

# Effect of acetylene content in working gas on microstructure and thermal stability of DLC coating

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**Abstract:** The DLC coatings were deposited onto the surface of 304 stainless steel by using PE-CVD method and Ar+C<sub>2</sub>H<sub>2</sub> as working gas. The effects of the methane content in the working gas on the structure, hardness, thermal stability of the coating were analyzed by means of SEM, FTIR, Raman and nano-indenter. It is found that controlling methane content in the work gas can be used as an effective means to modulate the structure and performance of the DLC coating. With reducing methane content in the gas mixture, the surface sputtering effect by Ar<sup>+</sup> is enhanced, which leads a drop of hydrogen content in the coating. A high sp<sup>3</sup>C-C content in the DLC coating can be obtained by selecting an appropriate methane flow, which derives a combination of high hardness and good thermal stability for the coating.

## 1 Introduction

DLC films have great application potential in mechanical, electronic, optical, even aerospace, biomedical and other fields because of their versatile property [1-4]. DLC films can be divided into two types: with hydrogen and without hydrogen. DLC films prepared from acetylene and other hydrocarbon gases often contain a large number of hydrogen elements. In addition to the sp<sup>3</sup>, sp<sup>2</sup> and a small amount of sp<sup>1</sup> C-C hybrid bonds, hydrogen can also be combined to form various hydrogenated C-H hybrid bonds [5]. The hydrogen content will affect the optical, electronic and mechanical properties of DLC films significantly.

There were a few study about the effects of hydrocarbon mixture gas on DLC, such as methane+hydrogen, and methane+butane argon [6,7]. However, it is not yet well known whether argon gas partly substituting for hydrocarbon gas is able to tune the performance of a DLC coating. In this paper, three DLC coatings were deposited onto the 304 stainless steel surface under the same processing condition, except for selecting a different C<sub>2</sub>H<sub>2</sub>/Ar flow ratio mixture gas, i.e., 100%, 75% and 50%. Before and after annealing, the structure and hardness of these samples were investigated.

## 2 experimental procedure

Prior to putting into the vacuum chamber, 304 stainless steel square specimens with 20×20×5 mm<sup>3</sup> were polished, ultrasonically cleaned and dried in nitrogen flow. Single crystal silicon wafer and pure aluminum foils were also

inputted to facilitate fractograph observation and DSC tests. The a-C:H coatings were prepared by using a PE-CVD technique Hauzer flexicoat850 (Netherlands) in Guangzhou Grantech Co. LTD. The preparation process is as following: firstly, the chamber was pumped to 5×10<sup>-3</sup> Pa and heated to 200°C. Secondly, high-purity argon is inlet till chamber pressure of 0.5 Pa, and then the substrate surface was etched for 90 minutes by Ar<sup>+</sup> ions with negative bias of -200 V. Thirdly, Cr/WC transition layer was deposited for 60 minutes by magnetron sputter with a power of 4 kW. After the transition layer finished, a-C:H layer was deposited in a mixture gas of C<sub>2</sub>H<sub>2</sub> and Ar under bias voltage -700V. During the a-C:H deposition, the vacuum chamber held 1 Pa, the auxiliary magnetic field current was 4A, and the deposition lasted for 90 minutes. Three working gas were chosen, i.e., Ar: C<sub>2</sub>H<sub>2</sub> flow ratio 0:100, 25:75, 50:50 respectively.

The aluminum foil coated with DLC was dissolved and immersed in 10% HCl electrolyte to peel off the DLC coating. The thermal behavior of the a-C:H coatings was measured by NETZSCH STA449 F3 differential scanning calorimeter (Germany), in which pure Ar gas with 500 sccm flow rate was used as protection, and linear temperature scanning kept 10 K / s. The 304 coating samples were isothermally annealed for 4 h in vacuum using IRLA-1200 (China), during which Ar gas protection was with 500sccm flow rate, and the pressure 5 Pa.

