Adherent diamond film deposited on Cu substrate by carbon transport from nanodiamond buried under Pt interlayer

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Abstract

Diamond film deposited on Cu suffered from poor adhesion mainly due to the large mismatch of thermal expansion coefficients and the lack of affinity between carbon and Cu. Enhancing diamond nucleation by carbon transport from buried nanodiamond through a Pt ultrathin interlayer, adherent diamond film was then deposited on Cu substrate without distinctly metallic interlayer. This novel nucleation mechanism increased diamond nucleation density to 10^{11} cm^{-2}, and developed diamond film with a composite structure of nano-crystalline diamond (NCD) layer and micro-crystalline diamond layer. Diamond film was characterized by the scanning electron microscope (SEM) and Raman spectroscope, respectively. The composition of diamond film/Cu substrate interface was examined by electron probe microanalysis (EPMA). The adhesion of diamond film was evaluated by indentation test. Those results show that a Pt ultrathin interlayer provides stronger chemically bonded interfaces and improve film adhesion.

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1. Introduction

Owing to its excellent thermal conductivity, chemical stability, low dielectric constant and high dielectric strength, diamond film is the most promising material for semiconductor industry [1,2]. An outstanding example is that the combination of diamond to Cu can provide very efficient heat sink, since diamond has the highest thermal conductivity of all known materials while Cu processes large heat capacity [3]. However, numerous works have suggested that diamond deposition on Cu is a difficult endeavor [4–7]. Cu, whose lattice parameter (a_{Cu} = 0.3615 nm) is very close to that of diamond (a_{diamond} = 0.3567 nm), belongs to the substrate that neither forms a carbide nor dissolves carbon. Because it is immiscible with carbon, graphite layer must be produced as an intermediate, which results in low density of diamond nucleation and long induction time (>10 h) [7]. Then, a number of surface pretreatment methods have been developed to enhance diamond nucleation. Ece et al. [8] developed a multi-step sequential hot-filament chemical vapor deposition (HF-CVD) process to deposit continuous diamond film on Cu substrates, consisting of seeding the substrate with diamond powder and annealing the seeded substrate in hydrogen at high temperatures (1300 °C). Ali et al. [9] reported an increase of 70% in the nucleation density was observed when the surfaces were polished with diamond paste and then negatively biased. Han et al. [10] adopted graphite seeding and CO_{2} laser irradiation to enhance diamond nucleation on Cu substrate. They pointed out that the defects and edges of the seeding graphite layer served as nucleation sites for diamond formation.

The other major problem is poor adhesion between diamond film and Cu [7]. The high thermal stress originated from the large mismatch of thermal expansion coefficients always cracks or peels off diamond film from Cu substrate when taking it out from the depositing chamber. Metal interlayer has been investigated to increase diamond adhesion on Cu, including Ti, Ni, Ni–Mo and Cr [11–14]. Ideal interlayer materials should offer high diamond nucleation density, matching thermal expansion coefficient, and enhanced interfacial adhesion. However, diamond nucleation density on the inter layer materials currently in use are not sufficiently high [15]. Thick metallic interlayer (several micrometers or higher) always deteriorates thermal and electrical properties of composition material [16].

In this paper, we investigated diamond nucleation and growth on Cu substrate by carbon transport from ultra-dispersed nanodiamond particles (UDDs) buried under an ultrathin Pt interlayer. Adherent diamond depositing on Cu substrate was obtained and no distinct metallic interlayer was observed between diamond film and Cu substrate.
2. Experimental

2.1. Substrate pretreatment

The substrate material used for diamond deposition was commercial Cu foil. The substrates were machined into specimens of 10 × 10 × 1 mm³ in size and mechanically polished with a sequence of SiC sand papers from 400# down to 1200# grid, and ultrasonically cleaned in acetone for 10 min. Then substrates were firstly immersed in aqueous colloid (0.05 wt%) of UDDs with ultrasonic bath for 30 min, followed by a rinsing in pure deionized water and air-dried. Mean particle size of UDDs was 6–15 nm. A Pt layer with about 40 nm thick was then deposited on substrates by vacuum evaporation at room temperature. After those treatments, Cu substrates changed to silver color.

2.2. Diamond film deposition

Diamond growth was carried out in a HF-CVD system which has been described in other literature [17]. The following deposition parameters were maintained constant throughout the entire study: a substrate temperature of 750 ± 50 °C, a deposition pressure of 3Kpa, a filament-to-substrate distance of 8 ± 1 mm, a methane concentration of 2%, and a total gas flow of 100 SCCM (cubic centimeter per minute at STP).

