

Effect of Film Thickness on Nano Columnar Diamond like Carbon Film Formation

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Abstract – Amorphous carbon with/without hydrogen (*a-C:H/a-C*), Diamond like carbon (DLC) films have been explored extensively in the past due to their highly attractive properties. They show promises in protective coatings, wear resistance and tribological performance. Thickness of the film is considered essential to be manipulated so to achieve desirable mechanical properties. Radio frequency (RF) sputtering is used for the film deposition on silicon wafer. The mechanical property response towards the sp^2/sp^3 matrix in the narrowed [H] zones, leads to the significant increase of hardness and elasticity. The magnificent of DLC is the hybrid system in the *a-C:H* films that can be controlled to suit for various application or to change their functionality. Nano-columnar *a-C:H* system is selected as a typical hybrid and formed by using electron beam (EB) irradiation. Through observation and characterization, this formed nano-columnar *a-C:H* films has a unique nano-structure and mechanical properties, due to the increased hardness and elasticity via nano-indentation results. **Copyright © 2015 Penerbit Akademia Baru - All rights reserved.**

Keywords: Amorphous Carbon, Nano-columnar DLC, RF-sputtering, EB-irradiation, Nano-Indentation

1.0 INTRODUCTION

Diamond-like Carbon (DLC), as the name suggested, is an amorphous carbon materials possessing unique properties similar to diamond. DLC is selected and widely used as a protective coating for tools and dies. The primary significant qualities are superior mechanical hardness, excellent wear resistance, chemical inertness, improved friction coefficient, and biocompatibility which are true as similar findings were reported by J. Robertson, P. Koidl et al, D.R. McKenzie and Y. Lifshitz. [1-10]. DLC shows great promises to increase the efficiency of conventional industries and able to open new doors to new applications and possibilities. However, majority of the commercial DLC films by previous work done have no intrinsic nano-structure, which leads to no option to improve their mechanical properties [11].

In 2008, T. Aizawa et al. conducted experiment and mentioned that a hybrid system in the amorphous carbon films is popular to make change in their functionality [12]. In order to have the desired hybrid system, physical vapour deposition (PVD) is used together with the post chemical treatment modification, electron beam (EB) irradiation. PVD oriented amorphous carbon films should have nano-columnar structure on the substrate by chemical modification via EB irradiation processing [13]. Self-organizing processes are able to generate nano-columnar amorphous carbon in the film through the PVD, followed by the EB irradiation. Vague nano-columnar amorphous carbon film is made by PVD process and then followed by

the columnar growth via EB-irradiation process [14]. Mechanical loading and unloading can characterize this nano-columnar a-C:H films by their reversible deformation. This reversible range of displacement is also dependent on different film thickness both in PVD coating and in EB-irradiation.

To date and to the best of author's knowledge, there are no comprehensive review or research on manipulating the film thickness to achieve various desirable mechanical properties. Therefore, the effect of film thickness is evaluated, in order to achieve the most favorable mechanical properties. The present paper is concerned with film thickness optimization during film deposition, and the effect of its graphitization and reordering via EB-irradiation setting, softening both in stiffness and hardness takes place generally with the different film thickness [14].

2.0 EXPERIMENTAL METHOD

2.1 Experimental Apparatus

RF-sputtering machine (Shinko Seiki Inc.; SRV6201) is used for depositing a-C:H film on silicon wafer. Figure 1 shows the system with matching box, vacuum chamber, and control-units. In this PVD approach, dc-bias as well as substrate temperature, are independently controlled from generated plasmas.

The a-C:H film is formed and deposited when carbon plume generated from carbon target is reacted with a carrier gas of argon-diluted methane. RF-power of 700W, DC-bias of 0V, target-substrate distance of 150 mm, and base pressure of 5×10^{-4} Pa are the setting used for the machine. Argon (Ar) with methane (CH₄) is used as carrier gas medium and being set to 90% in Ar and 10% in CH₄ ratio.

All these settings are to help sustain three dimensional growth of the a-C:H films. 10x10x0.5 mm³ silicon substrate size is used for microstructure analysis and observation. The pressure (P) is fixed at 0.5 Pa. The film thickness evaluated are 200 nm and 400 nm.



Figure 1: RF sputtering machine

While in the EB irradiation, the dose rate is dose rate of $6.0 \times 10^{11} \text{ s}^{-1} \text{ mm}^{-2}$ and the accelerated voltage and current set were 15 KeV, 0.15 mA with 1000s and 60 KeV, 0.3 mA with 2000s. The Ushio, Inc's mini-EB is used for low energy EB-irradiation of the PVD coated a-C:H

silicon substrate. In this process, electrons were uniformly irradiated to the a-C:H which to excite the carbon atoms.

