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2002 J. Phys.: Condens. Matter 14 5271

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A new quantitative determination of stress by Raman spectroscopy in diamond grown on alumina

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Received 21 December 2001

Published 16 May 2002

Online at stacks.iop.org/JPhysCM/14/5271

Abstract

Raman spectroscopy is used to study the residual stress in polycrystalline diamond grown on alumina by chemical vapour deposition. A new method for stress determination is first presented and used for the measurement of the stress evolution across the film thickness. The compressive stress in the very thin film is in good agreement with the thermal mismatch between diamond and alumina, and the stress declines with increasing film thickness due to the stress relief during grain growth. Within thickness up to about 20 μm , the stress values given by the singlet and doublet Raman modes correspond satisfactorily and the common assumption of biaxial stress in the plane of the film is confirmed. With further increasing film thickness, the quantitative measurement method seems to be inappropriate because of the more complicated stress state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Alumina ceramic substrate, mostly used in integrated circuits (ICs), has been faced with problems of heat production and signal delay during running, so many research studies have been carried out in order to improve the properties of this substrate. Mo *et al* [1] pointed out that a two-layer composite of diamond film and alumina was a promising and cheap substitute for monolithic alumina substrate. However, there are some problems associated with application of this composite as the substrate of electrical circuits. One of these is the large stress in the diamond films. It is therefore particularly necessary to measure quantitatively the stresses generated in diamond films on alumina substrates and consequently optimize the deposition conditions.

Raman spectroscopy is one of the most commonly used methods for evaluation of residual stresses in the diamond film. Von Kaenel *et al* [2] estimated quantitatively the relation between the residual stress and the corresponding Raman shift in heteroepitaxial chemical

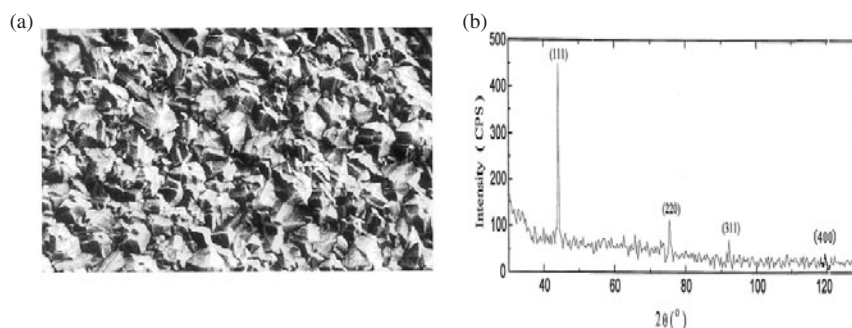


Figure 1. (a) SEM image and (b) XRD data of diamond films grown on alumina substrate for 15 h.

vapour deposition (CVD) diamond films. Ager [3] has also measured an in-plane stress gradient in diamond single crystals and in homoepitaxially grown CVD diamond films by Raman spectroscopy. Unfortunately, these quantitative stress measurements were practically possible only in these simplified cases of the highly oriented and textured films, where the crystallographic orientation was well known and the polarization selection rules in Raman spectroscopy could be applied unambiguously. No quantitative information has been given, as yet, on the stress for the randomly oriented diamond films. In this study, we study the Raman spectra of highly stressed, polycrystalline, CVD diamond films and develop a new model for determining the stress evolution quantitatively from detailed structure within Raman spectrum.

2. Experiment

Hot-filament chemical vapour deposition (HFCVD) techniques were used to deposit diamond film on alumina ceramic wafers. Prior to deposition of the diamond film, the substrate was pretreated in a fluidized bed of diamond particles to obtain a high nucleation density of diamond sites. Five parallel tungsten filaments of 0.4 mm diameter were used and the distance between filaments and substrate was fixed at 8 mm. A gaseous mixture of alcohol and hydrogen was introduced as working gas via the mass-flow controller. The total gas pressure of the reaction chamber was kept about 4×10^3 Pa. The substrate temperatures were measured by a thermal couple, which was embedded under the substrate.

After deposition, the diamond films were examined by scanning electron microscope (SEM) and x-ray diffraction (XRD). Raman spectroscopy, using the 632.81 nm line of a He–Ne laser, was utilized to characterize the stresses in the diamond films. The maximal power was 25 mW and the laser spot size was about $10 \mu\text{m}$. The shifts of different Raman peaks were measured compared with those from the stress-free natural diamond (1332.5 cm^{-1}). The measurements were performed for ten different points and averaged over five times at each point for the 60 s sampling time. Before each measurement, the Raman equipments were first calibrated against the standard laser line to minimize the system errors.

