

Nitrogen Doping of Amorphous Carbon Thin Film Prepared by Camphor using Thermal CVD

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Abstract— This research investigates on the nitrogen doping of amorphous carbon thin film that have been prepared by camphor using thermal CVD method at different temperature. This research used argon (Ar), camphor oil and nitrogen (N) as carrier source and dopant gases, respectively. The effect of nitrogen doping of the amorphous carbon thin film on electrical and optical properties were characterized by using Current-Voltage (I-V) measurement and UV-VIS-NIR spectroscopy. The I-V measurement studies demonstrate that the current measured for sample that have been deposited at higher temperature gives more conductivity. Optical band gap for the undoped thin film is about 0.1 to 0.4 eV. This study also shows that the optical band gap (E_g) for doped thin film decreased from 0.5 to 0.1 eV when the deposition temperature is increased.

Keywords— Nitrogen Doping, Amorphous Carbon, Thin Film, Camphor, Thermal CVD.

I. INTRODUCTION

CARBON (C) is an attractive material for low cost and high efficiency flexible solar cells. This remarkable element exists in different forms ranging from insulator diamond to metallic graphite to conducting/semiconducting nanotubes [1].

N can have numerous effects on diamond-like carbon: it can dope, it can form the hypothetical superhard compound C_3N_4 , or it can create fullerene-like bonding structures [2]. N is commonly used during sample preparation procedures for chemical analysis. Specifically, it is used as a means of concentrating and reducing the volume of liquid samples. Directing a pressurized stream of nitrogen gas perpendicular to the surface of the liquid allows the solvent to evaporate while leaving the solute(s) and unevaporated solvent behind.

Camphor ($C_{10}H_{16}O$) is the crystallized latex of a reproducible tree product. Camphor trees abundantly grow in almost all sub-tropical countries including China, India and Japan. They also thrive in Egypt, the Canary Islands, Argentina, Europe, Florida, California, Formosa, etc [3]. Camphor is very cheap, and also user-friendly for pyrolysis

due to its volatile and non-toxic nature. It is a white crystalline solid that sublimates even at room temperature and melts at 180°C [4]. Because of its typical molecular structure comprised of both hexagonal and pentagonal carbon rings, it is supposed to possess an inherent tendency to form fullerenes and nanotubes.

Amorphous carbon (a-C) has attracted great attention as a material for optical and electrical devices because of its semiconducting nature. Doping of impurities such as N, P and iodine (I) can modify optoelectronic properties of the films by increasing either the electron or hole concentration in the semiconductor device. The incorporation of N can strongly decreased defect density, which gives prospects on its use as a semiconductor material.

Plasma-deposited N doped amorphous carbon (a-C:N) films are of great technological importance as many of their properties can be tailored by varying the amount of N incorporation for divers industrial application. N being a gaseous phase has the advantage of better control of dopant concentration in a-C films, and the incorporation of N can strongly decrease the defect density, which gives prospects on its use as a semiconductor material. However, there are some problems such as low conversion efficiency due to the sp^2/sp^3 bonding structure and the difficulties in controlling the conduction type, carrier concentration and optical band gap [5].

Thus, some problems that will be observed are the doping concentration of nitrogen that used to ensure that electrical and optical properties remain unchanged after doping process. Research also will observe that effective doping can modify optoelectronics properties of semiconductor materials in particular optical band gap and photoconductivity. Besides that, samples will be taken depends on the deposition temperature and annealing time.

II. PROGRAM OBJECTIVES

In recent research [1, 5-7], a-C has been shown to behave as a semiconducting material, which is able to accept dopants, shows photoconductivity and suitable for optoelectronic

devices due to its chemical inertness, high electrical resistivity, high thermal conductivity, high dielectric strength, infrared transparency and band gap varying over a wide range from 5.5 eV for insulating diamond to 0.0 eV for metallic graphite [6].

It could be conveniently deposited on flexible plastic substrates at room temperature. However, there are some problems such as low conversion efficiency due to the sp^2/sp^3 bonding structure and the difficulties in controlling the conduction type, carrier concentration and optical band gap [5]. When we attempt to utilize a-C as an alternative material in photovoltaic devices, control of the conduction type of a-C film is indispensable [7]. Undoped C is reported to be weakly p-type.