2.2 Observation and Analysis Technique

Field emission scanning electron microscopy (FESEM) is used for cross sectional observation. While the characterization of ordered state in the a-C:H films would be using Raman spectroscopy. The deposited amorphous carbon on the silicon substrate initially has two broad peak; which is, D-peak and G-peak at the average wave number (Λ) of 1300 cm^{-1} and 1600 cm^{-1} respectively [14-17]. When self-organization occurs multiple-peaks are expected and will differ a bit compared to the initial D & G-peaks. The intensity ratio of both peaks makes quantitative characterization of ordered state formed in the amorphous carbon state.

2.3 Mechanical Characterization

Nano-indentation system (ENT-1100a), Berkovich type diamond indenter, is used for the purpose of mechanical characterization [18-20]. Since it is an indenter, the possibility of penetrating the coating and straight to the substrate exist. So, the indentation depth ratio is set to be around 1/6 of total film thickness so to eliminate the possibilities of substrate effect during the load-displacement measurement. From this nano indentation machine, the hardness (H) and the Young's modulus (E) can be obtained.

3.0 RESULTS

As mentioned, FESEM is used to observe and analyze the microstructure with after the EB irradiation. Finer columnar structure is observed after the EB irradiation as illustrated in Figure 2. During the irradiation process, agglomerated clusters make the growth even further and move towards the film surface uprightly. Thus, opening in matrix are left opened which the amorphous atoms started to make ordering and self-organizing.

The implanted atoms embedded in the matrix agglomerated and grows within the time frame of the EB-irradiation process duration, with no external influences of energy or load other than the EB-irradiation applied, heating effect through the EB-irradiation encouraged the formation of clusters, agglomeration and further growth. In short, by comparing the SEM microstructure, it is observed that a much finer nano-columnar structure is formed with the increase of irradiation time.

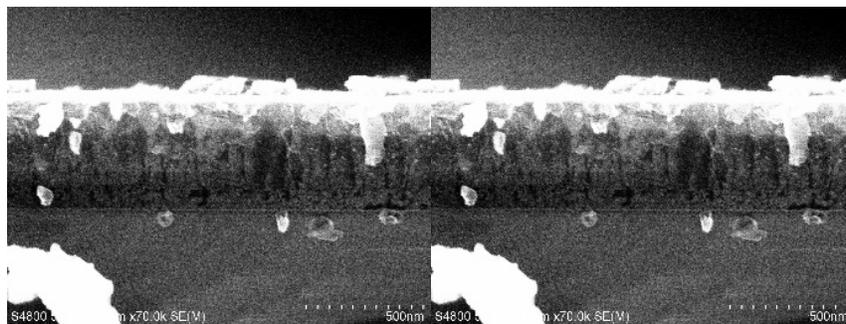


Figure 2: Cross sectional view of before (left) and after (right) EB irradiation

Figure 3 shows the measured Raman spectra by using Jasco NRS-2100. Raman-spectra are compared before and after EB-irradiation. The G-peak correspond to graphitic peak of higher wave number of C-C bonding and the D-peak correspond to disorder induced peak at its lower wave number [14]. The original peaks correspond to the amorphous carbon matrix, while the latter represent the new phases induced by EB irradiation. The position of D and G-peaks are listed in Table 1 below. New phase are being represented by this new peaks pair that is induced by the EB irradiation process. Therefore, EB irradiation energy increases the process of growth of atom from 1000s to 2000s.

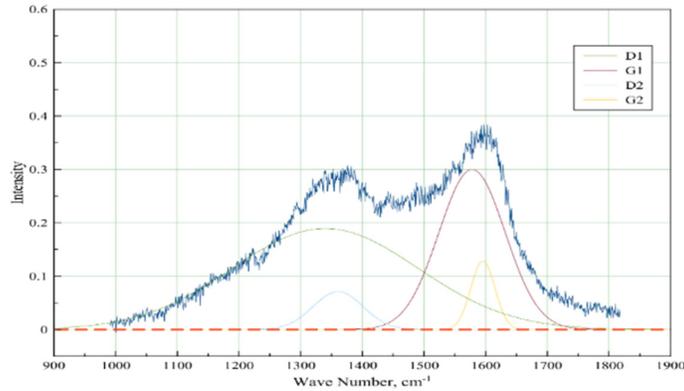


Figure 3: Comparison of Raman spectra before and after EB irradiation

Table 1: D and G peak positions before and after EB irradiation

As deposited	Centre (cm ⁻¹)
D1	1400
G1	1600
After EB irradiation	
D1	1387.4
G1	1575.6
D2	1359.9
G2	1589.4

