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# Improvement in adhesion of diamond film on Cu substrate with an inlay structured interlayer

W.Q. Qiu [a,b,*], A. Dasari [b], Y.-W. Mai [b]

[a] School of Material Science and Engineering, South China University of Technology, Guangzhou 510640, PR China
[b] Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronic Engineering (J07), The University of Sydney, Sydney, NSW 2006, Australia

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ABSTRACT

Diamond films were fabricated by using a two-step process on copper substrates in this study. The first step involved electroplating a chromium (Cr)–diamond composite interlayer on copper substrate and in the second step continuous diamond film was deposited on top using the hot-filament chemical vapor deposition (HFCVD) method. The interfacial characteristics was investigated by indentation tests and the thin film surface morphology, phase structure and residual stress analyzed by scanning electron microscopy (SEM), X ray diffraction (XRD) and Raman spectroscopy. The results show that the diamond particles are deeply imbedded in the chromium layer and the amorphous Cr in the composite interlayer was carburized to $Cr_3C_2$ during the CVD process. Low residual stress was detected in the diamond film and good adhesive strength between film and substrate was obtained due to the diamond particles anchored deep in the $Cr_3C_2$ matrix. Concentric cracks but no delaminated areas and radial cracks were observed on the periphery of the indentation at indentation load of 441 N.



## 1. Introduction

Chemical vapor deposited (CVD) diamond coatings have potential applications in mechanical, thermal, optical and electronic devices due to their outstanding combined properties including ultra-high hardness, low friction coefficient, superior wear resistance, high thermal conductivity and chemical inertness [1–4]. Most of these applications require superior adhesion properties between the diamond coating and the substrate employed. To improve the adhesion strength, a common approach is to use an 'interlayer' [5]. Interlayers are generally classified into two types depending on their interface structure: (a) a planar structured interface, where the interlayer material is simply deposited on the substrate and then the diamond film is grown on the interlayer [6–11]; and (b) an inlay structured interface, where some diamond particles are partially embedded in the interlayer and a homo-epitaxial diamond film is grown on the exposed diamond particles [12–14]. Generally, diamond coatings with an inlay structure show stronger interfacial strength as they are deeply anchored by the diamond grains into the interlayer. However, proper deposition of a composite interlayer comprising metal and diamond particles holds the key to success with this approach. An efficient methodology is by electroplating of metal–diamond where the diamond particles are suspended in a plating bath during the process [12–16]. Ni–diamond composite as an inlay structured interlayer is commonly used due to the relatively good wettability of nickel to diamond and the high cathodic current efficiency. However, nickel can catalyze diamond to graphite at the Ni/diamond interface during the CVD process [17–19]. Resende et al. [14] reported that the nickel layer was unsuitable for diamond deposition even though a $H_2$–plasma treatment was used to form a $Ni_4C$ layer that promoted diamond nucleation [20].

Chromium, the only carbide forming metal which can be electroplated from an electrolyte solution, has been utilized as a planar structured interlayer to improve the interface of substrate and diamond film and form a strong carbide bond [6,10,11]. Having no catalytic effect at the Cr/diamond interface during the CVD process, chromium is a suitable inlay structured interlayer metal. Here, we report the first results on the fabrication, structure and interfacial characteristics of diamond films deposited on copper substrates with a Cr–diamond inlay structured interlayer.

## 2. Experimental work

The inlay structured diamond coatings are fabricated using a two-step process on copper substrates. The first step was completed by electroplating. A 0.5–1 μm thick Cr layer was deposited on a Cu substrate, followed by the deposition of a Cr–diamond composite coating (1–1.5 μm thick) and another Cr layer (2.5–3 μm thick) to fix the diamond particles. The Cr layer was electroplated in a Cr (III) electrolyte solution containing 0.5 M $Cr^{3+}$, 0.6 M $HCOO^-$, 0.6 M $H_3BO_3$, 2.4 M $Cl^-$ and 0.1 M $Br^-$ at 30 °C and a current density of 12A/dm$^2$. The Cr–diamond composite coating was deposited in the Cr

* Corresponding author at: School of Material Science and Engineering, South China University of Technology, Guangzhou 510640, PR China.
*E-mail address:* mewqqiu@scut.edu.cn (W.Q. Qiu).

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(III) electrolyte added 25 g/l diamond particles with the sizes varied from 4.0 to 4.5 μm, at 30 °C with a current density of 10 A/dm$^2$. In the second step, a continuous diamond coating was deposited on the Cr–diamond composite interlayer coated on Cu substrate by the hot-filament chemical vapor deposition (HF CVD) process. Details were described elsewhere [9]. The fabrication process parameters used were: tungsten filament temperature, 2100 °C; gas pressure, 6.0 kPa; $CH_4$ concentration in $H_2$, 1.5 vol.%; distance between filament and substrate, 5 mm; substrate temperature, 800–860 °C; and deposition time, 18 h. The total thickness of diamond coating and inlay interlayer was ~22 μm.

All the samples were characterized by scanning electron microscopy (SEM), Raman spectroscopy (Argon laser, $\lambda = 514.5$ nm) and X-ray diffraction (XRD, $\lambda = 0.154$ nm from Cu $K_\alpha$ target) to examine the surface morphology, coating crystallinity and residual stress, and phase structure, respectively. Adhesion of diamond coatings was tested by a Rockwell hardness tester with loads of 147, 294 and 441 N, respectively, using a conical diamond indenter with a tip size of ~200 μm and an included angle of 60°.