The morphology and structure of diamond film was characterized by field emission scanning electron microscope (FE-SEM, Sirion200). Electron probe microanalyzer (EPMA, JXA-8230) was performed to investigate the composition at the interlayer of diamond film and Cu substrate. A micro-Raman spectroscopy (LabRaman, RH800) with an Ar-ion laser (488 nm) at 900–1800 cm⁻¹ was applied to evaluate the diamond film quality and the internal stress in the film by the shift of the diamond peak.

3. Results and discussion

3.1. Diamond nucleation

Fig. 1 shows the SEM surface images of Cu substrate after the treatment of UDDs seeding and Pt coating, respectively. Since Cu substrate and Pt interlayer are both favorable conductors, individual UDD on the seeding surface can be clearly observed. Fig. 1a shows the Cu substrate just after UDDs seeding. As it illustrates, mono-dispersed UDD seeding was obtained though the substrate surface was rough. The coverage of the Cu substrate is highly uniform and in high density. No distinct aggregation can be seen. The size of individual particles in the image was in the range of 6–15 nm. After coated with a 40 nm thick Pt interlayer, the image became vague under secondary electron (SE) mode (Fig. 1b). But diamond nanoparticles can still be fingered out. It validated that the thicknesses of Pt interlayer was at nano-scaled range. While in back scattered electron (BSE) mode (Fig. 1c), only flat Pt surface can be seen, which indicated that UDD seeds were buried under Pt layer. There were no micro-cracks existed in the Pt layer.

Fig. 2 is a SEM surface image after 0.5 h diamond growth. Since UDD seeds on Cu substrate were buried under the Pt, they were not direct exposed to radical species. It can be found that the whole surface of Cu is covered with faceted diamonds. A continuous diamond film forms and it exhibits a very denser structure, where no visible pinhole can be observed even at such high-magnification. In this case, the calculated nucleation density by counting the total number of diamond crystallites and dividing by the area was greater than 10¹¹ cm⁻². It was higher than two orders of magnitude reported in those literatures about diamond film deposited on Cu substrate [4,9]. The high nucleation density and uniformity of grain size across the film can be attributed to the well-distributed UDD seeds.

The high temperature interaction of carbon with Pt is interesting. On the one hand, Pt is a typical substrate for CVD diamond film that does not form carbide but can dissolve the carbon [18]. The dissolution of carbon into Pt film and the segregation of carbon on the metal surface during cooling are even used to prepare monolayer graphene [19]. While the solid solubility of C in Pt is
less than 1 at % at the CVD temperature (750 °C) according to the Pt–C binary phase diagram, it is likely that a Pt–C–H ternary system plays an important role in the occurrence of dissolution and recrystallization of diamond crystals on the Pt substrate [20]. On the other hand, Pt nanoparticles (2–3 nm) supported on few-layer graphene surfaces exhibit an extremely high stability towards temperature-induced sintering. While in Ref. [19], annealing a Pt film with a thickness of 100 nm on a 300 nm SiO2/Si substrate at 1050 °C in a 10% H2/Ar ambient, the surface roughness of Pt shows almost no change. It indicates negligible agglomeration during the annealing. Then, the diamond nucleation mechanism must be based on dissolving carbon from UDD particles into the Pt ultrathin interlayer followed by the transport of carbon atoms through Pt interlayer and formation of sp3-bonded diamond clusters at the Pt surface, which subsequently led to the formation of diamond nucleation when substrates were exposed to H2/CH4 plasma. In fact, Daenen et al. [21] confirmed the mechanism in the system of nanodiamond and TiO2 sol-gel with EELS and HRTEM data. Obviously, this nucleation mechanism was distinguished from diamond nucleation on Cu substrate without Pt layer. Under the later circumstances, diamond directly nucleated from pre-existing sp3 seeds [22].

3.2. The morphology of diamond film

The SEM microstructure of the diamond film deposited on the Cu substrate after 4h diamond growth is shown in Fig. 3a. The surface of diamond film became rugged once diamond nucleation stage was over and diamond began to grow. Due to different gas chemistry environment, some grains will grow faster. But the size of most of diamond grains is ranging from 2 μm to 3 μm and the diamond grains exhibit (111) facet face domination. Fig. 3b is a typical low-magnification SEM image of diamond film. As it illustrates, no local delamination or any micro-cracks can be observed.

