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HARD CARBON FILMS: DEPOSITION AND DIAGNOSTICS *

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We studied the growth of microcrystalline diamond films on pre-treated Si and WC-Co substrates by microwave plasma chemical vapour deposition (MPCVD). The pre-treatment was varied and its effect on diamond film was studied.

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1 Introduction

There are two major methods of diamond synthesis: one is the well-known method in the thermodynamic stability region of superhigh pressure and high temperature, and the other is that in thermodynamically hindered low pressure region. This paper deals with the second method, namely microcrystalline diamond growth by microwave plasma chemical vapour deposition (MPCVD).

The diamond film growth on the silicon surface is a subject of intense research due to its potential applications in microelectronics and optics. On the mirror-polished silicon surface the density of diamond nucleation is very low. Some surface pre-treatment is needed to enhance the nucleation density. In this work the abrasion of the substrate surface with different type of abrasives was used as a pre-treatment. The influence of methane concentration and the type of pre-treatment on the diamond nucleation density and the morphology of the final film was studied [1].

The machining industry is always seeking a means of improving productivity and machined part quality. Therefore there exist increasing demand for improved cutting tool materials that enhance productivity by extending tool life under increasingly aggressive machining conditions. For example, the aerospace and automotive industries are utilising increasing quantities of lightweight materials such as high-silicon aluminium alloys, fibre-reinforced composites, and metal matrix composites, which offer unique options for component design. Unfortunately, many of these enabling materials are very abrasive and difficult – if not impossible – to machine using conventional cutting tools. Therefore we studied the possibility of depositing μC-diamond on standard tungsten carbide cutting tools. This thin film technology can have perspective advantages over thick film freestanding diamond tips, especially to overcome the depth of cut limitations [2].

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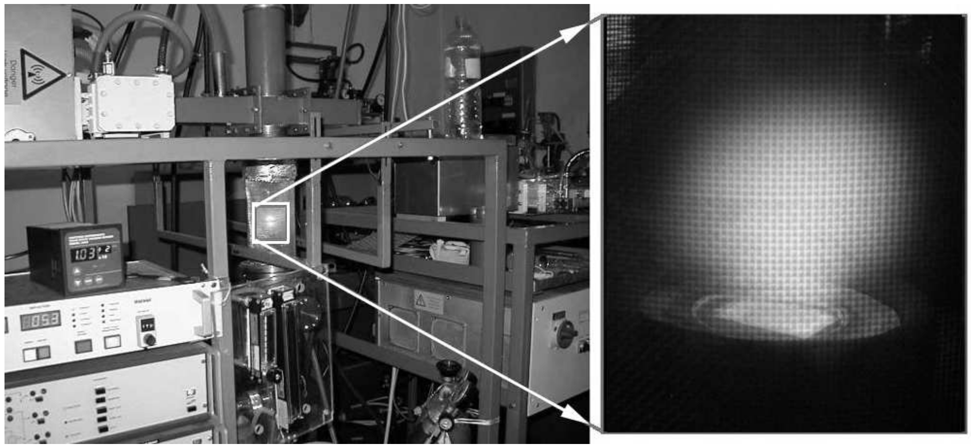

Fig. 1. ASTeX reactor (left) and detail of the substrate holder with plasma (right).

