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Microscopic mechanical characteristics analysis of ultranano-crystalline diamond films

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Abstract: The microscopic mechanical characteristics of ultranano-crystalline diamond films which were prepared in four different atmospheres were investigated for the applications in microelectron-mechanical system (MEMS). The loading−unloading curves and the change of modulus and hardness of samples along with depth were achieved through nanoindenter. The results show that the films which are made in atmosphere without Ar have the highest recovery of elasticity, hardness (72.9 GPa) and elastic modulus (693.7 GPa) among the samples. Meanwhile, samples fabricated at a low Ar content have higher hardness and modulus. All the results above demonstrate that atmosphere without Ar or low Ar content leads to better mechanical properties of nanodiamond films that are the candidates for applications in MEMS.

Key words: ultranano-crystalline diamond film; nanoindentation; mechanical properties; microelectron-mechanical system (MEMS)

1 Introduction

Due to its excellent mechanical properties, exceptional chemical inertness, outstanding thermal stability and superior tribological performance, ultranano-crystalline diamond (UNCD) film is a reliable ideal material for the microelectron-mechanical system (MEMS), aerospace, electronics and optical applications [1−6]. Most strikingly, the grain size of UNCD will not change with the thickness of the films. It may be the substitution material of Si and TiN. On the other hand, UNCD is a promising material for field emission owing to low electron affinity. Good chemical inertness, hydrophobicity and electrochemical sensitivity make it suitable for electrochemistry applications. However, there are some new requirements of mechanical properties test and failure mechanism of the materials because of the characteristics and service conditions of MEMS components. So, the research for mechanical properties of ultranano-crystalline diamond films is quite necessary.

The traditional test equipments are not suitable for such a small volume of thin-film materials whose testing range is required at micrometer or nanometer level [7]. For this reason, a more advanced testing method is used. Since OLIVER and PHARR [7,8] firstly put the concept of nanoindentation in 1992, it has gained an increasing popularity for the measure of a variety of mechanical properties, such as hardness and elasticity modulus with the help of the sensitive relationship between indentation and load as well as pressed depth. Most importantly, one can get the mechanical properties without imaging the hardness impression. The nanoscale pressure head displacement and force make test scope within the elastic limit of thin-film materials. Thereby, the blur and fracture of indentation edge are avoided and the validity, reliability and repeatability of tests can be assured. Many mechanical properties can be tested without separating films and substrate materials.

In this work, four ultranano-crystalline diamond films which are smooth, dense and uniform were deposited on silicon substrate in different atmospheres by hot filament chemical vapor deposition (HFCVD). The

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microscopic mechanical properties of these films were analyzed through nanoindentation to verify the application of ultranano-crystalline diamond films to MEMS.

2 Experimental

2.1 Preparation of ultranano-crystalline diamond films

The ultranano-crystalline diamond films were synthesized by HFCVD in a multifunctional vapor deposition system which is specially designed for diamond deposition. P-type (100) monocrystalline silicon discs with a diameter of 50 mm were used as the substrate. The Si substrates were mirror polished, and then ultrasonically cleaned in acetone, ethanol and nano-diamond powder suspension for 5, 5 and 30 min, respectively, and then rinsed by distilled water. Four kinds of deposition atmospheres were used. The proportions of ingredients and deposition time and the atmosphere pressure are shown in Table 1. The temperature of substrate was between 850 and 950 °C. During depositing, a 30 V DC negative bias was applied between hot filament and substrate.

Table 1 Detail parameters used in experiment

Film No.	Composition and proportion	Deposition time/h	Atmosphere pressure/kPa
A	During nucleation: $V(H_2):V(CH_4)$=100:3	1	2.5−3
	During growth: $V(H_2):V(CH_4)$=100:6	3.5	1−1.5
B	$V(H_2):V(Ar):V(CH_4)$= 16:80:4	12	1−1.5
C	$V(H_2):V(Ar):V(CH_4)$= 46:50:4	4.5	1−1.5
D	$V(H_2):V(Ar):V(CH_4)$= 76:20:4	4.5	1−1.5

