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CVD diamond film deposited on copper substrate enhanced by a thin platinum modification layer

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By coating a platinum layer of about 40 nm thickness to a copper substrate seeded with ultradispersed nanodiamond particles (UDDs), faceted diamond with high density was detected. It presents a novel nucleation mechanism – carbon in UDDs was dissolved in platinum and was transferred through the platinum interlayer, followed the formation of sp^3 -bonded diamond clusters at the platinum surface, which was distinguished from UDDs without platinum modification layer. The

diamond film was characterized by scanning electron microscope (SEM) with energy-dispersive X-rays, and laser Raman spectroscopy, respectively. After 4 h diamond growth, diamond film developed into two different layers: one nanocrystalline and one microcrystalline. Such a composite structure was attributed to the platinum layer that modified the interface properties of diamond nuclei and copper substrate at high temperature.

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1 Introduction Advanced high-power light-emission devices (LED) and nanominiaturized integrated circuits (IC) have significantly increased nowadays the power density of electronic devices [1, 2]. Highly localized high-power microelectronic devices demand high heat-spreading efficiency. Diamond is one of the best candidates for thermal-spreading materials due to its excellent thermal conductivity, chemical stability, low dielectric constant and high dielectric strength [3, 4]. Natural diamond (type II) has an extreme thermal conductivity of $2000 \text{ W m}^{-1} \text{ K}^{-1}$, which is the highest of all known materials and five times higher than pure copper ($395 \text{ W m}^{-1} \text{ K}^{-1}$).

However, natural diamond is too expensive to be widely used. At the same time, increasing evidence shows that the high thermal conductivity of diamond by itself is not enough to dissipate heat, as the heat capacity of diamond is limited [5]. Copper is a cheap material for thermal spreading with medium thermal conductance and large heat capacity. Therefore, chemical vapor deposition (CVD) of diamond film on copper substrate has attracted intensive attention. Copper, like diamond, has a cubic crystal structure, and its lattice mismatch with diamond is only 1.14%. Furthermore, copper does not form any carbide which makes it an excellent candidate for the heteroepitaxial growth of diamond [6, 7].

However, a number of investigations have suggested that diamond deposition on copper is a difficult endeavor [5, 8–12]. Major problems encountered with diamond deposition on copper are the low nucleation density, film cracking and poor adhesion.

In this paper, the nucleation and growth of diamond on modified copper by carbon transport from ultradispersed nanodiamond particles (UDDs) buried under a thin platinum layer was investigated. The possibility of heteroepitaxial growth by this novel nucleation mechanism, controlled carbon transport from the subjacent modification layer, was proposed.

2 Experimental details Diamond films were deposited in a hot-filament assisted CVD reactor designed and constructed in the Department of Physics at the Royal Institute of Technology, Stockholm (Sweden) [13], and subsequently transferred to Central South University [14, 15]. The reactor is a stainless steel chamber (300 mm inner diameter) to which are fitted various electrical, gas and liquid feedthroughs, as well as a magnetron cathode for sputtering. The process gas was activated using a spiral coil filament suspended between two molybdenum rods. The filament temperature (T_f) was measured by optical pyrometry. The

substrate temperature (T_s) was measured by K-type thermocouples attached to the substrate surface. The base pressure ($<1 \times 10^{-6}$ Torr) was maintained by a turbomolecular pump, and the deposition pressure (p) was monitored by a manometer. Deposition parameters were: filament power, $P = 361\text{--}394$ W; filament current, $I = 19.5 \pm 0.2$ A; $T_f = 2373 \pm 100$ K; $T_s = 1023 \pm 50$ K; $p = 3$ kPa; methane mole fractions, $C_m = 2\%$ in hydrogen.