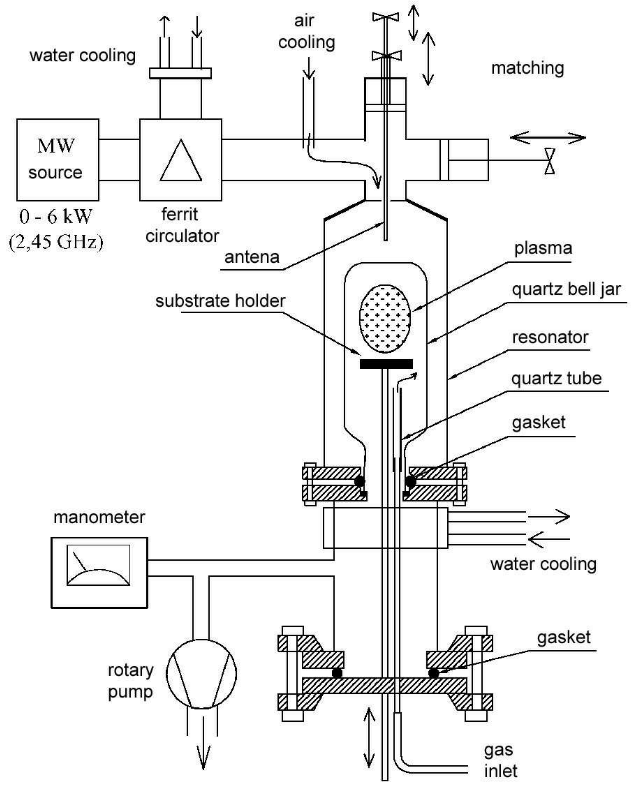

Fig. 2. Schematic drawing of experimental apparatus.

2 Experimental

The experimental apparatus was a conventional bell jar (ASTeX-type) MPCVD reactor with the frequency 2.45 GHz (λ=12.6 cm). The microwave power can be varied from approx. 0.5 to 6.0 kW. We used power about 1 kW. H_2 and CH_4 (a few vol%) were used as reactants [3], [4], [5].

For deposition on silicon wafers, the total pressure was kept at 10 kPa and the total flow rate was about 1000 sccm. The substrate temperature measured by optical pyrometer was 1050–1250 K. The substrate holder was made of graphite and it could be a secondary source of carbon in the plasma. The deposition time was 2 hours.

For deposition on WC-Co cutting tools the total pressure was kept at 11 kPa and the total flow rate was about 400 sccm. The substrate temperature measured by optical pyrometer was 1100–1250 K. The substrate holder was made of hexagonal BN and therefore it couldn't be a secondary source of carbon in the plasma. The deposition time ranged from 2 to 6 hours.

The photograph of the MPCVD reactor and the detail of the resonator with plasma ball are shown in Fig1. Schema of the apparatus is given in the Fig.2.

The influence of the gas mixture and the abrasive type on diamond deposition was investigated. The gas mixture was varied from 1% to 6% methane in hydrogen. Various SiC powders and diamond pastes with particle size from 10 to 1 μm were used for abrading. The films were analysed by the micro-Raman spectroscopy for existence of diamond and for the presence of graphite and by a scanning electron microscopy (SEM) for coverage and crystal morphology.

3 Results I: Diamond growth on silicon

We found out that the best quality films grow after abrading by 1 μm diamond paste, normally used for optical polishing. The nucleation density on substrates abraded by abrasives with greater roughness was poor. The experimental conditions for dense clear diamond film were the following: total pressure 10 kPa, microwave power 1 kW, concentration of methane $<1\%$, substrate temperature $\approx$1200 K. The growth rate ranged from 1 to 4 μmh^{-1} for methane concentrations from 1% to 5%.

The Raman spectra were recorded for samples grown from mixture with 5% and 1% methane concentration (see Fig.3). We can observe change of the graphite band and the diamond peak (at

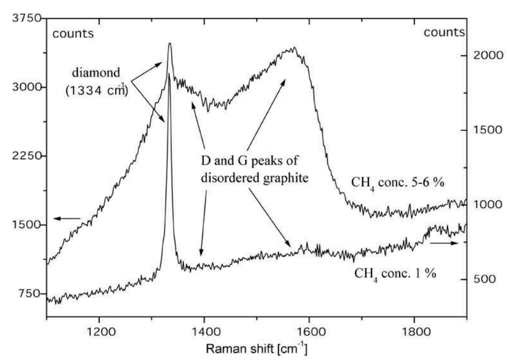

Fig. 3. The Raman spectra of the different diamond films.

