The dynamic sublayers for improving the adhesion of CVD diamond films on copper

A V Gaydaychuk, S A Linnik and V V Okhotnikov

National Research Tomsk Polytechnic University, 30 Lenin Avenue, 634050, Tomsk, Russia

E-mail: gaydaychuk@tpu.ru

Abstract. Polycrystalline diamond films were fabricated on copper substrates by a multi-step process comprised of physical vapor deposition of Al-based composite interlayer on Cu substrate and depositing continuous diamond film on composite interlayer by plasma assisted chemical vapor deposition (PACVD). The interface characteristics and adhesion strength were investigated by Auger electron spectroscopy, Raman analysis, calotest and indentation test. The results show that the continuous film without cracks is successfully obtained. The improved adhesion between diamond film and substrate results from the low residual stress in the film due to their compensation by Al interlayer in the sample cooling process.

1. Introduction

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 [1, 2]. However, the high thermal conductivity of diamond by itself is not enough to dissipate heat, as the heat capacity of diamond is limited [3]. Copper is a cheap material for thermal spreading with average thermal conductance and large heat capacity. Therefore, chemical vapor deposition (CVD) of diamond film on copper substrate has attracted great attention.

The main problem of diamond–copper heat spreader is adhesion failure. The poor adhesion of diamond film coatings has been attributed to the high residual stress in the coatings and the weak interfaces between the coatings and Cu substrates [3, 4]. In addition to reducing the residual stresses in diamond coatings, many efforts, including preseeding, scratching, and adding an interlayer, have been made to enhance the interfacial adhesion of the diamond/copper systems [5–9]. Appropriate interlayer between the diamond film and Cu substrate can effectively improve the interfacial adhesion. The interlayer is expected to perform the following three main functions: as adhesive layer, to enhance diamond/copper bonding strength; as diffusion barrier, to protect the detrimental element, which catalyzes diamond to graphite and consequently leads to the coating delamination; and as nucleation layer, to enhance diamond nucleation.

In this paper, Al-based composite interlayer for improving diamond–copper adhesion strength was investigated.

2. Experimental details

There are two methods to improve diamond/copper adhesion strength: method related to preparation of the substrate (preseeding, scratching etc.) and method directly associated with diamond film (residual stress reduction and interlayer adding). The first type of method initially ineffective because at a certain thickness of the diamond film (due to multiple internal stresses increase) regardless of diamond/substrate adhesion magnitude the film will peel off. For this reason, the second method (Al-based composite interlayer adding) was chosen.

Fusible Al was selected as composite interlayer base material. It must perform diamond film internal stress relaxation during the cooling process from growth to room temperature. Second material of the Al-based composite interlayer is cooper (as C diffusion barrier). The third one is Cr (as nucleation layer).

Cooper samples 20 mm in diameter and 5 mm thick were used as substrates. These were polished with a series of SiC sandpapers from 400 down to 1200 grit and ultrasonically cleaned in acetone for 10 min. For subsequent ion etching and deposition of Al-based composite interlayer, a PVD setup was used which was designed and manufactured in Tomsk Polytechnic University (Figure 1). Ion etching and interlayer deposition was performed in one continuous vacuum cycle. The main operating parameters are listed in Table 1. Two types of samples were prepared: 1) Al (520 nm)/Cu (80 nm)/Cr (210 nm); 2) Al (520 nm)/Cu (250 nm)/Cr (210 nm).

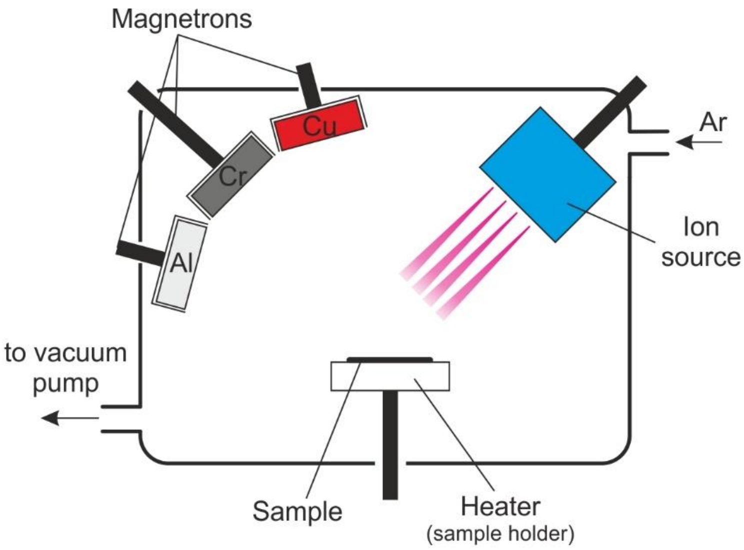

Figure 1. Schematic illustration of the PVD setup.

