The Effects of Concentration, Size, and Orientation on the Hardness of Nanoparticles Doped Diamond-Like Carbon Film

Chehung Wei, Chun-Hsien Yu

***Abstract*—The inclusion of nanoparticles in a material is a common strategy to improve mechanical properties such as Young's modulus or hardness. In most cases, the degree of improvement depends on the distribution and size of nanoparticles as well as the process condition. In order to investigate the effects of nanoparticles on the mechanical properties of a nanoparticles doped film, a nanoindentation finite element analysis is carried out. In this study, different concentration, size, and shape (spherical, elliptical) of nanoparticles were doped in diamond-like carbon (DLC) film on a silicon substrate and the mechanical property (hardness) is calculated based on a finite element analysis. The results indicate that for a given concentration, DLC doped with larger but less in quantites spherical nanoparticles has higher hardness than that in smaller but more dense counterpart. Meanwhile, large concentration of nanoparticle leads to higher hardness due to more population of nanoparticles. The orientation of elliptical nanoparticle also affects the hardness which means for non-spherical nanoparticle, the orientation is another factor that influences the hardness. The hardness enhancement mechanism for concentration, size and orientation is interpreted by the residual stress as well as projection area for particle inclusion which can be extended to other kind of inclusion.**

***Keywords*—nanoparticles, nanoindentation, finite element analysis, hardness**

I. Introduction

The advance of manufacturing process produces a variety of novel materials with high performance and light weight. Composite materials utilize the strength of inclusions, the strong interface as well as the varieties of the matrix. They have been applied in many fields such as microelectronics, biotechnology and aerospace industry. Among the various composites, nano-composites employ the strength of nanoparticles to improve material properties e.g. anti-corrosion, Young's modulus for epoxy coating containing SiO_2, Zn and Fe_2O_3 nanoparticles [1], hardness for ZnO/PMMA [2], hardness and fracture toughness for SiC/Si_3N_4 [3], and tensile strength, hardness for TiB_2/Cu [4].

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The inclusion of nanoparticles improves the material properties via cavity-filling [5], crack bridging or bowing [6] and defect reduction [7]. All these mechanisms depend on the microstructure which is sensitive to process parameters. As for mechanical property like hardness, the nanoparticles can affect the overall hardness in many ways such as concentration, size and orentation. In this study, we explore the role of the nanoparticles on the overall hardness via a nanoindentation finite element analysis. We try to investigate the mechanisms to explain all the hardness enhancement phenomena.

II. Hardness Modeling by Nanoindentation Finite Element Analysis

Indentation has been an effective tool to measure the hardness and elastic modulus of a material in a non-destructive way. Nanoindentation uses continuous measurements of indentation depths and the corresponding contact area by increasing loading to measure the hardness. The elastic modulus is derived by the slope of the elastic unloading. The theory of nanoindentation is based on the contact depth h_c which is calculated from the applied load P and the contact stiffness S as follows [8]:

$$h_c = h_{max.} - \varepsilon P_{max}/S \tag{1}$$

where h_{max} is the maximum indentation depth, P_{max} is the maximum applied load and ε is a geometry correction factor and for Berkovich indenter ε = 0.75. The projected area A_c of the actual contact area is a function of h_c and for a perfect Berkovich indenter, is given by

$$A_c = 24.56\, h_c^2 . \tag{2}$$

Hardness is the mean pressure under load supported by a material. In a nanoindentation experiment, it is calculated by dividing the applied load F with the contact area A_c as follows:

$$H = F/A_c. \tag{3}$$

The correctness of the hardness relies on the accuracy of the contact area under load. In a finite element analysis, contact area is calculated from the deformed mesh.

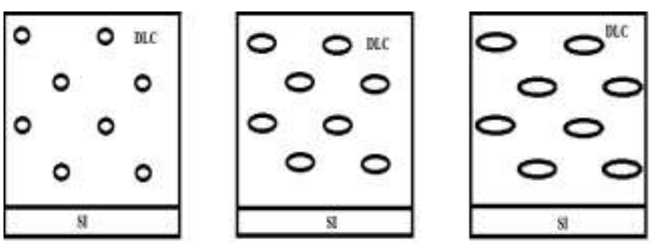
In this study, a 2D axisymmetric model is proposed. An equivalent conical indenter with a semi-apical angle of θ = 70.3 degree is used. This system has geometric and loading symmetry around the axis of the indenter. The specimen is modeled with 4-node axisymmetric quadrilateral, reduced integration, hourglass control elements (CAX4R element type). A high mesh refinement is used to model the large deformation area. The elements in the film are reduced in height to detect the behavior of the zone with greater accuracy. The total number of elements was generally 30,000 - 40,000. The finite element analysis was implemented by a commercial software ABAQUS (version 6.8.1, ABAQUS Inc., Pawtucket, RI). The ratio of thickness of the film and the substrate is 1:1000 and the film thickness is 1000 nm.