The a-C:H coatings were measured by LabRAM Aramis Raman spectrometer (France). The power of laser is 5 MV, the wavelength is 532 nm, and the cumulative time is 5s. Bruker VERTEX 33 infrared spectrometer (Germany) was used and the range is 400~4000cm<sup>-1</sup>. The surface nano-hardness of the coating 304 alloy samples were tested by nanoindentation

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instrument (NHTX S/N), using 5mN force and loading rate 10 mN/min. 6 points were randomly selected for each sample and the average value was calculated.

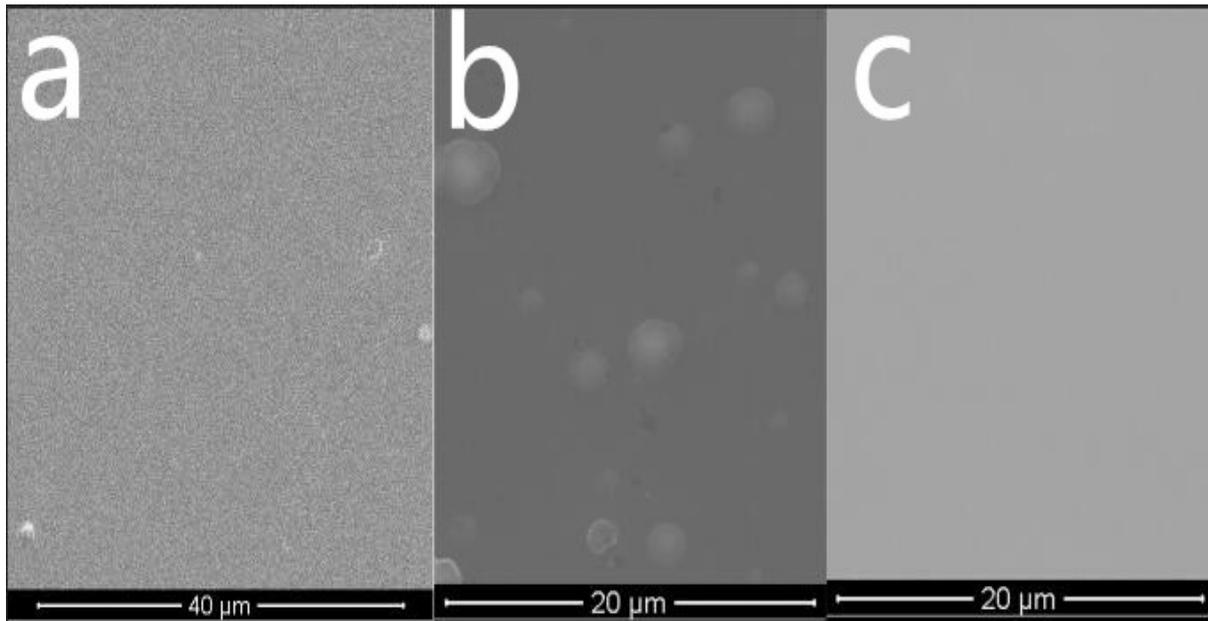
### 3 Results and discussion

#### 3.1 Surface and cross-sectional morphologies of coatings

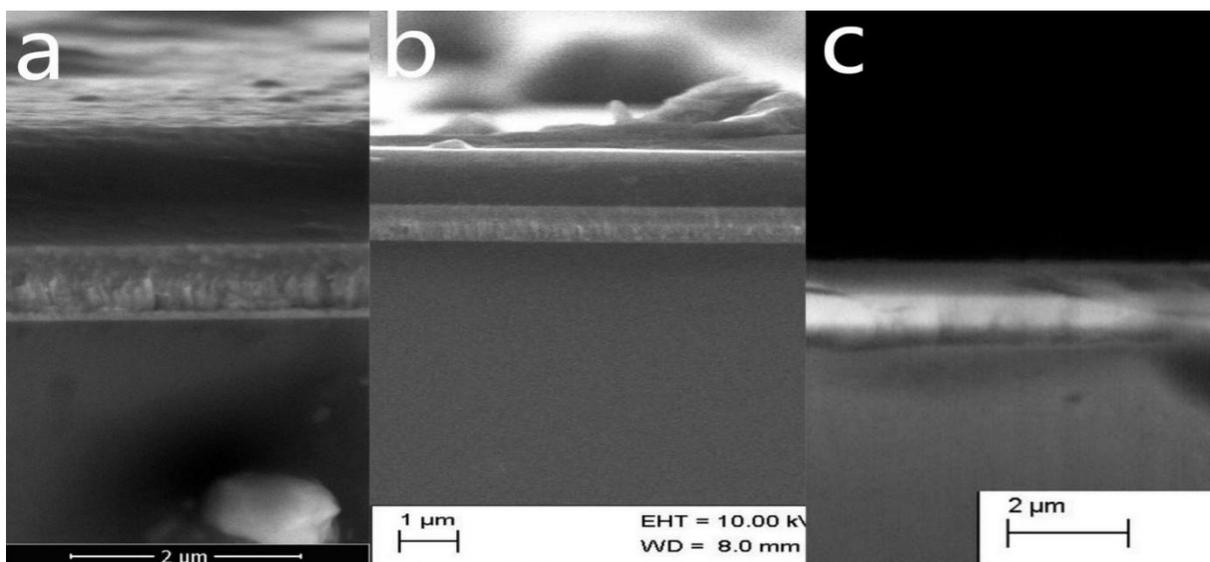
Fig.1 is the secondary electron microscopic morphology of a-C:H film deposited on stainless steel. With the

decrease of acetylene content in the working gas, the surface of the coating tends to be smoother and smoother.

Fig.2a-2c is the cross section morphology of DLC coating prepared by working gas containing 100%, 75% and 50% acetylene, respectively. The thickness of DLC surface layer in the coating is about 0.98  $\mu\text{m}$ , 0.92  $\mu\text{m}$ , 0.75  $\mu\text{m}$ , respectively. When the acetylene content in the working gas is higher than 75%, the thickness of DLC layer in the film decreases slightly, almost unchanged, but decreases significantly when the acetylene content is 50%. This is responsible for the intensifying of the  $\text{Ar}^+$  ion etching.