3. Results

Inspection of the sample with an SEM in figure 1(a) revealed that diamond films were polycrystalline and had no predominant crystallographic orientation. This observation was confirmed by the XRD data in figure 1(b). For the sake of clarity, the interfering peaks from the alumina substrate have been taken off with the aid of the standard PDF card of the alumina.

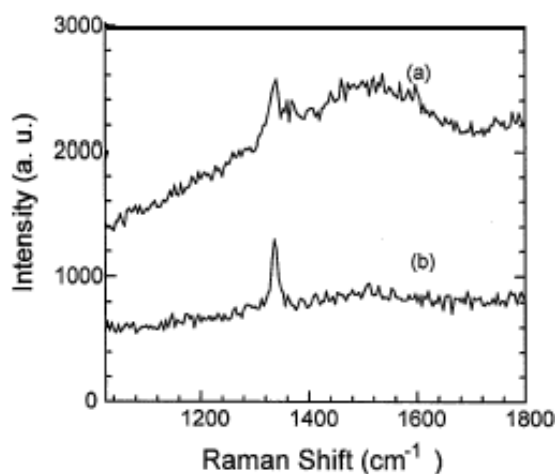


Figure 2. Raman spectra taken from diamond films on (a) alumina and (b) silicon substrates.

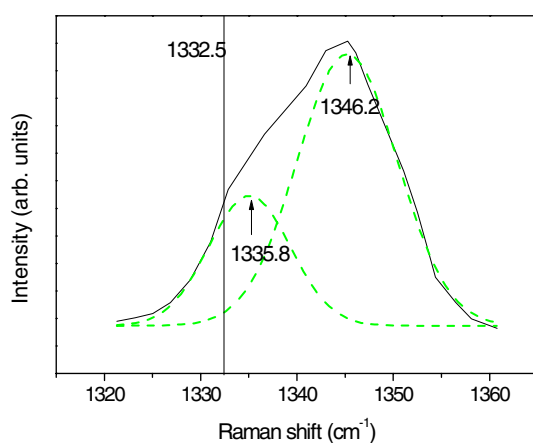


Figure 3. Part of the Raman spectrum of the diamond film in figure 2(a), excluding the Raman peak due to the sp^2 carbon and the PL background.

The sharp Raman peak near 1332 cm^{-1} in spectrum (a) of figure 2 confirmed that diamond films with good quality were deposited on alumina substrates, while the sp^2 band near 1550 cm^{-1} indicated the presence of a certain amount of amorphous carbon. Figure 2(b) showed the Raman spectrum of diamond films deposited on silicon substrates. It was found that the Raman spectra of the diamond films deposited on the alumina substrates were more complicated than those of the diamond films on silicon wafers. Figure 3 shows part of the Raman spectrum of the diamond film in figure 2(a), excluding the Raman peak due to the sp^2 carbon and the PL background. The solid straight line located at 1332.5 cm^{-1} indicates the peak position of the stress-free natural diamond. It was observed, from figure 3, that the splitting between the singlet and doublet components was not large enough to be observed clearly, so a Gaussian fit was applied to separate the two components completely and obtain their peak positions as precisely as possible. The lower frequency (1335.8 cm^{-1}) and higher frequency (1346.2 cm^{-1}) corresponded to singlet and doublet modes respectively, which was confirmed by Ager and Drory [6].

Table 1. Deformation potential and compliance constants of diamond.

Deformation potential constants (10^{28} s^{-2})		
p	-17.8	
q	-11.2	[4]
r	-12.0	
Compliance constants (10^{-13} Pa^{-1})		
S_{11}	9.524	
S_{12}	-0.9913	[5]
S_{44}	17.33	