## 3. Results and discussion

Fig. 1(a) shows the SEM micrograph of the as-plated Cr–diamond composite layer coated on Cu substrate. Diamond particles are well distributed in the chromium matrix and without any specific orientation or clear facets. It is also evident that most of the diamond particles are only partially embedded in the matrix. The density of the diamond particles is ~$2\times10^6$ to $4\times10^6$/cm$^2$. A high magnification micrograph of the embedded diamond particles (Fig. 1(b)) suggests the presence of cracks in their vicinity was probably attributed to the release of hydrogen during the Cr deposition [21]. This type of cracks was also observed in most of the trivalent chromium coatings [22]. The embedded portion of the diamond particles are firmly anchored in the chromium matrix, while the uncovered portion serves as seeds for subsequent CVD homo-epitaxial diamond growth.

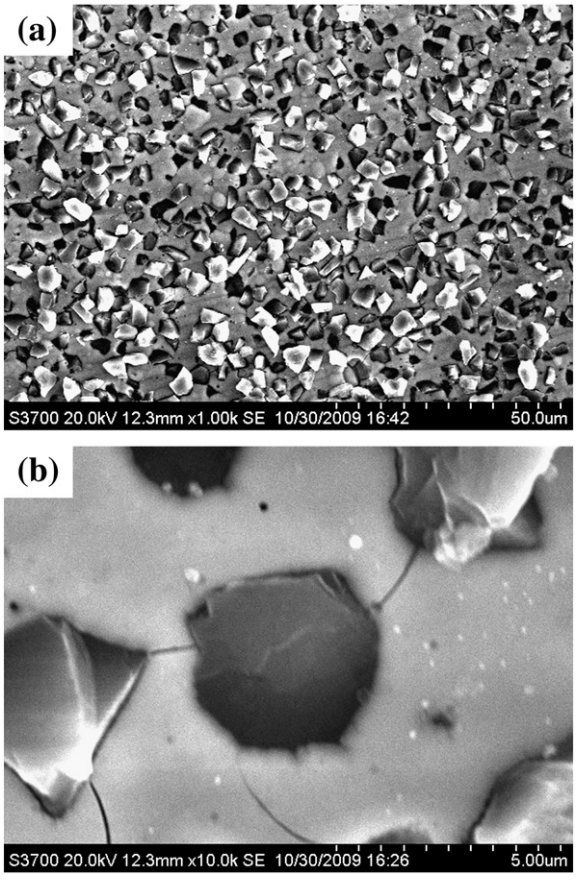


**Fig. 1.** SEM micrographs showing the surface of as-plated inlay interlayer. (a) The distribution of diamond particles, and (b) diamond particles embedded in Cr layer.

The surface morphology of the diamond film on Cr–diamond composite coated copper substrate after 18 h deposition of hot-filament CVD is shown in Fig. 2. A continuous diamond film with well-faceted grains is grown from the initial distributed particles. A broad size distribution (in the range of ~2–12 μm) of grains is evident as some are grown from the primary nucleating agents (homo-epitaxial growth of uncovered diamond seeds) and a few are secondary nucleated particles. XRD patterns of the films before and after the CVD process also confirm the continuity in the diamond film as high intensity Cu peaks are observed only before the CVD process (Fig. 3). Furthermore, the absence of Cr peaks in the pattern taken before the CVD process suggests the likelihood of the presence of Cr in amorphous state (similar to [22]). The weak diamond peak for the film before CVD is due to the combined effect of the dominance of the strong Cu substrate signal and only a small portion of diamond particles in the inlay interlayer. This is reconfirmed by the presence of a strong diamond peak in the pattern taken after the CVD process. The amorphous Cr reacted with carbon during the CVD process resulting in chromium carbide ($Cr_3C_2$), which is also identified in the XRD pattern.

Fig. 4 shows the Raman spectrum of the diamond film on the interlayer coated Cu substrate prepared by CVD. The strong and sharp peak at 1335 cm$^{-1}$ represents the good crystalline nature of diamond. However, as 1332.5 cm$^{-1}$ is the normal peak position of natural diamond, the shift in the diamond peak indicates that the film is under compressive stress. In the case of biaxial stress σ, the Raman line of polycrystalline diamond generally splits into singlet and doublets [23]. As no splitting peak is observed in Fig. 3, the peak at 1335 cm$^{-1}$ is assumed to be an overlap of singlet and doublets, and

$$\sigma(\mathrm{GPa}) = -0.567(\nu_m - \nu_o)\left(\mathrm{cm}^{-1}\right), \quad (1)$$

where $\nu_m$ and $\nu_o$ are measured and natural diamond wave number, respectively. Using this equation, the residual compressive stress in the diamond film grown on Cr–diamond composite interlayer coated copper substrate is 1.42 GPa. This is very much smaller than 6.7 GPa obtained in [5] for directly deposited diamond film on chromium substrate. It is believed that the soft copper substrate and Cr–diamond composite interlayer are responsible for the stress reduction in our present work.

Fig. 5(a) shows the SEM image of the residual imprint of the indentation with an applied load of 441 N. The diameter of imprint is ~870 μm and the diamond film has not been delaminated on the periphery of the indent. A high magnification micrograph shows concentric ring cracks evident on the surface of the film around the

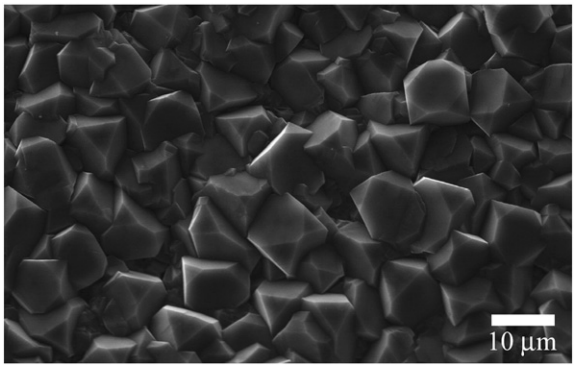


**Fig. 2.** SEM micrograph of surface morphology of diamond film.