Effective doping can modify optoelectronic properties, in particular optical band gap and photoconductivity, in semiconductor materials. Doping of a-C with n-type dopants such as phosphorus (P) and N has been attempted by several researchers [7]. N being a gaseous phase has the advantage of better control of dopant concentration over P in physical deposition systems [8]. The ability to dope N_2 gas has shown a new direction for application of C material in optoelectronic devices [9].

There are a few objectives that can be achieved in doing this research. The objectives are to prepare amorphous carbon thin film by thermal CVD method, to dope amorphous carbon thin film with nitrogen and to study electrical and optical properties of nitrogen doped amorphous carbon thin film.

III. EXPERIMENTAL DETAILS

Film deposition was carried out on the conning glass, quartz, p-type and n-type silicon (Si) wafer substrates. Before deposition, the substrates were cleaned before-hand by acetone and methanol for each at approximately 10 minutes in Power Sonic405 ultrasonic bath, rinsed by ultra-pure deionised water and then dried with nitrogen blower and only for Si substrates were etched with diluted hydrofluoric acid, $HF:H_2O$ (1:10) in order to remove the resistive native oxide formed over the surface [10]. Argon and nitrogen were used as carrier and doping gases respectively. The VT Furnace STF 40-1110 is set up with appropriate temperature and current flow. A double furnace was used for the deposition of carbon on a-C thin film by thermal CVD method. First furnace was used for the vaporization of natural precursor which is camphor and in the second furnace; pyrolysis was carried out at different temperatures.

Camphor ($C_{10}H_{16}O$), a source available in nature, has been used as a precursor for a-C thin film. A-C thin films were deposited on substrate by pyrolysis of camphor at different temperatures. After that, nitrogen will be introduced as a dopant to a-C thin film. Nitrogen will be introduced as dopant by changing the carrier gas, argon and

by annealing the samples in nitrogen atmosphere. Annealing will be done by varying the temperature and time.

Gold (Au) electrodes of about 15 nm is sputtered on a-C thin film for the top contact of conning glass and quartz substrates and for the back contact, about 100 nm Au electrode is sputtered on Si substrates by conventional electron beam sputtering method. And the ohmic contact verified by current-voltage (I-V) measurements. Junction I-V characteristics of dark and under illumination are measured by ST-103A Manual Prober and UV-VIS-NIR spectroscopy was used to investigate the optical properties of the films. Fig. 1 shows the project development process.

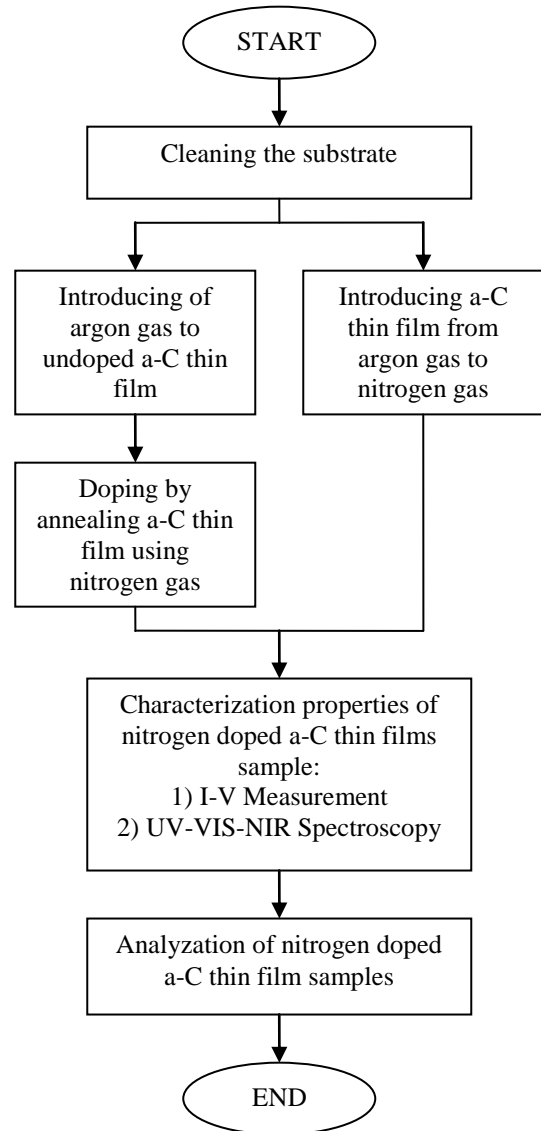


Fig. 1 Flow chart of project development

The growth of a-C thin film was obtained by thermal CVD technique which is performed in a horizontal tube furnace as shown in Fig. 2.