Polycrystalline copper foils (99%) with dimension of $10 \times 10 \times 1$ mm³ were used as substrates. These were polished with a sequence of SiC sandpapers from 400# down to 1200# grid and ultrasonically cleaned in acetone for 10 min. Nanoseeding was carried out by immersing copper substrates in an aqueous colloid of UDDs of 6–15 nm size in an ultrasonic bath for 30 min, which was then rinsed in pure deionized water and air dried. Ultrasonic agitation serves to disperse UDDs onto the substrate surfaces. Following the nanoseeding process, a platinum layer of about 40 nm thickness was sputtered on substrates to cover UDDs at a deposition rate of 0.25 nm s^{-1} .

Diamond films were characterized with field-emission scanning electron microscopy (FE-SEM FEI, Sirion200) with an energy-dispersive X-ray detector (EDX), and laser Raman spectroscopy (LabRAM HR800, Ar⁺ ion laser operating at 488 nm with an output power of 100 mW), where the transverse and the vertical resolution of laser Raman are 1 μm and 2 μm , respectively.

3 Results and discussion Because the copper substrate and platinum layer are both favorable conductors, We can directly examine the distribution of diamond nanoparticles on the seeding surface by SEM. Figure 1 shows the secondary-electron image (SE) and backscattering-electron image (BSE) of copper substrate after UDDs seeding and platinum sputtering at the same magnification, respectively. As shown in Fig. 1a, monodispersed nanodiamond seeding was obtained notwithstanding the wavy substrate topography. The diamond film on copper substrate is highly uniform with high density. No distinct aggregation can be observed. The size of individual particles in the image was in the range of 6–15 nm. When observed in BSE mode (Fig. 1b), only a flat platinum surface can be seen rather than UDDs, which indicated that UDDs were buried successfully under the platinum modification layer and that no distinct crack existed in platinum layer.

EDX analysis was also carried out to investigate the element composition of the corresponding surface. The result was shown in the inset of Fig. 1b. Three elements, Cu, Pt, and C, were detected. As we know, EDX is a microzone analysis method. But we still collect substrate signal (Cu) from the platinum surface, which validated that the thickness of the platinum layer and UDDs seeding layer are both in the nanoscale range.

A SEM image of the film after 0.5 h diamond growth is shown in Fig. 2a. UDDs on copper substrate were covered by the platinum sputtering layer. Apparently, they could not be directly exposed to radical species during diamond

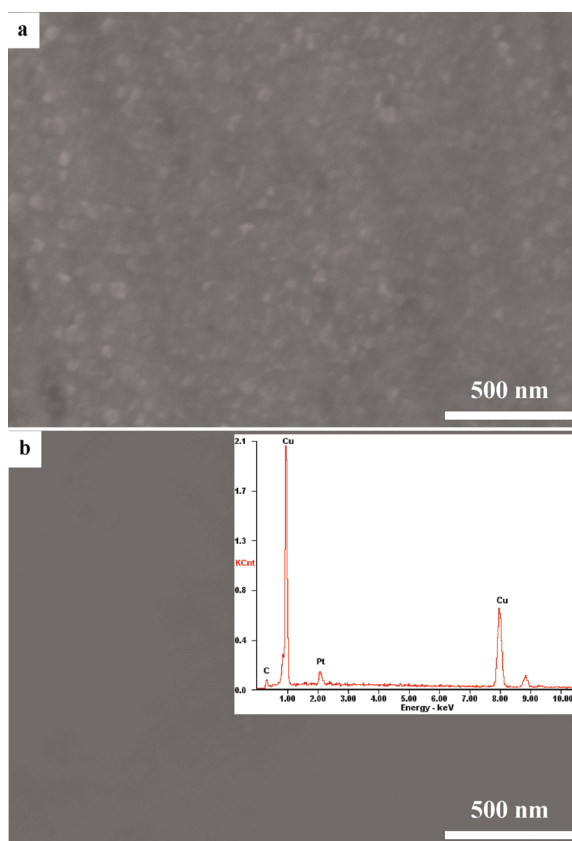


Figure 1 (online color at: www.pss-a.com) (a) SE image and (b) BSE image of UDDs seeded Cu substrate with Pt modification layer on top. The inset of Fig. 1b shows EDX results of treated substrate surface.