**Fig.1** Surface morphology of DLC coating prepared by different proportions of acetylene  
a)100%  $\text{C}_2\text{H}_2$ ; b)75%  $\text{C}_2\text{H}_2$ ; c) 50%  $\text{C}_2\text{H}_2$



**Fig.2** DLC coating cross-section morphology prepared with different proportions of acetylene  
a)100%  $\text{C}_2\text{H}_2$ ; b)75%  $\text{C}_2\text{H}_2$ ; c)50%  $\text{C}_2\text{H}_2$

#### 3.2 DSC behavior of DLC coating(Fig.3)

The hydrogen content in the DLC coatings obtained in this paper is high [8, 9, 10]. Most of the hydrogen is

present in open and closed defects in the form of H<sub>2</sub>; a small amount of H is present in the form of CH<sub>n</sub> bonds, which establish the trap defects to capture H<sub>2</sub> molecule. The mass loss in TG curve mainly comes from the effusion of those trapped gas, especially H<sub>2</sub> and probably little methane. After heated to 800 °C, the mass loss of coatings prepared by 100%, 75% and 50% acetylene was 1.8%, 0.9%, and 0.6%, respectively. As the acetylene content in the working gas is reduced, the amount of gas overflow also decreases obviously. The temperature for the intensive gas escape is inversely proportional to the acetylene content in the working gas, which is 600°C, 480°C and 400 °C, respectively for the DLCs prepared by gas with 100%, 75% and 50% acetylene.