Polycrystalline diamond films deposited on the Al-based composite interlayer applied on Cu substrate was carried out by a glow discharge plasma-assisted chemical vapor deposition system. The details were described elsewhere [10, 11]. The deposition parameters employed included the discharge current of 10 A, the gas pressure of 13.3 kPa, the CH_4 concentration in H_2 of 6%, the substrate temperature of 800−850 °C and the deposition time of 30 min.

Table 1. The main operating parameters.

	Al	Cu	Cr
Magnetron current [A]	4	2	2.3
Deposition rate [nm/min]	86	41.5	105
Working pressure [kPa]	10^{-3}	10^{-3}	10^{-3}
Ion etching (Ar^+ ions) [keV]	3.5	3.5	3.5

3. Results and discussion

Calotest was used to control the thickness of the Al-based composite interlayer (Figure 2). The micrograph shows three clearly visible interlayer: 1) Al, 2) Cu, 3) Cr. Calotest performed without diamond film.

The phase composition and the purity degree of the synthesized diamond films were determined using the most accurate method, i.e. Raman spectroscopy (NanoScan Technology Centaur I HR spectrometer). Figure 3 shows the Raman spectrum obtained in the area of the solid film. It is close to the spectrum characteristic to monocrystalline diamond. The line width, which characterizes sp^3-carbon (1333 cm^{-1}), is less than 50 cm^{-1}, which indicates the absence of amorphous sp^3-carbon. The lines of the parasitic inclusions typical for polycrystalline diamond [12] (lines of trans-PA (1450 cm^{-1}) and G band of graphite (1560 cm^{-1})) are also not observed in the spectrum. Thus, the deposited films consist of high-quality diamond material.

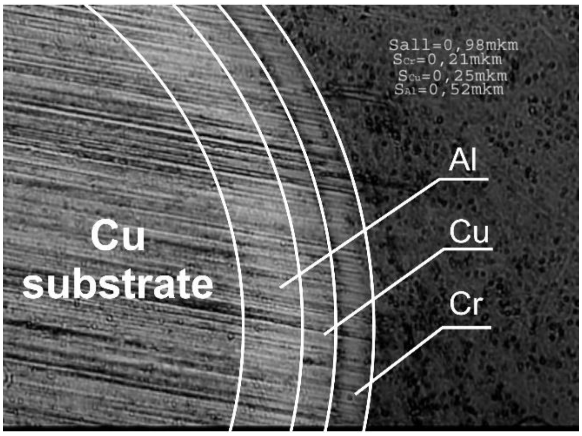

Figure 2. Optical micrograph of film thickness from calotest sample.

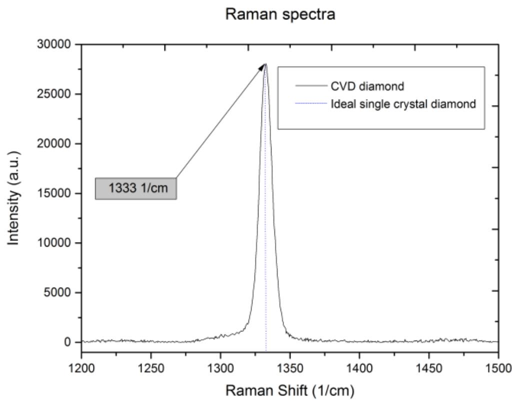

Figure 3. The Raman spectrum of deposited diamond film (Al (520 nm)/ Cu (250 nm)/ Cr (210 nm)).

Nevertheless, the shift in the peak from normal peak position of natural diamond (1332 cm^{-1}) indicates that the film is under compressive stress. According to Wan-qi QIU et al. [13] the compressive stress can be calculated by the following equation:

$$\sigma = -0.567(v_m - v_o) \tag{1}$$

where v_m and v_o are wavenumbers obtained from as-prepared diamond film and natural diamond, respectively. Using this equation, the compressive stress in the diamond film grown on Al-based composite interlayer is calculated to be 0.57 GPa, which is much lower than those in Refs. [14, 15]. The second sample compressive stress were also calculated (equation (1)) and amounted to 1.6 GPa.

