

Enhancement of nucleation of diamond films deposited on copper substrate by nickel modification layer

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Abstract: A Ni layer with a thickness of about 100 nm was sputtered on Cu substrates, followed by an ultrasonic seeding with nanodiamond suspension. High-quality diamond film with its crystalline grains close to thermal equilibrium shape was deposited on Cu substrates by hot-filament chemical vapor deposition (HF-CVD), and the sp^2 carbon content was less than 5.56%. The nucleation and growth of diamond film were investigated by micro-Raman spectroscopy, scanning electron microscopy, and X-ray diffraction. The results show that the nucleation density of diamond on the Ni-modified Cu substrates is 10 times higher than that on blank Cu substrates. The enhancement mechanism of the nucleation kinetics by Ni modification layer results from two effects: namely, the nanometer rough Ni-modified surface shows an improved absorption of nanodiamond particles that act as starting points for the diamond nucleation during HF-CVD process; the strong catalytic effect of the Ni-modified surface causes the formation of graphite layer that acts as an intermediate to facilitate diamond nucleation quickly.

Key words: diamond film; nickel interlayer; Cu substrate; chemical vapor deposition; nucleation kinetics; surface modification

1 Introduction

Due to exceptional properties of diamond, such as extreme hardness, high electrical resistivity, wide band gap, and the highest thermal conductivity, diamond film prepared by chemical vapor deposition on non-diamond substrates has been extensively investigated [1,2]. Cu is a crucial substrate because of its strong potential in electronic devices, such as thermal spreader [3,4]. Moreover, Cu is one of the few materials with lattice constant very close to diamond ($a(\text{Cu})=0.3615$ nm, $a(\text{diamond})=0.3567$ nm), which makes it a promising candidate for the heteroepitaxial growth of diamond film [5]. However, the existence of interfacial structure and thermal expansion mismatch between diamond and copper substrates is an inevitable obstacle to diamond nucleation and growth [6–8]. A thin graphite layer must be produced as an intermediate at the early stage, which results in low density of diamond nucleation and long induction time (>10 h) [9].

In order to enhance the nucleation and continuity of diamond film on Cu substrate, a number of surface pretreatment methods have been developed. ECE et al [10] developed a multi-step process to deposit continuous diamond film on Cu substrates. The Cu substrates were first scratched (or seeded) with diamond powder and then annealed in hydrogen at high temperature (1300 °C). Enhanced nucleation was observed on the molten Cu substrates since Cu does not interact with carbon and hydrogen to form $\text{Cu}_x\text{C}_y\text{H}_z$. This enhancement is attributed to the formation of a C-rich template on the melting Cu surface due to lower solubility of C in liquid Cu. ONG et al [11] implanted carbon ions into Cu surfaces prior to diamond deposition and observed the enhanced diamond crystallite nucleation. ALI et al [7] reported that 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 [12] adopted graphite seeding and CO_2 laser irradiation to enhance diamond nucleation on Cu substrate. The enhancement mechanism is attributed to

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the formation of defects and edges during the etching of the seeding graphite layers by the OH radicals in the flame.

In this work, the enhancement of nucleation and growth of diamond films on Cu substrate modified by thin Ni layers was studied. Based on the structural and chemical results of the samples obtained at different stages, a complete analysis of the process was given, and the mechanism for the enhancement effect of nickel modification layer was proposed.

2 Experimental

2.1 Diamond deposition and substrate pretreatment

A hot-filament chemical vapor deposition (HF-CVD) technique was used to grow the diamond films. Details of the experimental set-up can be found elsewhere [13]. Methane (CH_4) and hydrogen (H_2) gases were mixed at a volume ratio of 2:98. The total flow rate was $100 \text{ cm}^3/\text{min}$. The total gas pressure in the reaction chamber was 3 kPa. The gases were thermally activated by tungsten filament mounted 8 mm above the substrates. The substrate temperature was $(1023 \pm 50) \text{ K}$.

