Hydrogenated nanostructure boron doped amorphous carbon films by DC bias

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Abstract. Hydrogenated nanostructure-boron doped amorphous carbon thin film carbon was deposited at different negative bias using custom-made deposition bias assisted-CVD. Solid of boron and palm oil were used as dopant and carbon source, respectively. The hydrogenated nanostructure amorphous films were characterized by Field emission scanning electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, while the photo-response studies of thin film is done by I-V measurement under light measurement. The results showed the carbon film were in nanostructure with hydrogen and boron might be incorporated in the film. The Raman spectra observed the increase of upward shift of D and G peaks as negative bias increased which related to the structural change as boron incorporated in carbon network. These structural changes were further correlated with photo-response study and the results obtained are discussed and compared.

1. Introduction

Allotropes carbons have been prepared by multiple deposition techniques using different carbon precursor, palm oil for example has been successfully used for synthesize carbon nano-tubes by chemical vapor deposition technique. Palm oil contained carbon (67), hydrogen (127) and oxygen (8) to form the chemical binding of C_{67}H_{127}O_{8} and contained highest number of carbon compared to other carbon precursor used so far. It is reported that various properties of carbon films not only depend on their methods and conditions of deposition but also on the starting precursor materials [1,2].

Many deposition parameters have been introduced so far with the target to improve the quality of thin film such as temperature, dopant, deposition time, flow rate of carrier gas, position of substrate, etc. It was reported, DC bias voltage helped for improve quality of films through bombarding effect [3-5]. Among deposition parameters, negative bias applied to the substrates could significantly change film properties due to enhancement of adatom mobility and the effect of ion bombardment [3-5]. It determines the kinetic bombardment energies of the ions arriving on the substrate and can significantly affect the chemical composition, structure and residual stresses in the as-deposited films.
The hydrogenated amorphous carbon (a-C:H) deposited from many types of precursors and methods showed a good potential use in amorphous carbon solar cells. However, it was reported as weakly p-type in nature despite of very complex structure, high density of defect and those factors restricted to dope efficiently and the main barrier for its application in various electronic devices. In order solve that problem, the control of doping could reduce the existing of defect and modified the electronic properties [1,2].

Palm oil, a natural source is known so far as the highest carbon contents and may have both sp² and sp³ carbon. Application of light energy conversion for solar cell applications was reported using amorphous palm oil carbon film [1,2]. However, detail structural properties of palm oil carbon films related with photo-response were rarely discussed. In fact, there have been reports [3-5] about the influences of the substrate bias voltage on the structure and properties of carbon and as-deposited metal oxide films. However, there is no many literatures reporting on the effect of DC negative bias on hydrogenated nanostructure a-C:B films using this preparation.

2. Methodology

The a-C:B film was prepared by custom-made bias-assisted-CVD using the glass substrates (thickness: 1mm) and n-Si (100) (thickness 325 + 25 µm, resistivity 1-10 Ω cm). Substrates were cleaned with acetone (C₆H₁₂O) followed by methanol (CH₃OH) for 15 min in ultrasonic cleaner (power Sonic 405), respectively and the glass substrates were then rinse with deionizer water (DI) water for 15 min. Moreover, excess oxide layers of n-type silicon substrates were continued by the etching process with diluted hydrofluoric acid (10%) solution for about 3 min before rinsing in DI water. Substrates were then blown with nitrogen gas. The cleaned of substrates were finally placed inside the furnace chamber.

The deposition temperature was set at 350°C for 1h deposition. A liquid of palm oil precursor was heated in the bottle outside the chamber at around 150°C by using hot platter (Stuart CB162). The vaporized of palm oil was pressured into the furnace chamber using air pumps (model GA8000) where the flow rate of vaporized palm oil is controlled by adjustable valve. The amount of vaporized palm oil, carrier gas argon was set to be constant at 100 mL/min, 200 mL/min, respectively by using AALBORG flow meter. For doping process, approximately 1 g of boron was placed on the aluminium foil above the metal plate heater in the chamber.

Fourier transform infrared spectroscopy, JEOL JSM-7600F field emission scanning electron microscope (FESEM), Current-voltage measurement (I-V) (Bukuh Keiki EP200), and Raman spectroscopy are used to characterize the existing of hydrogen, particle size, structural bonding and electrical properties, respectively.