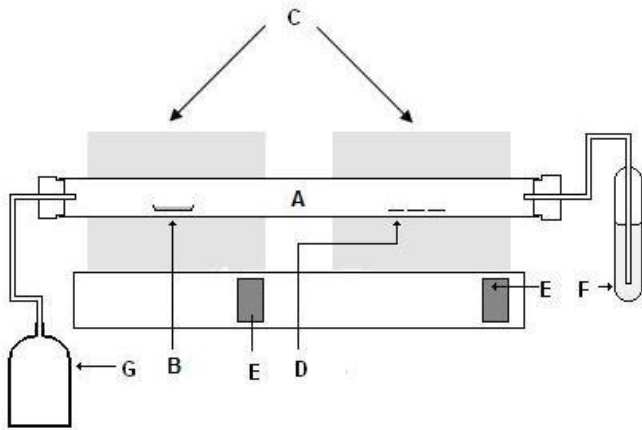


Fig.2 Schematic diagram of thermal CVD experimental set-up (A) alumina tube (B) combustion boat with camphor (C) double furnace setup (D) substrates (E) temperature controller (F) water bubbling system (G) gas cylinder

Different deposition temperatures in range 700°C, 750°C, 800°C and 850°C were exercised to obtain suitable optoelectrical properties. In this experiment, the vapors of 2ml camphor oil were carried by the flow of Ar gas with a flow rate of 30 bubbles per minute into the deposition furnace. The camphor oil was placed in the alumina boat and heated at 180°C. The experiment was done for about nearly 30 minutes deposition time resulting in a film thickness of about 46.3 to 240.0 nm.

IV. RESULTS AND DISCUSSIONS

A. Electrical properties

The electrical properties of the a-C thin films were carried out by temperature dependence conductivity and photoconductivity measurements. Fig. 3 shows the I-V measurement of undoped and doped thin film. Fig. 3 indicates that the current for the undoped thin film increases with voltage as the deposition temperature is increased. Thus, the conductivity of the amorphous carbon thin film is observed to increase with higher deposition temperature. The same results happen in doped a-C thin films as shown in Fig. 4. The results shown that the conductivity is increasing rapidly between undoped and doped a-C thin films. This variation of conductivity to doping of nitrogen in thin films can be related to graphitization.

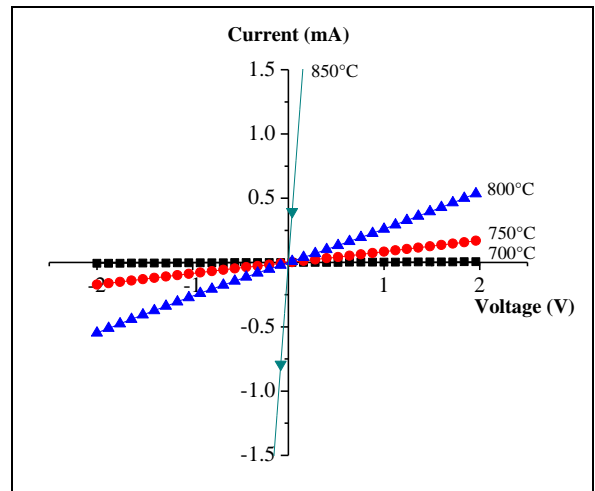


Fig. 3 Current-voltage measurement of undoped a-C thin films at various temperatures

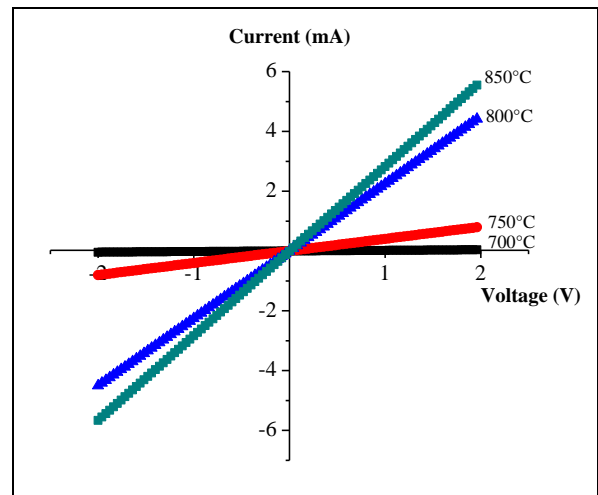


Fig. 4 Current-voltage measurement of doped a-C thin films at various temperatures

The electrical conductivity (σ) of the films as function of temperature (T) between 700 and 850 °C in Fig. 5 indicates that the σ increases with T in dark. The conductivity of the thin a-C:N increases with the temperature due to increase of sp^2 bonds and leading to more graphitization. The degree of doping in solid state semiconductors makes a large difference in conductivity. More doping on a-C thin films leads to higher conductivity.