growth. But faceted diamonds with high density were observed on copper substrate. We believe that diamond nucleated from the buried UDDs. As illustrated in Fig. 2a, no visible pinhole was observed on the diamond film even at current high magnification. The homogeneity of diamond nanoparticles across the film can be attributed to the well-distributed UDD seeds. Compared with diamond nucleation on UDD seeded copper substrate without platinum interlayer (Fig. 2b), diamond on platinum-covered substrate presents larger particle sizes.

The Raman spectra of diamond films deposited on those two specimens are shown in Fig. 3, which presents the same peak positions. The peaks at 1331.09 cm^{-1} were assigned to the diamond phase. The less-resolved peaks at around 1573.15 cm^{-1} corresponded to the G-band of graphite. In terms of crystal growth, diamond nuclei compete with each other to grow in the vertical direction. At this early stage of diamond growth, high nucleation density ensures the formation of grain boundaries. This coincides with the early competitive grain growth mechanism [16]. Consequently, G peaks were observed in the grain boundaries. The Raman peaks around 1138.26 cm^{-1} and 1485.91 cm^{-1} were assigned to trans-polyacetylene segments at grain boundaries and surfaces, which is one of the characteristics

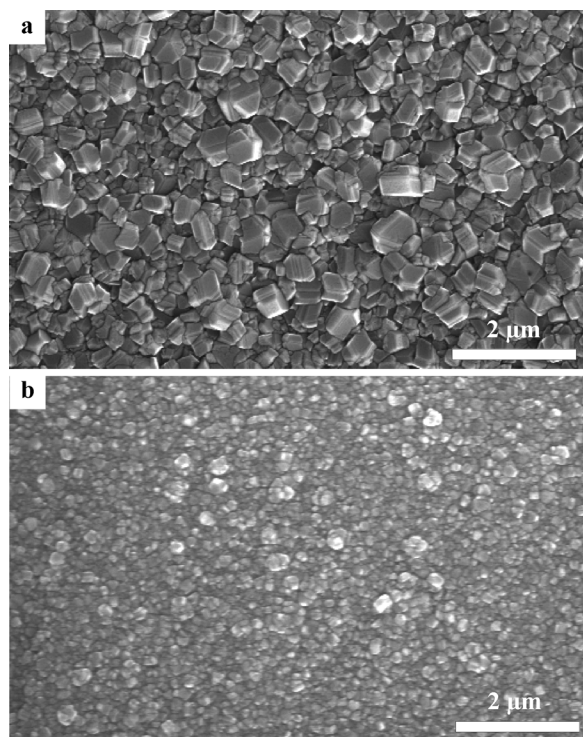


Figure 2 SEM images of diamond films with (a) and without (b) Pt interlayer after 0.5 h diamond growth.

of nanocrystalline diamond [17–19]. The major difference between them is that the diamond peak of diamond film grown with a platinum layer is sharper than the diamond peak of diamond film grown without a platinum layer, which indicated that the crystallinity of the former is better than the latter. This agrees with what the SEM images show.

UDDs seeding is a common approach to enhance CVD diamond nucleation [16, 20, 21]. Without a platinum interlayer, diamond nucleated from pre-existing sp^3 seeds distributed on copper substrate, yet, with a platinum layer

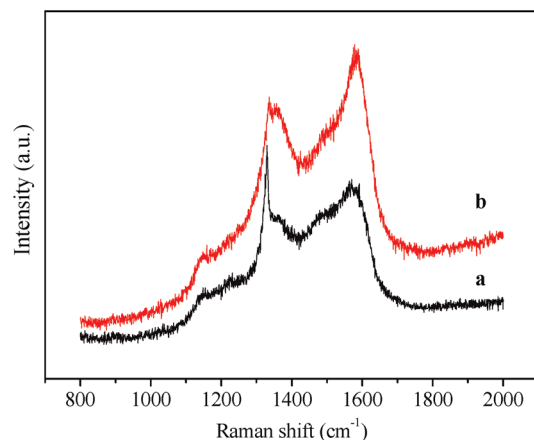


Figure 3 (online color at: www.pss-a.com) Raman spectra of diamond films with (a) and without (b) Pt interlayer after 0.5 h diamond growth.

sputtered on UDDs seeding layer, the nucleation mechanism is different.

