IOP Conference Series: Materials Science and Engineering

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To cite this article: J. Foo and T Aizawa 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **884** 012110

IOP Conf. Series: Materials Science and Engineering **884** (2020) 012110 doi:10.1088/1757-899X/884/1/012110

Wettability Control of Nano-Columnar Dlc Thin Films Via Eb-Irradiation

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Abstract. Amorphous carbon (a-C:H/a-C) or Diamond-like carbon, have a very high potential diverse engineering application especially in protective coating which made it an ideal method to be manipulated in process parameters so to achieve the desired mechanical and functional properties; this correlates to the smoothness, atomic density, and the sp^3 content. The nano-structure of this amorphous carbon is characterized by its disordered state of sp^2 and sp^3. The mechanical property would response to the sp^2/sp^3 matrix with the small hydrogen content which leads to the significant increases in hardness, tribological and also the wettability properties. This vague columnar structure of DLC is strictly modified to fine and self-organized structure, where high-density, graphitic inter-columnar structure is embedded into the low-density amorphous carbon phase as being confirmed through characterization, mechanical properties and response. This unique hybrid system in the a-C:H films would control the functionality of the final coating in customized way to suit multi-disciplinary engineering applications. This Nano-columnar a-C:H system. However, this hybrid system is still bound to the triangular diagram of sp^2-sp^3-H in the formation of a-C or a-C:H. This formed nano-columanar a-C:H films shows a unique nano-structure and its graphatized inter-columnar network with amorphous columns responsible the desired properties manipulation. In this paper, correlation between the degree of graphitization and wettability is established.

Keywords: Nano-columnar DLC, RF-sputtering, EB-Irradiation

1. Introduction

Amorphous carbon coatings, also known as diamond-like carbon (DLC), are mostly used as protective coatings; however, almost all of the commercial DLC films with or without doping have no intrinsic nano-structure and thus has no means to improve their mechanical properties. It is found out that the PVD-oriented DLC must have nano-columnar structure after chemical modification via EB-irradiation process (Aizawa, et al, 2006). In his previous paper, author proposed on the parameters setting, both PVD and EB-irradiation, must achieve the most desirable material outcome from the initial amorphous stage of the silicon wafer. It possesses some attractive properties, such as high hardness, elastic modulus, and etc, which are close to that of a diamond have motivated considerable interest in the deposition of DLC coatings and their use in tribological applications. (Aizawa, et al, 2010).

Through precise characterization of the nano-columnar DLC films, the reversible deformation during mechanical loading and unloading, indicating that the softening effects (Foo, et al, 2012) has taken place generally with the variation in parameters setting (Iwamura 2006, Aizawa, 2008), and this softening behavior is very much dependent on the processing parameters optimization (Foo, et al., 2011). With the EB-irradiation taken place, the self-organizing process taken place and must have modified the ratio of sp^2/sp^3, the quantitative relationship correlation between the different degree of graphitization and water contact angle of nano-columnar DLC film by post modification process, i.e. EB-irradiation. Thus, provides a further understanding on the evaluation of DLC coating.

2. Experiment

The DLC films were deposited on Silicon wafer substrates with the use of the custom made RF-sputtering machine (Shinko Seiki Inc.; SRV6201) with vacuum chamber, matching box, control units and chiller as shown in Fig. 1. In this PVD approach, DC-bias as well as substrate temperature, are independently controlled from generated plasmas.

Figure 1 RF-Sputtering system for DLC coating.

Carbon plume generated from carbon target is reacted with a carrier gas of argon-diluted methane; gaseous nuclei are deposited onto a substrate to form a-C:H film; and this coating method is controlled by RF-power, DC-bias, target-substrate distance and substrate temperature. On top of that, total carrier gas pressure and gaseous components have significant influence on this physical vapor deposition process.

Among these various parameters, the following parameters are fixed constant: RF-power is 700 W, target-substrate, 150mm, and base pressure of $5x10^{-4}$ Pa. The ratio of argon to methane carrier gas is set at the ratio of 90% /10%. The bias voltage is selected to be 0 V to sustain three dimensional growth of a-C:H films. Silicon substrate of size 10 x 10 x 0.5 mm^3 is used for microstructure analysis and observation. The pressure (P) is varied by P = 0.5, 1.0, 1.5 and 2.0 Pa. The film thickness (h) was varies from 100nm, 200nm and 400 nm for EB-irradiation without interlayer in between. The accelerated voltage and current set for the experiments were 60 KeV, 300mA and 15 KeV, 150mA; with a uniform distributed dose rate of $6.0x10^{11}$ s^{-1} mm^{-2}, and radiation time (t) of 1000, and 2000 seconds.

