the structure of the films is altered upon incorporation of N. Both, Raman D and G peaks are upshifted with increase of positive bias from 0 V to +50 V. This phenomenon might be indicated the component of the sp^2 bonds might be increased with the increase of nitrogen incorporation with carbon network. The upward shifting of Raman G peak together with the increase of Raman D peak position and intensity might reflect to the progress of graphitization which can occur by the increase of Csp^2 bonds and “ordering” of the Csp^2 domain because Raman D peak is reported to be assigned to sp^2 -bonded C which seems to be aromatic in structure [2,8,9]. Under this refinement process, the sp^2/sp^3 ratio may also be decreased to a certain value as supported by the upshifting of the D-position. The obtained result show the $I(D)/I(G)$ ratio fluctuated from 0.145 to 0.313 indicate the changing sp^2/sp^3 ratio. The same phenomenon was agreed by others when D-peak intensity increased. The changing of size particle in FESEM images might be related to the increasing of D-position. The main factor affecting bands position, width and intensity is the clustering of sp^2 phase [8,9]. The G band position measures topological disorder, which arises from the size and shape distribution of sp^2 clusters [9]. The changing of D and G position might be to a change in the clustering of sp^2 phase of a-C:N film. Although there is no evident to justify the clustering of sp^2 phase of a-C:N film changed, but changing of D position might be an indicator for changing of clustering of sp^2 phase. According to the literatures an increase in sp^2 -bonding resulted in a G peak shifted to a higher wave number and the upward shifting of the Raman D and G peak positions indicated the reduction of bond angle disorder and growth of graphitic domains [2,8,9]. Thus, the result implies that the a-C:N films prepared from palm oil precursor are dominated by sp^2 rather than sp^3 when the negative bias increase from 0 V to +50 V.

Table 1: Raman spectra characteristics parameters of a-C:N films at difference positive bias

Positive bias voltage (V)	Pos (G) (cm^{-1})	Width (G) (cm^{-1})	Pos (D) (cm^{-1})	Width (D) (cm^{-1})	$\frac{I(D)}{I(G)}$
0	1552.416	85.106	1314.344	83.566	0.1451
10	1555.037	66.912	1342.055	87.041	0.4875
20	1550.686	86.106	1340.972	44.583	0.1631
30	1562.83	86.384	1344.903	91.321	0.3165
40	1554.891	86.255	1344.567	91.181	0.3127
50	1562.829	86.234	1344.524	91.157	0.313

Figure 2 shows FTIR spectra of the a-C:N films at different positive bias voltages. The FTIR spectra were measured in the wave number range of 1000-2000 cm^{-1} to determine the vibration modes of deposited a-C:N films. Different types of band appearing in the a-C:N films which is, C=C, and CO₂ formed by the effect of positive bias voltage. The band appearing at the wave number in the range of 1050-1300 cm^{-1} is corresponding to C-O bond while in the range of 1500-1600 cm^{-1} is corresponding to C=C bond (the sp² bonding) [10,11]. The existing peak of C-O and CO₂ in FTIR spectra in carbon network might contribute for high defect in carbon network and therefore give agglomerated particles in FESEM images. The increase of D band and G in Raman spectra for graphitization of a-C:N film might be correlated with the microstructural change of carbon [9-11] due to true doping of nitrogen in carbon network and thus would improve the electrical properties of a-C:N film. It is usually stated that the effect of nitrogen into carbon films is to break the symmetry of the sp² carbon bonds making the Raman ‘G’ (graphitic) and ‘D’ (disorder) modes FTIR active [9-11], so the broad band between 1000-2000 cm^{-1} is quite similar in both FTIR and Raman spectra.