2.2 Materials characterization

Raman spectroscopy was used to characterize the quality of as-deposited films. The device model is the Almega XR laser Raman spectrometer of the Thermo Nicolet Corporation and its wavelength is 532 nm. Atomic force microscopy (AFM) was applied to characterizing the micromorphology of diamond films. The MTS Nano Indenter DCM test and diamond Berkovich indenter were used in the experiment. Load resolution was 1 nN and the displacement resolution was 0.2 nm. Continuous values of changes of hardness and modulus with pressed depth were adopted. The constant strain rate was 0.05 s^{-1} and the thermal drift rate was less than 0.05 nm/s by controlling parameter. Basic fixed indentation depth was 1 μm. Five points were measured with a 10 μm interval in each sample. A load−displacement curve can be drawn during the testing process of each point.

3 Results and discussion

3.1 Effect of Ar content on morphology and Raman spectra of diamond films

Figure 1 shows the Raman spectra of diamond films deposited at different Ar contents. When the content of Ar was 0, which was the gases mixture of depositing the micro-crystalline diamond (MCD) films by HFCVD, the spectrum had typical 1332 cm^{-1} peak of diamond band. When the content of Ar was 20%, the spectrum was different from the spectrum of the conventional diamond film. As the Ar content in the reactant gas was increased, carbon peaks around 1350 cm^{-1} and 1580 cm^{-1}, which were assigned to D and G bands, were significantly broadened. And an extra broad band near 1140 cm^{-1} appeared, which indicates the presence of nano-crystalline [9−12]. Broadening of the diamond band was the result of the nano-grain size, Raman scattering in the region of 1400−1600 cm^{-1} was attributed to sp^2-bonded carbon existing between the nano-crystalline diamond [13]. It is noted that the spectra had an extra Raman shift at approximately 1140 cm^{-1} compared with conventional diamond spectrum. Raman scattering is far more (nearly 50 times) sensitive to amorphous carbon and graphite phase than to diamond at the applied laser wavelength, hence the diamond component dominated in the films [14].

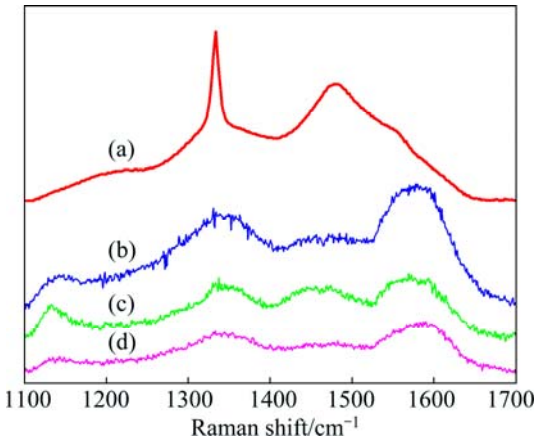

Fig. 1 Raman spectra of diamond films under different Ar contents by HFCVD: (a) Without Ar; (b) 20% Ar; (c) 50% Ar; (d) 80% Ar

The AFM images of diamond films are presented in Fig. 2. When the Ar content was 0, and the pressure was 1.5 kPa, the diamond grains were very large; but with increasing content of Ar, the diamond grains became small. It could be clearly seen that when the Ar content was increased to 80%, the surface of diamond films was