3.3. Diamond film/Cu substrate interlayer

The cross-section details of adherent diamond film on Cu substrate are shown in Fig. 4. As we known, in order to obtain a smooth surface for SEM investigation, the cross-section was mechanically lapping. Though the sample is accordingly subjected to a huge shear stress, The BSE image (Fig. 4a) illustrates that diamond film and Cu coalesced together, while it can hardly distinguish any individual layer at the cross-section. No gap or hole can be observed between diamond film and Cu substrate, which confirmed that diamond film was tightly bonded to Cu substrate. Further investigation reveals that diamond film presents a composite structure, which consists of two different layers in total: nano-crystalline diamond (NCD) layer and micro-crystalline diamond layer (Fig. 4b). The top layer is microcrystalline-diamond film and columnar crystal is its typical morphology, while the thickness is about 1.5 μm. The bottom is nano-crystalline diamond, with the thickness in the range of 0.6 μm. Applying an ultrathin interlayer on substrates always leads to the growth of NCD. It is ascribed to a nanoscale roughening of the interlayer surface and the rapid carburization of the thin interlayer [15,23]. Furthermore, Pt interlayer can stabilize the small diamond nuclei. Tachibana et al. [20] reported that at initial growth stage, small diamond particles at the Pt surface underwent positional and orientational changes.

To obtain further information of the composition and phase quality at the interface layers of the studied samples, EPMA analysis was performed on the cross-section of diamond film/Cu substrate. The corresponding content scanning on the same line is shown in Fig. 4c. Carbon signal was presented mainly in diamond film, and then the content decreased from film surface to Cu substrate. Cu signal was presented mainly in the substrate, even diffused from Cu substrate to diamond film, and then the content became weaker. As both content scan lines showed, there were no sudden changes, which testified diamond directly bonding to the Cu substrate. Pt content is very weak. The signal mainly presented at the diamond film/Cu substrate. It decreased more quickly in diamond film than in
Cu substrate. Interestingly, Cu is immiscible with carbon, but EMPA showed that mutual diffusion has happened at the cross-section of diamond film/Cu substrate.

From Cu–Pt binary equilibrium phase diagram, we know that Cu and Pt can form a solid solution (Cu, Pt) above deposition temperature. At the later of diamond nucleation, UDDs layer was depleted gradually. The direct contract of Pt layer and Cu substrate will facilitate Pt dissolving into Cu bulk. So Pt signal became very week.

![Image](image.jpg)

**Fig. 4.** (a) BSE image of the cross-section of adherent diamond film deposited on Cu substrate, (b) a magnified SE image of the cross-section and (c) EMPA analysis of diamond film/substrate interface.

Fig. 5 shows the Raman spectra of diamond films. As-deposited sample shows a diamond peak around 1345.80 cm$^{-1}$. The upward shift of the peak position from standard diamond at 1331 cm$^{-1}$, is attributed to a compressive stress accumulation in the film, and it is a sign of good adhesion of the film to the substrate [12,15,24]. The less resolved peaks at around 1593.10 cm$^{-1}$ correspond to G-band of graphite. The Raman peaks around 1135.54 cm$^{-1}$ and 1491.78 cm$^{-1}$ are assigned to trans-polyacetylene segments at grain boundaries and surfaces, which is one of the characteristics of nano-crystalline diamond [25]. Once the diamond film delaminated from Cu substrate, the diamond peak measured from the free-standing films exhibited sharp diamond peak at 1331.09 cm$^{-1}$, because it was free from biaxial stresses after debonding (Fig. 5b).

Raman spectra also testify the composite structure of NCD layer and micro-crystalline diamond layer viewed in SEM image. Since the confocal depth of Raman spectrometer was larger than 2 μm under measurement condition, it can collect the scattering signal from nano-crystalline to micro-crystalline diamond layer. Therefore, Raman spectrum assuredly presented the sharp diamond peak centered at 1331.09 cm$^{-1}$, and two nanocrystalline diamond peaks around 1138.26 cm$^{-1}$ and about 1485.91 cm$^{-1}$, simultaneously.