Peaks in the DSC curves is related to the following factors: 1) heat capacity change by release of the surface-adsorbed gas; 2) heat capacity change by effusion of trapped H<sub>2</sub> in the coating; 3) the sp<sup>3</sup>C-H transforming to sp<sup>2</sup>C; 4) the sp<sup>3</sup>C-C transforming to sp<sup>2</sup>C;

5) growth and crystallization of carbon clusters. The physical meaning behind each peak in Fig.1 can be reasonably stemmed from references reported. The peak in the vicinity of 200°C comes from the heat capacity change due to overflow of those H<sub>2</sub> in the open defect. Thus the acetylene content in the working gas does not affect this peak's temperature almost. It is plausible to suggest that the inflection point of mass loss in TG curves corresponds to the temperature, at which the enclosed-type defect is unlocked to release H<sub>2</sub> gas. This temperature can be defined as the sp<sup>3</sup>C-H transforming to sp<sup>2</sup>C completely. In that the content of acetylene in the working gas may have a significant effect on the sp<sup>3</sup>C-H to sp<sup>2</sup>C, that is, inversely proportional to acetylene content, which is 600, 480 and 400 °C, respectively. Other endothermic peaks are derived from the heat capacity change caused by the closed hydrogen release and the internal structure transition of the coating.