From the Pt–Cu and Pt–C binary equilibrium phases, we know that copper and platinum can form the fcc continuous solid solution (Cu, Pt) above 1089 K. While no carbide will form between platinum and carbon, carbon can dissolve in platinum [7, 22].

Initially, high mutual diffusion will occur between UDDs seeding layer and platinum layer under deposition temperature of 1023 K. Since the solid solubility of C in platinum is <1% at 1023 K according to the binary equilibrium phases, C will quickly precipitate from the platinum layer. The nucleation mechanism is expected to start by dissolving carbon from UDD particles into the platinum layer followed by transport of carbon atoms through the platinum layer and formation of sp^3 -bonded diamond clusters at the platinum surface. This subsequently leads to the formation of diamond nucleation when substrates are exposed to H_2/CH_4 plasma. Daenen et al. [23] confirmed this mechanism in nanodiamond and TiO_2 sol-gel composites with EELS and HRTEM data. The atomic hydrogen stabilized carbon atoms once they reached the platinum surface before those carbon atoms eventually aggregated into clusters and the formation of diamond sp^3 nuclei. Lifshitz et al. [24, 25] reported that diamond nuclei can be formed from sp^3 -bonded carbon that stabilized in a solid-state environment.

We also considered diamond nucleated from the unfolded UDDs when the above platinum covered layer was gradually exhausted by diffusing into copper bulk. This mechanism will be equal to diamond nucleation without a platinum layer. It will even present smaller particle size than the latter, since it needs time to diffuse. But this analysis is opposite to the experimental results. Diamond on platinum-covered substrate presents not only large particle size, but also high crystallinity.

Since the surface energy of diamond is much higher than that of copper substrates, a critical size of diamond nuclei has to be reached to prevent the diamond clusters from being decomposed or redissolved in the incubation stage. The low thickness of the platinum layer leads to fast saturation of carbon in the platinum interface and thus promoted diamond nucleation [16, 26–28]. The time it took to reach saturation increases with the thickness of the platinum interlayer. This carbon diffusion can significantly delay the onset of diamond nucleation, since a certain carbon concentration at the substrate surface should be reached before stable diamond nuclei can be formed [29].

Furthermore, the platinum interlayer not only brings about the change of nucleation mechanism, but also a modification of the interface properties of diamond nucleation at high temperature.

By nucleation, the change in Gibbs free energy is

$$\Delta E = V\Delta G_v + A'\gamma_N - A(\gamma_s - \gamma_{int}), \quad (1)$$

where V is the volume of the nuclei, ΔG_v is the variation in volumetric free energy, A' is the area of nucleus surface, A is the interface area, and γ_s and γ_N are the surface energies of

the substrate and the nuclei, respectively. γ_{int} is defined as the energy change for the formation of an interface from individual atoms [7]. As in Eq. (1), we can see that the substrate with large surface energy (γ_s) and smaller interface energy (γ_{int}) favors the wetting of diamond nuclei. Unfortunately, there is no actual data of γ_s and γ_{int} at 1023 K. Limited density functional theory (DFT) calculations showed γ_{Pt} (1.34 J m^{-2}) is larger than γ_{Cu} (1.28 J m^{-2}) [30]. Therefore, we can only presume that the platinum interlayer modified the high-temperature wettability between diamond nuclei and substrate and stabilized the small nuclei.

