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Nanocrystalline Diamond Matrix Deposited on Copper Substrate by Radical Species Restricted Diffusion

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Nanocrystalline diamond matrix (or patterned nanocrystalline diamond) have been grown by hot filament chemical vapor deposition (HFCVD) on copper substrates, which were masked by a copper template filled with through-holes. The influence of the mixing ratio for CH_4/H_2 source gases, total gas pressure and the aspect ratio (the ratio of hole depth to its diameter) on the morphology, grain size and quality of diamond films were investigated. Continuous diamond films were obtained under 2.0 kpa. When increasing the aspect ratio from 0.67 to 2.0, a gradual reduction of diamond grain size from micrometer to nanometers scale was observed. The formation of nanocrystalline diamond (NCD) matrix can be attributed to the restricted diffusion of radical species and the diamond nucleation kinetics on copper substrates. By through-holes of templates on copper substrates to restrict the diffusion and transport of radical species, NCD matrix was successfully deposited on copper substrates.

Keywords: Nanocrystalline Diamond Matrix, Hot Filament Chemical Vapor Deposition (HFCVD), Through-Hole Template, Copper Substrate.

1. INTRODUCTION

Owing to its promising mechanical, chemical, optical, thermal and electrical properties, CVD diamond is considered as an excellent candidate for micro-/nanoelectromechanical systems (MEMS/NEMS), low-field emitters and other advanced applications.^{1–3} Recent reviews^{4–7} have compiled different MEMS devices made from CVD diamond prepared by different research groups around the world. Those devices have been demonstrated for certain application areas such as gears, motors, burrs and scanning probe microscopy (SPM) tips. Especially, in the case of SPM tips, diamond has been proven to be an ideal material for its exceptional high hardness and low coefficient of friction.^{8–10}

However, three-dimensional (3D) devices in MEMS require deposition of diamond from the vapor phase inside the trenches and channels with an aspect ratios > 2.0,^{11,12} where, for a hole or a trench, the aspect ratio is the ratio of its depth to its dimension. Under those conditions, radical species diffusion is restricted. For the same

composition of feed gas, radical species concentrations vary along with the depth of the trench or the hole due to the surface recombination and restricted diffusion of gas-phase radicals inside micro-trenches, which could affect the ability to grow crystalline diamond films compared to non-diamond carbon at aspect ratios > 1.0. Eaton et al.¹³ presented a modeling approach utilizing a recently constructed C-H-O ternary diagram based on radical species composition to predict the diamond deposition into trenches with high aspect ratios under both Fickian and Knudsen diffusion conditions. When deposition of diamond thin films on pattered Si(100) substrates using a three-step process, Monteiro et al.¹⁴ have found that diamond films with uniform quality, morphology and grain size have been obtained on trenches with a diameter of down to 1 μ m and an aspect ratio of approximately 1, and a noticeable gradient in nucleation density and grain size was observed as a function of the depth.

Copper is one of the most common materials in electrical industry. Diamond deposition on copper substrate can enhance its mechanical, thermal and electrical properties. But a number of investigations have suggested that diamond deposition on copper is a difficult endeavor.^{15–19}

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Major problems encountered with diamond synthesis on copper are the low nucleation density, film cracking and poor adhesion.

In this study, nanocrystalline diamond matrix was successfully deposited on copper substrate by varying the aspect ratio of the template covered on copper substrate to restrict the diffusion and transport of radical species. NCD matrix in text is defined as patterned diamond film, which is different from textured NCD film. The later needs most grain of diamond film present preferential orientation. Furthermore, diamond film was analyzed by the scanning electron microscope (SEM) and Raman spectroscope, respectively.

2. EXPERIMENTAL PROCEDURES

The substrate was polycrystalline copper foil (99%) with a dimension of $\Phi 10 \text{ mm} \times 1 \text{ mm}$. Prior to diamond deposition, copper substrates were polished using SiC sandpapers. The polished substrates were then ultrasonically pre-treated for 15 min in diamond slurry, a mixture of 1 g diamond powder with an average particle diameter of 0.25 μ m and 10 ml of acetone. Afterwards, these substrates were cleaned in acetone for 5 min.