The Mini-EB (Ushio, Inc.) system for low energy EB-irradiation is deployed, with a dose rate of 6.0 x 10^{11} $s^{-1}mm^{-2}$. EB-irradiation is an effective processing method to control the phase and microstructure via solid-beam interaction. The dose of low energy irradiation leads to the chemical modifications as a post-treatment to tailor substrates into a desirable microstructure (Aizawa, 2007). Low energy electrons generate less heat; maximum temperature rise is still limited by 200K (Iwamura, 2003). Low energy electrons were applied to rearrange the structure during the irradiation (M. Singh, et al, 2007).

3. Graphitization of Nano-Columnar Dlc

In author's previous paper (Foo, et al., 2013) and PhD thesis, through AFM (Nanocute II system, Seiko Instrument Inc,) is deployed in order to topologically imaging so to understand the tribological phenomena in nano-scale that measures the local attractive or repulsive force between the probe tips and the DLC substrate. Whereas the DLC films responses to the inclination during measurement and it increases with the surface stiffness. The elastic distribution imaging for the DLC film and also the topographical image can be observed simultaneously. (Hisato, 2005)

During PVD, the uniform distribution of small clusters or island is generally formed on substrate and it is highly dependent on surface diffusion and substrate temperature. Surface diffusion allows the nuclei grows and bind together. A visible voids in the microstructure can be observed and it is generally the main reason of a voided columnar structure formation. The energy-enhanced post processes (EB-irradiation) can reduce the void through the self-organization process within the inter-columnar region.

Fig. 2 shows the AFM imaging for the DLC film. It is visible that before EB-irradiation, this DLC films was seen in the image as more vague, and a naturally grown columnar structure. After EB-irradiation, the original vague nano-structure is gradually changed to be more nano-columnar one through self-alignment.

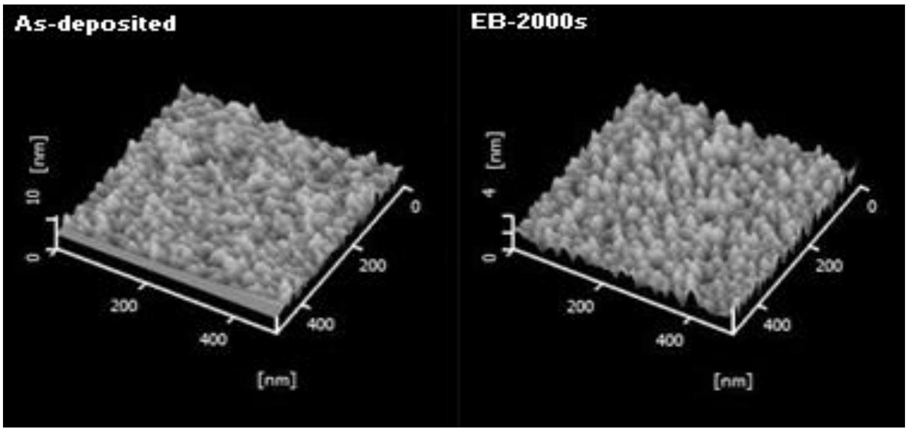

Figure 2 The AFM images and the topological profile image for as-deposited and after EB substrate.

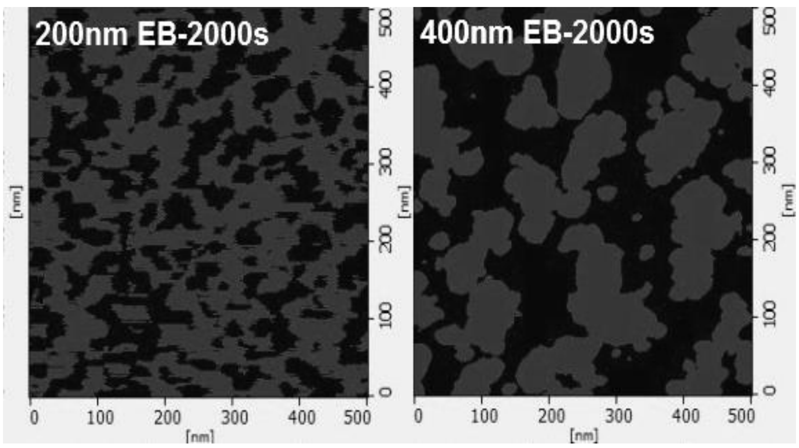

Figure 3 Topographic imaging profile for after EB substrate of 200nm and 400nm.