4. Discussions

The effect of stress on the zone-centre phonons in diamond films is well known. Without strain the Raman phonons are degenerate and have the same frequency $\omega_0 = 1332.5 \text{ cm}^{-1}$ in the centre of the Brillouin zone, but in the presence of strain the diamond symmetry is lowered and the degeneracy is lifted. The new frequencies of three optical phonons at $q \approx 0$ are given by the solutions of the following secular equation, which derives from the lattice dynamical equations:

$$\begin{vmatrix} p\varepsilon_{xx} + q(\varepsilon_{yy} + \varepsilon_{zz}) - \lambda & 2r\varepsilon_{xy} & 2r\varepsilon_{xz} \\ 2r\varepsilon_{xy} & p\varepsilon_{xx} + q(\varepsilon_{xx} + \varepsilon_{zz}) - \lambda & 2r\varepsilon_{yz} \\ 2r\varepsilon_{xz} & 2r\varepsilon_{yz} & p\varepsilon_{zz} + q(\varepsilon_{xx} + \varepsilon_{yy}) - \lambda \end{vmatrix} = 0$$

with $\lambda = \omega_i^2 - \omega_0^2$, $i = 1, 2, 3$, and $\Delta\omega_i = \omega_i - \omega_0 \sim \lambda_i/2\omega_0$ the stress-dependent Raman peak shift. The ε_{ij} are the components of the strain tensor ε referred to the crystal axes x, y, z and p, q, r are the deformation potential constants measured by many researchers.

Solving this equation for the general case (strain tensor with different and non-zero values for its six independent components) would be complex and would provide complex functions of the six strain tensor components and of p, q and r for the solutions. It is clear that certain assumptions concerning the magnitude of the different strain tensor elements are necessary in order to solve the secular matrix. Because the diamond films in our studies are polycrystalline, it is reasonable to assume that the strain is uniform in the diamond layer and in-plane stress is primarily biaxial. Using the constants given in table 1, the respective biaxial stresses for highly $\langle 111 \rangle$ -, $\langle 220 \rangle$ -, $\langle 311 \rangle$ - and $\langle 400 \rangle$ -oriented films can be easily calculated. The formulae obtained agree well with the already published data for diamond.

(1) Biaxial stress in the $\langle 111 \rangle$ plane:

$$\begin{aligned} \tau'_{(111)} &= -1.49\Delta\omega_s \text{ GPa} \rightarrow (\text{singlet}) \\ \tau''_{(111)} &= -0.35\Delta\omega_d \text{ GPa} \rightarrow (\text{doublet}). \end{aligned}$$

(2) Biaxial stress in the $\langle 220 \rangle$ plane:

$$\begin{aligned} \tau'_{(220)} &= -1.09\Delta\omega_s \text{ GPa} \rightarrow (\text{singlet}) \\ \tau''_{(220)} &= -0.37\Delta\omega_d \text{ GPa} \rightarrow (\text{doublet}). \end{aligned}$$

(3) Biaxial stress in the $\langle 311 \rangle$ plane:

$$\begin{aligned} \tau'_{(311)} &= -1.02\Delta\omega_s \text{ GPa} \rightarrow (\text{singlet}) \\ \tau''_{(311)} &= -0.41\Delta\omega_d \text{ GPa} \rightarrow (\text{doublet}). \end{aligned}$$

(4) Biaxial stress in the $\langle 400 \rangle$ plane:

$$\begin{aligned} \tau'_{(400)} &= -0.61\Delta\omega_s \text{ GPa} \rightarrow (\text{singlet}) \\ \tau''_{(400)} &= -0.42\Delta\omega_d \text{ GPa} \rightarrow (\text{doublet}). \end{aligned}$$

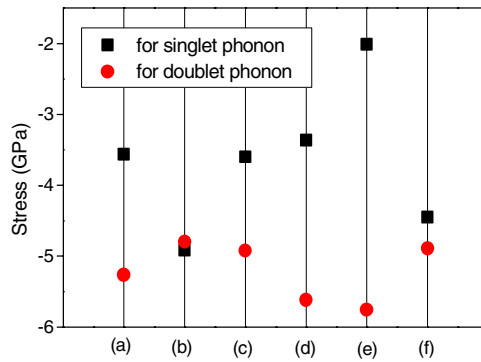


Figure 4. Stresses given by the singlet and doublet modes assuming biaxial stress in (a) the polycrystalline plane where Raman signals from different grains were equally averaged [6], (b) the (111) plane, (c) the (220) plane, (d) the (311) plane, (e) the (400) plane and (f) the polycrystalline plane where Raman signals were averaged by their respective content in XRD data.