The substrate was masked by a template full of array through-holes with different aspect ratio, and then placed in vacuum chamber for diamond deposition. The template was also made of copper foil with a thickness of 1 mm. Figure 1 shows the schematic illustration of the template and copper substrate. Diamond deposition was carried out in a hot filament CVD reactor, which has been described elsewhere.^{20, 21} A spiral coil filament (tungsten wire, diameter 0.38 mm, screw inner diameter 1 mm, 14 turns, 1 mm separation between adjacent turns, coil length 14 mm) suspended between two molybdenum rods was used to activate the process gas for diamond film deposition. In order to eliminate the influence of the template on the temperature distribution, the filament-substrate distance (d_f) was maintained at 8 mm. At the same time, we placed the thermocouple on the surface of copper substrate. The



Fig. 1. Schematic illustrations of the copper substrate masked by a copper template filled with through-holes.

typical growth condition used for diamond deposition is: methane concentration, 2%; hydrogen, 98%; total gas pressure, 2 kPa; substrate temperature, 750 ± 50 °C.

The diamond film was observed using FEI Sirion200 Field emission scanning electron microscope (FESEM) with energy dispersive X-ray detector (EDX). Raman spectroscopy (Lab Raman RH800 spectrometer (UK) with an argon laser source with a 488 nm wavelength) was applied to evaluate the quality of diamond film.

3. RESULTS AND DISCUSSION

Since the copper substrate was masked by a through-hole template, only those areas directly beneath the throughholes are exposed to radical species (Fig. 1). The first set of experiments was finished by varying gas pressure parameter while keeping the aspect ratio at 1.0, and the methane concentration at 2%. Figure 2 shows SEM images of diamond films prepared at different gas pressures which are 1.5, 2.0, 2.5 and 3.0 kPa, respectively. For the convenience of comparison, all SEM images unless otherwise specified were taken at the centre of diamond cylinder. Apparently, the central zone is enough typical for a specific deposition parameter set. With the increase of deposition pressure from 1.5 to 2.0 kPa, diamond nucleation density increased. However, when the gas pressure was increased further to 3.0 kPa, the nucleation density decreased. Obviously, it can be found that only at 2.0 kPa, the deposited diamond film is continuous. This indicates that highest nucleation density was achieved. Under the pressure of 2.5 kPa, diamond grains are more adequately developed. Faceted surface became more distinct. Besides, the grain size did not become smaller with the decrease of the gas pressure. This phenomena is deviated from other report²² in which diamond films were deposited on plain Si(100) wafers.



Fig. 2. Representative SEM images of the diamond films deposited at different gas pressures (a) 1.5 kPa, (b) 2.0 kPa, (c) 2.5 kPa and (d) 3.0 kPa.

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As we known, gas pressure affects diamond growth kinetics mainly by influencing thermal decomposition rate of the reacting gases and transportation of radical species to substrate surface.²³ Gas pressure serves as dual effects when depositing diamond on copper substrate with mask. On one hand, the concentration of thermally decomposed active species formed at the filaments is generally proportional to the concentration of source gas (the gas pressure). With increase of pressure, more active species (H atoms and CH₃ radicals, etc.) will be generated. However, when reaching a critical pressure threshold, the concentration of activated species at the filaments becomes saturated without further increasing with the gas pressure, as discussed in the investigations reported by Schwarz et al.²⁴ On the other hand, the thermally activated species must reach the substrate surface masked by the template to initiate diamond nucleation and growth. The fraction of activated gases that survive in collision, arrive and absorption onto the substrate surface also depends upon the gas pressure. When considering the surface recombination of gas-phase radicals inside micro-trenches, the mean free path for radical species diffusion is given by¹³

$$\lambda_k = \frac{RT}{\sqrt{2}\pi d_{m,k}^2 P N_A} \tag{1}$$

Where *R* is the gas constant, *T* is the assumed temperature, $d_{m,k}$ is the molecular diameter of *k* component, *P* is the pressure, N_A is Avogadro's number. As described in Eq. (1), the mean free path of the active species is inversely proportional to gas pressure. Therefore, with decreasing gas pressure, the mean free path increases. It leads to an increase in the number of active species or radicals that will survive in collisions and impinge on the surface of substrate.