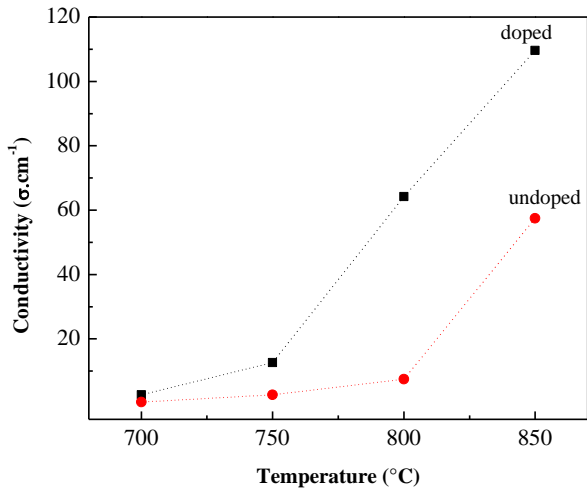


Fig. 5 In dark electrical conductivity (σ) as a function of deposition temperature for doped and undoped a-C thin films at various temperatures.

The photoconductivity measurements under constant photon energy illumination mode are also measured. The T dependence of ratio of conductivity on Fig. 6 shows that undoped thin films have effect to light compared to doped thin films. This is due to the nitrogen effect. The ratio of conductivity of doped thin films is higher compared to the films doped with nitrogen at the same parameters.

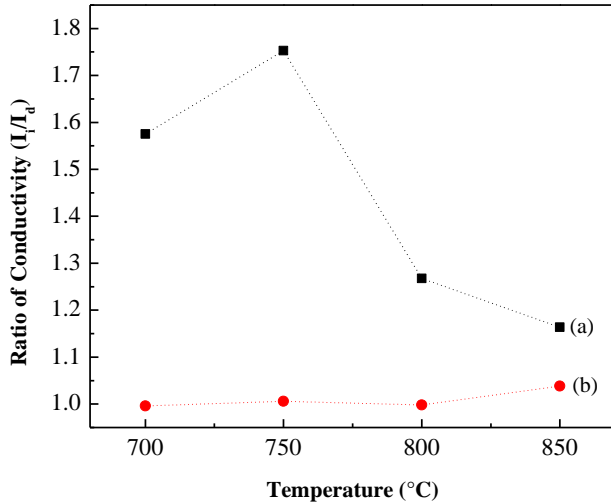


Fig. 6 Temperature dependent ratio of conductivity under illumination to in dark of (a) undoped and (b) doped a-C thin films

Also the photoconductivity measurement under constant energy illumination mode on Table 1 has shown the photoconductivity σ of the films undoped is higher for approximately double of the photoconductivity of σ of films doped with nitrogen at the same parameters. However, there

is no major change in the conductivity of doped a-C thin film when exposed to the light and in dark.

The present results suggest that it is possible to deposit a-C thin films with nitrogen due to more conductive. However, there is no significant changes of the electrical properties were observed on a-C:N between under illumination and in dark suggesting that the sp^2 domains did not present any evolution in size or ordering.

Table 1 Details of Photoconductivity Results of (a) undoped and (b) doped a-C Thin Films at Various Temperatures Ranging from 700 to 850 °C

Temperature (°C)	Conductivity (σ .cm ⁻¹)		Ratio of conductivity (I _i /I _d)
	In dark	Under illumination	
700	0.39	0.63	1.60
750	2.63	4.6	1.75
800	7.45	9.44	1.27
850	57.44	66.84	1.16

(a)

Temperature (°C)	Conductivity (σ .cm ⁻¹)		Ratio of conductivity (I _i /I _d)
	In dark	Under illumination	
700	2.60	2.60	1.00
750	12.61	12.69	1.01
800	64.18	64.06	1.00
850	109.63	112.89	1.04

(b)

The variation of the electrical properties of a-C:N thin films may be due to the development of graphite-like structure in these thin films with the increasing of temperature and the annealing effect.

