Electrical Properties Of Nitrogen Doped Amorphous Carbon Films Fromethanol Precursor

A. Ishak, M.Rusop

Abstract: The nitrogen doped amorphous carbon (a-C:N) thin films were synthesized for the first time by using mixing of nitrogen gas, argon and ethanol precursor by bias assisted pyrolysis-CVD in the range of 250^oC to 550^oC with fixed negative bias of -50V in 1h deposition. The a-C:Nthin films were characterized by current-voltage measurement, UV/VIS spectrophotometer, surface profiler, and atomic force microscopy. The resistivity of a-C:N thin films in the range 250^oC-550^oC was 4.97x10^{7}Ω.cm, 2.66x10^{5}Ω.cm 1.974x10^{4}Ω.cm,3.63x10^{3}Ω.cm, and 4.44x10^{3}Ω.cm, and 1.73x10^{4}Ω.cm, respectively. It was found that a-C:N thin filmshave responded with photon by created electron hole pair where the highest photo responseof a-C:N film was found at 350^oC.The substrate of deposition temperatures with the help of constant dc voltage influenced the electrical properties of a-C thin films.

Keywords: Amorphous carbon; Ethanol precursor; Negative bias; Boron doping; Carbon film Carbon solar cell

I. INTRODUCTION

A possibility of any hydrocarbon sources deposited directly from liquid precursor a to a vapor-phase state, growth onto non-crystalline substrate has a big advantage in technological viewpoint instead of high excellent in photoconductivity and high optical absorption of visible light [1-5]. The as-deposited (undoped) of amorphous carbon (a-C) is as weakly p-type in nature irrespectively with deposition method, deposition condition and precursor use. The a-C is reported as a complex structure and existing a high density of intrinsic defect [1-5] which contributed to the non ohmic form of slope, low conductivity and low photo-response, and therefore barrier to the well formation of p-n junction device solar cell. Furthermore, the difficulty for doping dopants such as nitrogen, boron and phosphorous incorporated with amorphous thin films for increase the conductivity is another issue to be concerned in improvement the deposited carbon thin films [6-8]. Until now, various standard deposition techniques are practically used [1-6] which have difference advantages ofparameters. In this study, the nitrogen doped a-C thin films is deposited by mixing nitrogen gas with ethanol vaporin the chamber by using bias assisted pyrolysis-CVD. Among deposition parameters, positive bias voltage applied to the substrates could significantly change film properties due to enhancement of adatom mobility and the effects of ion bombardment. The ion bombardment during coating deposition would play an important role in affecting the morphology, structure, composition and mechanical properties of coatings [1-4].

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Many attempts were studied by others on the effect of DC bias for instant through the use of pure lubricant coatings (MoS2) composite film which was able to provide good lubricious property due to the strong basal plane orientation and application of a bias voltage was found to reduce the coefficient of friction [8-11]. In this paper, we studied the effect of deposition substrate temperature on the physical properties of nitrogen doped of a-C thin films using ethanol precursor. To our knowledge, preparation and study on physical properties of nitrogen dope by using this precursor and technique has been rarely reported by other research groups.

II. EXPERIMENTAL

The cleaning of glass substrates has been reported elswhere[1,3,7]. A schematic diagramm of bias assisted pyrolysis-CVD is shown in Fig. 1.The ethanol was directly heated at around 65^oC by using the hot platter (Stuart CB162). The vaporized of ethanol was then pressured into the chamber by using two air pumps with a medium pressure. The amount of vapor of ethanol, argon pressured into the chamber were set at 100mL/min, 150mL/min, respectively. The argon gas was used for carrier of deposition particle onto the substrate and also to dispose contaminated particles outside the chamber.The samples were finally characterized by I-V measurement (Bukuh Keiki EP-2000), surface profiler (VeecoDektak 150), JASCO UV-VIS/NIR Spectrophotometer (V-670 EX) and Park system XE-100 atomic force microscope (AFM) for electrical, thickness, optical, atomic level properties, respectively.

III. RESULT AND DISCUSSIONS

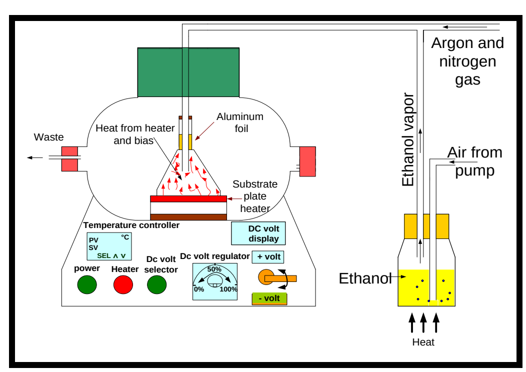

Fig. 1. A schematic diagram of bias assisted pyrolysis-CVD

Fig. 2 shows the current-voltage measurement of a-C:N film. An Aurum with fixed square area of approximately 0.09 cm2 is sputtered as a metal contact on a-C:N film. The resistivity and conductivity are calculated by using both equation (1) and (2) [8,9], respectively where R is the average of resistance; A is the area of metal contact and L is the length between metal two contacts. There were many forms of I-V relationships obtained in the literatures such as linear (ohmic), slightly linear, and nonlinear forms [10,11]. There is a need to form the linear behavior between current and applied voltage which is important for solar cell application. Besides the ohmic behavior, more importantly, the low resistivity and high conductivity a-C thin films as a semiconductor are required for solar cells application.