Under the pressure of 3.0 kPa, the concentration of radical species was the highest, but the lowest mean free path decreased the number of radicals which diffused and transported from the surface of the template into the bottom of through-hole. Most of radical species collided on the cylindrical wall of though-hole and recombined into nonactive species. Then residue radical initiated small amount of diamond nucleation and growth, which agreed well with SEM images.

While at 1.5 kPa, the mean free paths of radical species fall into the range of several millimeters, which is comparable with the distance between the top and the bottom of the through-hole of mask.²³ Then those radical species diffused and transported with only few collisions. Therefore, the kinetic energy of radicals can be reserved and more radicals are actually arrived on the surface of copper substrate. High kinetic energy results in enhanced surface mobility of these reactive species, which promotes an aggregation of the precursors and diamond growth.²² Therefore, diamond grains were more adequately developed than those under the pressure of 3.0 kPa.



Fig. 3. Magnified SEM image of diamond films prepared at 3.0 kPa. The inset shows the EDS analysis in the white rectangle region.

From the background of Figures 2(c) and (d), lots of small grains can be observed. EDX analysis validated that the element of small grains is copper rather than carbon. An enlarged SEM image was shown as Figure 3. Compared with nanoparticles prepared by other methods,^{25,26} those copper particles present favorable crystallinity and the particle size was in the range of 1–2 μ m, and it can be observed that most of the particles were of a truncated octahedral structure, an equilibrium form of cubic crystal. Even a very long induction time (>10 h) was adopted,²⁷ the small copper grains have never been reported when depositing diamond on plain copper substrate. In our experimental conditions, deposition temperature is lower than the melting point of pure copper (1085 °C). While its saturated vapor pressure at 722 °C is 10⁻⁸ Torr,²⁸ we speculate that gas-solid phase reaction has taken place, that is, copper diffused from the substrate to the gas phase and re-crystallized at the solid-gas interlayer. As the throughhole restricts the copper gas diffusion to the outside of the mask, the gaseous copper can easily reach critical saturation to motivate phase change. Besides, atom H with high activity may as well play an important part within this phase transformation, although more evidences and further research work are essential. In terms of the specific mechanism, we can expect a novel method to prepare small particles of some high melting point metal at medium temperature with controlled shape.

The continuous film formed under the pressure of 2.0 kPa was evaluated by Raman spectrum. As shown in Figure 4, the sharp peak at 1331 cm⁻¹ is the typical Raman peak of crystalline diamond. The broad peaks at approximately 1580 cm⁻¹ assigned to *G*-band for graphite. It is well known that the Raman scattering efficiency for the sp²-bonded graphite is more than 50 times greater than that for the sp³-bonded diamond.²⁹ It is clear that the diamond film holds favorable quality and crystallinity.

In order to reveal the relation between diamond nucleation and the radical concentration, diamond films were deposited with initial methane concentration increasing



Fig. 4. Raman spectra of diamond films deposited at 2.0 kPa.

from 0.5% to 5.0%. As illustrated in Figure 5, for 0.5% methane concentration, no diamond nucleation was found. In contrast, the surface of copper substrate underwent dramatic structural change as they suffered from H_2 plasma treatment.³⁰ It shows that the scratches and dimples on the initial surface have completely disappeared. Smooth surface was created in some area, while, in other areas, copper particles were produced.