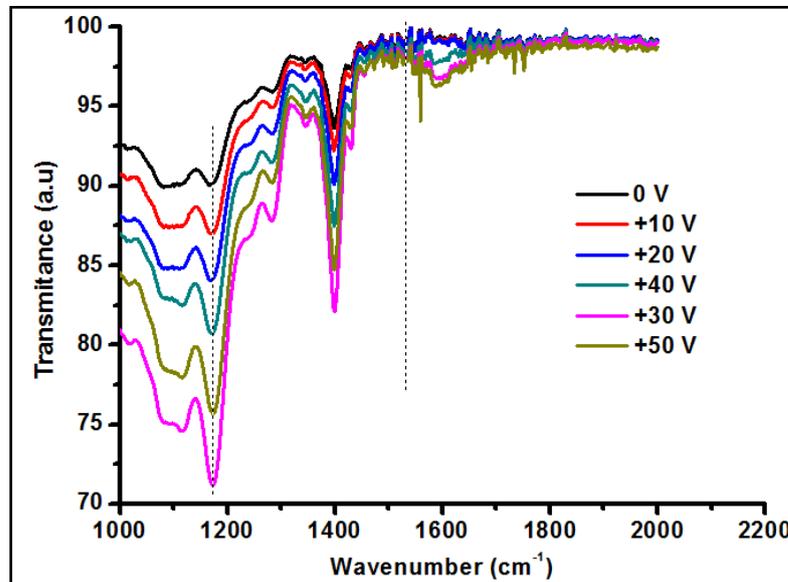


Fig. 2: The FTIR spectra of a-C:N films at difference positive bias

IV. CONCLUSION

In conclusion, the effect of positive bias voltage (0 to 50 V) at 500°C on Raman spectra was discussed and presented. The carbon film from ethanol and nitrogen gas was in amorphous nature. This result indicates the successful the existing of nitrogen and carbon atom in a-C:N films prepared at different positive bias. Raman scattering spectra of a-C:N film deposited at different positive bias showed similar peak structure, which might be indicated to similar sp³/sp² composition. The G and D bands observed from 0 to +50 V were relatively broad indicating that the crystallite size of the carbon in the a-C:N is small.

V. Acknowledgements

The authors thank to Ministry of Higher Education (MOHE) Malaysia, Universiti Teknologi MARA, Kota Samarahan Sarawak for the scholarship and Research Management Institute (RMI) Universiti Teknologi MARA (UiTM) for the facilities.

REFERENCES

- [1]. M. Rusop, X. Tian, T. Kinugawa, T. Soga, T. Jimbo, and M. Umeno, Preparation and characterization of boron-incorporated amorphous carbon films from a natural source of camphoric carbon as a precursor material, *Applied Surface Science*, 252 (2005) 1693-1703.
- [2]. F.W. Wang, M.W. Chen, Q.B. Lai, Metallic contact to nitrogen and boron doped diamond-like carbon films, *Thin Solid Films*, 518, 2010, 3332-3336.
- [3]. Ishak Annuar, Jalal Rouhi and Mohamad Rusop, Boron doped amorphous carbon film grown by bias-assisted pyrolysis chemical vapor deposition, *IEICE Electronics Express*, 12, 2015, 1-10.
- [4]. A. Ishak, K. Dayana, M. H. Mamat, M. F. Malek, M. Rusop, Nano-structured amorphous carbon films by novel palm oil precursor for solar cell applications, *OPTIK*, 126, 2015, 1610-1612.
- [5]. A. Ishak, M. Rusop, Deposition of Amorphous Carbon Film Using Natural Palm Oil by Bias Assisted Pyrolysis-CVD for Solar Cell, *Inter. J. of Power and Renew. Energy Syst.*, 1, 2014, 12-23.
- [6]. J. Podder, M. Rusop, T. Soga, and T. Jimbo, Boron doped amorphous carbon thin films grown by rf PECVD under different partial pressure, *Diamond and related materials*, 14, 2005, 1799-1804.
- [7]. R. Dey, S. Singh, A. Biswas, R. Tokas, N. Chand, S. Venkateshwaran, Substrate bias effects during diamond like carbon film deposition by microwave ECR plasma CVD, *Current Applied Physics*, 8, 2008, 6-12.
- [8]. N. Boutroy, Y. Pernel, J. Rius, F. Auger, H. Von Bardeleben, J. Cantin, Hydrogenated amorphous carbon film coating of PET bottles for gas diffusion barriers, *Diamond and Related Materials*, 15, 2006, 921-927.
- [9]. F. Alibart, O. Durand Drouhin, M. Lejeune, M. Benlahsen, S. Rodil, and E. Camps, Evolution of the opto-electronic properties of amorphous carbon films as a function of nitrogen incorporation, *Diamond and Related Materials*, 17, 2008, 925-930.
- [10]. A. Ishak, K. Dayana, and M. Rusop, Effect of Nitrogen Concentrations on Electrical Properties of Amorphous Carbon Thin Films by Using Palm Oil Precursor, Proc. IEEE Conf. on Electrical and Electronic Engineering 2013.
- [11]. A. Ishak, and M. Rusop, Effect of Low Positive Bias on Electrical Properties of Nitrogen Doped Amorphous Carbon Thin Films by Bias-assisted Pyrolysis-CVD, Proc. IEEE Conf. on Electrical and Electronic Engineering 2013.