Polycrystalline copper foil (99.9% purity) was cut into pieces of $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ and polished to serve as substrates. Prior to the deposition, nickel layers with a thickness of about 100 nm were deposited onto Cu substrate by magnetron sputtering at 1.5 Pa in an argon flow of $20 \text{ cm}^3/\text{min}$ and an sputtering power of 100 W. As a seeding pretreatment, the substrates were ultrasonically treated in an aqueous suspension of detonation nanodiamond powders (particle size about 10 nm) for 30 min, followed by a rinsing in acetone for 5 min.

2.2 Characterization

The morphologies of the deposited films were characterized by field emission scanning electron microscopy (FE-SEM, FEI Sirion200). Microstructural analyses of the diamond films were performed by micro-Raman spectroscopy (Lab Raman RH800) at room temperature using an Ar^+ ion laser (488 nm) at $800\text{--}2200 \text{ cm}^{-1}$. Prior to Raman characterization of the deposited films, the Raman system was calibrated using a Si substrate. X-ray diffraction tests (XRD, $D_{\text{max}}\text{-2500VBX}$ using Cu K_α radiation at a wavelength of 0.154 nm) were performed to study the phase formed on the substrate surface during diamond deposition.

3 Results and discussion

3.1 Ni modification and ultrasonic seeding

The morphological changes resulting from the surface modification of the Cu substrate by sputtering deposition of a Ni layer and the ultrasonic seeding with nanodiamond particles were investigated by SEM. Figure 1 shows SEM images of a blank Cu substrate and Ni-modified Cu substrate before and after ultrasonication in a nanodiamond suspension. As presented in Fig. 1(a), the untreated substrate surface is wavy, but scrupulously clean. No contamination can be observed. Some areas apart from lapping scratches are fairly smooth. Then, the substrate surface reveals a strong precipitation of nanodiamond particles after ultrasonic seeding for 30 min (Fig. 1(b)). The total number of nanoparticles was counted and divided by the area, then a relatively high number density of 10^{10} cm^{-2} of nanosized diamond seeds is observed. The reason that nanoparticles can be

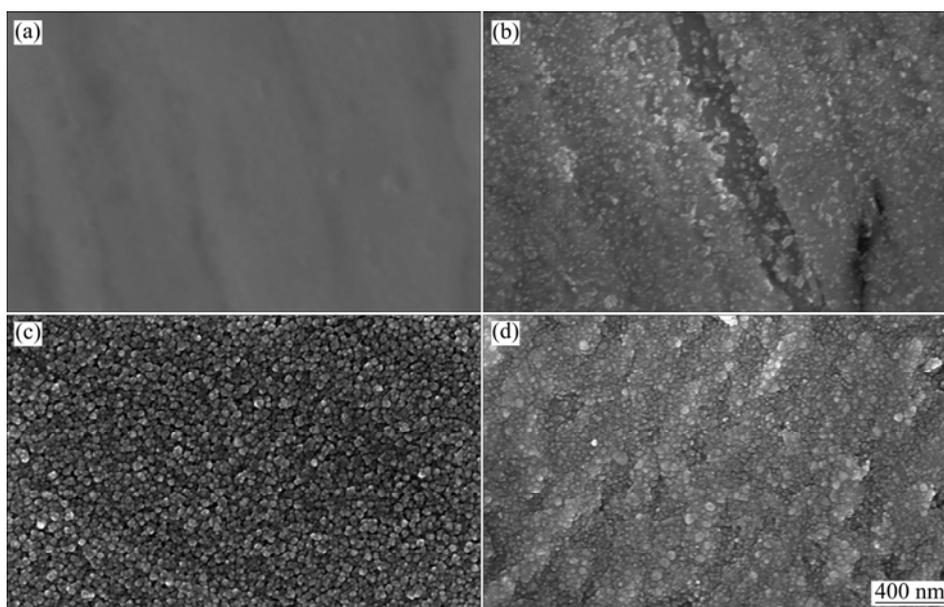


Fig. 1 SEM images of blank Cu substrate (a), ultrasonically seeded Cu substrate (b), Ni-modified Cu surface before (c) and after (d) ultrasonic seeding pretreatment in nanodiamond suspension

charged into Cu substrate must be explained by the interaction energy between Cu surface and nanodiamond. HOUŠKA et al [14] reported that the detonation nanodiamond particles have an extremely strong interaction with metallic targets.