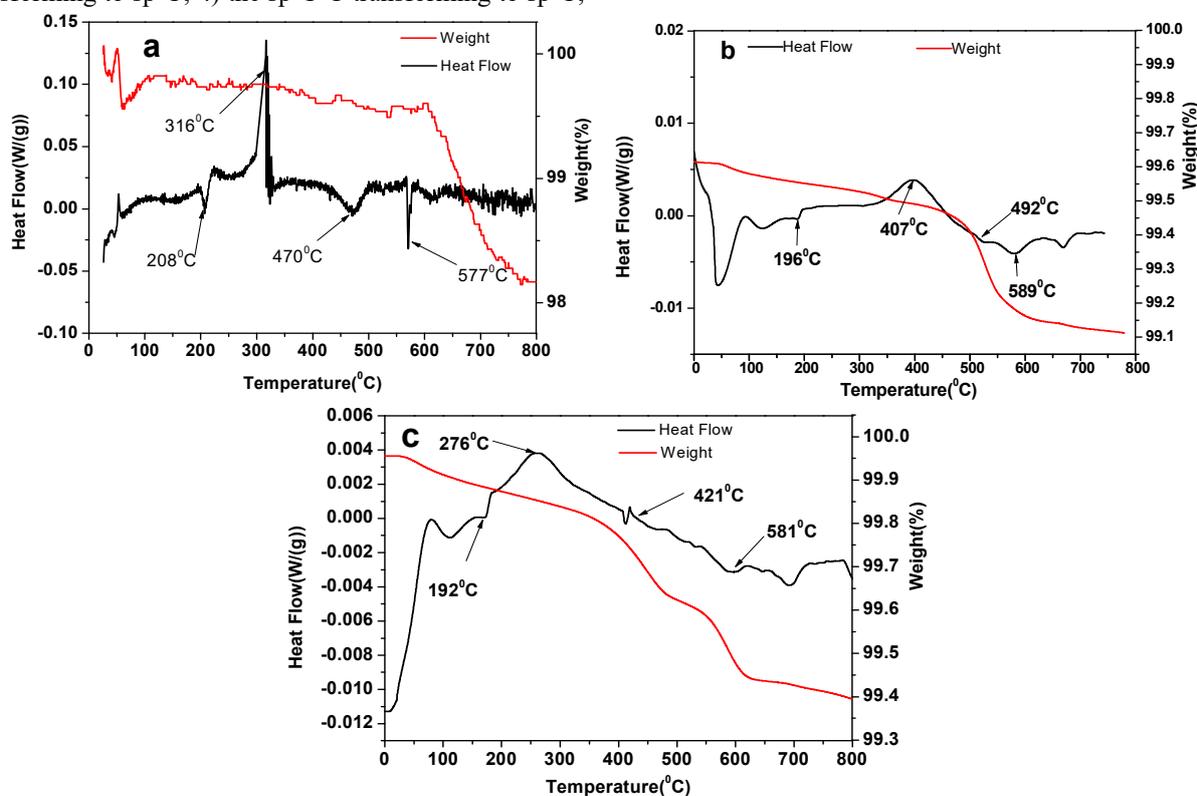
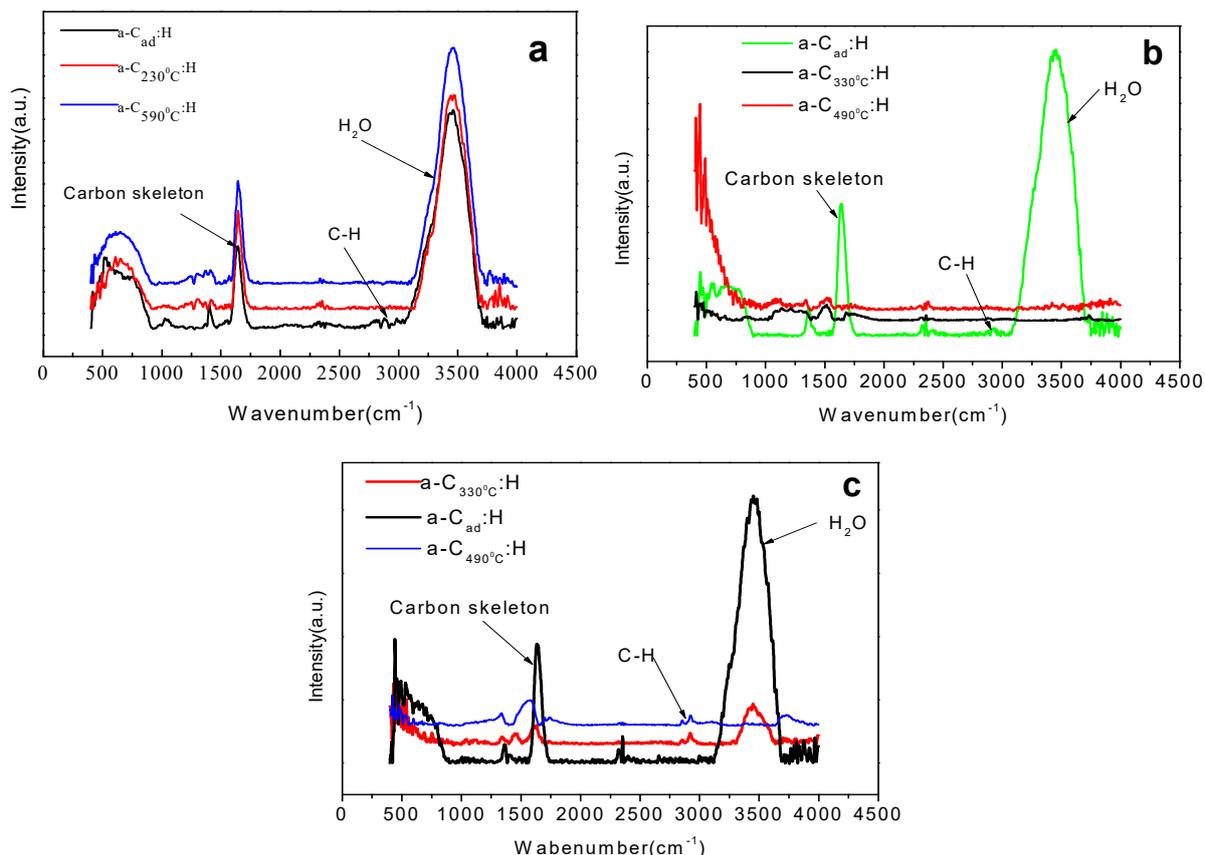


Fig.3 DSC curve of DLC coating prepared with different contents of acetylene  
 a) .100%; b).75%; c). 50%

