Boron-doped Amorphous Carbon Film Grown by Bias Assisted Pyrolysis Chemical Vapor Deposition

Ishak Annuar¹a), Jalal Rouhi¹, and Mohamad Rusop¹,²

¹NANO-ElecTronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
²NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
³Faculty of Electrical Engineering, UiTM Sarawak Kampus Kota Samarahan Jalan Meranek, Sarawak

a) ishak@sarawak.uitm.edu.my

Abstract: Boron-doped amorphous carbon (a-C:B) films were successfully synthesized via a bias-assisted pyrolysis-chemical vapor deposition (CVD). The effect of substrate bias on the thickness, surface morphology, electrical properties of a-C:B film were investigated. The AFM measurements and conductivity result show the surface roughness and resistivity of a-C:B films decreases with increasing substrate bias from 0 to -20 V. The fabricated films were evaluated for use in photovoltaic solar cells. The fabricated solar cell with the configuration of Au/p-C:B/n-Si/Au achieved conversion efficiency (η) of 1.431% at applied bias voltage of -20 V. This result showed the successful interstitial doping of boron in the amorphous carbon films deposited by this method.

Keywords: Substrate bias, Boron doped, amorphous carbon, solar cell

Classification: Semiconductor materials

References

[1] M. Rusop, X. Tian, S. Mominuzzaman, T. Soga, T. Jimbo, and M. Umeno: Solar Energy 78 (2005) 406-415.
[2] Y. Tang, Y. Li, Q. Yang, and A. Hirose: Applied Surface Science 257 (2011) 4699-4705.
[3] S. Adhikari, D. C. Ghimire, H. R. Aryal, S. Adhikary, H. Uchida, and M. Umeno: Diamond and related materials 15 (2006) 1909-1912.
[4] D. Mahadik, S. Shinde, C. Bhosale, and K. Rajpure: Journal of Alloys and Compounds 509 (2011) 1418-1423.
[5] T. T. Stapinski, B. Swatowska, S. Kluska and E. Walasek: Applied Surface Science 238 (2004) 367-374.
[6] Sudip Adhikari, Hare Ram Aryal, Dilip Chandra Ghimire, Golap Kalita and Masayoshi Umeno: J. of Diamond & Related Materials 17 (2008) 1666-1668.
[7] J. G. Buijnsters and L. Vázquez: Surface and Coatings Technology 201 (2007) 8950-8954.
[8] H. Dai, Y. Zhang, Z. Chen, and F. Zhai: Physica B: Condensed Matter 438 (2014) 34-40.
[9] G. Gottardi, N. Laidani, R. Bartali, M. Filippi, L. Calliari, R. Brusa: Diamond and Related Materials 14 (2005) 1031-1035.
[10] N. Dwivedi, S. Kumar, J. Carey, and H. K. Malik: J. of Applied Physics 112 (2012) 113706.
[11] X. Peng, Z. Barber, and T. Clyne: Surface and Coatings Technology 138 (2001) 23-32.
[12] T. S. Cale and V. Mahadev: Thin films 22 (1996) 175-276.
[13] L. D’Urso, G. Compagnini, and O. Puglisi: Carbon 44 (2006) 2093-2096.
[14] X. Tian, M. Rusop, Y. Hayashi, T. Soga, T. Jimbo, and M. Umeno: Solar Energy Materials and Solar Cells 77 (2003) 105-112.
[15] O. Panwar, M. A. Khan, B. Satyanarayana, and S. Kumar: Applied Surface Science 256 (2010) 4383-4390.
[16] L. Huang and L. Meng: Materials Science and Engineering: B 137 (2007) 310-314.
[17] Y. Hayashi, S. Ishikawa, T. Soga, M. Umeno, and T. Jimbo: Diamond and Related Materials 12 (2003) 687-690.
[18] M. Rusop, X. Tian, T. Kinugawa, T. Soga, T. Jimbo, and M. Umeno: Applied Surface Science 252 (2005) 1693-1703.