The microstructural image of Ni-modified Cu substrate prepared by magnetron sputtering is shown in Fig. 1(c). It displays an irregular, granular structure of features with lateral dimensions in the range of 40–50 nm. The nanocrystalline modification layer changes Cu surface into a nanometer rough one. After ultrasonic seeding, the Ni-modified surface (Fig. 1(d)) is significantly covered with high density of nanodiamond aggregates that adhere well to Ni surface via van der Waals interaction. Since the lateral sizes of the diamond seeds stay at a narrow distribution of 10 nm, which are smaller than Ni grains, it is easy to distinguish the diamond seeds from the Ni grains. The average density of nanodiamond seeds is in the order of 10^{11} cm^{-2} . This will be a lower limit for the nucleation of diamond during the subsequent diamond CVD growth since the multiple nucleation can take place at a single particle [15]. Comparing with blank Cu substrate, Ni-modified surface absorbs more nanodiamond seeds. The enhanced seeding is attributed to Ni modification layer. The nanocrystalline layer possesses a large number of structural defects (such as dinging bonds), which easily tends to minimize the surface energy by absorption, reconstitution or diffusion.

3.2 Diamond nucleation

In CVD diamond processes, the nucleation of diamond crystals is mainly determined by the availability

of diamond seeds. These seeds are typically induced on the substrate surface by ultrasonication using diamond particles, which act as starting points for the nucleation of diamond from the gas phase. The SEM images of the diamond nucleation and early stage formation of diamond films on pre-seeded Ni-modified Cu substrate and pre-seeded blank Cu substrate are shown in Fig. 2. The significant increase in the diamond nucleation site densities on Ni-modified Cu substrate is evident. As shown in Fig. 2(a), there is only a surface coverage of 80% on blank Cu substrate. This implies that the density of diamond nucleation is lower than the limit for continuous film formation. However, the diamond nucleation site density increases to nearly 10^{10} cm^{-2} on the Ni-modified substrate, which is an order of magnitude higher than that on the blank Cu substrate after a 30 min HF-CVD diamond processing (Fig. 2(b)). In addition, the diamond nucleation can take place at nanometer surface defects, such as scratches and pits, generated during the ultrasonic pretreatment [16]. Moreover, diamond nucleation on the unseeded Ni-modified Cu substrates already leads to diamond nucleation site densities of about 10^9 cm^{-2} (Fig. 2(d)), whereas it does not lead to notable diamond nucleation on unseeded Cu substrate at all (Fig. 2(c)). This implies that the Ni modification layer is an important source for diamond nucleation.

3.3 Crystalline development

It can also be observed that the nucleation on pre-seeded blank Cu substrate leads to the formation of nano-structured diamond with a lower crystalline order. This type of diamond film is commonly referred to as