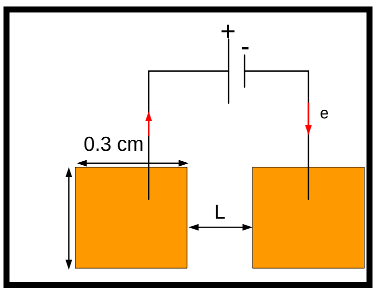

Fig. 2 A Current-voltage measurement of C:N thin films on the glass substrate

$$\rho = RA/L \quad (1)$$
$$\sigma = 1/\rho \quad (2)$$

Gold as a metal contact along with semiconductor thin films was studied by many researcher [10,12]. Metals contact such as titanium (Ti), chromium (Cr), aluminum (Al) and argentum (Ag) can reacted differently with thin film[10,12]. It was found all of the slopes are in linear region when the voltage is applied from -15V to +15V. The highest slope was found at 550°C while the smallest slope contact was at 250°C. Zeng et al [12] and Liu et al [13] reported the nonlinearity was attributed to the existence and magnitude of schottky depends on the Fermi levels of semiconductor and conducting metal. Other possibility factor causedthe nonlinearity were contributed by a dielectric layer formed betweengold and semiconductor thin films.

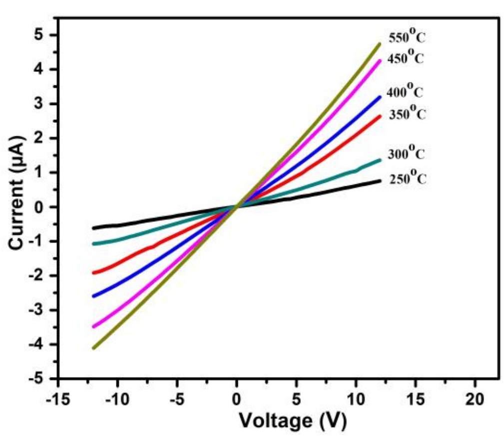

Fig. 3 Current voltage relationships of a-C:N films at various deposition temperatures

The smaller slope might be due to the additional of resistance come from high density of intrinsic defects. Zeng et al [12] discussed that increasing temperature can changed the structural to form more crystallite thereby decreased the resistivity. The decreasing of the resistivity due to increasing temperatures were discussed by others [13-17].

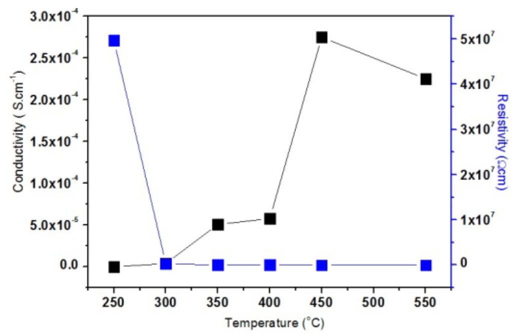

Fig. 4 Resistivity and conductivity of a-C:N films at various deposition temperatures

Fig. 4 shows the variation resistivity and conductivity of a-C:N thin films at different deposition temperature in the range of 250°C to 550°C. The resistivity of a-C:N thin films is calculated as 4.97x10^{7} Ω.cm,2.66x10^{5} Ω.cm, 1.974x10^{4}Ω.cm, 3.63x10^{3} Ω.cm, 4.44x10^{3}Ω.cm, 1.85x10^{4}Ω.cm, and 1.73x10^{4}Ω.cm, respectively.S .M. Sze [15] summarized the resistivity range of semiconductors was in between 1x10^{8} to1x10^{-3} Ω.cmand by comparing with our result, we have seen that the resistivity of a-C:N thin films are semiconductor thin film We predict that, a-C:N thin films might deform structure with dopant of nitrogen to provide excess of electron thereby reduce the number of defect of thin films. Beside other factors [13,14], deposition temperature is the main role to deform the existing structure together with crystallite form. The conductivity of doped a-C:N thin films is calculated by the reciprocal of resistivity values. Fig. 4shows the correlation of conductivity with changing deposition temperatures. The values of conductivity is 2.02x10^{-8} Scm^{-1}, 3.76x10^{-6} Scm-^{1}, 5.05x10^{-5} Scm^{-1}, 5.78x10^{-5} Scm^{-1}, 2.75x10^{-4} Scm^{-1}, and 2.25x10^{-4}Scm^{-1}, respectively. The conductivity of a-C:N thin films is gradually increased by the decreasing of substrate deposition temperature 250°C to 550°C. The effect of increasing deposition temperature and doping on the increment of conductivity of thin films were also agreed and discuss by others [18-22]. A photo response is defined as the ratio of conductivity under illumination to the conductivity under dark. Table 1 shows the effect of the temperature parameters on the photo response. The values of photo response from 250°C to 550oC are 1.3722, 1.1331, 4.3779, 1.4807, 1.0271, and 1.0314, respectively. The results showed the photo response is slightly decreased from 250°C to 300°C and showed dramatically increased from 300°C to 350°C. However, at 400°C to 500°C, it was strongly decreased. We found, the highest value of photo response is at 350°C while the lowest value is at 450°C. By comparing with sloped metal contact, resistivity, conductivity, and photo response results, at 350°C is the optimum deposition temperature. Table 1 shows the influenced of temperature toward the thickness of a-C thin films. The average of thickness in the range of 250°C to 550°C is 250 nm, 230 nm, 420 nm, 103.2nm, 383.2nm, and 680nm respectively. From Table 2, the highest thickness is found at 550°C while the lowest average thickness is 230nm at 300°C. We found, the average thickness is strongly dependence with deposition temperature However, the increasing of average thicknesses was not influenced resistivity as well as conductivity.

