CHARACTERISATION OF BORON DOPED DIAMOND THIN FILMS

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Received 07 May 2012; accepted 14 May 2012.

1. Introduction

The recent development of material deposition methods leads also to thin diamond film production on various substrates. The technologies used for the diamond thin film formation are based on chemical vapour deposition. Except for the natural diamonds as gemstones, which have superlative properties of hardness, highest room temperature thermal conductivity, etc., also the artificial ones have similar properties. Diamond thin films are very useful for many applications; the biological one seems the most attractive in these days [1].

The chemical vapour deposition (CVD) involves a gas phase chemical reaction occurring above a solid surface, which causes deposition onto that surface. Hot filament CVD (HF CVD) method is used for the growth of diamond thin films under low pressures, and is also the most popular method. The used hot filaments are heated up to 2 000 °C to activate the H_2 and CH_4 gases. The diamond film is then deposited onto a substrate, which is located about 10 mm under the filaments on molybdenum holder. The pressure in the chamber is up to 3 kPa and rotary pump is used for chamber evacuation. The HF CVD method is relatively cheap modification and diamond thin films can be relative easily produced. However, there is another method to produce diamond thin films, e.g., MW CVD (Microwave CVD), which uses microwaves to activate gases. It is cleaner as a HF CVD, but MW CVD reactor is more expensive [2]. Before starting the growth process, the substrate surface must be prepared for the growth. This step is described as a diamond seeding layer process or also nucleation [3].

The grown diamond layers can be analysed using analytical methods to specify their properties. They inform about surface morphology, crystalline structure or chemical composition of grown thin films. The surface morphology is studied with Scanning Electron Microscopy (SEM), which uses a focused beam of high-energy electrons to generate a variety of signals at the surface. Raman Spectroscopy can be used as a non-destructive technique to deduce easily and without contact the boron concentration of diamond thin films. Glow Discharge Optical Emission Spectroscopy (GDOES) provides rapid analysis of the atomic composition of thin films, which are sputtered by exposing them to Ar plasma and then characteristic photon spectra excited by sputtered atoms are observed [4]. Electrical properties were determined in the van der Pauw configuration.

2. Experimental Details

The diamond thin films were prepared by Hot Filament CVD. The nucleation process was initiated using diamond powder in ultrasonic bath in demineralised water after 15 minutes. Before nucleation, samples were cleaned in ultrasonic bath in acetone and next

they were rinsed in ultrasonic bath in demineralised water. Diamond thin films were prepared on SiO_2 thin layer (about 150 nm thick), which was prepared on Si substrate.

Table 1. *Gas flow and sample boron concentration*

Sample	CH_4 [sccm]	H_2 [sccm]	H_2+ TMB [sccm]	B/C [ppm]	Boron concentration GDOES [%]	Thick-ness [nm]
A	3	275	25	833	1.670	285
B	3	260	40	2 667	1.629	200
C	3	250	50	3 333	1.682	214
D	3	150	150	10 000	1.862	240

Using the hot filament CVD method the filaments in the reactor reach almost 2 000 °C and the substrate temperature is usually in the range from 600 °C to 800 °C. Samples were prepared at different gas flows of TMB (Trimethylboron), which is the source for B and B/C ratio is amount of TMB to CH_4 (ppm). In Tab. 1 gas flows during deposition are shown. All samples were prepared at 3 kPa in vacuum chamber and the time of the deposition was 120 minutes. GDOES measurement was done after deposition and boron concentration in diamond thin layer was determined.

3. Result and discussion

Scanning Electron Microscopy (SEM) was used to determine surface morphology and thickness. SEM images of samples A and D show the cross section. Surfaces are homogenously evenly covered with a diamond structure. A significant difference between samples is not observed (Fig. 1). B/C ratio is not influencing the BDD film thickness (200-285 nm).

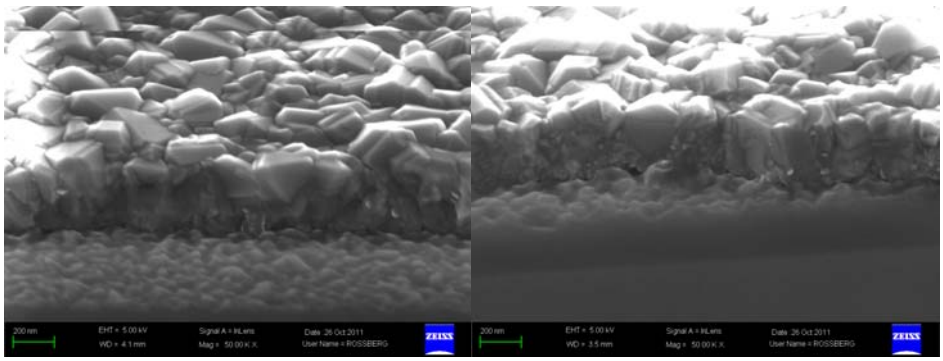

Fig.1: *SEM Pictures of sample A (left) and sample D (right)*

The Fig. 2 shows the Raman spectra, which were obtained at room temperature using a He-Ne laser with wavelength of 632 nm. The diamond peak at 1333 cm^{-1} decreases with an increased B/C ratio to 10^{20} cm^{-3} [5]. Raman broad bands centred at 500 cm^{-1} and 1 225 cm^{-1} are visible for high boron concentration. Peaks at 520 cm^{-1} and 925 cm^{-1} are characteristic for Si. For high boron concentration the peak at 1 580 cm^{-1} characteristic for micro-graphite is not visible [6]. The '500 cm^{-1}' peak in these films down-shifts systematically with increasing B/C ratio and it can be fitted. The boron concentration can be easily deduced from the Raman shift according to equation [5]:

$$[B]cm^{-3} = 8.44\times10^{30}\exp(-0.048W)(cm^{-1}) = 8.32\times10^{20}cm^{-3} \qquad (1)$$

Boron Raman peak in sample D was determined at 480 cm^{-1} and boron concentration of 8.32×10^{20} cm^{-3} was calculated.

