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COMMUNICATIONS

INVESTIGATION OF CARBON PHASES IN DIAMOND AND DIAMOND–LIKE CARBON HF CVD FILMS BY RAMAN SPECTROSCOPY

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Raman spectroscopy is employed to characterize thin diamond and diamond-like carbon (DLC) films deposited by HF CVD and MW CVD on sapphire, WC-Co and silicon substrates. Raman spectroscopy is able to identify different carbon phases. The technique allows to distinguish between various types of carbon such as diamond, nano-crystalline diamond, graphite, amorphous carbon, diamond-like carbon and hydrogenated carbon. The Raman spectra contain, besides the peaks of various phases of carbon, also a luminescence band.

K e y w o r d s: CVD, diamond, DLC, Raman spectroscopy

1 INTRODUCTION

Diamond layers have a high potential in diverse applications. The technologies of their deposition are intensely investigated and, similarly, techniques for their diagnostics are developing rapidly. The Raman spectrum is a fully credible, unambiguous sign of a given substance, hence Raman spectroscopy is an invaluable and at the same time fast and non- destructive analytical technique. It is widely utilized as a method for structural characterization of molecules and substances and for identification of the components of the systems being studied.

In this paper we analyze Raman spectra of diamond layers deposited on sapphire and on a WC-Co cutting tool by HF CVD (hot filament chemical vapour deposition) and of a layer deposited on silicon by MW CVD (microwave plasma chemical vapour deposition).

2 EXPERIMENT

The HF CVD technology employed to deposit thin films on sapphire and carbide substrates was described in [1]. The MW CVD differs from HF CVD in details but they have two common features. The first one is the substrate temperature of about 600-800 °C, the second common feature is a mixture of precursors — gaseous hydrogen and methane. The studied sample (44) was deposited by MW CVD in the conventional bell jar (ASTeX-type) reactor. The deposition pressure, microwave power, substrate temperature and total flow rate were maintained at 10^4 Pa, 1.2 kW, 800 °C and 300 sccm, respectively. A gas mixture of CH_4 and H_2 was used and the gas flow ratio of CH_4/H_2 was kept at 1.5 % for deposition on silicon. Before the deposition on silicon, the substrates were polished with a 1 μm diamond paste and then ultrasonically cleaned in alcohol. The films on silicon substrates were deposited for 9 hours.

Raman measurements were conducted on a Raman spectrometer DILOR-JOBIN YVON-SPEX, type LabRam. The sample was mounted in a micrometric manipulator of a confocal microscope (Olympus BX-40), and visualized, by means of a camera, on a monitor. The excitation source is a He-Ne laser (632.8 nm, 15 mW). The scattered radiation is focused onto the entrance slit of a grid monochromator (600 and 1800 grooves/mm), the spectral range being 450 nm to 1.05 μm. The spectrometer is equipped with an air-cooled CCD detector. The spectra (intensity of the scattered radiation versus wavelength or wave number) were processed by the software package LabSpec. The spectrometer was calibrated to the 520.7 cm^{-1} band of single crystalline Si and 1332 cm^{-1} of natural diamond. The measurements were performed at room temperature. Scanning electron microscopes Tesla BS 300 [2] and Philips 505 operating in the secondary electron mode were used to study the microtopography of diamond layers.

3 RESULTS AND DISCUSSION

3.1 Raman spectra of HF CVD thin films on WC-Co cutting tools

Refinement of the cutting tools for processing of hard materials (carbides, ceramics), non- ferrous metals, plastics and composites by depositing a diamond or DLC

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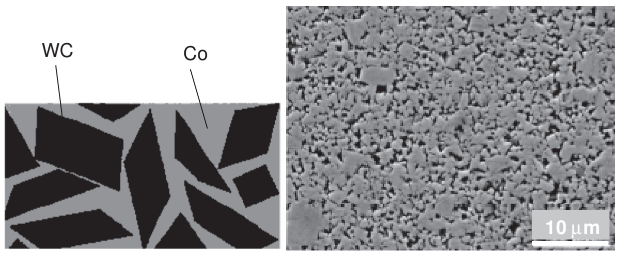

Fig. 1. Schematic representation of the WC-Co substrate and a SEM micrograph of WC-10 % Co.