From the point of view of kinetics, the platinum interface can enhance the diffusion of carbon atoms and control the transportation of carbon. The studies of the high-temperature interaction of carbon with transition metals and transition-metal carbides showed that surface phase transitions occur between multilayer graphite to monolayer graphite, named graphene, and further transition from this graphene to carbon aggregates on increasing the temperature. Stabilization at a high temperature of monolayer graphite on nickel and platinum has been explained by electronic transfer from the n electrons to the empty d orbital of the transition metals [31, 32]. Tachibana et al. [33] reported that at the initial growth stage, small diamond particles at the platinum surface underwent positional and orientational changes. The diamond growth at a later stage was governed by the van der Drift mechanism to form an azimuthally oriented (111) faces. Therefore, diamond grains with platinum interlayer presented high crystallinity (Fig. 2a), while diamond nucleated on copper substrate without any seeding required a very long induction time ($>10 \text{ h}$) [34].

When we increase the deposition temperature to 1123 K, which is still suited for diamond nucleation [12], however, high temperature destroys the continuity of the platinum interlayer. The result is that only substrate surface suffered from H_2 plasma treatment was obtained rather than nanocrystalline diamond film (Fig. 4). The majority of UDDs were etched by active atom H [35].

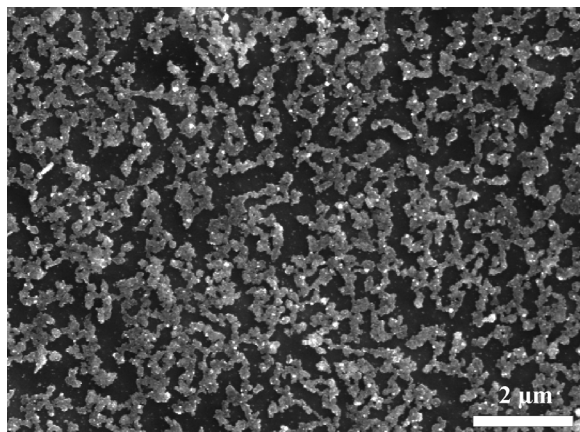


Figure 4 The SEM image of diamond film deposited at 1123 K.

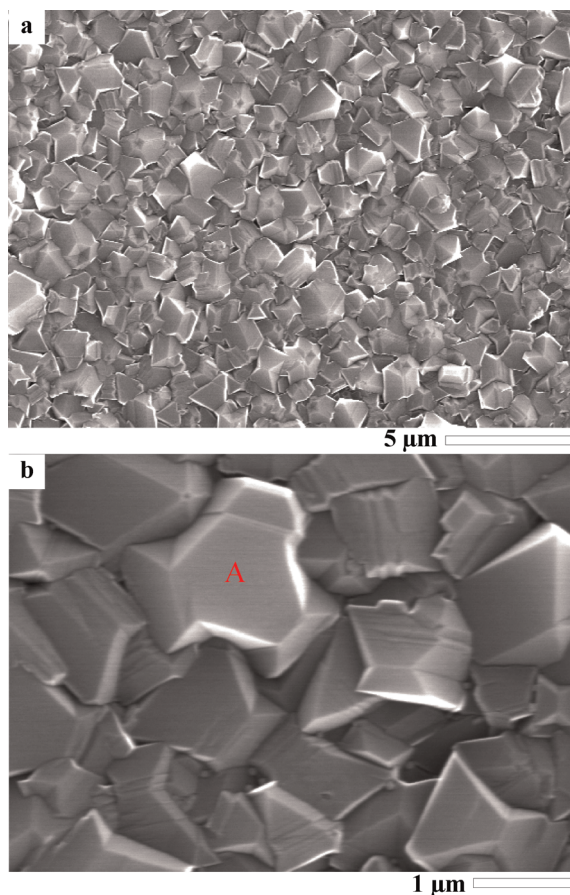


Figure 5 (online color at: www.pss-a.com) SEM images of diamond film at low magnification (a) and high magnification (b) after 4 h diamond growth.

