Complex And Nano-Structured Amorphous Carbon Films From Hydrocarbon Palm Oil As A P-Type In Photovoltaic Heterojunction Solar Cell Applications

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Abstract: The complex and nano-structured amorphous carbon as p-type films prepared from natural palm oil precursor for heterojunction solar cell were presented. Field-emission scanning electron microscopy (FESEM) revealed the nanostructured films had particle size in the range of 28 to 34 nm. The energy-dispersive spectroscopy (EDS) showed the existing of carbon in complex-structured amorphous carbon film and carbon together with boron in nano-structured amorphous carbon film. Solar simulator analysis results showed an open circuit voltage (VOC), current density (JSC), fill-factor (FF) and conversion efficiency (η) of Au/a-C:n-Si/Au were 264.62 mV, 1.50434 mA/cm², 0.32632, and 0.130154 %, respectively. Meanwhile, the VOC, JSC, FF and η of Au/a-C:B/n-Si/Au solar cell were 271.25 mV, 14.91723 mA/cm², 0.33582, and 1.542622 %, respectively. The conversion efficiency was increased as the p-type a-C:B film in the nanostructured form.

Index Terms: Amorphous carbon, Palm-oil, Negative bias, Boron doping, Carbon film

1 INTRODUCTION

Various types of carbon precursors have been discovered from renewable precursors: camphor powder, turpentine oil, coconut oil, etc [1], [2] and non-renewable sources; methane, acetylene, ethanol and ethylene for producing allotropic carbon such as carbon nano tubes (CNT), graphene, amorphous carbon, etc. using various method of depositions [1], [2]. Beside of those precursors, palm oil the other abundantly promising ‘green’ source was successfully synthesized the vertically aligned carbon nanotubes (VACNTs). Palm oil is scientifically known as hexaerocenic acid which was derived from fibrous exocarp and mesacarp of the fruits of palm tree. The palm oil is contained carbon (67), hydrogen (127) and oxygen (8) to form the chemical binding of $C_{67}H_{127}O_8$ (3). This compound has the highest carbon content among the known precursors. The synthesizing of a-C on the other hand, required less energy compared with other allotropes carbon for instant, the VACNTs need deposition temperature above 700°C [1]. Nevertheless, the a-C films are weak p-type in nature and they possess complex structure and high density of defects, thereby restricting their doping capacity; this low doping efficiency is the main obstacle for their application in various electronic devices. Amorphous carbon (a-C) films have gained considerable attention because of their controllable optical gap, which allows for its wide application in the manufacture of semiconductors. In order to solve that problem, it was suggested; the control of doping could reduce the existing of defect and at the same time modified the electronic properties [3], [4], [5]. Among deposition parameters, negative 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 [6], [7]. Many attempts were studied by others on the effect of negative bias for instant through the use of pure lubricant coatings (MoS$_2$) composite film. It was reported that, the increase of bias caused preferential re-sputtering of S resulting in a reduced S/Mo ratio, which can affect different properties of the film. A reported study on pure MoS$_2$ films deposited by bipolar pulsed DC showed that even an S/Mo ratio of 0.8 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], [9], [10]. Therefore, an understanding of substrate bias effects is necessary to improve the physical and mechanical properties of MoS$_2$-based coatings but also important for structural, electrical as well as electronic properties of any semiconductor film. In this paper, we report the micro-structured of as-deposited and nano-structured of boron doped amorphous carbon films deposited by using deposition temperature without bias (0 V) and deposition temperature with the help of a constant negative bias (-20 V). To the best of our knowledge, there is less report on natural bio-hydrocarbon of palm oil as a p-type of a-C film for heterojunction solar cell using negative bias technique.

2 Experimental Detail

The micro-structured a-C and nano-structured a-C:B films were deposited by using bias-assisted pyrolysis-CVD onto n-silicon (thickness 325 ± 25 μm, resistivity 1-10 Ω cm) and glass substrate (1 mm). Substrate was cleaned with acetone followed by methanol for 15 min in Ultrasonic Cleaner (power Sonic 405), respectively. Excess oxide layers were etched using diluted hydrofluoric acid and DI water with a ratio of 10:1 for about 2 min before rinsing in DI water. The substrates were dried with nitrogen gas and placed inside the chamber.