As for the material properties, the diamond tip was modeled with elastic modulus E=1140GPa and poisson ratio υ=0.07. The constitutive law is elastoplastic for DLC and is elastic for nanoparticles. The elastic constants for DLC and nanoparticles are E_{DLC}= 120 GPa, poisson ratio υ_{DLC}= 0.25 and E_{nano}= 1000 GPa, poisson ratio υ_{nano}= 0.3; respectively. As for plastic behavior, the von Mises yield criterion was used with the initial flow stress 4610 MPa. After yield, the power law hardening was employed and was expressed as follows:

$$\sigma = K\,\varepsilon^{n}, \text{ for } \varepsilon > Y/E. \qquad (4)$$

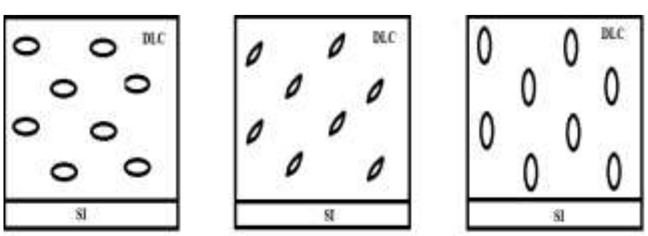
where K=120 GPa and n=0.55 for DLC.

To investigate many possible cases of nanoparticle inclusion, we vary the spherical nanoparticles into ellipsoid which is equivalent to fiber if the aspect ratio between the long axis and short axis is large. The effect of the orientation for these ellipsoidal inclusions is also studied. The distributions of different aspect ratio for long axis versus short axis with horizontally placed and different orientation ellipsoidal inclusion are shown in Fig. 1 and Fig. 2, respectively.



(a) (b) (c)

Figure 1. Different aspect ratio for long axis versus short axis for ellipsoidal inclusion (a) 1:1, (b) 2:1 (c) 4:1



(a) (b) (c)

Figure 2. Different orientation with respect to x-axis for ellipsoidal inclusion (a) 0 degree, (b) 45 degree (c) 90 degree

III. Results and Discussion

A. *Concentration, Size and Orientation Effect on Hardness*

For simplicity, a regular periodic distribution of nanoparticles is used to model the usual random distribution in nanocomposite (as shown in Fig. 1 and Fig. 2). In this case, the nanoparticles are embedded into the matrix (diamond-like carbon films) on a silicon substrate. This is similar to the CNTs inclusion in DLC [9]. The effects of concentration are carried out for 0.17%, 0.34% and 0.68% volume fraction of spherical inclusion, respectively. The percentage means the volume fraction of the inclusion with respect to the film. The nanoindentation hardness for different volume fraction is shown in Fig. 3. The order of the overall hardness is proportional the volume fraction which is consistent with Balog et. al [3] for SiC/Si_3N_4 composite where the micro/nano hardness are increasing with increasing SiC content. The hardness increase mechanism is attributed to the inclusion of hard nanoparticles and the degree of hardness increment is correlated with the volume fraction. The effects of different aspect ratio and different orientation of ellipsoidal particles under volume fraction 0.17% is shown in Fig. 4 and Fig. 5, respectively. In Fig. 4, the horizontally displaced ellipsoidal particles have long axis 20 nm, 40 nm, 80 nm and short axis 20 nm. The order of the hardness is 80 nm > 40 nm > 20 nm for volume fraction 0.17%. On the other hand, the effect of orientation of the ellipsoidal particles for same volume fraction (0.17%) is shown in Fig. 4 and the horizontally displaced ellipsoidal particles has the highest hardness while the vertically placed ellipsoidal particles has the smallest hardness. The mechanisms for the hardness enhancement are explained by residual stress and projection area of the inclusions.