When methane concentration increased to 1.0%, a remarkable change occurred. The surface of copper substrate was covered by measles-like dots, and according to the EDX analysis, the component of these dots is carbon. So, it can be concluded that, in this case, the methane concentration is still not sufficient to induce notable diamond nucleation. Only in favorable positions, such as crystal boundaries, limited amount of diamond nuclei can be generated. The white particle in the middle of Figure 5(b) was diamond grain which became fully developed and showed faceted surface. Those results were in agreement with the earlier results reported by Le Normand et al.^{31,32} and Li et al.³³ in which they observed carbon aggregates formed on copper under the conditions of diamond chemical vapor deposition. When methane concentration reached 2.0%, the diamond nucleation density increased (refer to Fig. 2(b)) and uniform diamond grains were obtained. Then, when methane concentration increased to 5.0%, it is clear that the particle size of diamond film decreases and secondary nucleation density increases. When depositing diamond film on a plain Cu substrate, it can obtain high nucleation density to grow continuous diamond film at 1.0% methane concentration. In other words, the template masked on copper substrate change gas chemistry and the balance of radical species. We will discuss the details in the following.

Figure 6 shows the SEM images of the diamond films prepared with template of different aspect ratios. During the desposition, the gas pressure was kept at 2.0 kPa and initial methane concentration was fixed at 2%. With the increasing of aspect ratios from 0.67 to 2.0, the diamond grain size decreased gradually from micrometer to nanometer scale. The large diamond grains shown in Figure 6(a) are the characterization of fully growth of diamond crystals without any appreciable formation of secondary nuclei. With the increase of the aspect ratio, as illustrated in Figures 6(b)-(c), the diamond grains became less developed and a large number of smaller diamond grains appeared at the neighborhood of larger ones. Smaller grains were formed as a consequence of the enhanced secondary nucleation effect. And, this effect can be intensified by further increasing of the aspect ratios to 2.0, resulting in the deposition of smooth nanocrystalline diamond (NCD) films, which is presented in Figure 6(d).

Figure 7 displays the relation between crystal size and aspect ratio. Average grain size is calculated by counting all diamond grains in the SEM image. It is evident that aspect ratio increases with average crystal size decreases. The y axis (crystal size) intercept of extrapolated fitting line goes to 5 μ m at 0 (aspect ratio), which coincides



Fig. 5. SEM images of the diamond films prepared at different methane concentrations (a) 0.5%, (b) 1.0%, (c) 3.0% and (d) 5.0%.



Fig. 6. SEM images of the diamond films deposited under the templates with different aspect ratios (a) 0.67, (b) 1.0, (c) 1.5 and (d) 2.0.

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Fig. 7. Average grain size of diamond films (determined by surface SEM analysis) plotted as a function of aspect ratio.

with measured size of diamond deposited on plain copper substrate.¹⁵

Raman spectra of films grown at different aspect ratios are shown in Figure 8. A common feature in the spectra is a sharp peak centered at 1331 cm⁻¹, which is the typical Raman peak of crystalline diamond. The broad peaks at approximately 1560 cm⁻¹ assigned to *G*-band for graphite. With the increase of aspect ratios, the 1331 cm⁻¹ diamond peak becomes weaker and broader. As the diamond grain size is reduced, grain boundaries increase, resulting in the increase of amorphous carbon (sp² C) content.³⁴ A closer observation reveals that two additional peaks at around 1140 cm⁻¹ and 1475 cm⁻¹ appear in the spectra and they become more prominent at high aspect ratios. The 1140 cm⁻¹ peak has been identified to be related to the diamond nanocrystallites.^{35, 36} It has been argued by some researchers that both peaks can be assigned to trans



Fig. 8. Raman spectra of the diamond films deposited under the templates with different aspect ratios (a) 0.67, (b) 1.0, (c) 1.5 and (d) 2.0.