1 Introduction
Amorphous carbon (a-C) thin films were extensively studied in the last two decades due to many excellent properties. This structure based on carbon materials has attracted a great interest for the potential applications in optoelectronic devices especially in the development of the photovoltaic solar cell, due to the fact that the cost of solar cell using silicon is much higher to meet the daily life expectations [1]. However, various properties of carbon thin films were directly influenced by methods, conditions of deposition and also on the starting precursor materials. Until now many sources from non-renewable carbon sources were studied using different method and carbon targets [2]. However, these carbon sources obtained from fossil fuels are very limited in the near future [3]. In consequences, renewable natural hydrocarbon sources were suggested [4] can be used to replace non-renewable carbon sources due to sufficiently available in nature.

The conduction type of carbon films can be controlled by depositing dopants [5, 6]. Boron is widely used as a p-type impurity in Si semiconductor and carbon films. Boron-doped films are employed in fabricating heterojunction solar cells using different precursors and techniques, such as chemical vapor deposition (CVD), ion implantation, and pulsed laser deposition, etc. However, most of the techniques require the use of sophisticated reactors inducing high costs. By contrast, traditional low-cost techniques, such as CVD, have several limitations in terms of the selection and delivery of multi-component products [6]. For example, the hollow of quartz and glass chambers are small, thereby limiting the number of substrates that can be placed in the chamber and increasing the difficulty of sample
extraction. In this study, a bias-assisted pyrolysis-CVD is designed with a large chamber and equipped with a unique parameter. DC bias is assembly in many high-cost deposition techniques to improve film quality and consequently increase deposition rate, thereby effectively minimizing defects and attracting dopant atoms [7] through kinetic bombardment energies of the ions arriving on the substrate.

To the best of our knowledge, this method have rarely been used to deposit a-C:B films used in heterojunction solar cell applications. In the present study, a-C:B films were synthesized by bias-assisted pyrolysis-CVD on n-type silicon (n-Si) using palm oil as carbon source. In addition, the surface morphology, electrical, and electronic properties of a-C:B films are investigated.

2 Methodologies

Bias-assisted pyrolysis-CVD was used to deposit a-C:B onto corning glass substrates (thickness: 1 mm) and n-Si (100) (thickness: 325+25 µm; resistivity: 1 cm to 10 Ω cm). The substrates were cleaned with acetone followed by methanol for 15 min in an ultrasonic cleaner (power Sonic 405), and subsequently rinsed with deionized (DI) water for 15 min. Excess oxide layers of n-Si substrates were then etched with diluted hydrofluoric acid (10%) solution for approximately 3 min before rinsing with DI water. The substrates were dried using nitrogen gas and then attached inside the chamber as shown in Sub-E (Fig. 1).

The deposition temperature was set at 350 °C for 1 h. The palm oil precursor was heated in a bottle at approximately 250 °C using a hot plate (Stuart CB162, Fig. 1, Sub-A). The vapor of palm oil was flowed into the chamber through subsystems B and C using aquarium air pumps (model GA8000). The flow rate of the vapor palm oil was controlled by subsystem D (adjustable valve). The flow rate of vapor palm oil and the carrier gas argon were set at 114 and 200 mL/min, respectively.
Calibration was achieved using AALBORG flow meter. For the doping process, approximately 1.5 g of boron was placed on the aluminum foil above the metal plate heater (subsystem E).

In the evaluation of the fabricated solar cell device, the bottom and top sides of silicon were sputtered with approximately 100 nm and 10 nm of gold, respectively. Another gold film (thickness: 60 nm) was deposited on the top surface of the 10 nm gold film to verify if the probe point established proper contact with the gold metal. To establish a complete circuit, the other probe is connected to a conductive metal holder. Atomic force microscopy (AFM XE-100 park system), surface profiler (Veeco Dektak 150), current-voltage measurement (I-V), JASCO UV-vis/NIR spectroscopy (V-670 EX), and solar simulation (Bukuh Keiki EP200), were used to characterize surface morphology, thickness, optical, electrical, and electronic properties, respectively.