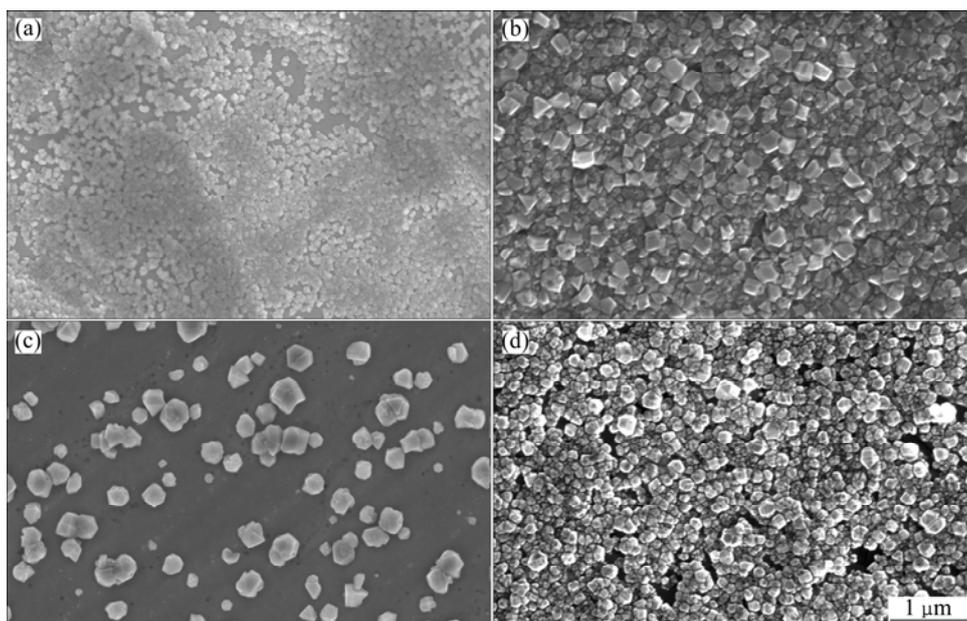


Fig. 2 SEM images of nucleation of diamond on pre-seeded blank Cu substrate (a), pre-seeded Ni-modified Cu substrate (b), blank Cu substrate (c) and Ni-modified Cu substrate (d) without nanodiamond seeding after HF-CVD processing for 30 min

cauliflower- or ballas-type growth morphology. However, the diamond crystallites grown on the pre-seeded Ni-modified Cu substrates are well-faceted. The enhanced diamond nucleation kinetics on the Ni-modified layer induces the development of more uniform diamond films, where no pinholes can be seen. Furthermore, Raman analysis was performed to investigate the crystalline development on diamond deposits after HF-CVD growth for 30 min. The results are shown in Fig. 3. The diamond peak is centered at 1334 cm^{-1} (peak 2), while the Raman peak at 1363 cm^{-1} (peak 3) and 1567 cm^{-1} (peak 5) are corresponding to the D-band and G-band of graphite, respectively. The peaks at 1139 cm^{-1} (peak 1) and around 1492 cm^{-1} (peak 4) are related to trans-polyacetylene(t-PA) at grain boundaries and surfaces, which is one of the characteristics of nanocrystalline diamond [17]. In summary, the following two important trends from the Raman analyses can be observed: 1) both blank Cu substrates and Ni-modified Cu substrates present very similar carbon-related Raman signals; 2) Ni-modified Cu substrates present stronger signals of diamond phases. These evidences testify that the presence of the Ni modification layer improves the kinetics of diamond nucleation and diamond film formation, but does not deteriorate the carbon phase purity of the diamond. On the contrary, the relative Raman intensity of graphitic carbon on Ni-modified Cu substrate is somewhat lower.

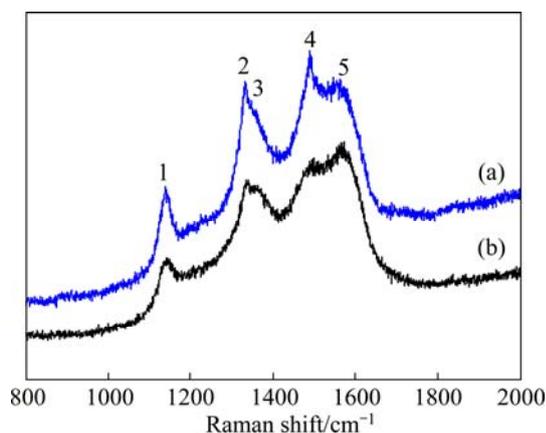


Fig. 3 Raman spectra recorded on Ni-modified Cu substrate (a) and blank Cu substrate surfaces (b) after HF-CVD processing for 30 min (Raman signals numbered 1–5 correspond to signals form t-PA (1, 4), diamond (2), and D-band (3) and G-band of graphite (5), respectively)