![Fig. 1 A schematic diagram of bias assisted-pyrolysis-CVD](image)
The deposition substrate temperature was set at 350°C for 1h deposition with a constant of negative bias voltage -20V and without negative bias (0 V). A liquid palm oil precursor was heated outside the chamber at 180°C by using hot platter (Stuart CB162). A vaporized of palm oil was pressured into the chamber using aquarium air pumps (GA8000). The amount of the vaporized palm oil, carrier gas argon used into were set to be constant at 114 mL/min, 180 mL/min, respectively. For doping process, 150mg of boron was placed on an aluminium foil inside the furnace of chamber.

Fig. 2 A schematic diagram of heterojunction solar cell devices

In the evaluation of the fabricated heterojunction solar cell device, the bottom and top sides of silicon were deposited with approximately 60 and 12 nm gold, respectively. Another gold film (thickness: 60 nm) was deposited on the top surface of the 12 nm gold film to verify if the probe point established proper contact with the gold metal. Light closure was attached on top of the device (Fig. 2) to ensure that light strikes only the 2 cm² target area. To establish a complete circuit, then other probe is connected to a conductive metal holder. Surface profiler (Veeco Dektak 150), FESEM (ZEISS Supra 40VP), and energy-dispersive spectroscopy (EDS), Atomic force microscopy (AFM, XE-100 Park Systems) and Solar simulator (Bukuh Keiki EP200) were used to characterize the surface morphology, atomic level, and electronic properties, respectively.

3 Result and Discussions

Fig. 3 Surface morphology of (a) Complex-structured a-C film and (b) nano-structured a-C:B film

Fig. 3 (a) and (b) show the FESEM images of micro-structured and nano-structured of a-C and a-C:B films, respectively. The images were taken with magnification of 50K and 100K using 5.0kV voltage. The images in Fig. 1 (a) shows the irregular pattern of structure synthesized from pure hydrocarbon precursor of palm oil with the diameter in size of below 382-669 nm without the use of negative bias of -20 V. As can be observed from FESEM images, the micro-structured a-C film consists of irregularly scattered micro ball-like of agglomerated particles. In contrast, the nano-structured a-C:B film has particles in diameter of 28-34 nm. As bias voltage of -20 V and boron applied, the size of particles becomes significantly decreased. This difference 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. More specifically, during the deposition of a-C:B film with applied of -20 V, an intense positive-ion bombardment on the growing film surface is occurred. The flux and the energy of these species affect the mechanisms that govern the incorporation of boron in the a-C network and the formation of a-C:B bonding groups. The negative bias of -20 V increases the energy of the bombarding ions, enhancing the chemical reactions between different species and their mobility at the growing film surface. As a result, the high-energy gas ions dissociate the deposition carbon clusters affecting the boron distribution, and the bonding structure of the a-C:B film. Accordingly, without bias voltage (0 V) applied to substrate, the ions energy is too weak to penetrate into the growing surface and most of the ions are only trapped on the growing surface, resulting in the formation of the loose cross-linking [10], [11] resulting to the irregularly scattered micro ball-like of agglomerated particles.
Fig. 4 (a) and (b) show the EDS images of micro-structured a-C film and nano-structured a-C:B film, respectively. The composition of carbon arise at 0.4K eV in a-C film while composition of boron together with carbon in a-C:B film arise at around 0.4 and 0.3K eV, respectively. We observed the compositional element of carbon is quite similar with the compositional element of silicon and only small number of oxygen found in is EDS result. In contrast, the compositional element of carbon decrease as boron introduce in a-C film. With negative bias (in this case -20 V), the ion current drew towards the substrate increases along with the flux of neutral and charged species. This further cause an increase in preferential nucleation sites so that individual grain growth is arrested, hence expected to reduce the grain size as shown in Fig. 3 (b). However, the content of the elements are decreased, which possible allowed the grains to expand, since with increase in dopant content, the crystallite size of a-C:B film decrease. The same phenomena were reported [6], [12], [13] for TiN-MoS$_2$ and CrB$_2$-MoS$_2$ composite coating when the increasing of negative bias.