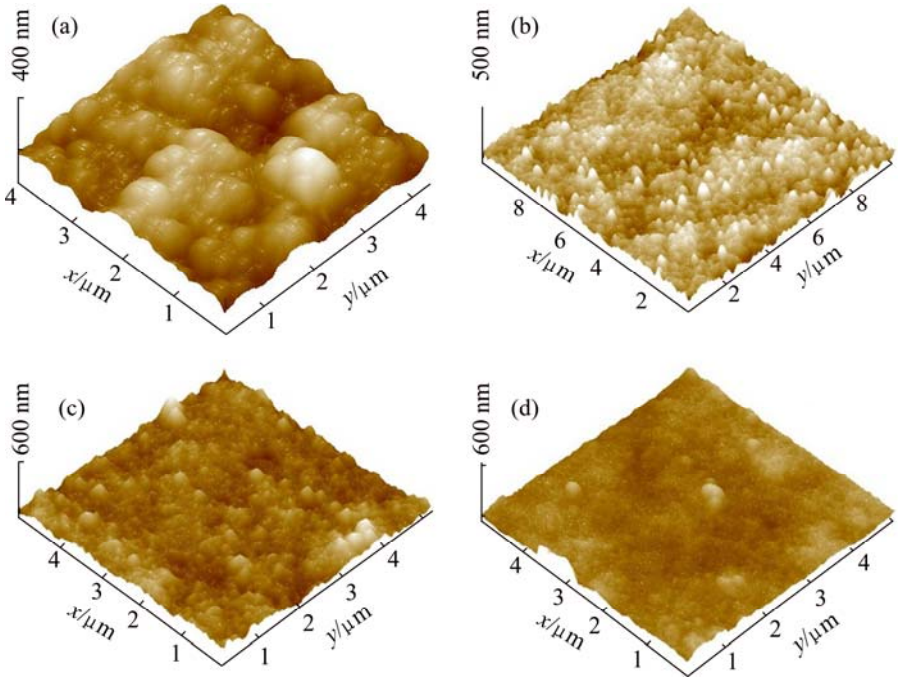

Fig. 2 AFM images of NCD films with different Ar contents: (a) Without Ar; (b) 20% Ar; (c) 50% Ar; (d) 80% Ar

the smoothest, and the grains size was the finest. The surface roughness (R_a) of diamond film deposited with without Ar in a 5 μm × 5 μm area was about 50 nm. While when the Ar contents were 20%, 50% and 80% and the pressure was 1.5 kPa, the R_a values were 28, 17.5 and 10.1 nm, respectively. This can be attributed to the fact that Ar can improve the re-nucleation of diamond films, thus finer grain size and smoother surfaces were obtained. This result was also corresponding to the Raman spectra above and was also confirmed by other researches [15].

3.2 Nano-properties

The corresponding loading−unloading curves of four samples at the same pressed depth are shown in Fig. 3. The residual pressed depths of Samples A and B, which were made in atmosphere without Ar or with lower Ar content, are significantly lower than those of the Samples C and D which were made with higher Ar content, which implies that the films of Samples A and Sample B have better elastic recovery ability.

The curves of four samples whose hardness and modulus change with pressed depth are shown in Fig. 4. Five points were tested in each sample with the same pressed depth. The hardness and modulus of silicon substrate are very steady, which is equal to 12.5 GPa and 180 GPa, respectively. Hardness and modulus of Samples A and B are higher than those of the silicon substrate. Additionally, hardness and modulus of Sample D are similar to those of the substrate, and the same properties of Sample C are a little higher than those of

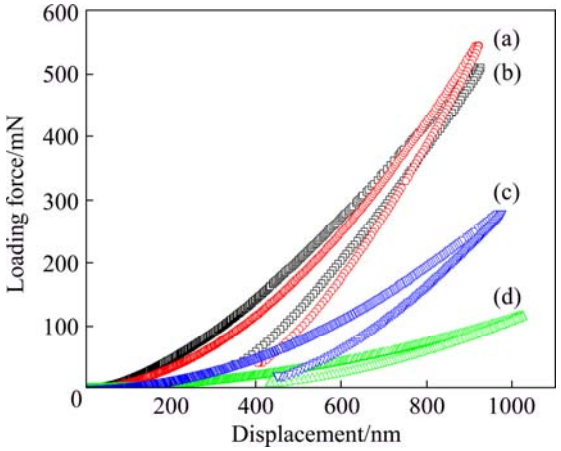

Fig. 3 Loading−unloading curves of four samples: (a) Without Ar; (b) 20% Ar; (c) 50% Ar; (d) 80% Ar

the substrate. The hardness and modulus of Samples C and D grow slightly as pressed depth increases, while the same properties of Sample A lessen as the pressed depth increases. Additionally, hardness and modulus of Sample B keep steady. It suggests that the silicon substrate has a slight effect on Samples C and D while the same effect on Sample B is the smallest. And the effect of silicon substrate on Sample A is the most serious among the four samples. The substrate begins to deform when the pressed depth increases to a certain degree. The measured results should be the composite hardness and modulus of the thin film−substrate system. The test results gradually approach the properties of substrate because the effect of substrate becomes more obvious as the pressed depth increases.