The topographic imaging profile clearly shows that with the increment of film thickness, the column formed become increasingly interconnected as shown in Fig. 3. This graphitization of inter-columnar region is changing the mechanical properties, where, the soft inter-columnar region becomes harder. Apart from that, through the AFM measurement and observation, apparent roughing occurs, as shown in Fig. 4. This roughening is corresponding to the nano-columnar formation. Again, with the increment of film thickness, the after EB-irradiation columnar size grow in a directly proportional trend from 22.17nm (100nm thickness) to 62.17nm (400nm thickness) as shown in Fig. 5.

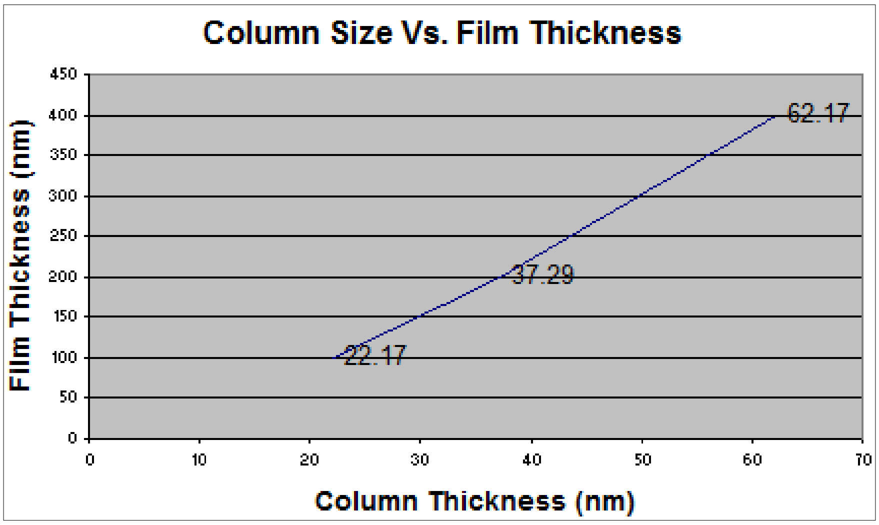

Figure 4 Column size vs. film thickness.

4. Wettability Analysis Results

Wettability means the ability of liquid o maintain in contact with solid surface, while maintaining the balance between the intermolecular interactions of adhesive type and cohesive type irradiation (Kurusu, et al, 2018). The degree of wetting is determined b a force balance between the adhesive and cohesive forces. In this contact angle measurement, the angle between the Nano-columnar DLC surface and the tangent of the droplet's ovate shape at the edge of the droplet (Ghosh M., 2018). A dedicated system was deployed in order to perform contact angle measurement as shown in Fig. 5. And the result obtained is analyzed by the ImageJ freeware.

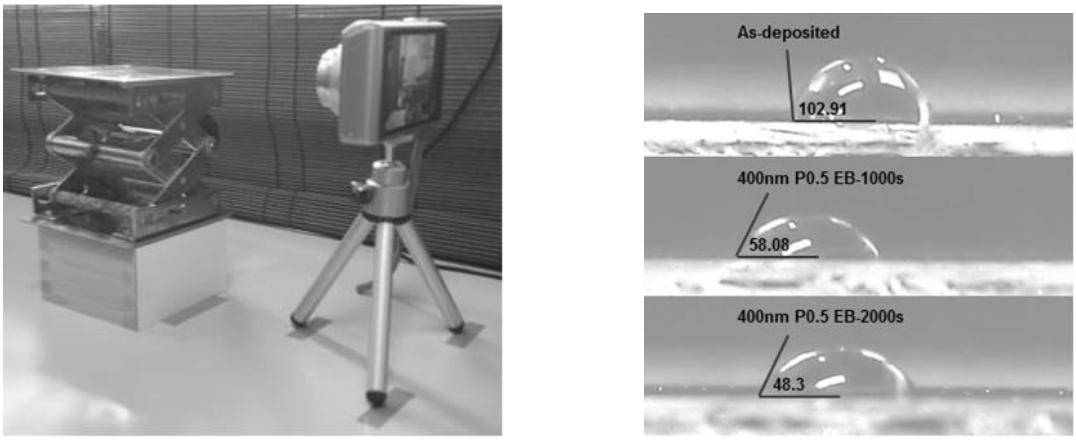

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Figure 5 Contact angle measurement setup **Figure 6** Contact angle measurement

The surface wetting by polar liquid of the Nano-columnar DLC coating shows that before EB-irradiation, it possess a more hydrophobic (poor wetting) properties with contact angle of around 103^o. Meanwhile, the contact angle decreases remarkably to around 48^o after 2000 seconds of chemical modification process, i.e. EB-irradiation, hence, hydrophilic properties. This indicates that the graphitization must have reduce the hydrophobicity property of the DLC film, i.e. increment of the sp^2 phase. Some other parameters affecting the contact angles are the sputtering pressure and also the coating thickness as shown in Fig. 6 and Fig. 7. The graphitization taken place due to the thermal effect in the sp^2/sp^3 matrix that must have transform from a more sp^3 (diamond like) into a more sp^2 (graphite like). With the higher the thermal effect during the EB-irradiation, the better the wettability; hence, the lower the contact angle, i.e. hydrophilic.