3.4 Growth of diamond film

The enhanced nucleation kinetics of diamond on Ni-modified Cu substrate facilitates the rapid formation of dense and smooth nanocrystalline diamond. When the deposition time extends to 4 h, as shown in Fig. 4, the surface of diamond crystals becomes rugged once

diamond nucleation stage disappears and diamond begins to grow. It can be seen that diamond film with well-faceted grains is adequately developed, as the sizes of all the crystalline grains range from 2 to $5\text{ }\mu\text{m}$. Due to different gas chemistry environments, some grains will grow faster. There is no dissociated nickel diffused from the substrate to diamond film. Compared with diamond film deposited on copper substrate by typical condition [8], it can be seen that the diamond crystal in Fig. 4 is more close to thermal equilibrium shape, such as octahedron, rhombic-dodecahedron and truncated octahedron. The flake grain due to twin crystal is scarce in these results. The quality improvement is attributed to the Ni modification layer.

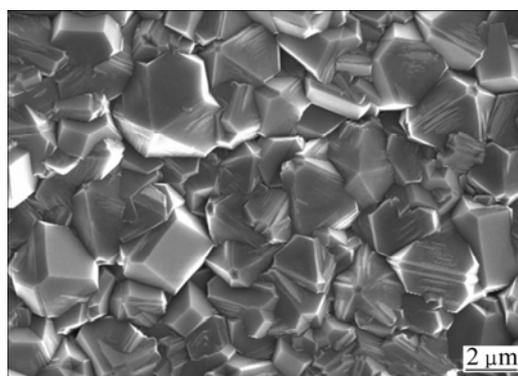


Fig. 4 SEM image of diamond film deposited on Ni-modified Cu substrate after HF-CVD processing for 4 h

The crystallinity of diamond film was further characterized by Raman spectrum. As shown in Fig. 5, an intense and narrow peak is obtained at 1331 cm^{-1} in the Raman spectrum, corresponding to a high degree of sp^3 carbon bonding with the full-width-half-maximum (FWHM) being 8.33 cm^{-1} . Sharp peaks with small FWHM indicate high crystal quality. The scattering intensity is centered at 1570 cm^{-1} , corresponding to negligible sp^2 carbon bonding.

It was reported that the Raman signal is 50 times more sensitive to non-diamond carbon than to crystalline diamond [18]. The percentage of sp^3 carbon in the total carbon content can be quantified with a purity index (Q) that is calculated as follows[19]:

$$Q = \left(\frac{I_D}{I_D + I_C / 50} \right) \quad (1)$$

where I_D is the integrated peak intensity of diamonds at around 1331 cm^{-1} ; I_C is the integrated peaks intensity of non-diamond carbon phase at 1345 , 1470 and 1570 cm^{-1} . By a mixed Lorentzian function, the area of the fitted curves corresponding to non-diamond phases was calculated to be 5.56% of the total carbon content (Fig. 5).

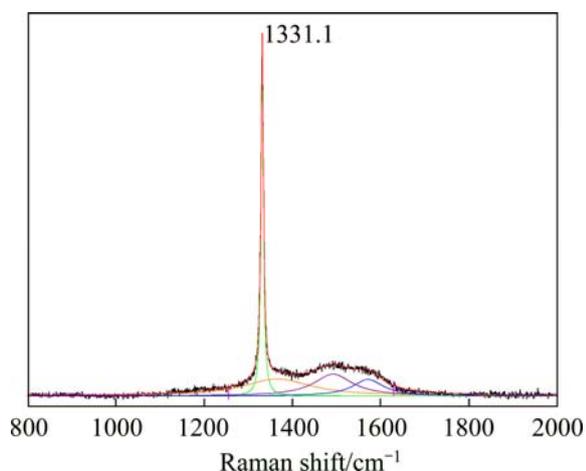


Fig. 5 Raman spectrum of diamond film deposited on Ni-modified Cu substrate after HF-CVD processing for 4 h