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polyacetylene situated at the grain boundaries of diamond nanocrystals.^{27, 34}

Regarding the restricted diffusion and transport of those radical species participating in the growth processes, diamond deposition inside a hole is quite complex. The concentration of radical species C_k inside a cylindrical hole can be described by the following one-dimensional, reaction-diffusion equation:¹³

$$\frac{d^2 C_k}{dz^2} = -\frac{1}{D_{E,k}} \left(\frac{4}{d_t} r_{k,\text{surface}} + r_{k,\text{gas}} \right)$$
(2)

Where r_k represent the reaction rates at the surface and at the gas phase, d_i is the effective trench diameter and $D_{E,k}$ is the effective diffusion coefficient for radical species k through the stagnant gas phase. Considering of each individual elemental reaction with the appropriate rates,³⁷ Eaton et al.¹³ have resolved the concentration of the main species present in diamond deposition by Eq. (2). They have proved that radical species concentration is a function of aspect ratio. There is a concentration gradient in gas phase composition from the top of the hole to the bottom. Compared to other major radical species (e.g., CH₃), the concentration of atomic hydrogen decreases faster when aspect ratios < 2.0. This would favor growth of nondiamond phases at the bottom of the hole for atomic hydrogen serves as an effective etching for sp² C.¹⁴

As is known to all, diamond cannot nucleate on copper through carbide, nor can it be dissolved in copper. It has been shown that diamond will nucleate from carbon layers on Cu(111) surface when five to six carbon layers was reached.²⁷ Constant et al.³⁸ proceeded reporting that the diamond nucleation occurred through a phase transformation from later transformed graphite layers, not directly from diamond seeds preliminary deposited on the surface. Singh et al.³⁹ further divided the diamond nucleation from carbon phase precursor nucleation process into two steps. For the first stage, diamond-like amorphous carbon layer was formed in which small diamond nanocrystallines were embedded. Then large diamond crystallites were grown from those nanocrystallines with the consumption of diamond-like amorphous carbon layer. Nevertheless, more non-diamond phase was produced on the substrate under the mask with high aspect ratio which enhances secondary nucleation of diamond films, and then NCD film was formed. In other words, by restricting diffusion and transportation of those radical species using the through-holes of variant aspect ratio in the template, NCD film on copper substrate can be deposited.

Figure 9 presents the results of NCD matrix on copper substrate deposited for 2 h. Periodic NCD patterns were deposited successfully by restricting the diffusion and transportation of radical species (Fig. 9(a)). As shown in Figure 9(b), the diameter of diamond cylinder was 520.66 μ m, which is comparable with the diameter of through-hole. What deserves special attention here is working error of the holes led to several NCD cylinders



Fig. 9. NCD matrix on copper substrate deposited for 2 h.

with various diameters. Furthermore, Figure 9(c) (the center) and Figure 9(d) (the edge) are the magnified SEM images of different sections of a diamond cylinder. Comparing with those two images, marginal effect is visible. Diamond crystal size became uneven at the outside of diamond cylinder, which may be originated from the disturbance of cylindrical wall, and further research will be carried out to interpret this phenomenon.

4. CONCLUSIONS

The relationship of deposition pressure and aspect ratios of the through-hole on the morphology, grain size and crystallinity of the diamond films grown on the masked copper substrate was comprehensively investigated. Two opposite effects of pressure were found balanced and largest nucleation density and continuous diamond film was achieved under the pressure of 2.0 kpa. When increasing the aspect ratio from 0.67 to 2.0, a gradual reduction of diamond grain sizes from micrometer to nanometers was observed. The formation of NCD films was attributed to the restriction on the diffusion of radical species and diamond nucleation kinetics on copper. By varying the aspect ratio of the template covered on copper substrate to restrict the diffusion and transport of radical species, NCD matrix was successfully deposited on copper substrate. Besides, diamond growth by radical restricted diffusion and transport provides another pathway to investigate diamond coating on 3D devices in MEMS.

Acknowledgments: We gratefully acknowledge the Nature Science Foundation of China (No. 21271188), the China Postdoctoral Science Foundation (No. 2012M521541), the Fundamental Research Funds for the Central Universities (No. 2012QNZT002), the State Key Laboratory of Powder Metallurgy (No. 20110933K), and the Open-End Fund for Valuable and Precision instruments

of Central South University (No. CSU2012024) for financial support.

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Received: 25 September 2012. Accepted: 10 April 2013.