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The diffusion behavior of carbon in sputtered tungsten film and sintered tungsten block and its effect on diamond nucleation and growth

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ABSTRACT

Diamond was done on sintered tungsten block with or without sputtered tungsten films. The effects of various depositing conditions, including methane concentration, temperature, pressure, the diamond seeding step and reaction time, on diamond growth were investigated in detail. The results show that the sputtered tungsten film has a dual effect on diamond growth. Firstly, after ultrasonication with diamond slurry, the tungsten film will adsorb a large number of diamond nanoparticles. Therefore, the nucleation density of diamond will be substantially improved. Secondly, the film will be carbonized during the deposition process and the carbon on the surface of the film will decrease. Methane concentration generally does not affect the carbonization level of the tungsten film but higher temperature will lead to a higher level of carbonization. The carbonization process of sputtered tungsten films during deposition is made up of two steps. Also, the nucleation surface of diamond was revealed. The nucleation surface was a layer of ultrasmooth and seamless nanocrystalline diamond film with high-quality and special surface architecture (tiny peaks arrays), which is potential to be applied in MEMS and field-emission devices. A potential method to prepare ultrasmooth nanocrystalline diamond films is proposed.

1. Introduction

Diamond has been regarded as a precious material for centuries and it has many good properties, such as extreme hardness, low friction coefficient, chemical stability, wide band gap, negative surface emission energy, the highest thermal conductivity [1] and good biocompatibility [2]. Therefore, diamond is a very attractive material for a large number of applications, including cutting tools [3,4], artificial joints [5,6], thermal conductors [7,8], field-emission devices [9] and MEMS [10,11].

During chemical vapor deposition (CVD) of diamond films, some substrates (W, Mo, Ta, etc.) are likely to form an interfacial carbide layer, which serves as a buffer layer. The buffer layer limits carburization (the dissolution of activated carbon source into the substrate) and relieves the stress at the interface [12]. Among these substrates, tungsten is one of the best substrates for diamond growth because of the low thermal expansion mismatch between tungsten and diamond. So the diamond film coated tungsten blocks are used as electrodes to degrade organic substance in sewage [13]. Researchers also prepared boron-doped diamond films on tungsten wires to produce diamond microelectrodes, which have remarkable electrochemistry properties [14,15]. Others deposited diamond films on tungsten wires and then corroded the core to prepare diamond micro-tubes [16–18]. These diamond micro-tubes can be used in microfluidic applications [19,20].

On the other hand, it is difficult to grow diamond on substrates containing iron group elements (Fe, Co, Ni). These elements have high solubility of carbon. Diamond can hardly nucleate on these substrates. Also, these substrates can serve as catalysts for graphite formation during the CVD process, making diamond nucleation even difficult [21–23]. To solve this problem, tungsten was deposited on these substrates as an interlayer before diamond preparation [24]. The tungsten interlayer can enhance the nucleation density and surface coverage and reduce the surface roughness for micro/nano crystalline diamond (MCD/NCD) films. Many articles proved that the interlayer enhanced the nucleation density of diamond dramatically [25] and this technique was a potential way to produce ultra-smooth nanocrystalline diamond films for MEMS and field-emission applications. Buijnsters and co-workers examined diamond growth on six different metallic sputtered seed nanolayers (Cr, Mo, Nb, Ti, V and W). They found that the highest seed density of diamond nanoparticles anchored to the metallic (W) surface [26]. Also, the tungsten interlayer will shield the adverse impact of the substrates. Therefore, diamond films with good quality and adhesion were prepared on tungsten-coated steel substrates [27] and tungsten-coated

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WC–Co substrates [28]. Another benefit of sputtered interlayer is that it provides a new way to prepare ultrasmooth nanocrystalline diamond films. This was proved to be quite effective using Mo interlayers [29,30].

The published literatures mainly focused on the effect of interlayer on adhesion, diamond nucleation and surface roughness after diamond deposition. But the diffusion behavior of interlayer and its influence on nucleation and surface morphology did not receive enough attention. Also, the phase transformation and the reaction process of tungsten and carbon during HFCVD are not fully understood. In this paper, the diffusion behavior of carbon in tungsten interlayer and its effects under the different methane concentration, pressure, growing time and pretreatment methods are discussed. Unlike regular pretreatment procedures, most of the sputtered substrates used in the experiment were not submerged into diamond powder slurry in order to eliminate the influence of adsorbed diamond particles. The impacts of various deposition parameters on the surface morphology and growth rate of diamond films were investigated by field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), focused ion beam (FIB), STEM and Raman spectroscopy. The composition of the tungsten film was analyzed in detail. The results show that the tungsten interlayer has a dual effect. With diamond ultrasonic agitation, diamond particles will absorb on the interlayer, which has a positive effect on diamond nucleation. But activated carbon atoms will also diffuse into the tungsten interlayer because of the defects in sputtered tungsten film (holes, dislocations and grain boundaries). As a result, the concentration of activated carbon will decrease and the nucleation time will be prolonged. Without the seeding step, diamond will not nucleate until the tungsten interlayer is carbonized. In other words, the nucleation of diamond is delayed. Also, we observed the morphology of the nucleation surface of the grown diamond film. The nucleation surface is a layer of high quality, ultra-smooth nanocrystalline diamond film, with an array of tiny roughness peaks. The results of this study are expected to provide guidance to researchers in order to evaluate the effect of tungsten interlayer and help researchers choose interlayers wisely.