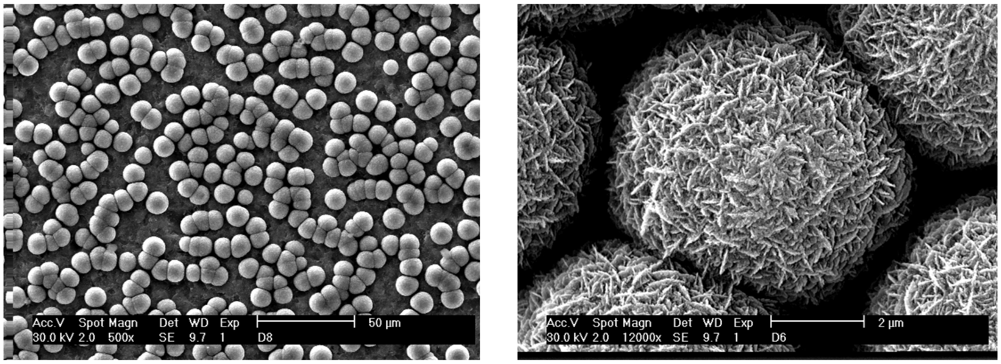

Fig. 4. Morphology of the layer deposited with 6% methane concentration

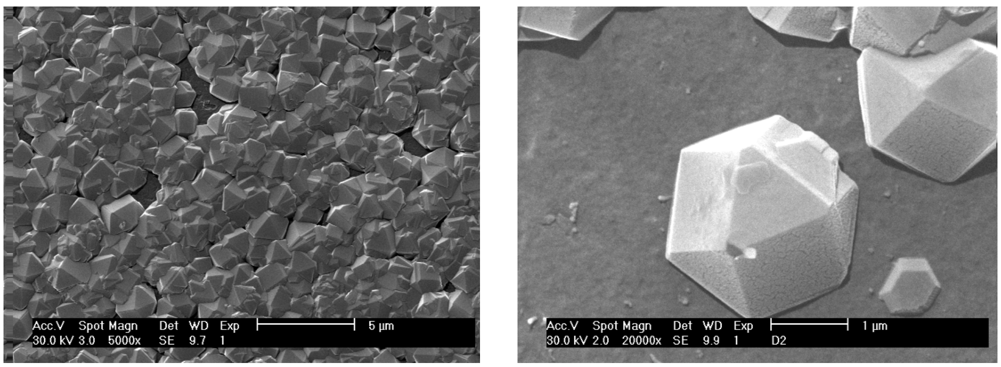

Fig. 5. Morphology of the layer deposited with 1% methane concentration

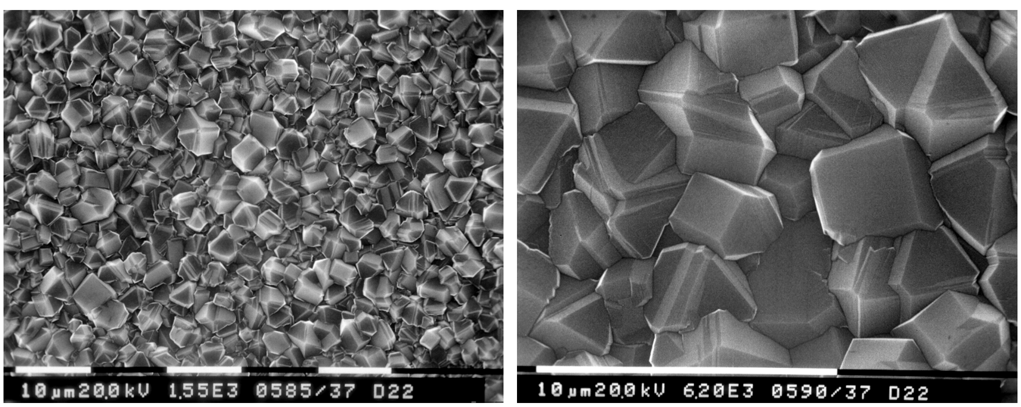

Fig. 6. Microcrystalline diamond layer obtained by 6 hours deposition with 1% methane concentration and sample temperature about 1230K.