When the deposition time was extended to 4 h, as shown in Fig. 5a, the surface of diamond crystals became rough once the diamond nucleation stage is over and diamond grains begin to grow. During the deposition process, diamond nuclei compete with each other to grow in the vertical direction. Some grains growing preferentially due to a different gas chemistry environment immersed the small ones. But the size of most diamond grains ranges from 2 to $3 \mu\text{m}$ and exhibited (111) facet face preferential orientation.

Diamond growth using an electron cyclotron resonance CVD apparatus showed that diamond grains on copper substrates grew not only through an increase of the size of grains but also through their combination, and that isolated grains at an early stage of growth migrated on the substrate as if they were attracted by each other [6]. Highly oriented and spontaneously coalesced diamond films with (111) crystal surfaces can be heteroepitaxially grown by microwave plasma CVD after 50 h [33]. Those growth trends were not very apparent in our experiment. But it can be deduced from Fig. 5b that the crystal labelled A developed from three (110)-oriented crystals.

Some reasons for this discrepancy can be summarized as follows. One reason is that those authors employed high-

density plasma, which increased the concentration of radical species and enhanced their diffusion on the substrate. We will carry out more investigations in our newly designed equipments – a periodic magnetic field (PMF) enhanced CVD systems [36]. Further results will be presented in another paper. Another reason is their growth time is much longer than ours. Suppose that using single-crystal copper substrate, modifying the thickness of platinum interlayer and applying diamond growth environment with a high density plasma can lead to more favorable results. In addition, the crystallinity of the platinum interlayer is highly dependent on deposition conditions [37, 38]. We will carry out a series of dedicated experiments to check the effect of the preferential growth direction of platinum interlayer on diamond nucleation and growth in further investigations.

The Raman spectrum of diamond film (4 h) is shown in Fig. 6. The diamond peak, centred at 1331.09 cm^{-1} , is sharp and high. It is well known that the Raman scattering efficiency of sp^2 carbon is stronger than sp^3 diamond [39], though the scattering intensity of amorphous sp^2 -bonded carbon is found to vary considerably as a function of the incident photon energy as compared to the strength from sp^3 -bonded diamond. Excitation in the infrared range is shown to give a high sensitivity to scattering from amorphous sp^2 -bonded carbon, whereas ultraviolet excitation enhances sp^3 -bonded signal from crystalline diamond considerably even in nanocrystalline films [40, 41]. Therefore the sharp diamond peak indicated the high quality and perfect crystallinity of diamond grains. The peaks at around 1573.15 cm^{-1} corresponded to the G-band of graphite. The two other peaks around 1138.26 cm^{-1} and 1485.91 cm^{-1} were assigned to trans-polyacetylene segments.

Figure 7a is the cross-sectional image of diamond growth with platinum interlayer, it can also be determined that diamond film presented composite structure. There are two different layers in total: one nanocrystalline and one microcrystalline. The top layer is a microcrystalline diamond film and columnar is its typical morphology, while the

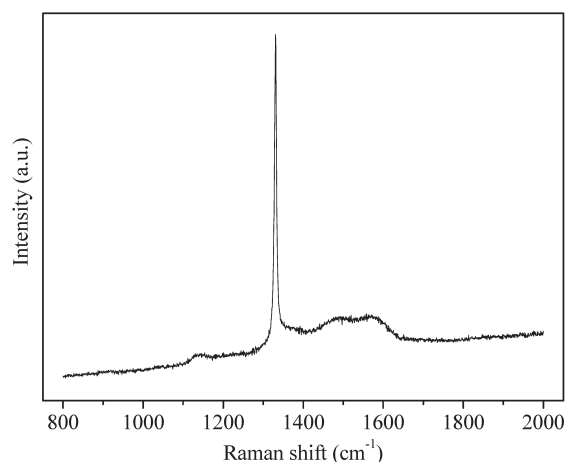


Figure 6 Raman spectrum of diamond film after 4 h diamond growth.