3. Results and discussion

Figure 1 show FTIR spectra of the carbon films deposited at different negative bias. The absorption bands in the spectra were assigned based on comparison with the standard patterns reported in the literature [6-9].The FTIR spectra were measured in the wave number range of 1000-3000 cm⁻¹ to determine the vibration modes of deposited films. Different types of band appearing in the films which is, C=C, CO₂, and C-H formed. 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) [6-9]. The band situated in the range of 2950-3060 cm⁻¹ is attributed to C-H stretching vibration of sp²-C, while for sp³-C in the range 2850-2945 cm⁻¹ range [6-9]. It was clearly observed the bonding of hydrogen with carbon films deposited at -10 V to -50 V, the films exhibit ‘characteristic C-H related absorption’ in the range 2800-3000 cm⁻¹ and therefore we called it as hydrogenated boron doped amorphous carbon thin film.
However, the carbon film at 0 V is found almost no C-H peak but we predict small number of hydrogen existed. Since the C-H bond signal is found very weak for 0 V, so it is assumed the attachment of H bond is less. It was predicted; the passivated of hydrogen in carbon thin film might reduce defect and therefore can increase conductivity. In contrast, C-H stretching peaks indicates at -10 to -50 V and might be successfully incorporated into carbon network thus might be passivated dangling bonds. The high C-H stretching peaks might be the role of negative bias to attract more opposite ion, in this case positive ion hydrogen to binding with the carbon network. In contrast, the existing peak of CO$_2$ and no hydrogen bond in FTIR spectrum in carbon network might contribute for defect in carbon network and therefore might suggest the low conductivity carbon film at 0V.

Figure 2 shows the FESEM images of hydrogenated a-C:B films deposited at different negative bias. The surface morphology images were captured by the JEOL JSM-7600F field emission scanning electron microscope (FESEM) between 100kx to 250kx magnification, using 5kV. It clearly observed, the images were really in amorphous nature, since no sharp images were determined. FESEM images consist of irregularly scattered ball-like particles in between 90 nm to less than 10 nm. The sample at 0 V (by only using thermal process only) shows the nanostructure particles with average size in between 51 nm to 27.5 nm. A gradual refinement of the nanostructure particles sizes slightly observed as bias voltage at -10 V (Figure 2 (II)). The nanostructure particles sizes were almost constant at -20 V (Fig. 2 (III)) and deteriorated at -30 V (Figure 2 (IV)) to -50 V (Figure 2 (V)). This suggest that, negative bias from -10 to -50 V give less significant effect on the particles sizes of hydrogenated nanostructure of a-C:B films. The agglomerated particles contain C-O binding might produce defect and C-H binding might passivated the dangling bond as supported by FTIR analysis. It is observed that, the lowest size of particles with less agglomerated form was found at -20 V.

The possibility mechanism of this process can be explained as follow; during the deposition, the palm oil precursor decomposed in a variety of forms (molecule, ion, etc.) and they are moving randomly in the chamber. Similarly, boron powder heated by thermal process released boron ion, molecule. The negative bias attracts more positive ions boron and carbon beside other elements to the substrate by carrier argon. This effect will fill the voids between the grains, break down the large particles growth and create more nucleation sites, thereby promoting the particles refinement [3-5].
Figure 2. The FESEM images of hydrogenated nanostructure a-C:B films deposited at different negative bias.

An intense positive-ion bombardment on the growing film surface is occurred when the optimum condition achieved. In contrast, at less optimum condition only thermal process (0 V), the ions energy is less effective to penetrate into the growing surface and most of the ions are only trapped on the growing surface, resulting in the formation of the large particles size.

The study on nanostructure materials was successfully done by different preparation technique for crystalline material such as zinc oxide (ZnO), compound semiconductor, silicon material, etc. [7, 8]. The result showed nanostructure film has improved efficiency in dye sensitized solar cell [7, 8], increased sensitivity and reliability of humidity sensor[205], and increase high surface area in silicon solar cell [7,8]. However, there is less report on the nanostructure of a-C alone or with other dopants in the literatures. K. Dayana et al [9] reported that nanostructure iodine doped (a-C:I) film was achieved particle size of nanostructure of about 45 to 65 nm by thermal CVD using camphor precursor. In addition, D.B. Mahadik et al [10] reported a nanostructure carbon thin film by thermal CVD process about 1000°C using turpentine oil achieved by SEM images showed the particles size of 80 to 9 nm. In
technological point of view, the result prepared by this technique achieved the size of particles nanostructure a-C:B lower than in the literatures [9,10]. The result showed that, the nanostructure a-C film can be achieved not only by conventional techniques using camphor and turpentine precursors but also can be prepared by this technique.