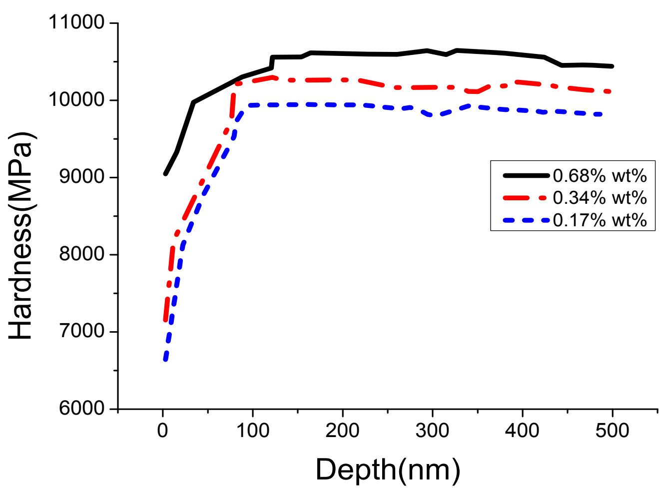


Figure 3. The concentration effect on the hardness variation

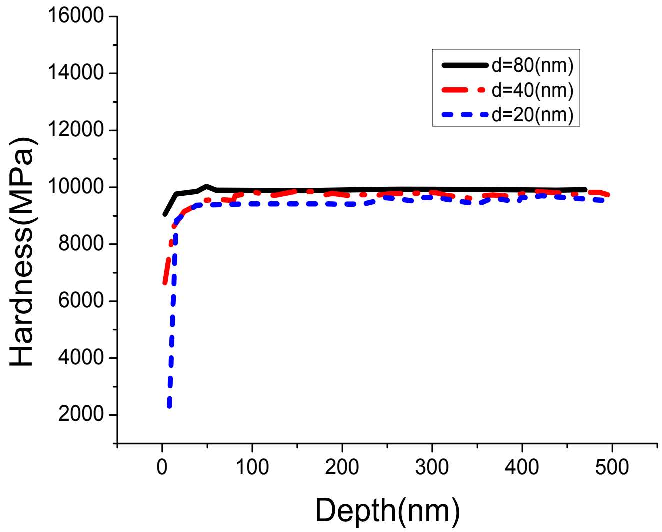


Figure 4. The size effect on the hardness variation

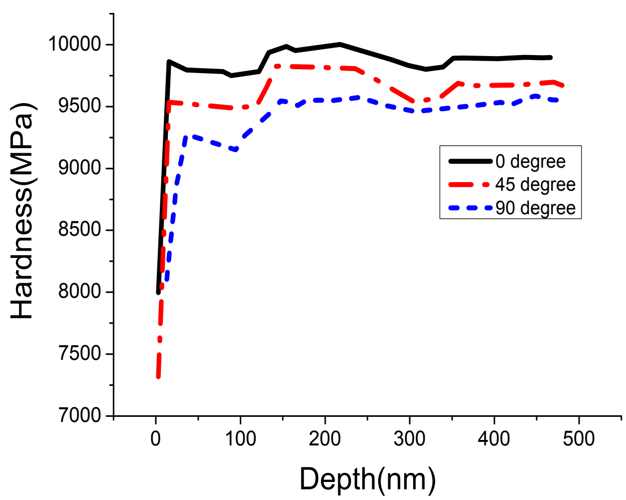


Figure 5. The orientation effect on the hardness variation

B. *Hardness Enhancement Mechanism: Residual Stress*

Many mechanisms have been proposed to interpret the hardness variation such as residual stress, interface strength or defects. For reidual stress, Suresh and Giannakopoulos has suggested that internal stress has no effect on hardness for bi-axially stressed thin film and viewed hardness as an invariant that can be used to measure the stress [9]. However, Wei and Yang found that hardness is affected by the residual stress when the diamond-like carbon films deposited on rough substrate or doped with carbon nanotubes [10,11]. The discrepancy among these cases might be the stress state is different. For nanoparticles doped DLC, the stress state is not biaxial and the residual stress might affect the hardness. In a 2D analysis, the difference in normal stress is negligible due to the continuity condition. Therefore, only the shear stress is considered. The shear stress is taken from the element under indentation where the stress is maximum. The stress variation during indentation for different concentration, size and orientation is shown in Fig. 6, Fig. 7 and Fig. 8, respectively. In all cases, the maximum hardness (0.68%, 80nm, 0 degree) occurred where the shear stress is maximum. Also, the least shear stress belongs to the least hardness (0.17%, 20nm, 90 degree). This indicates shear stress has certain effect on the hardness enhancement. However, this effect does not seem to be linear and other mechanism might be critical as well.