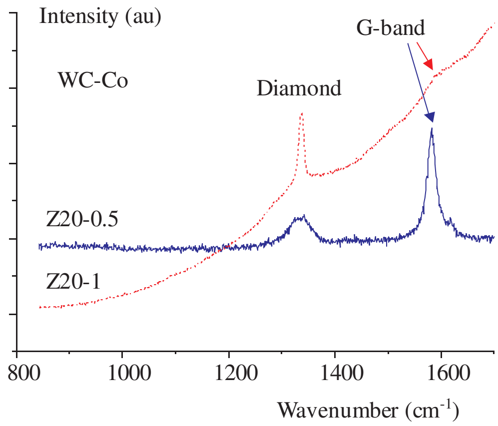

Fig. 2. Raman spectra of D/WC-Co.

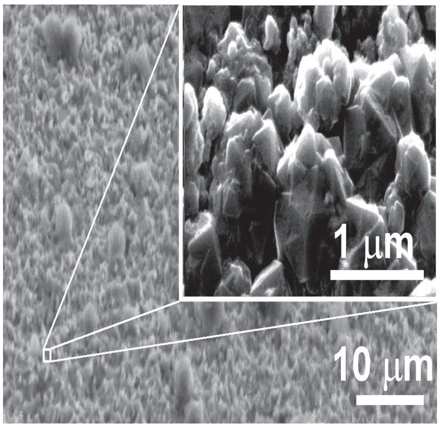

Fig. 3. SEM micrograph of the surface of the cutting tool Z20-0.5 (microcrystalline graphite), prepared by HF-CVD.

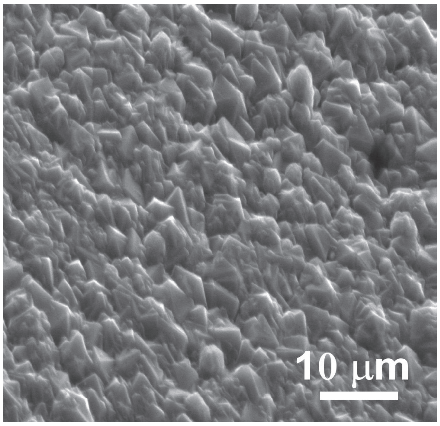

Fig. 4. SEM micrograph of the cutting tool Z20-1 (diamond film), prepared by HF-CVD

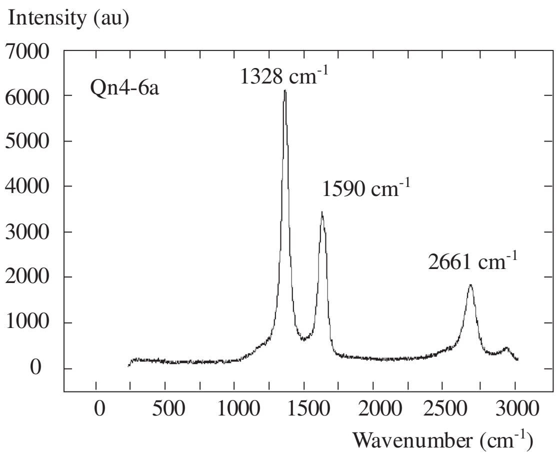

Fig. 5. Raman spectrum of a diamond film on sapphire with a high content of graphite (nucleation time 5 hours, growth time 3 hours, gas flow ratio $CH_4 : H_2 = 4.5 : 300$).

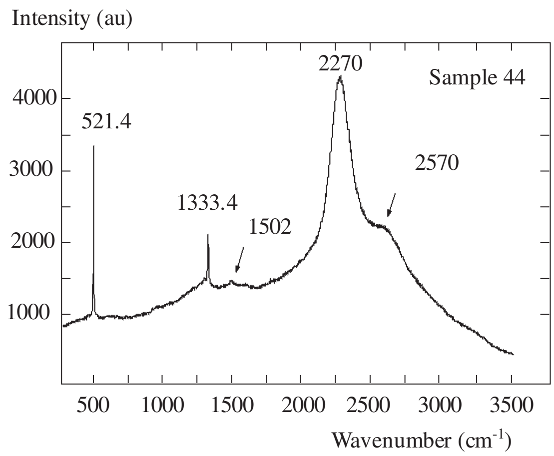

Fig. 6. Raman spectrum of a microcrystalline diamond film grown on Si by MW CVD.

layer prolongs their operation life, increases the rate of cutting and, which is in some cases very important, allows a better, sharper termination of the cutting than it is possible with today's conventionally used carbide tools. The most often used material for coating is WC/Co. The cutting tools contain WC crystals of various size (0.4 to 10 μm) in a matrix containing Co (4 to 25 %) as shown in Fig. 1.