Figure 3 shows the Raman spectra nanostructure a-C:B films deposited at different negative bias. The G and D bands observed from 0 to -50 V are relatively broad indicating that the crystallite size of the carbon film is small [12]. The peak around 1550 cm$^{-1}$ shows the amorphous nature of the a-C films [6,9,12]. This same phenomenon has been reported by other groups [6,9,12] but using other methods, precursors, and dopants sources [6,9,12] and also supported by FESEM images as discussed previously. At no bias applied (0 V), the D band position is low compared to a-C:B film deposited with negative bias voltage and slightly increase thereafter until -20 V. The D band of hydrogenated nanostructure a-C:B film for the negative bias between -20 V to -30 V remains almost unchanged after which it has changed obviously from 0 V to -20V. The D band peak height in Raman spectra reported by Pardanoud et al [13] was correlated with the H content in graphene and therefore might be correlated with H incorporated in nanostructure a-C:B film.

This phenomenon might be indicated the component of the sp$^2$ bonds increased with the increased of boron 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” because Raman D peak is reported to be assigned to sp$^2$-bonded C which seems to be aromatic in structure [14-16]. 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 same phenomenon was agreed by others [6,12] when D-position increased. The changing of size particle in FESEM images and C-H binding from FTIR spectra might be related to the increasing of D-position by the structural disorder. The main factor affecting bands position, width and intensity is the clustering of sp$^2$ phase. The G band position measures topological disorder, which arises from the size and shape distribution of sp$^2$ [15] clusters.

The changing of D and G position might be to a change in the clustering of sp$^2$ phase of nanostructure a-C:B film. Although there is no evident to justify the clustering of sp$^2$ phase of hydrogenated nanostructure a-C:B film changed, but changing of D position might be an indicator for changing of clustering of sp$^2$ phase.
Table 1. Raman spectra parameters of a-C:B films deposited at difference negative bias

| Negative bias voltage (V) | $\text{Pos} \ (G) \ (\text{cm}^{-1})$ | $\text{Width} \ (G) \ (\text{cm}^{-1})$ | $\text{Pos} \ (D) \ (\text{cm}^{-1})$ | $\text{Width} \ (D) \ (\text{cm}^{-1})$ | $I(D)$ | $I(G)$ |
|--------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--------|--------|
| 0                        | 1582.436                        | 448.861                         | 1332.504                        | 212.642                         | 0.447  |        |
| 10                       | 1587.133                        | 182.979                         | 1319.889                        | 642.474                         | 0.778  |        |
| 20                       | 1560.283                        | 182.978                         | 1344.504                        | 194.825                         | 0.969  |        |
| 30                       | 1560.283                        | 182.979                         | 1344.503                        | 194.825                         | 1.069  |        |
| 40                       | 1620.337                        | 137.796                         | 1410.199                        | 319.879                         | 1.785  |        |
| 50                       | 1552.452                        | 140.871                         | 1340.450                        | 334.438                         | 1.829  |        |

The refinement of a-C:B films particle size by negative bias of FESEM images might be correlated with a dense of boron and carbon peaks together with other elements which might contribute for the change of clustering $sp^2$ phase and therefore attribute for a change in D and G in Raman spectra. The change in bond hybridisation ($sp^2/sp^3$) and density of the particles as revealed from EEL analysis was reported more sensitive to starting precursor [17]. According to the literatures [6,9,12] 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. Thus, the result implies that the hydrogenated nanostructure a-C:B films prepared from palm oil precursor are dominated by $sp^2$ rather than $sp^3$ as negative bias increased from 0 V to -50 V.

Figure 4. The current-voltage relationships of hydrgenerated nanostructure boron doped amorphous carbon under dark and light measurement

Figure 4 illustrates the current voltage (I-V) characteristic of a-C:B films under dark and illumination. All a-C:B films do not show rectifying behavior either in dark or under illumination. The
reason is that the work function of Aurum is larger than a-C:B and might be due to low resistivity of a-C:B which attributed to the existence of sp²-rich interfacial layer [18, 19].