B. Annealing effect

The undoped a-C thin film with 750 °C was taken as the as-deposited thin film since at this temperature it gives the dominant changes in conductivity. Fig. 7 shows the I-V of as-deposited and annealed a-C:N thin films with various annealing time at 750 °C with various annealing time between 30 to 120 minutes. It can be seen that the current of annealed a-C:N thin films increases after thermal annealing. Furthermore, the conductivity increases with the annealing time. The changes in the conductivity of annealed thin films as a function of measurement time is similar to that of Ar change to N gas a-C thin films. The annealing behavior of electrical conductivity of a-C:N thin films indicates the development of graphite-like structure in thin films. This is because of the stability of sp^2 bonds higher than sp^3 bonds at longer time.

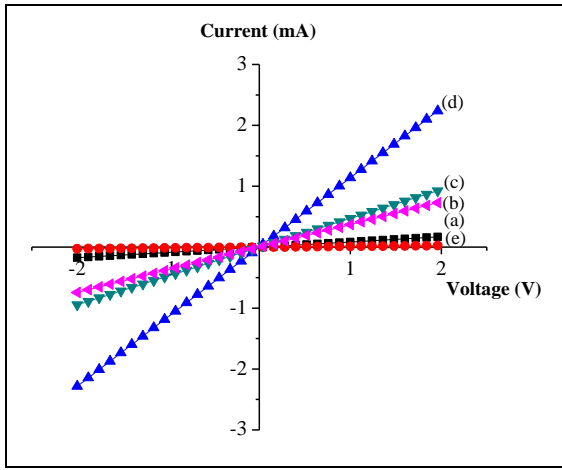


Fig. 7 Current-voltage measurement of (a) as-deposited and (b) to (e) annealed a-C:N thin films at various annealing time ranging from 30 to 120 minutes

The electrical conductivity (σ) of the films as function of annealing time between 30 and 120 minutes in Fig. 7 indicates that the σ decreases with time at 60 minutes and increased again at 90 minutes and dropped again.

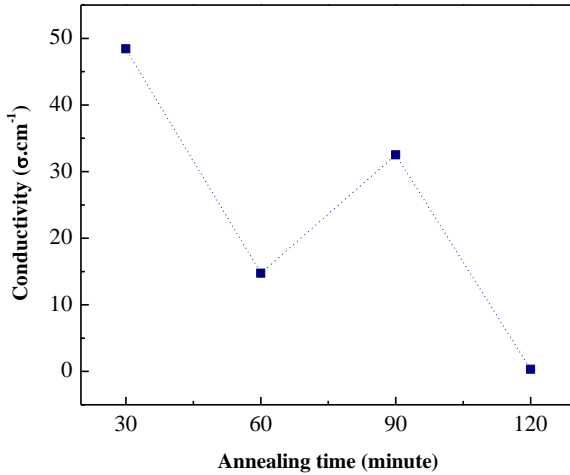


Fig. 7 Electrical conductivity (σ) as a function of annealing time for annealed a-C:N thin film in dark

C. Optical properties

To study the optical characteristics of a-C thin films, experiment was carried out the reflectance and transmittance measurements by UV-VIS-NIR spectroscopy in the range of 200-2000 nm using a Cary Win UV Scan spectrophotometer in transmission mode. From Fig. 8, it can be seen that spectrum of a-C:N thin films gives high transmission (T%) compared with the undoped thin films. As the deposition

temperature increased, the transmission is decreased. This is due to the thickness of thin films are thicker thus make the thin films less transparent.

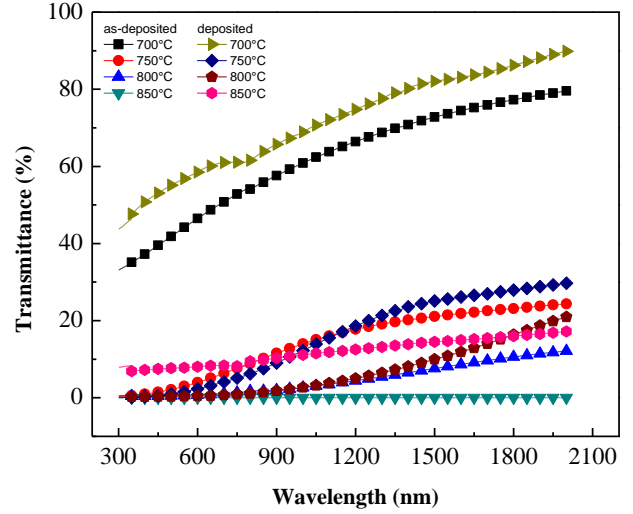


Fig. 8 UV-VIS-NIR transmission spectra of the undoped and doped a-C thin films at various temperatures