However, these data cannot be applied directly to the diamond films on alumina substrates because the films are polycrystalline and have no preferential orientation. It is advisable to consider the polycrystalline diamond films as a mixture of various highly oriented grains. The observed Raman signals, likewise, are the joint results of the grains probed in the film. That is, the polycrystalline nature of the film allows both doublet and singlet Raman modes to be observed in backscattering from most crystal orientations. For example, only the singlet mode can be observed in backscattering from a $\langle 100 \rangle$ -oriented single crystal, while both the singlet and doublet are observed in backscattering from (100) and $(11\bar{2})$. Ager and Drory [6] also mentioned this issue in their articles and thought the individual contributions from all the different crystals to the Raman signal were definitely equal, but we think it is more reasonable to assume that the contributions of differently oriented particles to the singlet and doublet Raman modes are in proportion to their respective contents in the film, which can be roughly indicated by XRD data. We thus deduce that the biaxial stresses corresponding to singlet and doublet modes, τ' and τ'' , can be quantified respectively by the following equations:

$$\tau' = \sum_i I_{ri} \tau'_i \text{ (for the singlet phonon)}$$

$$\tau'' = \sum_i I_{ri} \tau''_i \text{ (for the doublet phonon)}$$

where τ'_i and τ''_i are the stresses calculated above for various highly oriented grains and I_{ri} the relative intensities of different particles in the XRD data. Using the average by individual content for figure 1(b) data (excluding the (400) doublet value since Raman scattering from the phonon is forbidden in backscattering) yields the following relation between the stress and the two Raman shifts:

$$\tau' = -1.348 \Delta\omega_s \text{ GPa}$$

$$\tau'' = -0.357 \Delta\omega_d \text{ GPa.}$$

The stress values given by the singlet (1335.8 cm^{-1}) and doublet (1346.2 cm^{-1}) in figure 3 correspond to 4.45 and 4.89 GPa respectively. Figure 4 shows the details of comparative calculations using different assumptions. It is clear that the stresses from singlet and doublet phonons which were averaged by the individual contents of different oriented grains were of better consistence. The stress evolution across the film thickness is demonstrated in figure 5. When the film was very thin, the stress obtained from the Raman spectrum (-6.8 GPa) was in

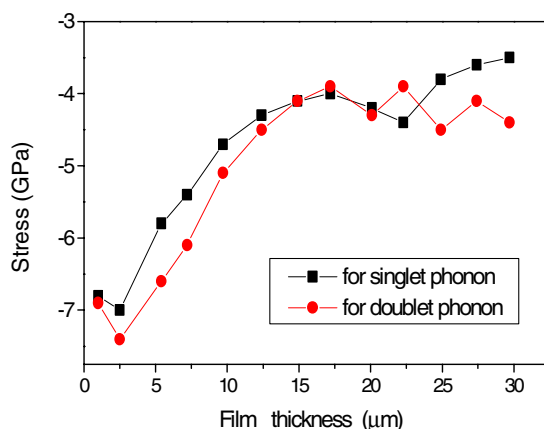


Figure 5. Evolution of compressive stresses given by the singlet and doublet with the film thickness.

good agreement with the thermal stress estimated by the thermal expansion mismatch between diamond and alumina (-6.56 GPa). Within thickness up to about $20 \mu\text{m}$, the compressive stresses in the diamond films declined smoothly with increasing film thickness, which can be attributed to the stress relief during grain growth [7]. In addition, the stress values given by the singlet and doublet corresponded satisfactorily across the whole thickness, which provided further support for our interpretations. However, when the film thickness increased beyond $20 \mu\text{m}$, the obtained stress varied irregularly and the assumption of biaxial stress in the film plane seemed to be inappropriate. It is assumed that a more complicated stress tensor will be necessary for the thicker film to acquire quantitative data.

5. Conclusions

A new method for quantitative stress determination based on Raman spectroscopy has been applied to diamond films grown on alumina substrates. It is found that thermal mismatch is highly responsible for the compressive stress in the very thin film. The stress will then decline with the film depth, which is caused by the stress relief during grain growth. The assumption of biaxial stresses in the film plane is confirmed for film thickness up to about $20 \mu\text{m}$, because the compressive intrinsic stresses given by singlet and doublet Raman modes are of good consistence, but the strain tensor has to vary and a more complicated stress tensor will be needed for the thicker films.

Acknowledgment

This work was supported by the Shanghai Foundation of Applied Materials Research and Development.

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