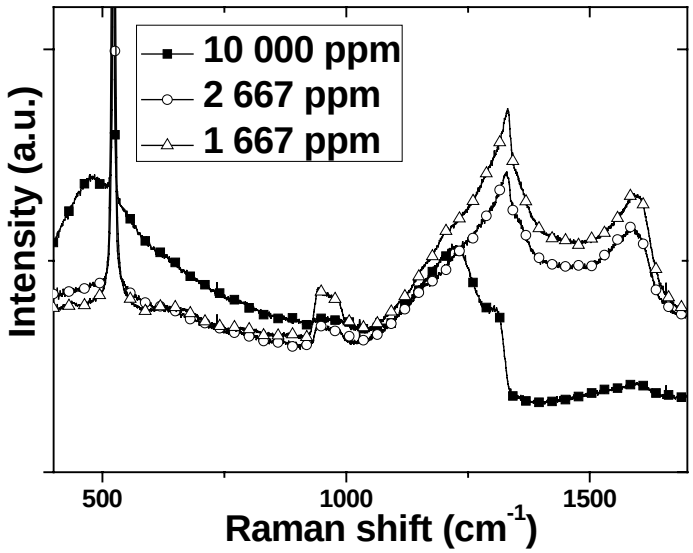

Fig.2 Raman spectra of samples with different B/C ratio

Electrical characteristics as a sheet resistance R_s, resistance R and carrier concentration N were determined in the van der Pauw configuration (Tab. 2). Sheet resistance is increased with boron concentration from 136. 5 Ω/sq to 1 245 Ω/sq. Carrier concentration is increased with boron concentration from 5.59×10^{18} cm^{-3}(sample A) to 3.61×10^{22} cm^{-3} (sample D) [7]. Before boron concentration was determined with Raman spectroscopy to be 8.32×10^{20} cm^{-3}. However, measurement in the van der Pauw configuration is strongly influenced by imperfect electrical contacts. Sheet resistance R_s and carrier concentration N are shown in Fig. 3 and they are influenced by B/C ratio.

Table 2. *Sample electrical characteristics*

Sample	Electrical characteristics		
	R_s [Ω/sq]	R [mΩ·cm]	N [cm^{-3}]
A	1 245.0	35.4	5.59×10^{18}
B	645.1	12.9	1.49×10^{19}
C	518.3	11.0	5.18×10^{19}
D	136.5	3.2	3.61×10^{22}

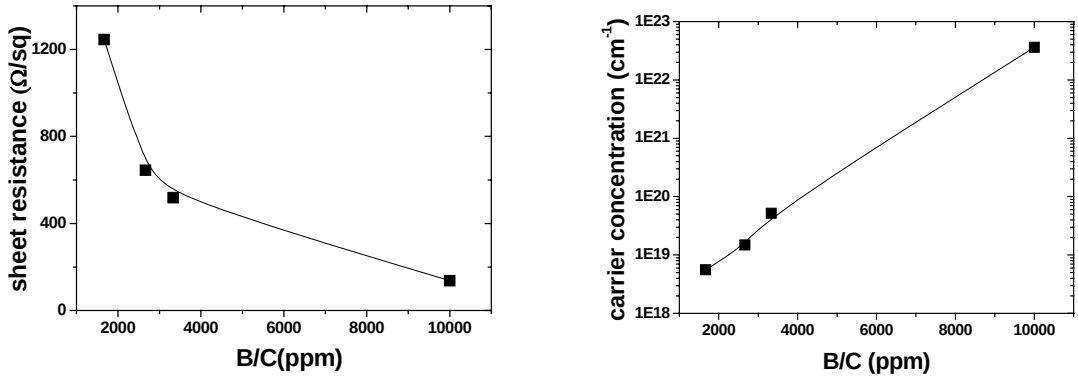

Fig.3: *Sheet resistance and carrier concentration are influenced by B/C ratio*

4. Conclusion

In this contribution we compared a series of diamond thin film samples produced by HF CVD method prepared with different boron concentrations. Characterizations by SEM, GDOES and Raman spectroscopy methods were carried out. Electrical properties were determined in the van der Pauw configuration. Boron doped diamond thin films can be produced and they will be used in other areas of science and industry, for example, now they are used in electrochemistry [1].

Acknowledgement

The authors would like to thank to J. Král for technical support. This work was done with a support of Slovak Research and Development Agency project No. LPP-0094-09, APVV-0548-07, VEGA projects 1/1103/11 and 1/1102/11 and DAAD project 507 552 00.

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