The film thickness was measured using surface profiler. The average thickness of undoped and a-C:N films was calculated as the measured average film thickness. Should be noted here that, when calculating the film thickness, the changes on the roughness of the films have not being taken into account [10, 11]. Table 2 indicate that thickness of thin films increased proportionally with deposition temperature for both thin films; undoped and doped. In addition, the thin film thickness is higher as the deposition temperature increased.

Table 2 Details of Thin Film Thickness at Various Temperatures Ranging from 700 to 850 °C

Temperature (°C)	Thickness (nm)
700	46.3
750	193.9
800	212.7
850	240.0

The absorption coefficient (α) was calculated by the spectral reflectance and transmittance, and the film thickness data. The optical band gaps were obtained by Tauc plot [12]. The Tauc optical band gap (E_g) was obtained from the extrapolation of the linear part of the curve at $\alpha=0$ by using the Tauc equation,

$$(\alpha h\nu)^{1/2} = B(E_g - h\nu) \quad (1)$$

where B is the density of the localized state constant [13]. As shown in Fig. 9 we found the optical absorption coefficient of a-C film deposited increased as the deposition temperature increased, while at deposition temperature 850°C showed the opposite nature.

The energy ($h\nu$) dependence of α of a-C:N is shown in Fig. 9. From the measurements of optical transmittance, an optical absorption coefficient (α) was calculated to be on the order of 10^3 cm^{-1} . As shown in Fig. 9, the optical absorption edges of these a-C thin films are increase upon heating, gradually increased with deposition temperature up to 800 °C however, rapidly decreased thereafter with higher temperature, 850°C.

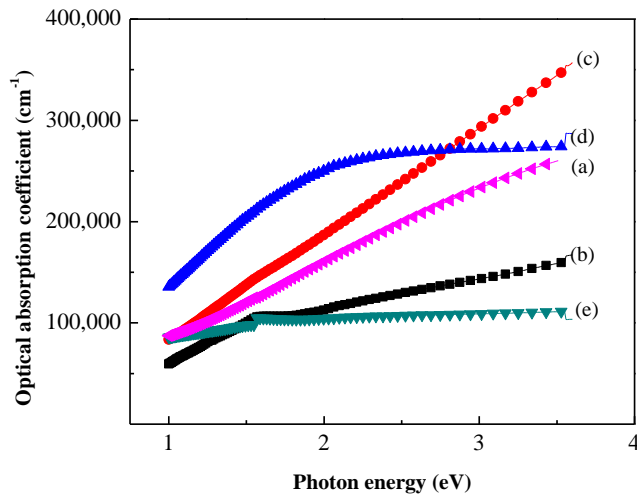


Fig. 9 Optical absorption coefficient edge for (a) as-deposited and (b) to (e) a-C:N thin film at various temperature: (b) 700 °C, (c) 750°C, (d) 800 °C, and (e) 850°C

The results shown that the absorption coefficient edge where it shifts towards lower photon energy (higher wavelength) region with increasing temperature has a reduction in transparency [11]. The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. In a material with a low absorption coefficient, light is only poorly absorbed, and if the material is thin enough, it will appear transparent to that wavelength. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed. Since light which has energy below the band gap does not have sufficient energy to raise an electron across the band gap. Consequently this light is not absorbed.

The optical band gap is the measure of the gap between the extended state in the valence band and the conduction band. Optical band gap for the undoped is about 0.1 and 0.4 eV while the optical band gap for a-C:N is in

range of 0.1 and 0.5 eV. The results of optical band gap as a function of photon energy is shown in Fig. 10. The optical band gap decreased for high deposition temperature. Since both of the optical band gap and resistivity are decreased with further increase of deposition temperature up to 0.1 eV and 0.011651Ω , respectively, this phenomenon can be related to graphitization of a-C:N thin films. Hence, the results are related to electrical properties where as the deposition temperature increases, the conductivity is also increased. This shows that the a-C thin films tend to be more graphite where there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically. The band gap energy of semiconductors tends to decrease with increasing temperature. When deposition temperature increases, the amplitude of atomic vibrations increase, leading to larger interatomic spacing. The interaction between the lattice phonons and the free electrons and holes will also affect the band gap to a smaller extent [14].