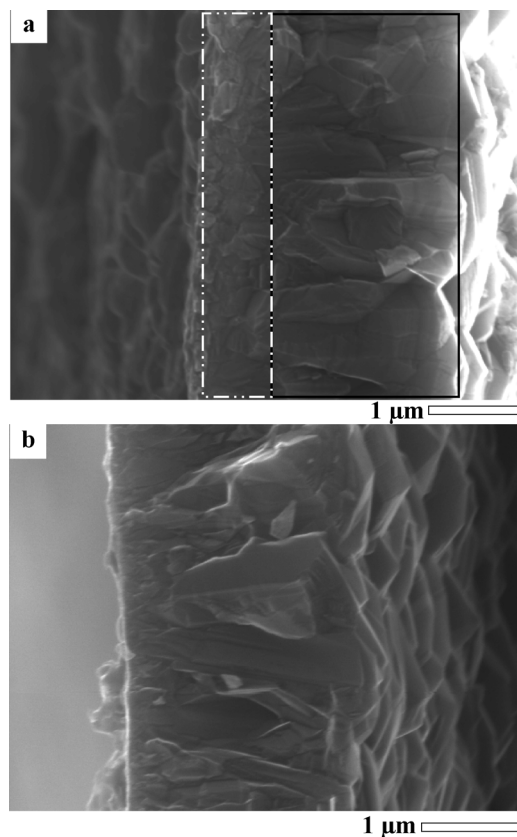


Figure 7 Cross-sectional SEM images of diamond films with (a) and without (b) Pt interlayer after 4 h diamond growth, where the left surface of diamond films corresponds with the nucleation surface, while the right side represents the growth surface, respectively.

thickness was about $2\text{ }\mu\text{m}$ (marked by the solid line). The bottom is nanocrystalline with a thickness in the range of $0.5\text{ }\mu\text{m}$ (marked by the dashed line). The nanocrystalline diamond film gradually developing into a microcrystalline one. The Raman spectrum also supports the composite structure. It presents the sharp diamond peak centered at 1331.09 cm^{-1} , and two Raman peaks around 1138.26 cm^{-1} and about 1485.91 cm^{-1} of nanocrystalline diamond simultaneously. Since the confocal depth of the Raman spectrometer is larger than $2\text{ }\mu\text{m}$ under our condition, it has collected the scattering signal from the nanocrystalline diamond layer to the microcrystalline one.

Diamond film deposited on UDDs seeded substrate without platinum coverage did not present such special structure (Fig. 7b). Therefore, we attributed the special structure to the platinum interlayer. In the growth stage, diamond nuclei competed with each other to grow in the vertical direction. While a platinum interlayer can stabilize more diamond nuclei, this affect prohibited some grains aggregated from the small ones. Only those diamond nuclei far enough from the platinum interlayer can finally grow preferentially and lead to microcrystalline diamond. Therefore, the growth rate of nanocrystalline diamond film

developed into a microcrystalline one is lower than those without a platinum interlayer.

4 Conclusions By sputtering a platinum layer of about 40 nm thickness onto UDDs-seeded copper substrate, diamond nucleation was promoted by carbon dissolving from the UDDs to the platinum interlayer followed by carbon atom transport through platinum layer and formation of sp^3 -bonded diamond clusters at the platinum surface. A nanocrystalline diamond film with faceted diamond was detected. After 4 h diamond growth, diamond film was composed of two different layers: nanocrystalline diamond film in contact with platinum and microcrystalline diamond film further away from the substrate. Such a composite structure was attributed to a platinum diffusion layer that modified the interface properties of diamond nuclei and copper substrate at high temperature. Diamond nucleation by this novel mechanism of controlled carbon transport from the buried UDDs provides a new way to investigate diamond heteroepitaxial growth on copper.

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