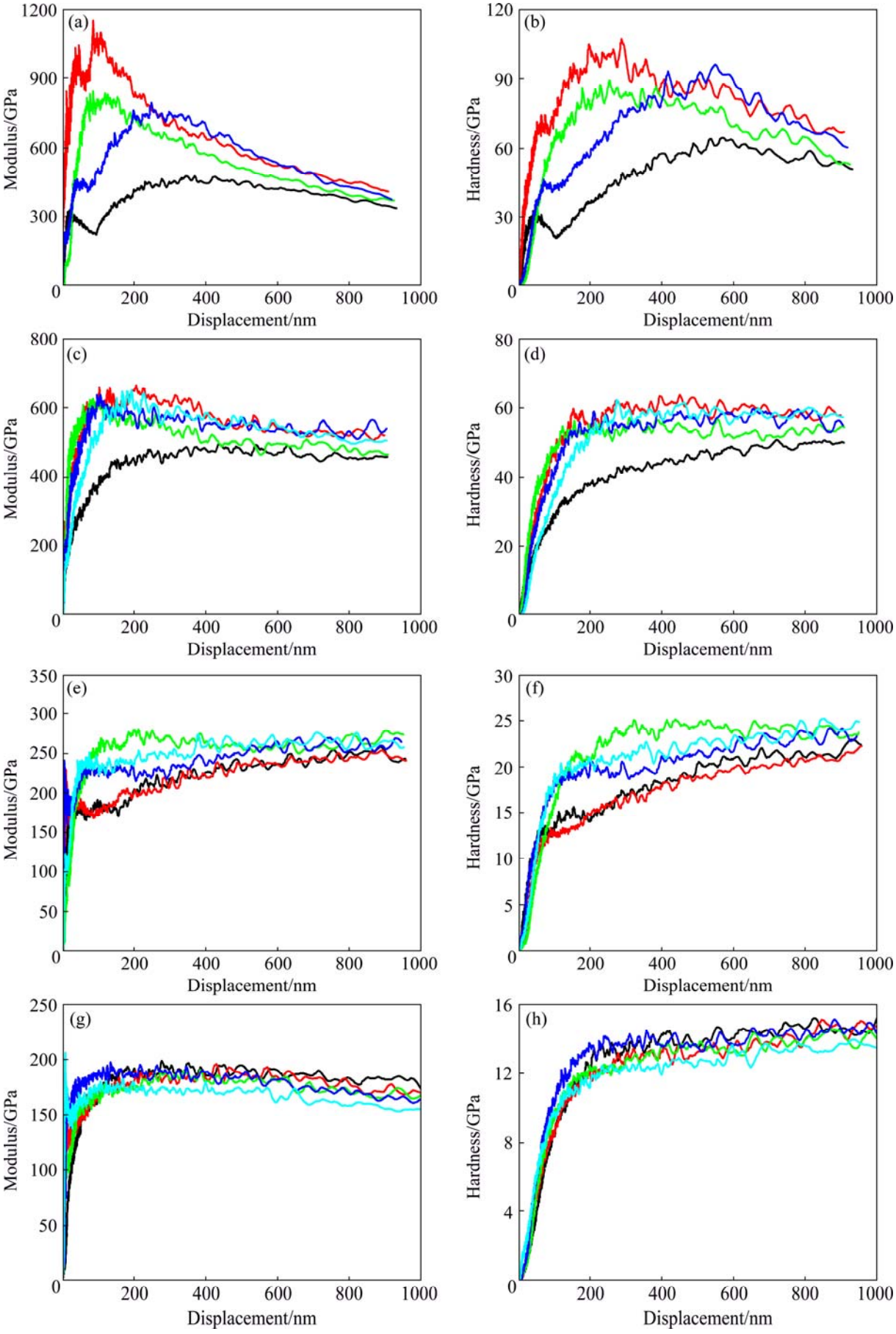

Fig. 4 Change of modulus and hardness along with depth: (a,b) Without Ar; (c,d) 20% Ar; (e,f) 50% Ar; (g,h) 80% Ar

