

## Raman spectroscopic and X-ray investigation of stressed states in diamond-like carbon films

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The non-destructive characterization of intrinsic stress is very important to evaluate the reliability of devices based on diamond-like carbon (DLC) films. Whereas the only requirement for the X-ray diffraction method is a crystalline state of specimen, Raman spectroscopic stress analysis is restricted to materials showing intensive and sharp Raman peaks. On the other hand, Raman spectroscopy offers the possibility to measure stress profiles with lateral resolution of about 1 micron. The results of stress measurements in DLC films using both X-ray diffraction and Raman spectroscopy are found in very good correspondence. Mean stress in carbon films consisting of very small crystallites on silicon substrates has been determined by measuring and fitting the stress profiles in the substrate near artificial vertical film edges.

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*Dedicated to Professor Peter Paufler on the occasion of his 65<sup>th</sup> birthday.*

### 1 Introduction

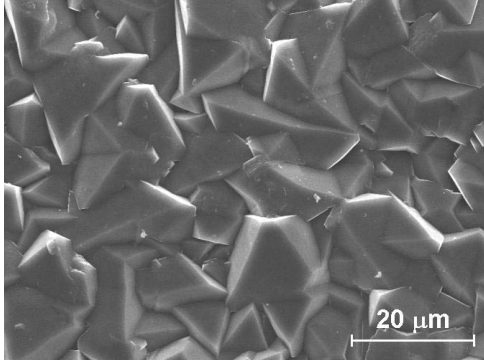
Diamond-like carbon (DLC) films consist of predominantly  $sp^3$  bonded carbon atoms. Outstanding physical properties like extreme hardness, low friction coefficient, and low electrical conductivity led to a broad variety of applications in manufacturing engineering, electronics, and microsystems engineering [1-3]. Moreover, chemical inertness and biocompatibility offer the use of carbon coatings in medical technology too [4]. However, in all cases the reliability of DLC coatings and of devices based on such films is strongly affected by intrinsic stresses. Both the deposition process and the substrate material can be the origin of residual stress.

The stress state in diamond films showing a high degree of crystallinity as to be seen in the SEM micrograph in fig. 1 can be analysed by X-ray diffraction and by Raman spectroscopy. Using X-ray diffraction, the change of lattice spacing due to the occurrence of strains is measured [5]. Otherwise, stress values can be determined by measuring the shift of characteristic Raman lines in comparison to stress-free samples [6]. Although the Raman spectroscopic method is restricted to only a few materials compared to X-ray analysis, it allows to measure local stresses with the lateral resolution provided by the applied microscope. Therefore, stress profiles or mappings can be attained easily. In the present paper DLC films prepared by hot filament chemical vapour deposition (HF-CVD) on tungsten carbide and silicon nitride designed for cutting tools [7] are investigated by both methods and the results are compared.

If the diamond crystallites are very small, i.e. if the films appear to be amorphous both in X-ray diffraction and in the Raman spectrum, the mean film stress can be estimated only indirectly by a Raman experiment. The stress field in the substrate concentrated near a vertical film edge contains important information about the film stress. Therefore, stress values are obtained by finite element assisted model calculations [8]. This method is

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demonstrated on example of carbon films produced by pulsed laser deposition on single crystalline silicon, because the Raman spectrum of silicon contains a very sharp triply degenerate peak and the relation between stress and the shift of the Raman lines is well known [9].



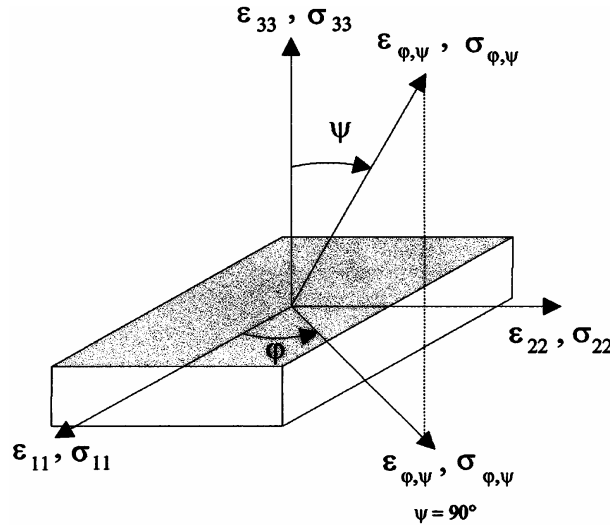
**Fig. 1** Top view of a 28  $\mu\text{m}$  thick DLC film on a  $\text{Si}_3\text{N}_4$  substrate obtained by SEM.