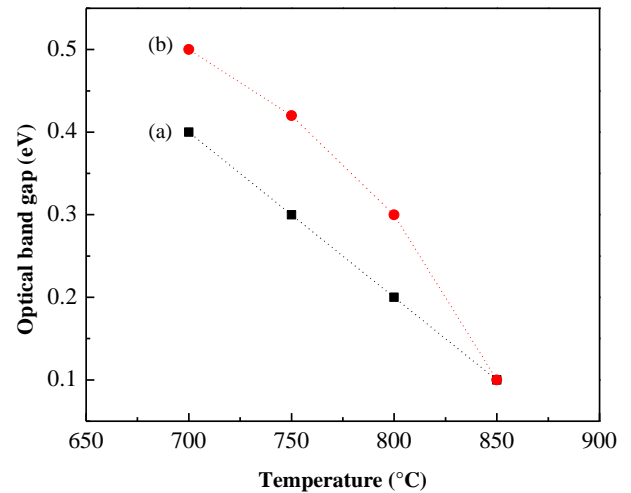


Fig. 10 The optical band gap as a function of photon energy (eV) for (a) as-deposited and (b) a-C:N thin films deposit at various temperatures at 700 to 850 °C

The decrease of E_g with higher temperature can be related due to the structural, bonding and doping in the a-C:N thin films. The change of optical properties might be due to the changes in the bonding and band structure of the amorphous carbon thin films.

Fig. 11 shows a plot of $(\alpha h\nu)^{1/2}$ versus photon energy, E (eV) of the films and the change of E_g as a function of deposition temperature is shown in Fig. 10. The E_g of a-C:N thin film was found to be approximately 0.5 eV, gradually decrease with higher deposition temperature to approximately 0.3 eV at 800 °C, after which it rapidly

decreased with higher temperature to approximately 0.1 eV at 850 °C.

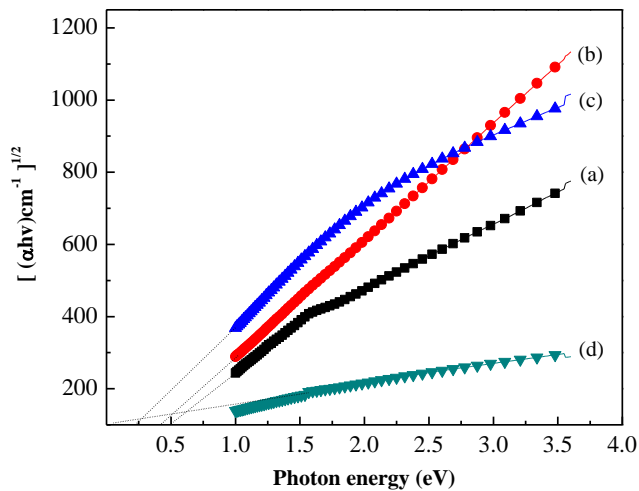


Fig. 11 The Tauc plot of $(\alpha hv)^{1/2}$ as a function of photon energy (eV) for a-C:N thin films at various temperatures at (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 850 °C

V. CONCLUSIONS

The effect of nitrogen incorporation in camphoric a-C thin film by thermal CVD method and the effects of deposition temperature in the range from 700 to 850 °C have been investigated. The thickness, electrical and optical properties of the as-deposited and a-C:N thin films were measured and compared. The film thickness is increased rapidly with increasing deposition temperature. The results indicate successful doping of nitrogen to a-C thin films. The electrical properties of the a-C:N thin films were found increasing and more conductive. The optical band gap of the a-C:N thin films was found to be approximately 0.5 eV and beyond that it decreased up to 0.1 eV at 850 °C. As nitrogen is incorporated, the optical gap decreased and conductivity increased indicates doping of nitrogen in a-C thin films. With increase temperature during deposition, the reduction in optical gap is due to graphitization of a-C thin films. The variation of electrical and optical properties can be related to interstitial doping of N in a-C thin films by rearranging of N atoms upon increase of deposition temperature. The results indicate it is possible to control optical band gap of a-C:N thin films by doping nitrogen for getting suitable optical band gap. Recommendation for the future work of this research is to perform this research by using other deposition method and analyze the nitrogen content using Fourier Transform Infrared (FTIR), Raman spectroscopy and the surface morphology using Atomic Force Microscopy (AFM) to be applied on solar cell applications.