The thermal stress caused by the different coefficients of thermal expansion can be expressed by the following equation assuming elastic deformation [26]:

$$\sigma_{th} = \frac{E}{1-v} \int_{T_1}^{T_2} \left( \alpha_s - \alpha_f \right) dT$$

(1)

where $E$ and $v$ are the Young’s modulus and the Poisson constant of the diamond film, $\alpha_s$ and $\alpha_f$ are coefficients of thermal expansion of the diamond film and the substrate, respectively. $T_2$ is the deposition temperature and $T_1$ is the room temperature. If we ignore the temperature effect on coefficients of thermal expansion, the calculated value is $-12.81$ GPa. The value is much greater than diamond film deposited on most of metal substrates [27].

The internal stress can be determined by the shift of the diamond peak in the Raman spectrum. Raman shift is proportional to biaxial stresses in the diamond film. It can be expressed by the following equations [28]:

$$v_D = -1.08 \text{ GPa cm}^{-1}(v_s - v_D)$$

(2)
for a singlet phonon

\[ \nu_D = -0.384 \text{ GPa cm}^{-1}(\nu_d - \nu_0) \]  

(3)

for a doublet phonon where \( \nu_0 = 1332 \text{ cm}^{-1}, \nu_d \) and \( \nu_D \) are the observed maxima. Since the splitting of the peak is not obvious, we used the average value \( \nu_m \) of the factors for the singlet and the doublet evaluated by Ager et al. [29].

\[ \nu_D = -0.49 \text{ GPa cm}^{-1}(\nu_m - \nu_0) \]  

(4)

Using Eqs. (4), we found that the residual stress in the diamond film was \(-7.56 \text{ GPa}\), which was comparable with the thermal stress. Therefore, it implies that no relaxation of thermal stress presents due to diamond film cracking or peeling off. Ma Zhibin et al. [13] reported that the intrinsic stress of the diamond film can be adjusted by the deposition conditions. Adherent diamond film coating on Cu substrate with low residual stress can be anticipated in further investigation.

3.5. Diamond film adhesion

The bonding ability of the diamond film to Cu substrate was evaluated from Rockwell-C point indentations. Since diamond film was deposited on a soft substrate, a load of 40 kgf was applied. The loading speed was set at a value for 20 N/min to avoid any sudden damage to the fragile film. A SEM image of the imprint with a crater diameter of 80 \( \mu \text{m} \) is shown in Fig. 6. No propagation of crack from the indentation edge and no significant peeling of the film were observed around the crater. It confirms that the diamond film deposited on Cu substrate possesses high adhesion strength [27,30].

On the one hand, the enhanced diamond nucleation density and formation of NCD film provide higher contact area between the diamond film and Cu substrate. NCD layer adjacent to Cu substrate has lots of grain boundaries, which provides the channel for the diffusion of Cu or Cu–Pt.

The diffusion of Cu or Cu–Pt into NCD layer will obtain the same bonding performance of brazed diamond grits with Ni–Cr–P alloy [31]. In face, even without any chemical bonding, the mechanical anchor existed in the interface of diamond film and pure Cu substrate is stronger than 1800 N/cm² [32].

On the other hand, a Pt ultrathin interlayer significantly modified the chemical bonding between diamond film and Cu substrate. As EMPA indicated, the Pt ultrathin interlayer promoted carbon diffusing into the Cu substrate (Fig. 4c). When Pt and Cu form a Cu–Pt alloy, the Pt rich area can still dissolve carbon because the continuous diffusion of carbon from the diamond particles to metallic glass can generate a thin carbon rich reaction layer [33]. Besides, the chemical bonds of Pt–C–H bonds may take place [20]. The adhesion improvement by forming a nickel–carbon–hydrogen (Ni–C–H) eutectic layer has been proposed when diamond film deposited on Cu substrates using a nickel interlayer [13].

4. Conclusions

The application of a 40 nm Pt interlayer has markedly enhanced diamond nucleation and adhesion. Diamond nucleation was based by carbon dissolving from UDDs to Pt interlayer and formation of \( \text{sp}^2 \)-bonded diamond clusters at the Pt surface, which increased the nucleation density to \( 10^{13} \text{ cm}^{-2} \) and finally promoted a composite structure of NCD layer and micro-crystalline diamond layer. The internal stress made diamond Raman peak shift to 1345.80 cm⁻¹. Indentation test showed that there were no propagation of cracks from the indentation edge and no significant peeling of the film around the crater. The adhesion improvement can be mainly attributed to the diffusion between Cu substrate and NCD film and the modification of the chemical bonding between diamond film and Cu substrate by the Pt interlayer.

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References


Fig. 6. A SEM surface image of diamond film deposited on Cu substrate after indented with a load of 40 kgf.