## 2 X-ray analysis of film stress

X-ray stress analysis has been performed using a diffractometer with an open Eulerian cradle (Philips X'Pert MPD). The stress state in the DLC films is assumed to be plane and parallel to the film surface. According to the coordinate system shown in fig. 2 it can be written as:

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & 0 \end{pmatrix}. \quad (1)$$

By varying of the sample tilt  $\psi$  at constant direction  $\varphi$  (see fig. 2) the diffracted intensity of several lattice planes is measured and the strain  $\varepsilon_{\varphi\psi}$  can be determined according to eq. (2).



**Fig. 2** Coordinate system used for X-ray stress analysis.

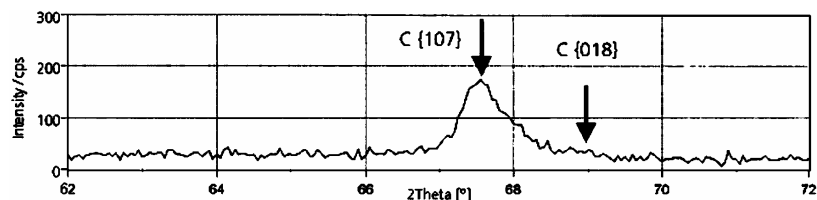
$$\varepsilon_{\varphi\psi} = \frac{1}{2} S_2 (\sigma_{11} \cos^2 \varphi + \sigma_{12} \sin 2\varphi + \sigma_{22} \sin^2 \varphi) \sin^2 \psi + S_1 (\sigma_{11} + \sigma_{22}), \quad (2)$$

with

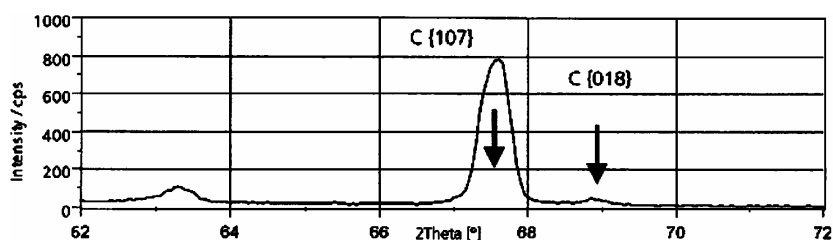
$$S_1 = -\frac{\nu}{E}, \quad \frac{1}{2} S_2 = \frac{\nu+1}{E}. \quad (3)$$

$\nu$  is the Poisson ratio and  $E$  the Young's modulus of the film material. In this paper  $E = 1034.47$  GPa and  $\nu = 0.1597$  [10] was used for diamond. The components of the stress tensor, see eq. (1), have been calculated by applying eq. (2) and (3) with  $\varphi = 0^\circ$ ,  $\varphi = 45^\circ$ , and  $\varphi = 90^\circ$ , respectively. In fig. 3 and 4 typical X-ray diffraction results of DLC films on tungsten carbide and on silicon nitride are shown. Table 1 contains the stress tensors which have been determined for the corresponding films.

**Fig. 3** X-ray diffraction diagram for a 28  $\mu\text{m}$  thick DLC film on a tungsten carbide substrate.



**Fig. 4** X-ray diffraction diagram for a 28  $\mu\text{m}$  thick DLC film on a silicon nitride substrate.



**Table 1** Measured stress tensor in DLC films.

Sample	28 $\mu\text{m}$ DLC/WC	28 $\mu\text{m}$ DLC/Si <sub>3</sub> N <sub>4</sub>
$\underline{\underline{\sigma}}$ (DLC) in MPa	$\begin{pmatrix} -1573 & -43 & 14 \\ -43 & -1663 & -36 \\ 14 & -36 & 0 \end{pmatrix}$	$\begin{pmatrix} 267 & -88 & -2 \\ -88 & 214 & 7 \\ -2 & 7 & 0 \end{pmatrix}$

In both cases absolute values of the shear stress components are essential smaller than values of the normal stress components. Taking into consideration the accuracy of the measurement, the component  $\sigma_{13}$  can be assumed to be nearly zero and also the stress components  $\sigma_{12}$  and  $\sigma_{23}$  are very low. The normal stress components are approximately equal:  $\sigma_{11} \approx \sigma_{22}$ , i.e. the stress state in the films is radially symmetric.