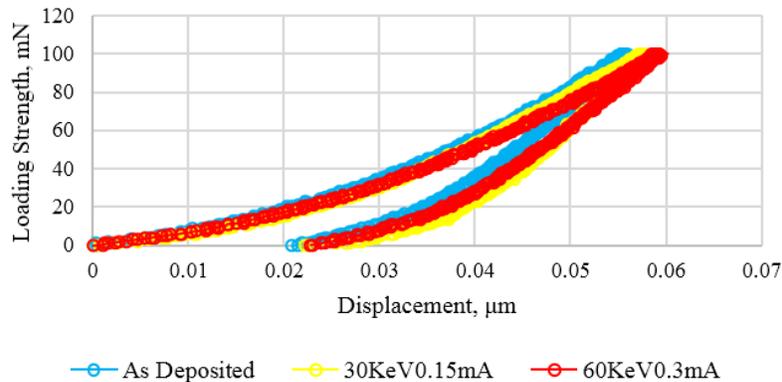


Figure 4: Nano-indentation results for 200 nm DLC film

Figure 4, Figure 5, Table 2, and Table 3 shows the nano-indentation results for 200 nm and 400 nm. As can be observed from both 200 nm and 400 nm film, it has a non-linear elasticity relationship whereas the load-displacement curved becomes reversible to the film thickness. The maximum displacement increases at the same loading limit as the irradiation time increases. Softening effect occurred here by the decreasing of Young's modulus and hardness corresponding with the duration factor [21].

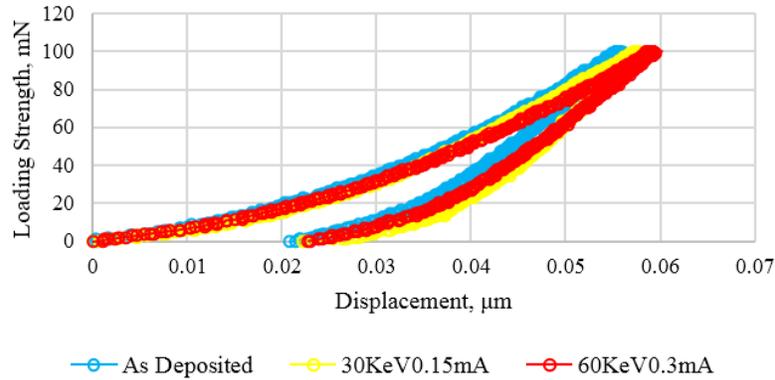


Figure 5: Nano-indentation results for 400 nm DLC film

Table 2: Hardness and Young's modulus for 200 nm DLC film

DLC Film	Hardness	Young's Modulus
As Deposited	28.95 GPa	23.40 Gpa
30KeV0.15mA EB	27.37 GPa	26.4 GPa
60KeV0.3mA EB	27.13 GPa	23.5 GPa

Table 3: Hardness and Young's modulus for 400 nm DLC film

DLC Film	Hardness	Young's Modulus
As Deposited	27.42 GPa	24.5 GPa
30KeV 0.15mA EB	27.37 GPa	26.4 Gpa
60KeV 0.3mA EB	28.01 GPa	22.5 GPa

4.0 DISCUSSION

The hardness will increase and Young's modulus will decrease with the increasing EB-irradiation time as noticed from Fig. 4 and 5. The results get better with the increase in thickness as well. In Fig. 3, proven that even with EB-irradiation taken place, the D and G-peaks are equivalent to each another. Apart from that, it also proves that the self-organization will be taken place once the present of the sufficient amount of concentration in the a-C:H matrix.

Originally, the a-C:H film has a vague columnar structure with relatively high-density columns covered by lower density one with similar sp²-sp³-H formulation. However, after the EB-irradiation, high-density inter-columnar with higher sp²/sp³ bonding ratio is embedded into the original a-C:H matrix, which made it homogenizing as the original as-deposited a-C:H

film. It can also be noticed that thicker DLC film such as 400 nm gives more promising results and there are still room for improvement and potential.

The vertical alignment intercolumns in the matrix were shown on the mechanical responses during the nano-indentation test. This again proven that the softening and hardening of the nano-structure can be controlled alone by the effect of film thickness.

5.0 CONCLUSION

In conclusion, RF sputtering are used to form the amorphous carbon film with vague columnar structure. Then, the DLC film be irradiated with electron beam further enhancing the structure via chemical modification. Due to this irradiation, the self-organization take place in the intercolumn from low density to high density amorphous carbon, hence, forming of vertically aligned graphite. This formation can be reflected from its mechanical properties.

The loading/unloading curves has non-linear elasticity and reduction in stiffness and increase in hardness taken place accordingly to the irradiation time and different thickness with the graphite formation in the intercolumns.

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