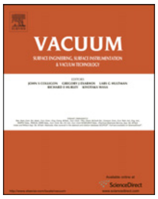
Vacuum 85 (2010) 518–522

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum



Structure of diamond polycrystalline films deposited on silicon substrates

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Keywords:
Diamond films
Residual stress
EBSD
Raman spectroscopy

ABSTRACT

The article presents results of structural studies of polycrystalline diamond thin films deposited by hot filament CVD on silicon substrates. The films were characterized using Scanning Electron Microscopy (SEM), Raman Spectroscopy (RS), Electron Backscattered Diffraction (EBSD), Energy Dispersive Spectroscopy (EDS) and Secondary Ion Mass Spectroscopy (SIMS). Both the EBSD patterns and Raman spectra confirm that the grains visible in the electron micrographs are diamond micro-crystallites. The residual stress in the films is found to be in the range between −4.29 GPa and −0.56 GPa depending on the sample thickness. No evidence of lonsdalite and graphite has been registered in the polycrystalline material of the investigated samples. Evidence of the existence of silicon carbide at the diamond/silicon interface is presented. It is also suggested that an amorphous carbonaceous film covers the silicon surface in the regions of holes in the thin diamond layers.

1. Introduction

Despite the fact that there are many results of structural investigations of diamond and diamond-like carbon films deposited on silicon substrates (see e.g. Refs. [1,2]), the EBSD investigations of diamond films are not very common. Only a few papers concerning the EBSD studies of diamond films are available [3–6]. The papers focus on the structure of films on a micro-scale. In this paper detailed investigations of the structure of thin diamond films deposited on silicon substrates using EBSD and other techniques are presented. The residual stress in the films deposited on variously oriented silicon substrates was calculated in order to determine the relationship between the substrate orientation and the stress value. It is also shown that silicon carbide (SiC) exists at the silicon/diamond interface. This should be taken into account when the electrical properties of silicon/diamond junctions are discussed.

2. Experimental

Diamond films were grown on silicon substrates using the hot filament chemical vapour deposition (HF CVD) method. A mixture of methanol and hydrogen was used for the deposition process. The amount of methanol was changed in the range between 1.0% and 2.5%, the total gas flow rate was between 100 sccm and 150 sccm and the gas pressure in the reaction chamber was changed between 50 mbar and 60 mbar (Table 1) and the substrate temperature was 1100 K. The films were deposited on n-type silicon substrates which were cut out from a single crystal silicon wafer oriented (100) or (111). The details of the deposition system used and typical deposition conditions are described elsewhere [7].

The quality of crystalline structure of diamond films was evaluated using Raman Spectroscopy. The Raman spectra were recorded at room temperature in backscattering geometry using a Jobin-Yvon T64000 Raman micro-spectrometer. The 514.5 nm line from an Argon laser was used for excitation. Morphology of the films was examined in a scanning electron microscope (SEM, Hitachi S 3000N). Electron backscattered diffraction (EBSD) [8] of the investigated diamond films was carried out using the EBSD ThermoNORAN equipment attached to the SEM. In order to identify the chemical composition in selected areas of the samples an Energy Dispersive Spectrometer (ThermoNORAN) was used.

In order to find the spatial distribution of chemical elements in the films Secondary Ion Mass Spectroscopy (SIMS) measurements were also carried out. The measurements were carried out with a Secondary Ion Mass Spectrometer (ToF-SIMS IV, Ion-ToF GmbH, Muenster Germany) with $^{69}Ga^{+}$ primary ion source and time-of-

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doi:10.1016/j.vacuum.2010.01.025

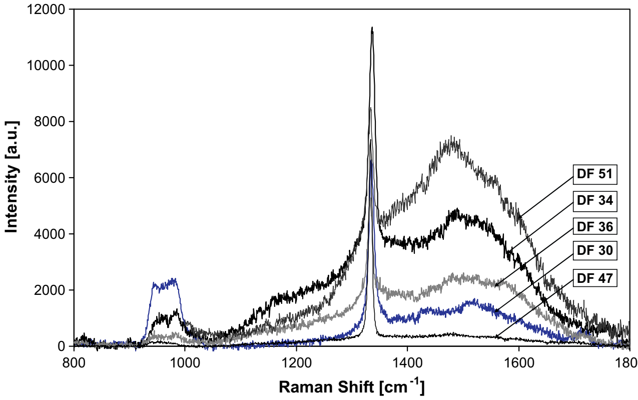

Fig. 1. Raman spectra of the investigated samples. The spectrum for the thinnest sample DF 30 shows a broad peak at approximately 960 cm^{-1}, which is the second-order peak of the Si substrate [12].

flight (ToF) secondary ion mass analyzer with high mass resolution $m/\Delta m = 7500$ at $m/z = 29$.

3. Results and discussion

Raman spectroscopy is a standard method to identify the presence of the diamond phase of carbon in polycrystalline diamond and diamond-like carbon films grown by CVD techniques on non-diamond substrates [9,10]. In general, the CVD diamond films may contain some amorphous carbon (graphite-like) phase. In this case the Raman spectra show, apart from the well-defined diamond Raman peak at 1332 cm^{-1}, the broad peak at 1530 cm^{-1} attributed to this form of carbon [11].