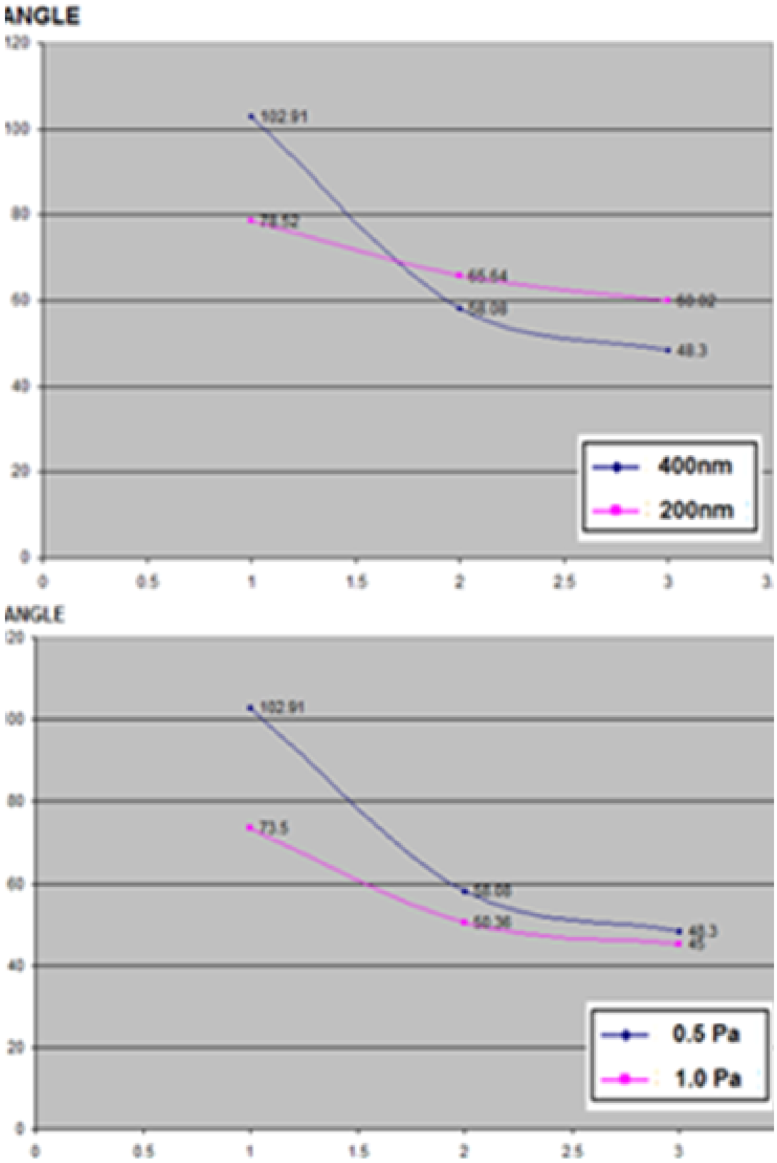

Figure 7 Graphitization effect: Film thickness and Deposition pressure.

5. Conclusion

The analysis using AFM shows that the microstructure and topography formation is highly dependent on the deposited film thickness. Formation of these films strongly related to graphitization process of amorphous carbon. It is concluded that the EB-irradiation is effective in affecting the adhesive and frictional force of the Nano-columnar DLC surface, and owing to the graphitization effect, also with the increment of the columnar size, increasing the area of contact, directly resulting to the hydrophilic properties with high surface energies. Note that the area of contact plays a very dominant role in the adhesion and frictional behavior of DLC films. The finding i.e. the ability to control the wetting properties dynamically does provides a vague application of nanocoating for various industries who might desire the product surface to be either hydrophobic or hydrophilic depending on its suitable application and desired wetting property.

Acknowledgment

First and foremost, I would like to thank God Almighty, without his blessing, this research would not have been posible. I would like to express my special appreciation and thanks to the most beloved Proessor Aizawa for his continual advice, inspriration, positive and constructive input for this research topic. I would also like to thanks Universiti Teknologi Malaysia's School of Mechanical's committee members in MRCG groups for their support especially in funding for this conference paper. Last but not least, I would like to also thanks my parents, my two kids and Miss Sharon Hii for their continuous support and believe in my work and ability.

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