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Influence of seeding pre-treatments on mechanical properties of ultrananocrystalline diamond films on silicon and Si_3N_4 substrates

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ABSTRACT

Ultrananocrystalline diamond (UNCD) films on silicon and Si_3N_4 substrate were prepared by microwave plasma chemistry vapor deposition method using argon-rich $CH_4/H_2/Ar$ plasmas. The influence of the nucleation density on the development of morphology of UNCD films and their mechanical properties has been investigated by varying pretreatments. Their morphology and topography have been characterized by scanning electron microscopy and surface profilometer. The influences of pretreatments on mechanical properties of the deposited UNCD films are investigated by using nano-indentation and nano-scratch tests. It was found that grain size, hardness, and elastic modulus are less dependent on nucleation density change, which is caused by different pretreatments. Changes in grain size are more dependent on deposition temperature and plasma atmosphere. As compared to the nucleation density pretreated by the suspension of diamond (0.25 μm) powder mixed with nano-diamond (3–5 nm), nucleation density is obviously enhanced by pretreatments with W powder (0.25 μm) or Ti powder (0.25 μm) mixed with nano-diamond (3–5 nm). It was also observed that there is no difference in nanohardness and elastic modulus with different substrates (Si and Si_3N_4 substrates). But the UNCD's adhesion on Si_3N_4 substrate is obviously higher than that on Si substrate. The determined hardness was about 54–58 GPa for all samples under investigation, the elastic modulus 542–667 GPa, and the elastic recovery 74–81%. The scratch tests proved a strong adhesion of the UNCD coatings and their protective effect on silicon substrates and Si_3N_4 substrates. Detailed experimental results and mechanisms for UNCD film deposition in argon-rich plasma are discussed.

1. Introduction

The deposition, characterization, and application of UNCD (ultrananocrystalline diamond) films have been extensively studied in the past few years [1,2], due to the excellent combinations of the chemical and physical properties of the UNCD films including the excellent corrosion resistance, good chemical inertness, high hardness, very smooth surface, and excellent mechanical properties [3,4], such as high Young's modulus, fracture toughness, and low friction coefficient [5,6]. The nucleation phase of the deposition process is a key period of the UNCD film development to the property optimization. Therefore, some researches about the enhancement of nucleation density have been reported recently. To achieve the compact and smooth film, a lot of pretreatments were also conducted, for example, Mo transition layer, W transition layer, Ti transition layer, Ti powder with various grain size suspension, scratch on the substrate, and some other methods [3,7–18]. The adhesion of diamond on several substrates, including Si, cemented carbides and Si_3N_4, has also been investigated [19–23]. As reported [24–27], UNCD films are a candidate for being applied in tribology and biomedicine, own its predominate properties which might be impacted by pretreatments. Therefore, it is very important to know the effect of various pre-treatments to mechanical properties, particularly in the interface adhesion. However, the comparison analysis of mechanical properties, particularly in the aspect of the adhesion, for the various pretreatments was, in fact, really rare.

In this paper we report the influence of various seeding pretreatments on UNCD film mechanical properties. Morphology and structure of these films were investigated by XRD, Raman spectroscopy and scanning electron microscopy; mechanical and tribological properties were evaluated by nano-indentation and nano-scratch tests.

Table 1
Deposition parameters for preparation of UNCD films.

Ar/sccm	H_2/sccm	CH_4/sccm	Pressure/kPa	Time/h	Power/kW
88.5	10	1.5	11.8	1.5/8	1

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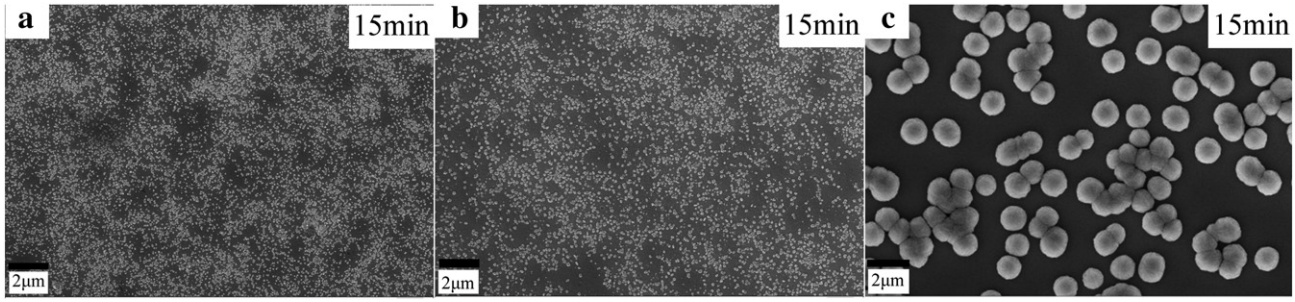

Fig. 1. FESEM photographs of silicon-based UNCD films deposited with different pre-treatments: a) pre-treated by Ti + ND; b) pre-treated by W + ND; and c) pre-treated by Dia + ND.