Since Co etches diamond, it is inevitable to prevent Co from a direct contact with the diamond layer. This is why the surface of the substrate is processed. We have experimentally tested several methods of pre-deposition treat-

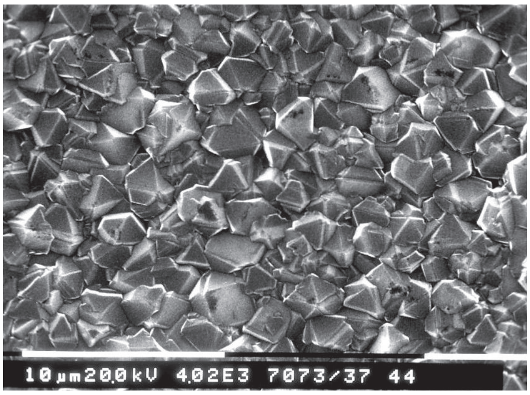

Fig. 7. Microcrystalline diamond CVD film on Si prepared by MW-CVD

ment [3]. As for film adhesion, the best way proved to be etching the substrate by a commercially available etchant Murakami for 20 minutes and to anneal it at a temperature of 600 °C and pressure 10^{-4} Pa for 10 hours. The layers were deposited on pre-treated surfaces. The common parameters during nucleation and growth: 3 tungsten filaments, filament temperature 2100 °C pressure in the bell jar 3000 Pa.

Nucleation voltages: between the filaments and the grid $U_G = 100$ V, on the substrate $U_S = -170$ V (with respect to the filament). The flux of gasses was variable.

Figure 2 shows Raman spectra of films deposited at a concentration of 0.5 % of CH_4 in H_2 (referred to as sample Z20-0.5), and at a higher concentration of 1 % of CH_4 in H_2 (Z20-1). Sample Z20-0.5 exhibits a broad diamond band centred at approx. 1335 cm^{-1} along with a narrow graphitic band (G) centred at approx. 1583 cm^{-1}. Such a spectrum is typical for microcrystalline graphite. SEM micrograph of microcrystalline graphite on a WC-Co substrate is in Fig. 3. The Raman spectrum of sample Z20-1 contains a diamond maximum at 1337.2 cm^{-1}, its FWHM being 13 cm^{-1}. The developed diamond grains coalesced into a continuos film are shown in Fig. 4. The result of the experiment is optimization of the CH_4/H_2 flow for deposition on WC-Co. The film of microcrystalline graphite proved to be unsuitable for coating also after a load test because of poor adhesion.

3.2 Raman spectra HF CVD deposited diamond films on sapphire

Similarly like in the case of deposition on the WC-Co substrate, we have studied the effect of the CH_4-to-H_2 ratio on the quality of the film on a non-conducting, optically transparent substrate. In the case of the sapphire substrate, the effect of a higher content of CH_4 in H_2 proved to be adverse. With a higher content of CH_4 v H_2 the conditions for conversion of sp^2 hybridized carbon in the inter-layer into sp^3 hybridized carbon became worse. Besides diamond, the layer contains a lot of graphitic phase forming an inter-layer. Carbon exhibiting the spectral behaviour shown in Fig. 5 is crystallographically disordered.

3.3 Raman spectra of MW CVD-grown diamond films on silicon

Figure 6 shows the Raman spectrum of a diamond film grown on silicon by MW CVD. The spectrum of the layer has three dominant features: sharp lines centred at 521 and 1333 cm^{-1}, known to be the characteristic line of silicon and diamond, and a broad band centred at about 2270 cm^{-1}. The latter is most likely a band of structural defects in diamond, which reveals a lower quality of the silicon/diamond buffer interface. This dominant band has also been observed when analyzing diamond films deposited in the HF CVD reactor. A SEM micrograph of microcrystalline diamond film on silicon is shown in Fig. 7. The micrograph shows triangular facets typical for (111)-oriented crystallographic planes of the grown diamond crystals. One can also see doubled edges and crystal twinning.

4 CONCLUSION

On several examples, we have demonstrated the potential of Raman spectroscopy to identify the state of the film-to-substrate interface after single technological steps. We have resolved diamond and non-diamond phases of carbon. A serious problem in the use of polycrystalline CVD coating in electronics, optics as well as in cutting tools is the surface roughness. The roughness can be estimated from the Raman spectra. Nanocrystalline and microcrystalline types of diamond have their typical Raman spectra. The most interesting result of the paper is the presence of the band at approx. 2270 cm^{-1} in Raman spectra of the films with pronounced diamond crystal twinning.

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