**3 Results and Discussion**

Under the employed deposition conditions, the obtained a-C:B films demonstrate homogenous thickness and composition throughout the entire silicon substrate. With the bias voltage, the ion energy (E) is proportional to substrate bias voltage (V_b) [8]:

$$E = \frac{(kV_b)}{P^{0.5}}$$  \hspace{1cm} (1)

where P is discharge pressure and k is a constant. According to formula (1), the energy of carbonaceous species increases with the increase of substrate bias from 0 to -20 V. The film thickness slightly increased from 150 nm to 220 nm with the increase in negative bias substrate. The change of thickness in the a-C:B films deposited with different substrate bias can be explained by the sub-plantation model [9]. When the energy of an impinging species (E_{im}) is lower than that of penetration threshold (E_p), the impinging species cannot penetrate the surface, so it just stick to surface, and remain in their lowest energy state, at this case thickness.
is low. When $E_{im}$ is higher than $E_p$, the species have a probability to penetrate the surface, and enter a subsurface interstitial site leading to an increase of the thickness. Under this condition, the local bonding will then reform around that atom according to this new density [9], where the feature of the film deposition is characterized by internal growth. Based on the sub-plantation model [7, 10], the fraction of carbonaceous species trapped in subsurface position is increased with increasing substrate bias, therefore the thickness of a-C:B film is also increased. At 0 V bias, less species can reach the film surface due to less optimized energy. Therefore, a-C:B film growth depends only on physisorption, chemisorption, and incorporation of hydrocarbon growth precursor. However, at negative bias voltage (-10 and -20 V), additional energy by the impinging positive ions enhance the sticking of the negative radical growth precursors by creating dangling bonds, which can ultimately enhance film growth.

![Graph](image)

**Fig. 3.** The thickness of boron doped amorphous carbon by difference substrate bias voltage

AFM micrographs of the a-C:B films are given in Fig. 3. It can be seen that the average particle size on the film surface becomes smaller with increasing substrate bias from 0 to -20 V. At the bias voltage 0 V, the a-C:B film showed high peaks grain particles on the a-C:B film surface. When the bias voltage increased from 0 V to -20 V the grain peaks particles of a-C:B film became low and dense, and the surface roughness decreased significantly from 7.65 nm to 1.65 nm. The general trend observed for the evolution of the a-C:B film as follows. At 0 V, the film morphology is cauliflower-like with protruding structures. This type of morphology is similar characteristic implying an unstable growth as reported by [11]. According to sub-plantation model, the growth of the film is a surface growth processes when $E_{im}$ is lower than $E_p$. Surface diffusion on the surface causes the growth of the large clusters of $sp^2$ component leading to substantial roughening [11]. In this case (0 V), this unstable growth would be due to the fact that the growth takes place under diffusion limited conditions which agreed by [7, 12]. The depositing particles undergo several collisions before they can reach the growing
interface. Thus, the particles arrive following trajectories with different angles with respect to the growing surface. This scenario leads to shadowing effects during the growth process as the protruding surface structures receive more depositing particles than the depressed regions and grow at a higher rate [12]. When $E_{im}$ is higher than $E_p$, the growth of the film is internal growth process. The impinging species can penetrate into the subsurface, surface diffusion is reduced and the boron and carbonaceous species energy tends to be dissipated into a relatively large volume in the interior. The surface morphology thus remains relatively unaffected by the penetration of the species, which leads to the smoother surface [13]. Therefore, the surface roughness decreases slightly and the slope distribution becomes narrower and the cauliflower-like morphology disappears to lead to a rather granular morphology. This is probably due to the fact that some physical deposition of the growing film is already taking place. At -20 V these effects become more evident since the surface roughness drops sharply. In addition, the energy released by the incoming ions can induce downhill currents in the top layer of the growing film contributing to its smoothening [7, 13].