### 3 Raman spectroscopic stress determination in diamond

If diamond is irradiated by visible light, e. g. by a laser, a small part of the light energy is scattered inelastically by interaction with the diamond lattice vibrations resulting in a frequency shift of the incident radiation. This phenomenon is known as Raman effect [11]. The so-called Raman frequency gives the wave number shift related to the exciting radiation. Raman spectra have been taken using a RENISHAW 3000 microprobe equipped with an argon ion laser (wavelength 514.5 nm) [12].

The Raman spectra of the DLC films prepared by HF-CVD (fig. 5) shows a sharp peak at a wave number of about  $1332\text{cm}^{-1}$  caused by crystalline diamond [13]. If the film is stress-free, this peak is triply degenerate. The broad and low intensive peaks at higher wave numbers can be assigned to ordered and disordered graphite [14].

If diamond is strained, the vibrational frequency is changed and the Raman frequency is shifted due to the piezo-spectroscopic effect. Assuming elastic behaviour according to Hooke's law, the stress induced Raman shift  $\Delta\omega^{(k)}$  of the mode  $k$  is given empirical by the following tensorial relation [6]:

$$\Delta\omega^{(k)} = \sum_{ij} \Pi_{ij}^{(k)} \sigma_{ij} . \quad (4)$$

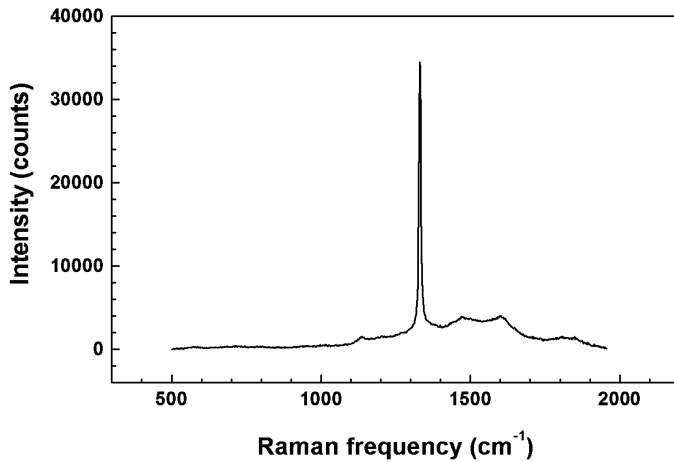
$\sigma_{ij}$  are the components of the stress tensor  $\underline{\underline{\sigma}}$ ,  $\Pi_{ij}^{(k)}$  are the piezo-spectroscopic coefficients of mode  $k$ . The stress state in the investigated DLC films has been approximated by the following stress tensor:

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{\text{film}} & 0 & 0 \\ 0 & \sigma_{\text{film}} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5)$$

Eq. (4) together with eq. (5) allows to determine the mean film stress  $\sigma_{\text{film}}$  from the measured Raman frequency shift  $\Delta\omega$ . If the film stress is high, the diamond mode splits into a singlet and a doublet [13]. This splitting could not be observed in the Raman spectra of the investigated DLC samples. In that case eq. (4) reduces to

$$\Delta\omega = \Pi_{\text{film}} \cdot \sigma_{\text{film}}. \quad (6)$$

The piezo-spectroscopic coefficient of diamond is  $\Pi_{\text{film}} = -2,13 \text{ cm}^{-1} \text{ GPa}^{-1}$  [13].



**Fig. 5** Raman spectrum of a DLC film prepared by HF-CVD.

#### 4 Raman spectroscopic stress analysis in amorphous carbon films

In the Raman spectra of amorphous carbon films or of DLC films with very small crystallite sizes the diamond peak disappears and stress values cannot be derived. But, there is the possibility to determine the film stress from measured substrate stress profiles, if the substrate material can be investigated by piezo-spectroscopy. Fig. 6 shows schematically a film structure with a vertical edge on a thick substrate. If the film is stressed, the edge causes measurable stress in the substrate. The substrate stress oscillates perpendicular to the edge. The mean film stress can be estimated as free parameter by fitting a finite element model to the measured substrate stress curve [8].