3.5 Enhancement mechanism of diamond film deposited with Ni modification layer

The XRD diffraction was used to identify the crystalline phase in the Ni-modified Cu substrate before and after diamond nucleation. As shown in Fig. 6(a), the XRD pattern recorded on Ni-modified Cu substrate before diamond nucleation is dominated by Cu features, where peaks at 2θ diffraction angles of 43.29° and 50.43° are corresponding to the (111) and (200) reflections of Cu structure, respectively. The as-sputtered Ni modification layer is polycrystalline and is clearly identified by the corresponding (111) reflections at 44.51° . After a CVD diamond processing of 30 min, the XRD pattern shows that the Ni layer begins to dissolve into the Cu substrate (Fig. 6(b)). No reflections from Ni phase can be detected at all. Because the strong peak of Cu will enshroud any weak signal emitted from nickel, more phase information of Cu–Ni alloy must be investigated by the grazing incidence XRD [15].

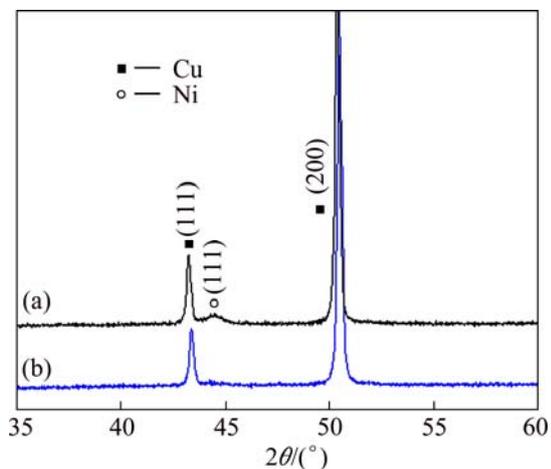


Fig. 6 XRD patterns recorded on Ni-modified Cu substrate before (a) and after (b) diamond nucleation

From binary alloy phases, it is known that Cu and Ni can form an infinite solid solution, (Cu,Ni), above 354.5°C . Mutual diffusion will happen between Cu substrate and Ni layer at a treatment temperature of 900°C . $D(\text{Cu})$ (Intrinsic diffusion coefficient) is one magnitude higher than $D(\text{Ni})$. When Cu/Ni diffusion couple is annealed at 950°C for 100 h, the formation mechanism of diffusion-solution layer is that Cu atom diffuses into Ni block, while Ni atom hardly diffuses into Cu [20]. However, as a thin Ni layer deposited on Cu substrate, its nanocrystalline structure presents high activity. The diffusion kinetics of Ni modification layer and Cu substrate in these experiments must be distinguished with bulky Cu/Ni diffusion couple. It is deduced that Ni modification layer tends to dissolve into Cu substrate. Besides, the atom hydrogen may play an crucial role on the diffusion performance [21].

Introducing Ni-modified layer to diamond deposition seems to be contrary to some well established conclusions, since its high solubility for carbon and its strong catalytic effect on hydrocarbon decomposition and subsequent graphite formation at low pressures prevent CVD diamond nucleation. The graphite interlayer generally forms immediately after a Ni substrate is placed into a methane-hydrogen CVD environment. To suppress the graphite formation, SITAR et al [22] once annealed the seeded Ni substrates in hydrogen at high temperatures (1200°C). In this work, the deposition temperature is $(1023\pm 50)\text{K}$. Obviously, it cannot suppress the graphite formation. Furthermore, the catalytic property of Ni is utilized. On one hand, when the Cu substrate is modified with Ni thin layer, Ni with empty 3d or 4s electronic states facilitates the transformation of diamond seeds absorbed on the substrate into graphitic layers quickly. In Refs. [23,24], it is believed that the diamond seeds only partially dissolve. Carbon reacts with the Ni lattice, and forms a nickel–carbon eutectic phase (or maybe a $\text{Ni}_x\text{C}_y\text{H}_z$ ternary phase). Both carbon and hydrogen dissolve into the Ni lattice, but remain mainly in the surface region. Once the Ni–C–H intermediate states form, the locally supersaturated sites (with sp^3 carbon) on the Ni surface serve as diamond nucleation centers [24]. On the other hand, the hydrocarbon can also be decomposed into carbon by nickel. Because Cu is immiscible with carbon, the formation of graphite layers precedes the diamond nucleation and growth. WEI et al [13] studied diamond growth on Cu (111) via the HF-CVD method with an in situ AES and XPS. The results suggested the following three-step process: first two graphite layers form, then the very slow growth of graphitic layers increasingly distorts when going away from the copper surface and finally, when a critical size corresponding to 5–6 layers