In a dark measurement (refer Figure 4), the conductivity of a-C thin film deposited by negative bias compared with zero bias (2.048x10⁻⁷) is gradually increases from 4.53x10⁻⁶ to 4.878x10⁻⁶ S cm⁻¹. The result shows with the help of negative bias increase the conductivity of hydrogenated a-C:B film. This phenomenon might be correlated with the increase of true dopant of boron in the thin film. Similar result was found by W. Chan et al [20] conductivity increase with increasing boron concentration in reliable boron-doping. The electrical properties could be related with the changing density of crystal defects, such as the vacancy, grain boundary and film surface, carrier concentration and mobility of the electron [21]. It is reported that the surface morphology (grain size), carrier concentration and carrier mobility also play an important role in the electrical conductivity [10, 22].

Deposition by negative bias showed higher conductivity compared to thermal process only. This might be increased carrier concentration due to ability of negative bias attract positive boron, increase true doping boron incorporated in the film and this might explained why conductivity increased as negative bias increased. In addition, the electron mobility of the a-C:B film might be increased due to the film in nanostructure and ability hydrogen passivated in film as discussed previously.

**Table 2.** Conductivity and photoresponse of a-C:B films by applied negative bias

| Applied DC bias voltage (V) | Conductivity (σ) | photoreponse |
|----------------------------|------------------|---------------|
|                            | Under dark       | Under illumination | \(\sigma_{\text{illumination}}/\sigma_{\text{dark}}\) |
| 0                          | 2.048x10⁻⁷       | 3.126x10⁻⁶     | 1.531 |
| -10                        | 4.536x10⁻⁶       | 8.407x10⁻⁶     | 1.856 |
| -20                        | 4.878x10⁻⁶       | 9.746x10⁻⁶     | 1.998 |

Table 2 shows photo-responses of a-C:B films with a function of DC applied bias. Increment in conductivity values under illumination indicate photoresponse characteristic for thin films. Photoconductivity of thin films is important in addressing the suitability of thin films to be evaluated in photovoltaic solar cell applications. The photoresponse of a-C:B film ranging from 0 V to -20 V is 1.531, 1.856, and 1.998, respectively. It observes that a-C:B films have the overall range photoresponse below 2 with the highest one 1.998 at -20V. Although photo-responses are low, all hydrogenated nanostructure a-C:B films are rarely reported by using this preparation. The film shows the ability to absorb light by producing current flow in the external circuit. Current flow is the results of the photoexcited carriers drift before recombination [23]. For hydrogenated a-C:B films under illumination, the ohmic form is similar with hydrogenated nanostructure a-C:B films under dark but higher than under dark measurement is due to the higher generation of excess carriers. We predict, negative bias as discussed previously gives more excess of holes and thereby generates more excess carriers. The nanostructure of a-C:B film drift electron-hole pair in the load rather and thus slow recombination time . The hydrogen terminated the dangling bond reduced less defect in hydrogenated nanostructured a-C:B film and thus prevent recombination excess of carrier in the film surface.

4. Conclusion

The hydrogenated nanostructured a-C:B films were successfully prepared by bias assisted-CVD. FTIR and FESEM images confirmed the carbon is C-H binding and in nanostructure, respectively. The FESEM images at 0 V showed particles size was less than 45 nm. Furthermore, a more uniform of particles size less than 25 nm was achieved at -20 V. Raman spectra showed the a-C:B films deposited by different negative bias were amorphous in nature. Raman analyses showed a change of structural properties was correlated with incorporated of carbon, boron, hydrogen and other elements in carbon
network. Hydrogen was believed to be incorporated with dangling bonds near the surface as correlated with vibration peaks at 28850 cm$^{-1}$ of FTIR spectra. The overall of photo-response is below 2 with the highest one 1.998 at -20V. Current flow is the results of the photoexcited carriers drift before recombination. For hydrogenated a-C:B films under illumination, the ohmic form is similar with hydrogenated nanostructure a-C:B films under dark but higher than under dark measurement is due to the higher generation of excess carriers. The nanostructure of a-C:B film drift electron-hole pair in the load rather than recombine and thus reduce recombination time. The hydrogen terminated the dangling bond reduced defect in hydrogenated nanostructure a-C:B film and thus slower recombination of excess carrier in the film surface.

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