2. Experimental details

2.1. Preparation of UNCD films

One-side-polished single crystal Si (100) wafers and sintered Si_3N_4 were used as substrates for UNCD film deposition. Smooth UNCD films were deposited on the substrate in a commercial 5 kW microwave plasma-assisted chemical vapor deposition (MWPACVD) apparatus using Ar-rich $Ar/H_2/CH_4$ gas mixture (Model: MPG-2050C, Chengdu Newman-Hueray Microwave Tech.). Prior to UNCD deposition, Si (100) substrates were thoroughly degreased by sonicating in acetone and methanol, each for 10 min; afterward they were subjected to 2 min surface etching in a 40% HF solution to remove the native oxide layer. Then the substrate was ultrasonically abraded for 40 min in a suspension which contained 100 mg of ultra-disperse diamond powder with a mean grain size of 3–5 nm and 100 mg of 0.25 μm grain size Ti, W, or diamond powder. The samples are labeled as Ti + ND (nano-diamond, 3–5 nm), W + ND (nano-diamond, 3–5 nm), and Dia (diamond, 0.25 μm) + ND (nano-diamond, 3–5 nm), respectively, according to seeding pretreatment (the powders were supplied by Beijing DK Nano technology Co., LTD). Subsequently the substrate was again ultrasonically cleaned in de-ionized water to remove the nanocrystalline diamond particles sticking to the surface and was dried in nitrogen gas blow before inserting into the reactor chamber. Si_3N_4 substrates were subjected to the same pretreatment procedure. The plasma was induced with a microwave power of 1 kW at a total pressure of 11,800 Pa and total gas flow rate of 100 standard $cm^3\ min^{-1}$ (sccm). The substrate temperature, measured by optical pyrometer through a quartz bell jar, was maintained at 600 °C. The growth duration for UNCD films was 8 h and 1.5 h. The deposition parameters used in the present investigation are listed in Table 1.

2.2. Characterization of UNCD

Field emission scanning electron microscopy (FESEM, LEO ULTRA55, 0.1–30 kV) was used to characterize the surface morphology of the samples before and after diamond nucleation and UNCD film growth. Glancing-incidence X-ray diffraction (GIXRD, PANalytical X Pert PRO, Cu, Kα1, λ = 0.154056 nm) was used to characterize the phase composition and the grain size of the UNCD films. Microstructural analysis of the diamond deposits was performed by micro-Raman spectroscopy at room temperature using an Ar-ion laser with a wavelength of 532 nm and a scan range at 800–2000 cm^{-1} (Renishaw System 1000 with a spot size of about 1–2 μm). The hardness was determined from the load versus displacement curve obtained on a nanoindenter (Nano-indentor™ II, MTS) at a maximum displacement of about 300 nm. For the nanoscratch tests (NST, CSM Instruments), a diamond Rockwell C indenter with a radius of 2 μm was used. Tests on each sample were performed with a progressive loading rate of 160 mN/min at a scanning speed of 1.6 mm/min. The critical loads for full delamination were determined from the recorded normal force vs. penetration depth curves along the scratch; the respective images had also been taken. All mechanical measurements were performed at room temperature in air with 25% relative humidity.

3. Results and discussion

3.1. Nucleation of UNCD onto differently pre-treated silicon substrates

Fig. 1 shows the morphology of UNCD deposits obtained after 15 min CVD on silicon substrates pre-treated with different suspensions (Ti + ND, W + ND, and Dia + ND), in the atmosphere of 88.5% Ar, 10% H_2 and 1.5% CH_4. It can be seen that the nucleation density of substrates

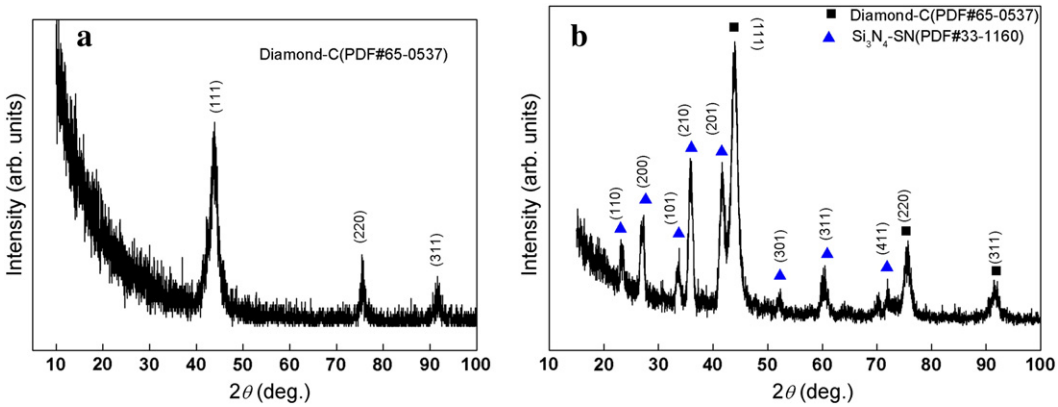

Fig. 2. XRD patterns for carbon films deposited with various substrates a) Si substrate; and b) Si_3N_4 substrate in the Ar-rich source gas mixture.