![AFM images](image)

**Fig. 5** Two typical 3-dimentional AFM images of (a) as deposited a-C film and (b) boron doped a-C film

AFM images shown in Fig. 5 illustrate the effect of the bias voltage and without bias voltage on the surface roughness and feature. The films deposited at all conditions show very smooth with agglomerated 'island' form. The films deposited without bias (0 V) are denser as compared to negative bias of -20 V but more higher of surface roughness as compared with the applied of negative bias voltage (-20 V) as shown in Table 1. In the case of applied the substrate without negative bias (0 V), the denser of particle at atomic level is attributed by the combination of unwanted macro-particles and neutral atoms. Most of the unwanted maro-particles and neutral atoms are remained under deposition temperature at 350°C. While the surface of a-C:B film became smoother with applied of negative bias (-20 V), resulting in an obvious reduction in surface roughness from 7.605 nm to 0.386 nm. The decreasing tendency of surface roughness with increasing of negative bias voltage can be suggested by the energy of impinging ions to the growing film that help improve the roughness by the surface diffusion [10], [11], [12], [13].

The current density–voltage (J–V) characteristics of Au/a-C/n-Si/Au and Au/a-C:B/n-Si/Au solar cells in dark environment are shown in Fig. 6 (a). The Au/a-C/n-Si/Au and Au/a-C:B/n-Si/Au solar cells display rectifying curves, which indicate the formation of heterojunction between the a-C:B film and silicon. The a-C and a-C:B layers acted as a $p$-type semiconductor with respect to silicon substrate, thus forming the rectifying curve. 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. At forward bias, the current increases exponentially, indicating a good quality of $p$–$n$ junction. The ideality factor is approximateley 2, indicating the dominance of the recombination current rather than the diffusion current. Many deviances from the ideal $p$–$n$ characteristics are observed, which can be due to the high low doping efficiency and posses complex structure and high density of defects [14], [15], [16]. The $I$–$V$ characteristics of Au/a-C/n-Si/Au and Au/a-C:B/n-Si/Au devices under illumination at 100 mW/cm$^2$ are illustrated in Fig. 6 (b). A dissimilar trends in the form of curves are observed for micro-structured film used for Au/a-C/n-Si/Au solar cell and nano-structured film used for Au/a-C:B/n-Si/Au solar cells by the. The obtained curve of Au/a-C/n-Si/Au solar cell is less broad and small area as compared with the obtained curve of Au/a-C:B/n-Si/Au solar cell. A slightly broad curve indicates reduced area (fill factor, FF) or maximum output power, and thus, the overall conversion efficiency is minimized. This phenomenon is attributed to series and shunt resistances, which are caused by metal contact and material...
defect, respectively. The open circuit voltage \( (V_{oc}) \), current density \( (J_{sc}) \), fill factor \( (FF) \) and efficiency \((\eta)\) of Au/a-C/n-Si/Au is \( V_{oc} \), \( J_{sc} \), FF and \( \eta \) is 0.265 V, 1.505 mA/cm\(^2\), 0.327, and 0.130154 \%, respectively. Meanwhile, the \( V_{oc} \), \( J_{sc} \), FF and \( \eta \) were 0.272 V, 14.91723 mA/cm\(^2\), 0.33582, and 1.542622 \%, respectively. The conversion efficiency was increased as constant negative bias of -20 V applied for doping boron into a-C film. Although the conversion efficiency of heterojunction solar cells are considerably low, it shows a prospect of using palm oil as the carbon source of the nano and micro-structured a-C film for the improvement of the energy conversion efficiency by optimizing the deposition conditions.

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**REFERENCES**


[8]. Xiufeng Tang, fa luo, fang Ou, Wangcheng Zhou, Dongmei Zhu, and Zhibin Huang, Effect of negative bias substrate voltage on the structure and properties of aluminium oxide films prepared by DC reactive