The Raman spectra of the investigated samples (Fig. 1) show a well-developed diamond band at 1332–1336 cm^{-1} and a broad band at about 1530 cm^{-1} typical for imperfect diamond structures. The full width at half maximum (FWHM) of the diamond Raman peak is often used as a measure of the diamond quality. The deposition parameters and Raman data are shown in Table 1, where parameter of the film quality Q was calculated from the formula given by Sails et al. [13]. The standard deviation of the mean value of FWHW and ν_m for polycrystalline diamond films obtained from 30 measurements are equal to 0.07 cm^{-1} and 0.1 cm^{-1} respectively. This gives the average error of calculated residual stress in the range between 5% and 7% for the lower values of stress and between 10% and 20% for the higher values of stress.

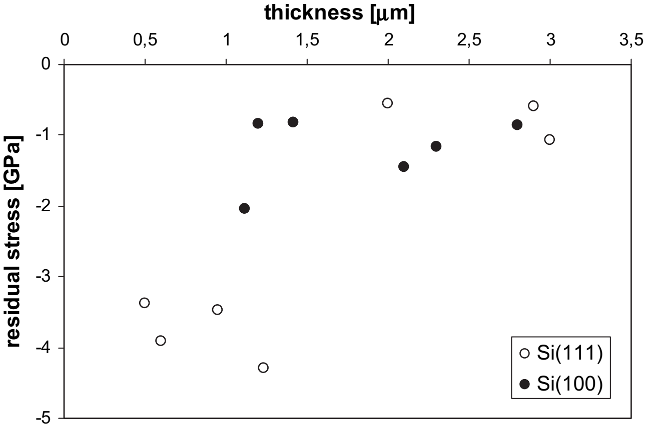

Fig. 2. Relationship between the residual stress and thickness for the polycrystalline diamond films. ○ – films deposited on (111) oriented silicon wafer; • – films deposited on (100) oriented silicon wafers.

As seen in Table 1, both the FWHM and the values of the quality parameter Q suggest that the deposited diamond films are of good quality, although they contain some disordered phase. No graphite was detected in the diamond crystallites which means that the disordered graphite-like phase is primarily in the inter-grain regions. The broadening and small shift of diamond Raman peak from 1332 cm^{-1} may result from some residual stresses caused by the presence of amorphous carbon in the inter-grain regions [11,14–16]. The values of the shift and splitting of Raman spectra depend on the magnitude of the stress [17]. A Raman peak of diamond shifts to a higher or lower value than ν_o under compressive or tensile stresses, respectively, where $\nu_o = 1332$ cm^{-1} is the peak position for a perfect diamond crystal under no stress. In the investigated diamond films, the splitting of the Raman peak is not visible, so the residual stress σ in the diamond film was calculated from the relationship [18]:

$$\sigma = -1.08\left[\frac{\mathrm{GPa}}{\mathrm{cm}^{-1}}\right](\nu_m - \nu_o) \qquad (1)$$

where ν_m is the observed diamond peak position for the investigated diamond films. The values of σ for the investigated films are shown in Table 1. It was suggested by Fan et al. [19] that the stress evaluated from the shift of the diamond Raman peak usually decreases with increasing film thickness, but the thickness of samples investigated by these authors [19] was much greater than 1 µm. The relationship between the residual stress and the diamond film thickness is shown in Fig. 2. As expected, the magnitude of residual stress decreases with increasing sample thickness and reaches a value of about 0.6–0.7 GPa. The values of residual stresses found in the investigated films are rather typical for diamond films

Table 1
Parameters of the HF CVD process and Raman data.

Sample symbol/ orientation of Si substrate	Content of methanol [%] in mixture of CH_3OH and H_2	Pressure [mbar]	Gas flow rate [sccm]	Deposition rate [µm/h]	Thickness [µm]	Raman shift of the diamond peak maximum [cm^{-1}]	FWHM [cm^{-1}]	$Q_{[514\ nm]}$ [%]	Residual stress σ [GPa]
DF30/Si(111)	1.0	55	150	0.30	0.50	1335.12	11.21	97.04	−3.37
DF 31/Si(111)	2.0	55	150	0.46	0.60	1335.63	16.60	91.90	−3.92
DF 32/Si(111)	2.5	55	150	0.52	0.95	1335.21	14.62	96.77	−3.47
DF 34/Si(111)	1.5	50	110	0.41	1.23	1335.97	13.33	95.50	−4.29
DF 35/Si(111)	1.7	50	110	0.36	2.00	1332.52	12.21	92.31	−0.56
DF 36/Si(100)	1.5	60	110	0.38	1.42	1332.76	10.06	93.85	−0.82
DF 37/Si(100)	1.5	50	110	0.39	1.12	1333.90	9.71	97.33	−2.05
DF 46/Si(100)	1.5	50	100	0.32	2.80	1332.80	10.56	97.83	−0.84
DF 47/Si(100)	1.0	50	100	0.20	2.10	1333.34	6.86	99.71	−1.45
DF 49/Si(100)	1.2	50	100	0.23	1.20	1332.78	5.31	99.12	−0.84
DF 51/Si(100)	1.7	50	100	0.49	2.30	1333.07	11.12	91.40	−1.16
DF 52/Si(111)	1.2	55	100	0.23	3.00	1332.99	9.63	98.34	−1.07
DF 53/Si(111)	1.5	55	100	0.35	2.90	1332.56	11.54	96.45	−0.60