2. Experimental details

2.1. Pretreatment of the samples

The substrate used in this work is tungsten substrate with the size of 8 mm × 8 mm × 4 mm. First, the polished substrates were washed with alcohol and acetone in ultrasonic bath for 10 min. Then, the substrates were cleaned with a Kauffman ion gun in order to eliminate contaminants and adsorbed gas molecules. The applied voltage was 70 V, with 1.25 A current. The coil current was 6 A, whereas the acceleration voltage and current was set to 500 V and 40 mA, respectively. The gas source was Ar and the pressure in the vacuum chamber was 0.05 Pa. The beam operation voltage was 1.5 kV and beam current was kept at 78 mA.

After ion cleaning for 30 min, the tungsten interlayer was prepared by the DC magnetron sputtering technique in a high vacuum chamber with base pressure < 10^{-4} Pa. The purity of the tungsten target and the purity of the argon gas were 99.99 wt.% and 99.99 vol.%, respectively. Pure tungsten thin film was sputtered with sputtering voltage of 350 V and current of 0.4 A. The sputtering pressure of the pure tungsten thin film was kept at 1.0 Pa and sputtering time was 30 min. The target-substrate distance was 70 mm. 300 °C was chosen in order to optimize the adhesion and deposition rate of tungsten thin film.

2.2. Diamond deposition

The diamond films were grown by hot filament assisted CVD in a multifunctional vapor deposition system specifically designed for diamond deposition. The reactor is a stainless steel chamber with an inner diameter of 300 mm to which various electrical, gas and liquid feeds are fitted, as well as a magnetron cathode for sputtering. A spiral coil tungsten filament is used to activate the gas for diamond film deposition. The filament temperature (T_f) was measured by an optical pyrometer. The reaction gas was a mixture of H_2 and CH_4. The flow rate of H_2 and CH_4 was controlled by mass flow controller (MFC). Substrate surface temperature (T_s) was measured by a K-type thermocouple. The experiment conditions are listed in Table 1. In this table, the samples are divided into six groups to investigate the influence of interlayer (i), methane concentration (M, Mi), pressure (P), temperature (T), reaction time (t) and pretreatment process (Pr).

2.3. Characterization of the samples

Samples were characterized by field-emission scanning electron microscopy (FE-SEM FEI, Sirion200) to reveal the surface morphology of the diamond film. Raman spectroscopy (LabRAM ARAMIS) was employed to characterize the quality and bonding structures of diamond film. The wavelength of the laser is 532 nm with a typical resolution of 1–2 cm^{-1} in the back-scattering geometry. The diameter of the laser spot is 2 μm. The phases in the samples were analyzed by X-ray Diffraction (XRD, Dmax-2500VBX using Cu Kα radiation at a wavelength of 0.154 nm). Focused ion beam (FEI Helios X600, Interface Analysis Centre, University of Bristol) was applied to illustrate the cross-section morphology of the sample.

3. Experiment results

3.1. Seeding process

Samples i1, i2, i3 and i4 aim to investigate the influence of interlayer and diamond seeding step on nucleation stage of diamond growth. The SEM results are shown in Fig. 1. It is evident that the nucleation density is different for substrate with and without tungsten interlayer. The nucleation density is in the following order: i3 < i1 < i2 < i4. For tungsten block substrates, it is difficult for them to form a continuous diamond film within 180 min, whether or not the substrate was ultrasonically abraded by micro-sized diamond, as shown in Fig. 1 (a, b) and (c, d). However, for i4, which was ultrasonically agitated in diamond slurry, after deposition for 20 min, nanocrystalline diamond film grew continuously on the surface. For i3, diamond only nucleated at defect places, such as scratches, craves and gaps. On an intact surface of tungsten film, diamond can hardly nucleate in such short period of time. The nucleation density of i3 was much lower than that of i1. In Fig. 1(f), diamond nuclei are observed near the cleft because the energy of the surface near the cleft was higher than non-defect places and diamond is prone to nucleate near those defects [31]. Fig. S1 (a, b) further proved this assumption. In Fig. 1(h), diamond mainly nucleated on the bottom of the hole, where sputtered tungsten film was peeled off. In Raman patterns, it is clear that the signal–noise ratio of i4 is much better than i3. The peak located at 1150 cm^{-1} is the Raman peak of trans-polyacetylene and it cannot be observed in the Raman pattern of i3. The results of samples i1, i2, i3, and i4 indicated that the nucleation and growth of diamond on sputtered tungsten coating were different from those on sintered tungsten block because the reaction activity of sputtered tungsten is much higher than sintered tungsten. Therefore, the effect of different conditions on diamond film grown on sputtered tungsten coating was investigated in detail.

3.2. Methane concentration

Fig. 2 compared the surface morphology, cross-section morphology and XRD patterns of samples M1, M2 and M3. These samples were sintered tungsten substrate without diamond seeding step. In Fig. 2 (a, d, g), there are four phases in all three samples, that is WC, diamond, tungsten and carbon. XRD results show that as methane concentration increases, the WC layer thickness decreases. The thickness of diamond and WC layers was relatively small and XRD ray can penetrate