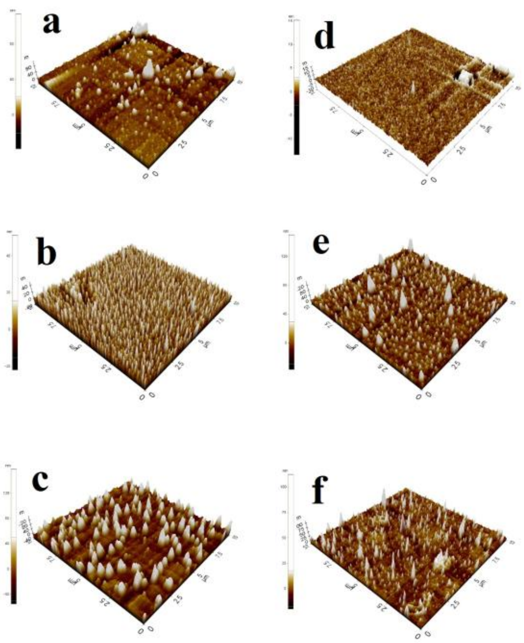

Fig.5. The AFM images of a-C thin films by in-situ doped at various temperatures

AFM images of a-C:N thin films were characterized by atomic force microscopy (AFM, XE-100 Park Systems), as shown in Fig. 5 with a scan rate 1Hz and scan size of 10µm. The images show different forms of particles on the surface for all a-C:N thin films. The surface roughness from 250°C to 550°C are 1.842, 0.828, 0.053, 0.244, 0.828,and 1.448 nm while the average grain sizes are 0.802, 0.935,0.124, 0.661, 0.526, and 0.326, respectively. Table 2 The surface roughness and average grain size of a-C:N thin films in the range of 250°C-550°C

Temperature (°C)	Surface Roughness (nm)	Average Grain Size (µm²)
250°C	1.842	0.802
300°C	0.82	0.935
350°C	0.053	0.124
400°C	0.244	0.661
450°C	0.828	0.526
550°C	1.148	0.326

The highest surface roughness is 1.842 at 250°C while the lowest surface roughness is 0.053 at 350°C. For the average grain size, 0.935 is the highest average grain size at 300°C while 0.526 is the lowest average grain size at 450°C. It is believed that grain boundary and surface roughness are directly related with the electrical properties especially carrier concentration and mobility of the electron. It was observed that both surface roughness and conductivity were decreased as the temperature was increased from 250°C to 300°C. Furthermore, the conductivity is strongly increased when the surface roughness was decreased. Similarly, the conductivity was increased as the average grain size was decreased. The effects of grain boundary and surface roughness on electrical properties were also reported by other [20-23]. AFM measurement reveals the average grain sizes for the sample at 250oC is the highest as compared with others temperatures and therefore restricts the ability for electron movement. Huang et al [23] reported thickness could also affect the conductivity. In our experiment, we found as the thickness increased, the average grain size is increased causing to decreasing the conductivity. Thisdifference in the size of the surface film can be attributed to the ion bombardment during the growth of the films which is controlled by the applied of negative bias onto the substrate.

IV. CONCLUSIONS

The semiconducting a-C:N thin films was successfully deposited by bias assisted pyrolysis–CVD from ethanol precursor. The resistivity of a-C:N thin films deposited at 250°C to 550°C were $4.97 x 10^7$Ω.cm,$2.66 x 10^5$Ω.cm, $1.974 x 10^4$Ω.cm, 4.44x103Ω.cm, $1.85 x 10^4$Ω.cm, and $3.63 x 10^3$ Ω.cm, respectively. Meanwhile, the conductivity of a-C thin films were $2.012 x 10^{-8}$ Scm^{-1}, $3.76 x 10^{-6}$ Scm^{-1} , $5.05 x 10^{-5}$ Scm^{-1}, $5.78 x 10^{-5}$ Scm^{-1}, $2.75 x 10^{-4}$$Scm^{-1}$, and $2.25 x 10^{-4}$ Scm^{-1}, respectively. The resistivity was decreased as the temperature increased. The highest and the lowest photo response of a-C:N film were found at deposition temperature of 350°C, and 250°C, respectively.

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