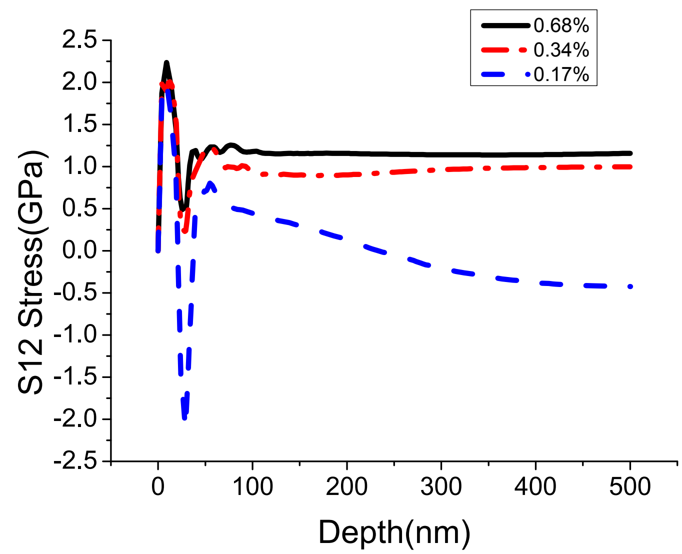


Figure 6. Shear stress variation for different concentration

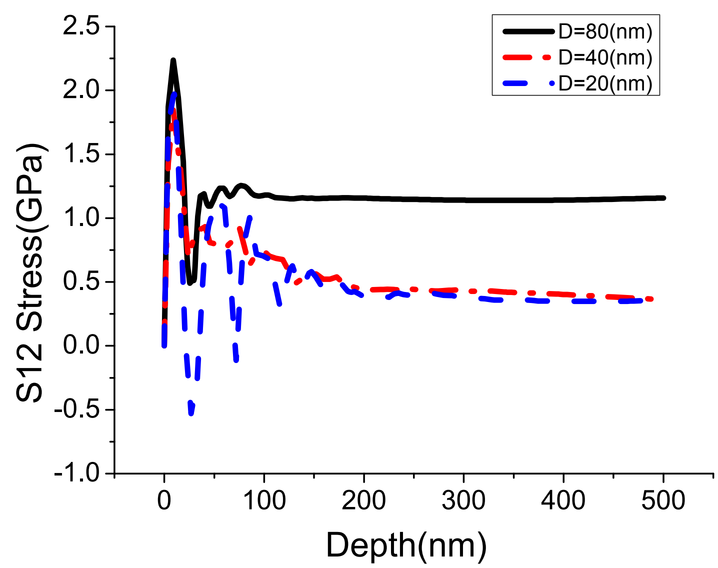


Figure 7. Shear stress variation for different inclusion size

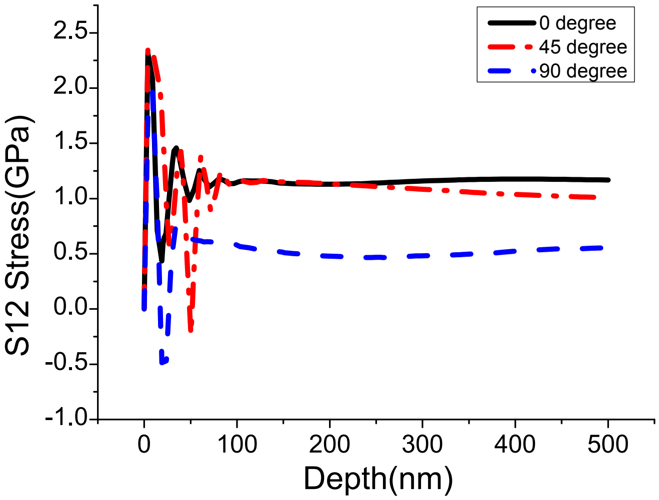


Figure 8. Shear stress variation for different orientation

C. *Hardness Enhancement Mechanism: Projected Area*

Apart from residual stress, the hard inclusion itself might affect the hardness. From mechanics point of view, the hardness is calculated by the applied loading over the deformed area as shown in (3). Therefore, the hard inclusions like nanoparticles increase the hardness by supporting the load with stiff projection area (the area projected on the loading direction as shown in Fig. 9). Therefore, the nanocomposite with the highest projection area accounts for the highest hardness. High volume fraction (0.68%), horizontally displaced (0 degree) and larger long axis (80 nm) all has the maximum projection area in each group and they should have the highest hardness. To confirm this observation, we compare the average hardness of the continuous indentation with the overall projection area for different concentration, size and orientation and the results are shown in Figs. 10-12. The linear correlation indicates that the contribution of projection area of the inclusions is linear. Therefore, high concentration, big diameter and horizontal orientation tend to have higher hardness due to the bigger projection area. This offers an explanation how the volume fraction, size and orientation affect the hardness. However, the overall hardness might be affected by the combination of residual stress and inclusion placement.