Fig. 4. The AFM images of a-C:B films at different substrate bias voltage
Fig. 3 indicates the current-voltage (I-V) characteristics of a-C:B films in the dark and under illumination. All of the a-C:B films did not show rectifying characteristics either in the dark or under illumination, which can be attributed to the larger function of the gold film compared with the a-C:B film, as well as the low resistivity of the a-C:B films because of the presence of the sp²-rich interfacial layer[13, 14]. For a-C:B films under illumination, the linear increase in current along with the decrease in voltage is more apparent compared with that of the films in the dark because of the generation of excess carriers.

In dark environment (Fig. 6), the conductivity of a-C thin film deposited by negative substrate bias voltage gradually increased from $4.536 \times 10^{-7}$ S.cm$^{-1}$ (0 V) to $4.738 \times 10^{-6}$ S.cm$^{-1}$ (-20 V). The electrical properties could be related to the changing density of crystal defects, carrier concentration, and electron mobility at different film thickness values. The smoothness of the surface roughness applied by negative bias substrate was confirmed by AFM images (Fig. 4(c)) might be a good agreement for the high conductivity of a-C:B film. Variations in film thickness can influence the conductivity because of the relation between carrier concentration and the grain size of film [15, 16]. Negative bias has a significant function in attracting positive B ions for incorporation with a-C film, thereby generating excess holes in a-C:B films. The increase in average thickness contributes to the increase in the number of excess holes generated through boron incorporation, and thus, increasing a-C:B film conductivity. As shown in Fig. 6, resistivity decreases when negative substrate bias increases. This result can be attributed to the increase in boron concentration with reliable boron-doping.
Table 1 shows the conductivity and photoresponse of the a-C:B films with functions of applied negative substrate bias voltage. The photoconductivity of thin films is important in determining the suitability of thin films for photovoltaic solar cell applications. As shown in Table 1, a-C:B films exhibit an overall range photoresponse <2, with the highest value of 1.931 at -20 V. Although the photoresponses of the films are low, all of the a-C:B films obtained using palm oil as precursor demonstrate the capacity to absorb light, as evidenced by the generation of current flow in the external circuit.

Table 1. Conductivity and photoresponse of a-C:B films

| Applied DC bias voltage (V) | Conductivity (σ) Under dark | Conductivity (σ) Under illumination | Photoresponse (σ_{illuminated}/σ_{dark}) |
|----------------------------|-----------------------------|------------------------------------|----------------------------------------|
| 0                          | 4.536x10^{-7}               | 8.407x10^{-7}                      | 1.853                                  |
| -10                        | 1.478x10^{-6}               | 2.746x10^{-6}                      | 1.857                                  |
| -20                        | 4.78x10^{-6}                | 9.22x10^{-6}                       | 1.931                                  |

The current density-voltage (J-V) characteristics of Au/a-C:B/n-Si/Au solar cells in dark environment are shown in Fig. 7a. The Au/a-C:B/n-Si/Au solar cells display rectifying characteristic at 0% fill factor, which indicate the formation of different layers between the a-C:B film and silicon. The a-C:B layer acted as a p-type semiconductor with respect to n-silicon substrate, thus forming the rectifying characteristics. The reverse saturation current, which is low as compared with the forward current, gradually increases with reverse bias (photocurrent increases). These behaviors can be attributed to the generation of minority carriers within the depletion region. On the otherhand, the current increases exponentially at forward bias, indicating a good quality of the a-C:B film as the p-type on n-Si.
substrate to perform the p-n abrupt junction. The fast response of increasing current at forward bias at -20 V is a good agreement with high conductivity and low resistivity results as shown in Fig. 6.