### 3.3 Infrared Spectral of DLCs (Fig.4)

The 2800-3100 cm<sup>-1</sup> band corresponds to the stretching vibration modes of different CH<sub>n</sub> radicals. The H<sub>2</sub>O peak is around 3500cm<sup>-1</sup>. sp<sup>3</sup>-CH<sub>n</sub> is 3000 -3100 cm<sup>-1</sup>, while unsaturated aromatic sp<sup>2</sup> CH<sub>n</sub> is 2800 - 2950 cm<sup>-1</sup>. The DLCs prepared with different acetylene content contain more or less sp<sup>3</sup>CH<sub>n</sub>, but it disappears at the temperature corresponding to the inflection temperature of TG curves. It is exactly the reason why we suggest it is related to the sp<sup>3</sup>C-H transforming to sp<sup>2</sup>C completely. However, when the acetylene content of the working gas is 50%,

although sp<sup>3</sup>-CH<sub>n</sub> disappears, the unsaturated aromatic sp<sup>2</sup>CH<sub>n</sub> appears, which indicates that the hydrogen atoms obtained after the decomposition of hydrogen or water vapor in the DLC are recombined with aromatic carbon atoms to form sp<sup>2</sup>CH<sub>n</sub> bonds. The different intensity of H<sub>2</sub>O peak in the as-annealed coatings indicates that Ar content in working gas influences the capacity of the coating to absorb water vapor. This tributes to Ar<sup>+</sup> ion-etch and Ar-inclusion in the coating. It also shows that the content of acetylene in the working gas affects the stability of the structure, especially sp<sup>3</sup>-CH<sub>n</sub>.



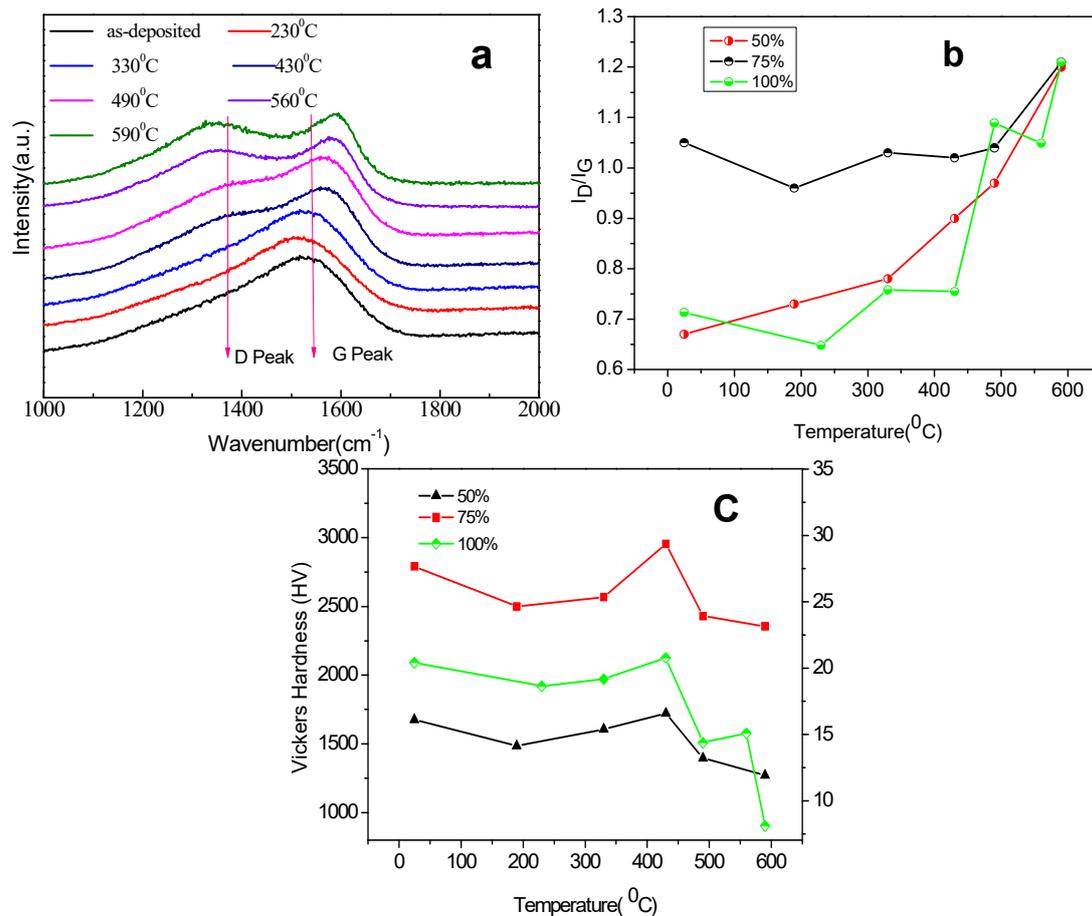
**Fig.4** IR spectrum of DLC coating prepared with different contents of acetylene  
 a) 100% ; b) 75% ; c) 50%