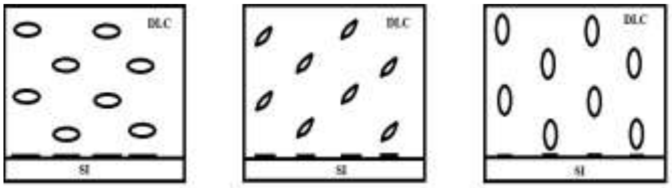


Figure 9. The schematics of projected area for different orientation

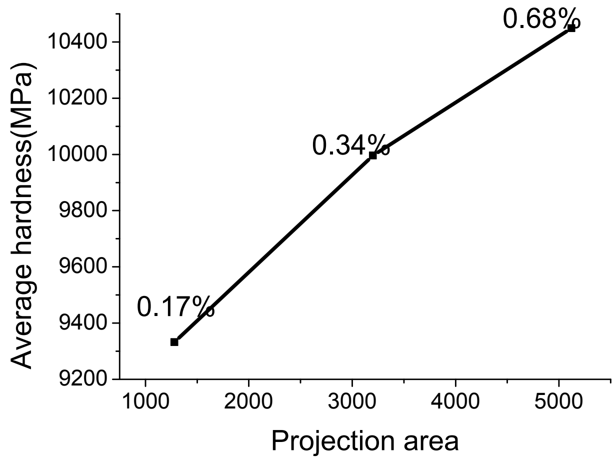


Figure 10. Average hardness versus projected area for different concentration

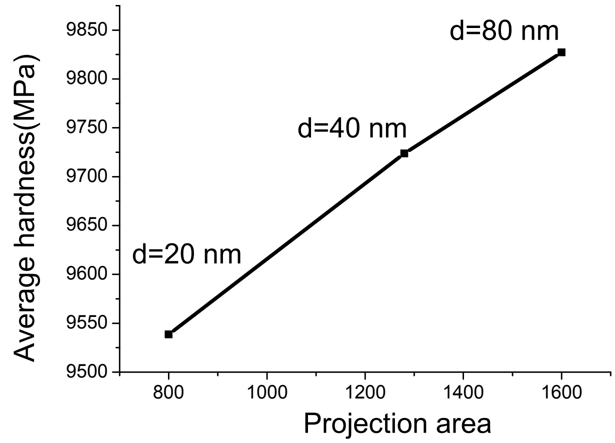


Figure 11. Average hardness versus projected area for different inclusion size

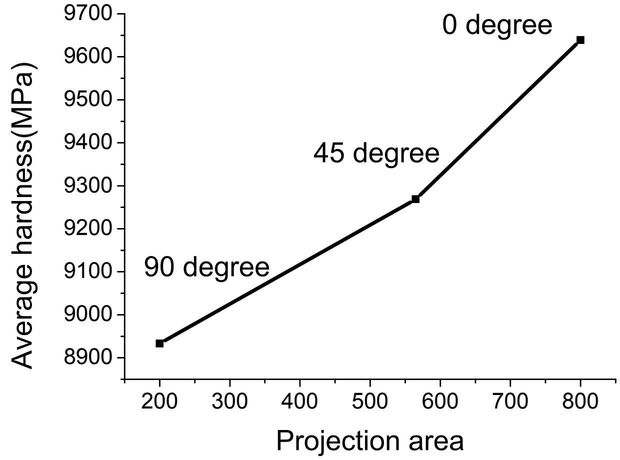


Figure 12. Average hardness versus projected area for different orientation

IV. Summary

The hardness of the nanoparticles doped diamond-like carbon films is carried out by a finite element analysis. The effects of volume fraction, size and orientation are investigated for different application. The results show high volume fraction, large aspect ratio and horizontally displaced inclusion has higher hardness. These phenomena are explained by residual stress and projection area of the inclusion and the results can be extended to other shape of inclusion.

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High volume fraction, large aspect ratio and horizontally displaced inclusion has higher hardness. The hardness enhancement mechanisms are residual stress and projection area of inclusion.