

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

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**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

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### 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

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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  $1550\text{ cm}^{-1}$  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].

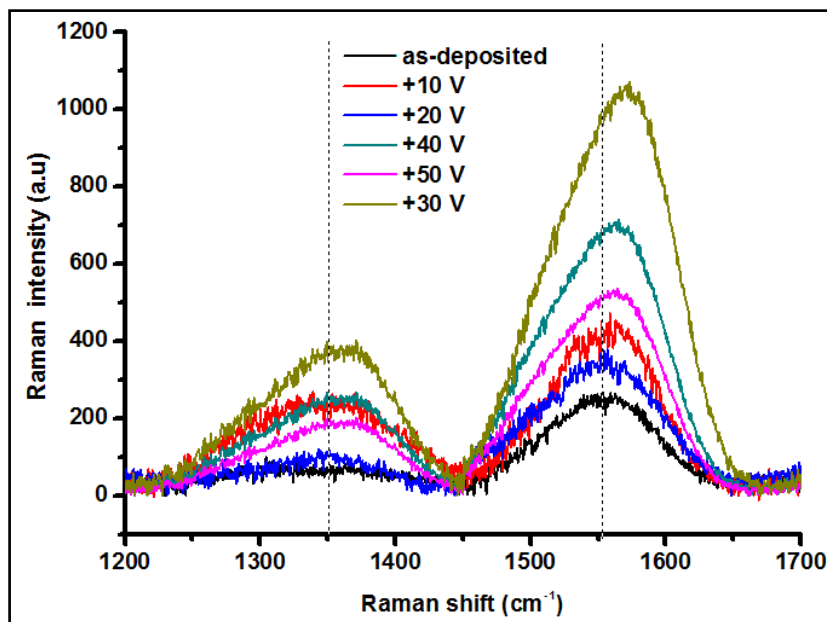


Fig. 1. The Raman spectra of a-C:N films at difference positive bias voltages

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  $\text{sp}^2$  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  $\text{Csp}^2$  bonds and “ordering” of the  $\text{Csp}^2$  domain because Raman D peak is reported to be assigned to  $\text{sp}^2$ -bonded C which seems to be aromatic in structure [2,8,9]. Under this refinement process, the  $\text{sp}^2/\text{sp}^3$  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  $\text{sp}^2/\text{sp}^3$  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  $\text{sp}^2$  phase [8,9]. The G band position measures topological disorder, which arises from the size and shape distribution of  $\text{sp}^2$  clusters [9]. The changing of D and G position might be to a change in the clustering of  $\text{sp}^2$  phase of a-C:N film. Although there is no evident to justify the clustering of  $\text{sp}^2$  phase of a-C:N film changed, but changing of D position might be an indicator for changing of clustering of  $\text{sp}^2$  phase. According to the literatures an increase in  $\text{sp}^2$ -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  $\text{sp}^2$  rather than  $\text{sp}^3$  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) | $\text{Pos (G)}$<br>( $\text{cm}^{-1}$ ) | $\text{Width (G)}$<br>( $\text{cm}^{-1}$ ) | $\text{Pos (D)}$<br>( $\text{cm}^{-1}$ ) | $\text{Width (D)}$<br>( $\text{cm}^{-1}$ ) | $\frac{I(D)}{I(G)}$ |
|---------------------------|--|--|--|--|---------------------|
| 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  $\text{cm}^{-1}$  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 CO<sub>2</sub> formed by the effect of positive bias voltage. The band appearing at the wave number in the range of 1050-1300  $\text{cm}^{-1}$  is corresponding to C-O bond while in the range of 1500-1600  $\text{cm}^{-1}$  is corresponding to C=C bond (the sp<sup>2</sup> bonding) [10,11]. The existing peak of C-O and CO<sub>2</sub> 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 sp<sup>2</sup> carbon bonds making the Raman ‘G’ (graphitic) and ‘D’ (disorder) modes FTIR active [9-11], so the broad band between 1000-2000  $\text{cm}^{-1}$  is quite similar in both FTIR and Raman spectra.

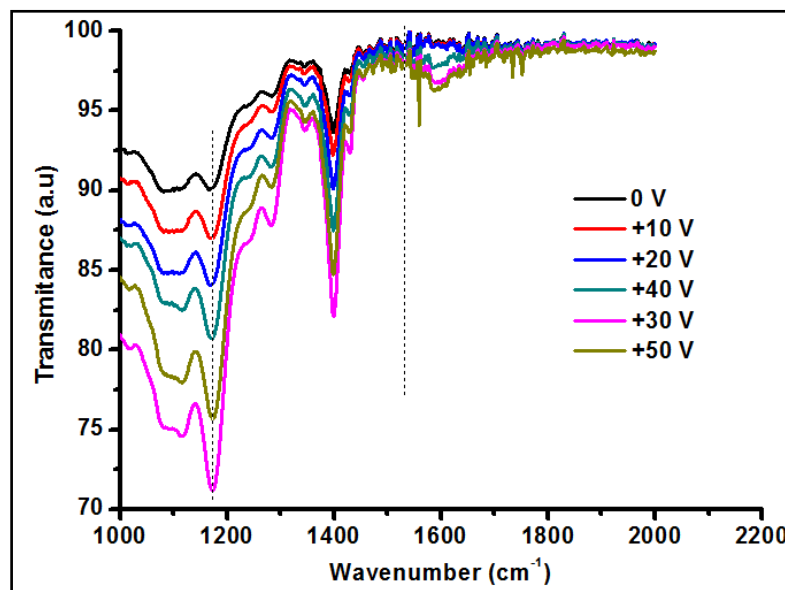


Fig. 2: The FTIR spectra of a-C:N films at difference positive bias

#### 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 sp<sup>3</sup>/sp<sup>2</sup> 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.

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