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REFERENCES

- [1] K. M. Krishna, T. Soga, K. Mukhopadhyay, M. Sharon, and M. Umeno, "Photovoltaic solar cell from camphoric carbon a natural source," *Solar Energy Materials and Solar Cells*, vol. 48, pp. 25-33, 1997.
- [2] B. Kleinsorge, A. C. Ferrari, J. Robertson, W. I. Milne, S. Waidmann, and S. Hearne, "Bonding regimes of nitrogen in amorphous carbon," *Diamond and Related Materials*, vol. 9, pp. 643-648, 2000.
- [3] M. Kumar and Y. Ando, "Camphor—a botanical precursor producing garden of carbon nanotubes," *Diamond and Related Materials* vol. 12, pp. 998 - 1002, 2003.
- [4] S. P. Somani, P. R. Somani, M. Tanemura, S. P. Lau, and M. Umeno, "Carbon nanofibers and multiwalled carbon nanotubes from camphor and their field electron emission," *Current Applied Physics*, vol. 9, pp. 144-150, 2009.
- [5] Y. Hayashi, S. Ishikawa, T. Sogaa, M. Umenob, and T. Jimboa, "Photovoltaic characteristics of boron-doped hydrogenated amorphous carbon on n-Si substrate prepared by r.f. plasma-enhanced CVD using trimethylboron," *Diamond & Related Materials*, vol. 12, pp. 687 - 690, 2003.
- [6] S. M. Mominuzzaman, K. M. Krishna, T. Soga, T. Jimbo, and M. Umeno, "Optical Absorption and Electrical Conductivity of Amorphous Carbon Thin Films from Camphor: A Natural Source," *Japanese Journal of Applied Physics*, vol. 38, pp. 658-663, 1999.
- [7] M. Rusop, S. M. Mominuzzaman, T. Soga, T. Jimbo, and M. Umeno, "Characterization of Phosphorus-Doped Amorphous Carbon and construction of n-Carbon/p-Silicon Heterojunction Solar Cells," *Japanese Journal of Applied Physics*, vol. 42, pp. 2339-2344, 2003.
- [8] M. Rusop, S. M. Mominuzzaman, X. M. Tian, T. Soga, T. Jimbo, and M. Umeno, "Nitrogen doping and structural properties of amorphous carbon films deposited by pulsed laser ablation," *Applied Surface Science*, vol. 197, pp. 542-546, 2002.
- [9] A. M. M. Omer, M. Rusop, S. Adhikari, S. Adhikary, H. Uchida, and M. Umeno, "Photovoltaic characteristics of nitrogen-doped amorphous carbon thin-films grown on quartz and flexible plastic substrates by microwave surface wave plasma CVD," *Diamond & Related Materials*, vol. 14, pp. 1084-1088, 2005.
- [10] A. M. M. O. M. Rusop, S. Adhikari, S. Adhikary, H. Uchida, T. Soga, T. Jimbo, M. Umeno, "Effects of annealing temperature on the optical bonding, structural and electrical properties of nitrogenated amorphous carbon thin films grown by surface wave microwave plasma chemical vapor deposition," *Journal of Material Science*, vol. 41, pp. 537-547, 2006.
- [11] X. S. L. K. Cheah, J. R. Shi, E. J. Liu, S. R. P. Silva, *Journal of Non-Crystalline Solids*, vol. 40, p. 242, 1998.
- [12] J. Tauc, *Amorphous and Liquid Semiconductors*. London: Plenum Press, 1974.
- [13] S. M. M. M. Rusop, T. Soga, T. Jimbo, and M. Umeno, "Characterization of Phosphorus-Doped Amorphous Carbon and construction of n-Carbon/p-Silicon Heterojunction Solar Cells," *Japanese Journal of Applied Physics*, vol. 42, pp. 2339-2344, 2003.
- [14] H. Unlu, "A Thermodynamic Model for Determining Pressure and Temperature Effects on the Bandgap Energies and other

Properties of some Semiconductors," *Solid State Electronics*, vol. 35, pp. 1343-1352, 1992.