Fig. 7. Measured J–V characteristics of the of Au/a-C:B/n-Si/Au solar cell under (a) dark and (b) light illumination conditions at different negative bias

The I-V characteristics of Au/a-C:B/n-Si/Au devices under illumination at 100 mW/cm² are listed in Fig. 6b. Similar trends in the form of curves are observed for all Au/a-C:B/n-Si/Au devices (Fig. 7b). The obtained curves are less broad compared with an ideal solar cell curve. A slightly broad curve reduces a fill factor or maximum output power, and thus, the overall conversion efficiency. This phenomenon is attributed to series or shunt resistances, which are caused by metal contact and material defect. The series resistance results in voltage drop, thus preventing full photovoltaic voltage across the external load; likewise, series resistance affects open circuit voltage ($V_{oc}$) [17, 18]. By contrast, internal resistance of material is due to the device edges and grain boundaries as correlated with AFM images as shown in Fig. 3 which directly influence the resistivity of a-C:B film as correlated with resistivity result in Fig. 6. Shunt resistance significantly contributes to the reduction of solar cell performance. In shunt resistance, a fraction of photo-generated carriers are diverted away from the external load, thereby reducing current density ($J_{sc}$).

The electronic properties of Au/a-C:B/n-Si/Au solar cell, including its open $V_{oc}$, $J_{sc}$, FF, and efficiency are presented in Table. II. Low $V_{oc}$ and $J_{sc}$ are found for all a-C:B films, which directly indicate low FF and conversion efficiency. The low $V_{oc}$ and $J_{sc}$ values are attributed to the low built-in voltage, which are caused by the high amount of defect in the a-C:B films. The electronic properties of Au/a-C:B/n-Si/Au solar cells remarkably improved by the increase in the bias of the substrate. The Au/a-C:B/n-Si/Au solar cells fabricated through the deposition at -20 V applied bias shows the highest conversion efficiency. The improvement of conversion efficiency can be attributed to the successful boron incorporation, which increases the number of excess carriers and therefore increases the current density of the a-C:B film. The bombardment of ions produced by -20 V is important in minimizing defects which reflect to the low resistivity (Fig. 6). The reduction of defects increases the built-in voltage, thereby prolonging the lifetime.
of excess carriers and providing wide diffusion. Although the energy-conversion efficiencies of the fabricated solar cell devices are considerably low, the present study presents a viable alternative through the use of natural palm oil precursor in developing solar cells. Moreover, the energy-conversion efficiency achieved in this study (1.411% at -20 V) for boron doped a-C film is higher than that reported by [14, 17, 18].

### Table II. The electronic properties of Au/a-C:B/n-Si/Au solar cell devices

| Substrate bias voltage (V) | Open-circuit voltage, V_{oc} (V) | Current density, J_{sc} (mA/cm²) | Fill Factor, FF | Conversion efficiency, η (%) |
|----------------------------|---------------------------------|----------------------------------|----------------|-----------------------------|
| 0                          | 0.1906                          | 2.9886                           | 0.1831         | 0.104                       |
| -10                        | 0.2707                          | 3.8648                           | 0.3152         | 0.335                       |
| -20                        | 0.4192                          | 7.9035                           | 0.4281         | 1.431                       |

### 4 Conclusions

The change in the thickness, surface morphology, electrical and electronic properties of the a-C:B films deposited by the bias-assisted pyrolysis-CVD method in a mixture of hydrocarbon palm oil, boron and argon gas, have been studied. The results show that with increasing substrate bias the thickness increase and surface roughness becomes lower. In other words, a lower surface roughness is corresponding to a higher conductivity and higher conversion efficiency for the a-C:B films. These results strongly suggest that increasing the substrate bias produced more energetic ions, and these ions led to surface modifications of a-C:B films during the film deposition. The I-V measurement using the solar simulator revealed the formation of p-n abrupt junction due to the different layers of a-C:B film and n-Si. The conversion efficiency increased from 0.104% to 1.431% with the increase of negative bias voltage from 0 V to -20 V. Although the conversion efficiency is considerably low, the present study presents a viable alternative through the use of palm oil as precursor, which can improve energy-conversion efficiency as the deposition conditions are optimized.

### 5 Acknowledgments

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.