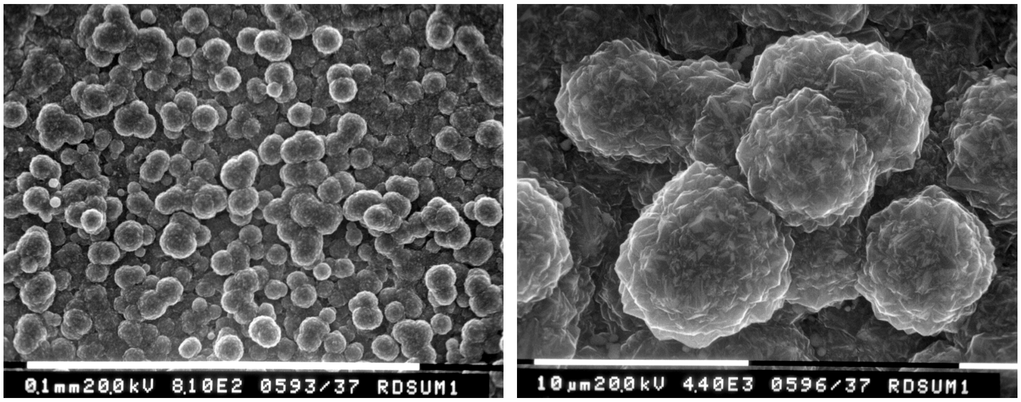

Fig. 7. CVD diamond layer structure affected by Co binder phase during nucleation.

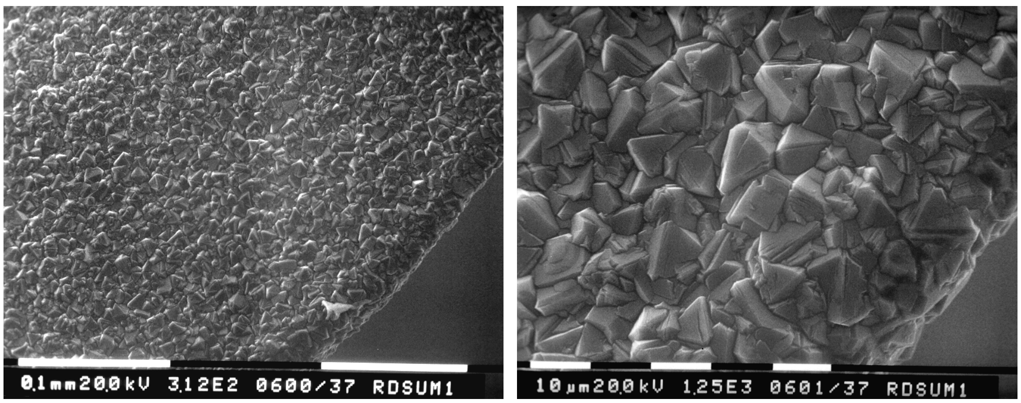

Fig. 8. CVD diamond layer on the cutting edge of WC-Co tool

1334 cm^{-1}) intensity. From this measurement we can easily find out diamond phase purity.

Scanning electron microscopy of the samples (Figs. 4 to 6) have shown spherical particles consisting of graphite and diamond splinters for films grown with 6% methane concentration (Fig. 4). For 1% methane concentration the diamond crystals are formed (Figs. 5 and 6).

4 Results II: Diamond growth on WC-Co cutting tools

The greatest problem of diamond deposition on cutting tools is the adhesion of coating [2] [6]. To achieve stable film, one must minimalise interfacial defects, maximize chemical bonds density and provide crack deflection mechanism. In the case of WC-Co, we must therefore ensure that the interface is chemically stable and suppress the formation of soft nondiamond phases at the interface.

Because cobalt catalyses the formation of nondiamond carbon (sp, sp^2 bonded carbon) in the diamond CVD growth environment, it is important that the Co binder phase is absent from the substrate surface during nucleation and the diffusion of the binder phase from the bulk to the free surface is suppressed. It seems that the presence of Co at the growth surface or at a region of already formed diamond can perturb the phase stability of the deposit (see Fig.7). Under typical CVD growth conditions, this may result in a phase transformation from diamond to graphite or other nondiamond carbon phases. We have succesfully tested pretreatment of the substrate by high temperature etching [6] in hydrogen plasma to remove the cobalt layer. Substrate temperature was kept at approx. 1400 K and pretreatment time was 1 hour. We performed this pretreatment directly in the deposition reactor. SEM image of good quality coating is presented in Fig.8.

5 Conclusion

The growth of diamond films on Si and WC-Co substrates was investigated. The nucleation density on polished silicon wafers was enhanced by abrasion pre-treatment of the substrates. The diamond paste (1 μm) was found to be the best abrasive. We found the optimum deposition parameters for the diamond film growth.

We have successfully tested MPCVD deposition on WC-Co cutting tools. To increase the layer adhesion we have pretreated the substrate by plasma etching. We made scanning electron microscopy (SEM) analysis of the finished diamond layers to observe the homogeneity of the deposits and its roughness.

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