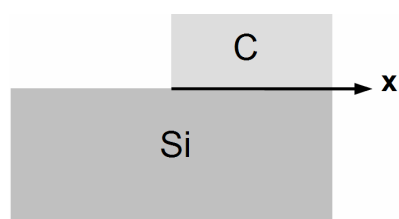
A 80 nm thick carbon film on a single crystalline silicon substrate has been investigated. Parts of the film have been removed by ion etching to form a steep edge with the silicon substrate. The measured mean normal stress in the silicon is to be seen in fig. 7. Because the Raman spectra have been taken with a light microscope a lateral resolution of about  $1\mu\text{m}$  could be reached.

The substrate stress is compressive left to the edge (substrate area not covered by the film), indicating that the film stress is compressive. The model curve fitted to the data points represents the weighted sum of stress contributions from different depth in the substrate convoluted by the probe function given by the dimensions of the laser spot on the sample surface [12].

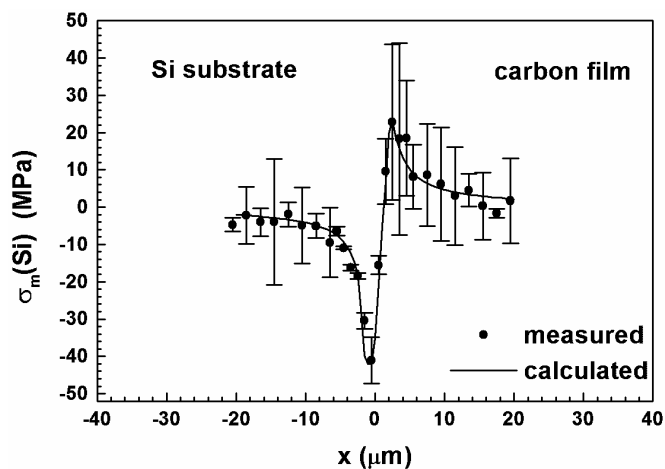
#### 5 Results and discussion

Stress values determined in DLC films on different substrates by X-ray diffraction and by Raman spectroscopy are compared in table 2. The values are the means from repeated experiments. The films deposited on tungsten

carbide are under compressive stress higher than 1 GPa whereas the films on silicon nitride are under tensile stress ranging from 300 to 400 MPa. Within the limits given by the accuracy of the method of measurement the normal stresses determined by X-ray diffraction and by the piezo-spectroscopic experiment are in accordance. The only exception is the measurement on the thin film on the silicon nitride substrate.



**Fig. 6** Scheme of a carbon film with vertical edge on a silicon substrate.



**Fig. 7** Measured mean normal stress distribution in the silicon substrate perpendicular to the substrate/80 nm carbon film edge (at  $x = 0$ ) and fitted model curve.

The carbon film on the silicon crystal also shows very high compressive stress. It cannot be compared directly with the other films because of the different deposition technique and of deviating thickness. Nevertheless, the result of the indirect measurement method seems to be realistic in terms of the order of magnitude of the stress values.

**Table 2** Stress values measured on DLC films on different substrates by X-ray diffraction and Raman spectroscopy.

Substrate	thickness (DLC) in $\mu\text{m}$	$\sigma_{\text{film}}$ (Raman) in MPa	$\sigma_{11}$ (X-ray) in MPa
Si <sub>3</sub> N <sub>4</sub>	6	300 ± 40	-12 ± 61
	28	390 ± 150	323 ± 116
WC	6	-1670 ± 200	-1133 ± 95
	28	-1440 ± 130	-1317 ± 409
Si	80	-2000 ± 400	—

## 6 Conclusions

Residual stress in DLC films caused by the deposition technique and by differences in the thermal expansion behaviour between substrate and film have been analysed using two methods independently: X-ray diffraction and Raman spectroscopy. The X-ray diffraction results confirm the assumptions concerning the stress state made to determine stress from the Raman data. Nearly all investigated films have plane stress with negligible shear stress. The normal stress values determined by both methods are in good agreement.

Additionally, a method to evaluate stress in amorphous carbon layers has been demonstrated by measuring the stress in a silicon substrate near a vertical carbon film edge. The result is in the order of magnitude of the directly determined stress values.

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