It is widely known that diamond film deposited on cooper substrate usually crack or peel off during post cooling process due to the poor bonding strength and the large mismatch of thermal expansion coefficients between diamond and copper [16]. For a comparative analysis of diamond/cooper adhesion strength, a microhardnes tester with spherical indenter with d = 180 μm and 15 kg load was used. The microstructures of the film after test are shown in Figure 4. The diamond film delamination regions was not observed in the case of 250 nm Cu interlayer thickness (Figure 4a). When the thickness of Cu interlayer is 80 nm, delamination region about 1 mm in diameter is present (Figure 4b). This suggests that the diamond /cooper adhesion strength decreases.

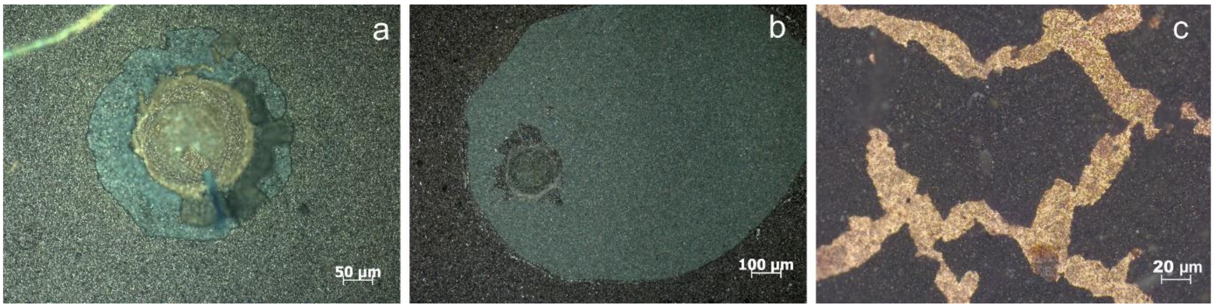

Figure 4. Optical image of indentation imprint: a) sample with 250 nm Cu interlayer in Al based composite interlayer; b) sample with 80 nm Cu interlayer in Al based composite interlayer; and c) sample without Al based composite interlayer.

For a detailed study of Cu interlayer thickness influence on the diamond/cooper adhesive strength, element composition of Al based composite interlayer was investigated (Figure 5).

AES pattern shows the presence of carbon in the interlayer of aluminum in the case of 80 nm Cu interlayer (Figure 5b). At the same time, the 250 nm Cu interlayer completely blocks carbon diffusion in Al (Figure 5a). This explains the enhancement of the diamond film adhesion on a sample with a 250 nm copper interlayer. If thickness of the Cu is sufficient, Al retains its properties and compensates the compressive stresses occurring in the diamond film in the postcooling process. Otherwise, the resulting aluminum carbide has a higher melting point than aluminum, which reduces the efficiency of stress compensation. With high probability at the Cu/Al-based composite interlayer interface, Al/Cu intermetallic compound is formed. It also increases the adhesion strength of the system Cu/Al based composite interlayer/polycrystalline diamond film.

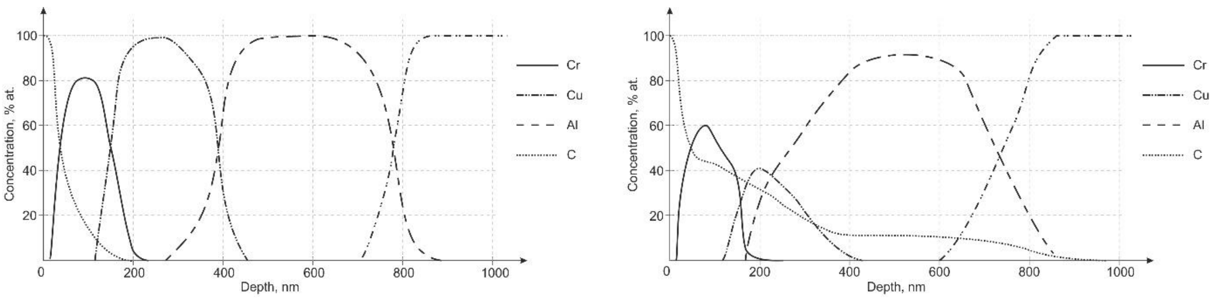

Figure 5. Auger electron spectroscopy pattern of obtained samples: a) Al (520 nm)/ Cu (250 nm)/ Cr (210 nm); b) Al (520 nm)/ Cu (80 nm)/ Cr (210 nm).

4. Conclusion

During this work, the continuous polycrystalline diamond films of high purity were deposited on Al-based composite interlayer coated on copper. The improved adhesion between diamond film and Cu substrate results from the internal stress of the diamond film compensated by fusible Al interlayer and Al/Cu intermetallic compound formation at the Cu/Al-based composite interlayer interface.

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Acknowledgments

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