Table 2 Modulus and hardness of as-deposited diamond films

Testing No.	Sample A		Sample B		Sample C		Sample D	
	Modulus/ GPa	Hardness/ GPa	Modulus/ GPa	Hardness/ GPa	Modulus/ GPa	Hardness/ GPa	Modulus/ GPa	Hardness/ GPa
1	475.8	64.4	465.5	48.7	222.3	17.5	191.6	12.6
2	828.3	81.7	650.1	56.7	206.2	18.4	188.9	14.5
3	713.9	85.0	584.2	55.4	277.8	25.1	177.2	13.8
4	744.4	67.0	577.4	58.0	230.7	23.1	187.9	12.1
5	706.4	66.6	647.1	56.8	252.7	22.5	170.7	11.9
Mean	693.8	72.9	584.9	55.1	237.9	21.3	183.3	13.0
Standard deviation	131.1	9.6	74.8	8.1	27.9	3.2	8.9	1.1
COV/%	18.9	13.2	12.8	6.7	11.7	15.2	4.9	8.7

The film thicknesses of Samples A, B, C and D were estimated as 7, 20, 9 and 10 μm by deposition time and rate, respectively. It can be regarded that the silicon substrate of Sample B, which has the thickest film, has no effect on the test results. But the hardness and modulus of Samples C and D are close to those of the silicon substrate, and substrate effect gives rise to the rise of testing results. With higher hardness and modulus than those of silicon substrate, the testing result of Sample A declines because of substrate effect.

Surface roughness and curvature of pressure needle tip have effect on nanoidentation test results. Thereby, the properties of samples cannot be well reflected by experimental data when the pressed depth is less than 100 nm. The effect of substrate on mechanical properties of films is not obvious when pressed depth is about 1/10 of the film depth. The hardness and modulus of ultrananо-crystalline diamond films can be approximately gotten from hardness curves and modulus curves when the pressed depth is 200 to 300 nm. The results are shown in Table 2.

The hardness and modulus of Samples C and D are inferior to those of Samples A and B, while hardness and modulus of Sample D are less than those of Sample C. It means that the atmosphere has effects on the mechanical properties. A higher Ar content brings lower hardness and modulus of sample. At the same time, the hardness and modulus of Sample B are inferior to those of Sample A. It can be achieved that Ar content has stronger effect than methane content on mechanical properties.

Ar atmosphere helps grain refinement, and high amorphous phases combined by sp^2 bonds have been brought out. At the same time, the diamond will be purer with lower methane content. The content of sp^3 bonds will be more as well. The microscopic mechanical properties of films are determined by the contents of sp^2 and sp^3 bonds.

From Fig. 4, it can be gotten that the hardness and modulus of elasticity have discreteness. The reason is that the thickness and homogeneity of film quality are inconsistent. Meanwhile, the structural imperfection of films will cause the differences of test results. But the microscopic mechanical properties variation trend of ultrananо-crystalline diamond films, which are prepared in different atmospheres, can be reflected by test data in general.

4 Conclusions

1) The ultrananо-crystalline diamond films made in atmosphere without Ar have better elastic recovery ability.

2) The hardness and modulus of ultrananо-crystalline diamond films which were made in atmosphere with Ar are relatively low, and lessen as the content of argon increases.

3) The hardness and modulus of ultrananо-crystalline diamond films which were made in atmosphere without Ar are relatively high, but the diamond grains are very large, and the hardness and modulus of elasticity have more discreteness.

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超纳米金刚石薄膜的显微力学性能表征

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摘 要：研究 4 种不同气氛下制备的可应用于 MEMS 方面的超纳米金刚石薄膜的显微力学特征。利用纳米压痕技术得到样品的加载−卸载曲线及硬度和弹性模量随压入深度的变化关系。结果表明，无 Ar 条件下制备的薄膜具有最好的弹性回复能力、最高的硬度(72.9 GPa)和弹性模量(693.7 GPa)。同时低 Ar 含量更有利于提高薄膜的硬度和弹性模量。以上结果说明无 Ar 或低 Ar 含量更有利于提高纳米金刚石薄膜的力学性能，以更好地应用于 MEMS 方面。

关键词：超纳米金刚石薄膜；纳米压痕；力学性能；微机电系统(MEMS)

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