reaches, diamond nucleation and growth take place. An incumbent time of more than 10 h is needed before the growth of graphitic layers. Then, Ni modification layer significantly shortens the incumbent time. While there is a thin nickel layer, it has abundant grain boundaries to provide the channel for carbon atom diffusion. Then, thin nickel layer does not need a long time to compensate for the loss of carbon dissolved into nickel.

Once a critical thickness of carbon deposition is satisfied, diamond nucleation will occur. Two important explanations were proposed on diamond nucleation from carbon phase precursor (graphite, amorphous carbon, glassy carbon, diamond-like carbon, fullerenes, etc). One was proposed by SINGH and VELLAIKAL [25], which divides the nucleation process into two steps. For the first step, diamond-like amorphous carbon layer formed in which small nanocrystalline diamond was embedded. Then, large diamond crystallites grow from those nanocrystalline grains with the consumption of diamond-like amorphous carbon layer. The other explanation was direct heteroepitaxy of diamond from graphitic prismatic planes [26], which considered a direct transformation of graphite into diamond through the distortion of the angles and the bonds of the carbon starting at the edge and corner sites of graphitic planes that will lead to oriented nucleation [27]. Nevertheless, Ni modification layer finally enhances nucleation kinetics of diamond film by its strong catalytic effect.

At the growth stage, Ni modification layer has little effect on diamond film since it diffuses into bulk Cu substrate. During the transformation of Ni modification layer into Cu–Ni alloy, the carbon solubility gradually decreases. The carbon dissolved into Ni modification at an early nucleation stage begins to separate out. It acts as another carbon source for the growth of diamond crystals. Therefore, they tend to present high crystallinity.

4 Conclusions

1) By sputter deposition of Ni modification layer with a thickness of 100 nm, the modified Cu substrate shows the improved absorption of nanodiamond particles which act as starting points for the diamond nucleation.

2) The fast nucleation kinetics on Ni-modified surfaces yields diamond nucleation site density up to about 10^{10} cm⁻², which is 10 times higher than that observed on blank Cu surfaces. The strong catalytic effect of the Ni-modified surface causes the formation of graphite layer that acts as an intermediate to facilitate diamond nucleation quickly.

3) High-quality diamond film with its crystalline grains close to thermal equilibrium shape is deposited on Ni-modified Cu substrate, and the sp² carbon content is less than 5.56%.

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镍改性层增强铜基底沉积金刚石膜的形核

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摘要: 在铜基底溅射约 100 nm 厚的镍改性层, 然后置入纳米金刚石悬浮液中超声震荡加载籽晶, 随后在热丝化学气相沉积设备中制备出晶体颗粒接近热力学平衡形态的高质量金刚石膜, 其中 sp^2 碳相含量低于 5.56%。分别采用激光拉曼光谱、扫描电镜与 X 射线衍射对金刚石膜的形核与生长进行研究。实验结果表明: 在溅射有镍改性层的铜基底上, 金刚石的形核密度比在无改性层的铜基底上的形核密度高 10 倍。镍改性层的增强机制主要来源于两个方面: 镍改性层的纳米级粗糙表面增强金刚石籽晶颗粒的吸附; 镍改性层的强催化效应加速铜基底上金刚石形核生长所需的石墨过渡层的形成, 从而促进金刚石的快速形核。

关键词: 金刚石膜; 镍过渡层; 铜基底; 化学气相沉积; 形核动力学; 表面改性

(Edited by Wei-ping CHEN)