### 3.4 Raman spectrum and hardness of DLC Coatings

The D peak in the DLC coating comes from the disorder of the carbon atomic arrangement, the disorder of the bond angle and bond length, the carbon cluster size, the  $sp^3$  content in the coating, etc. There is an inverse relationship between the  $sp^3$  content and the  $I_D/I_G$  in the DLC coating. When the size of the cluster is more than 2 nm, there is an inverse relationship between the cluster size and the  $I_D/I_G$  ratio. According to the Raman spectrum after annealing (Fig.5a), the  $I_D/I_G$  obtained by using the double-Gaussian fitting varies with the annealing temperature (Fig.5b). The hardness of the coating changes with the annealing temperature (Fig.5c). For those as-deposited DLCs, the concentration of acetylene in the working gas influences the  $I_D/I_G$ : the  $I_D/I_G$  of the coating prepared by 50% acetylene is the lowest, while the highest one is for the coating prepared by 75% acetylene. However, the highest hardness was exhibited

in 75% acetylene-prepared DLC coatings in this experiment, whether as deposited or as annealed. This indicates that the acetylene concentration not only affects the content of hydrogen in the coating, but also affects the content of  $sp^3CH_n$  and  $sp^3C-C$  in the coating, and the size and density of the carbon cluster in the coating.

According to the above experiment, the following speculation can be reasonably proposed out. The lower is the acetylene concentration in the working gas, the lower H is trapped in the coating. One hand,  $Ar^+$  bombardment is helpful to form C-C bonds by breaking the weak  $CH_n$  bonds; Another hand,  $Ar^+$  bombardment is also conducive to produce a higher defect density in the coating, which promotes more dangling bonds and recombination with hydrogen atoms. Therefore, the  $sp^3$  bond content in the 75% acetylene-prepared coating is low, but  $sp^3C-C$  bonds dominates. For the 50% acetylene-prepared coating, there are carbon clusters with high density and large size, and  $sp^3C-H$  constitutes mainly those  $sp^3$  bonds.



**Fig.5** Raman spectra and hardness of DLCs

a) Raman spectra of 100% acetylene-prepared DLC; b) ID/IG after annealing; c) hardness after annealing

## 4 Conclusion

When the hydrogen-containing DLC coating is prepared by using the mixed working gas of Ar+C<sub>2</sub>H<sub>2</sub>, the C<sub>2</sub>H<sub>2</sub> content in the work gas can be used as an effective means to modulate the structure and properties of the DLC coating. With the increase of acetylene content, the sputter etching effect from Ar<sup>+</sup> ion is enhanced, which leads to the decrease of hydrogen content in the coating. A high sp<sup>3</sup>C-C content in the DLC coating can be obtained by selecting an appropriate methane flow, which derives a combination of high hardness and good thermal stability for the coating.

## Acknowledgement

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