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Calculation of the stress in large square facets of MPCVD grown diamond from cathodoluminescence and raman spectroscopy measurements and comparison to stress predicted from finite element models[1]

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Abstract

Thin films of diamond grown by microwave plasma assisted chemical vapour deposition on silicon substrates have been observed to be under stress. Large (100) oriented square facets were observed in the films examined. The size of these crystallites allowed large numbers of readings to be taken by the different techniques illustrated at different points within a single crystallite. Stress in diamond crystals has been shown to affect the peak position and splitting of the 575 nm luminescence peak system in diamond. By the application of different accelerating voltages in a SEM at different positions on the square facet, the stress distribution in the crystallite could be mapped. Stresses in diamond are known to affect the triply degenerate first order phonon line observed by Raman spectroscopy. Using backscattered Raman on a confocal Raman spectrometer a map of the variation of biaxial stress within a volume could be built up. The stresses observed by these techniques and those predicted by finite element modelling of the diamond crystals were compared and the results were found to be in general agreement. © 1997 Elsevier Science S.A.

Keywords: Cathodoluminescence; Diamond Films; Raman Spectroscopy; Stress

1. Introduction

It has been known for some time that diamond films can be deposited by low pressure chemical vapour deposition processes onto a variety of substrates [1]. The unique properties of diamond make such films attractive for a number of technological applications. It has been observed that such films are under stress [2,3] and this is known to affect the properties of the film including its adhesion and fracture strengths. The cause of this stress may include mismatches between the lattice constants and thermal expansion coefficients of the film and substrate as well as stresses from defects and inclusions. The quantitative determination of the stresses in these films will be useful in characterising and optimising their structural properties.

Two methods are presented here for determining the stresses in particular growth features of diamond films. Cathodoluminescence measurements relate the splitting of the 575 nm peak to the stresses in the crystal. This relation has been accurately determined for uniaxial stress in bulk diamond [4] and the analysis is carried over to biaxial stress. The movement of the peaks of the first order Raman spectrum of a diamond crystal can be related to the stresses in that crystal [5–9]. The stresses obtained from such methods are compared to predictions derived from finite element models [10,11].

2. Growth and SEM characterisation

The film under investigation was grown by J.E. Butler at the Naval Research Laboratories in Washington DC by microwave plasma chemical vapour deposition (MPCVD). The planar geometry of the film and the results of similar investigations lead to the assumption that the stress in the film is biaxial to a first approxima-

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tion. The film is made up of a large number of diamond crystallites with a variety of orientations. The largest and most easily identifiable crystals were cubo-octahedral growths with ⟨001⟩ orientations which were truncated to give square (001) facets. A single large crystallite was selected in order to obtain comparative measurements. This crystallite will be referred to as Facet A. Fig. 1 is an SEM micrograph of this crystallite, which shows that the square facet is raised above the surface of the film. It is known from work on heteroepitaxial growth of semiconductors that such raised structures can contain large variations of stress. It has been observed by optical methods that the surface of facets similar to these is deformed in a manner that suggests that the in-plane stress is tensile at the surface of the crystallite.

3. Cathodoluminescence

Both natural and synthetic diamond have complex and well studied cathodoluminescence spectra. It has been shown that certain peaks in this spectrum are sensitive to stress. In particular it is known that the trigonal defect related 575 nm CL system is split by stress and Davies [4] has evaluated the relationship between the amount of applied uniaxial stress and the position of the components of the 575 nm system in bulk diamond. Similar splittings have been observed in small crystallites with a similar structure to that of Facet A within the same film.

CL investigations were carried out on an optical system attached to a JOEL 6400 SEM. The sample was cooled to liquid nitrogen temperatures within the SEM on a specially built stage. Spectra were obtained with the electron probe at certain positions on Facet A with

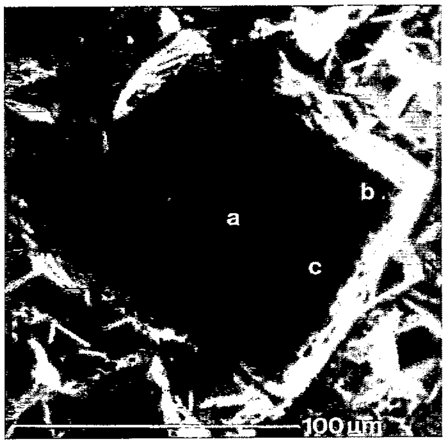

Fig. 1. An SEM micrograph of a ⟨001⟩ oriented cubo-octahedral crystal with a square [001] facet labelled as Facet A. The dimensions of the square facet are measured from this micrograph as being 95 × 105 μm. Labels a, b and c indicate the points below which the Raman and cathodoluminescence measurements were taken.

SEM beam voltages in the range 10–30 kV. Variation of the electron beam voltage varies the depth and size of the interaction volume and therefore the region from which the CL is obtained.

Splittings between the two major peaks of the 575 nm system were observed at almost all the positions on the facet that were studied. Notably, no splitting was discernible below position a at the centre of the facet, implying a low value for the stress in that area. The additional peak in the stressed 575 nm system that occurs because of a dynamic Jahn–Teller effect was observed but without the consistency necessary to obtain measurements from it. Initial polarisation studies have enabled an identification of the two major peaks. This identification indicates that the peaks are split in an opposite sense to that observed by Davies and hence the stresses that we observe in the crystal adjacent to the surface are tensile. The out-of-plane stress at the surface must be zero. It will be assumed that the out-of-plane stresses are much smaller than the in-plane stresses in the crystal volume adjacent to the surface and can therefore be ignored in an analysis based on CL. A reworking of the theory employed by Davies to understand the behaviour of the 575 nm system for the case of tensile in-plane stress leads to the conclusion that the magnitude of this stress can be found from the splitting of the two major components without the need to make any further assumptions about the stress being uniaxial or biaxial. The magnitude of the stress can therefore be found from

$$\sigma(\mathrm{GPa}) = (\omega_a - \omega_b)(\mathrm{cm}^{-1})/60.$$

The numerical factor comes from Davies line fitting analysis on the uniaxial stress data.

4. Raman spectroscopy

Raman spectroscopy was performed using a Renishaw 2000 confocal Raman system. The system operates at 20 mW using a 325 nm He–Cd laser as the light source.

The lattice theory of morphic effects in diamond relates the stresses in a diamond crystal to the frequency of the zone centre phonon modes. The relationship is given in terms of the elastic and anharmonic force constants for diamond. Different patterns of stress in the diamond will split the triply degenerate first order Raman line in different ways. A complete determination of all the components of the stress tensor would be possible by analysis involving different polarisations of the incident and scattered light and different angles of incidence to the film. This method of tilted backscattered Raman will be described fully at a later date.

Raman microscopy has been used previously to discover the stresses in both silicon and diamond [5–9]. With a backscattered Raman laser probe incident normal to an [001] crystal facet the Raman polarisation selection rules forbid the observation of the transverse optical components of the zone centre optical phonon and only the position and relative shift of the LO phonon may be determined. As only one piece of information can be obtained with this set-up, certain assumptions must be made about the form of the stress tensor. It was assumed that the stress in the crystallite was biaxial in form with the two in-plane components equal and the out-of-plane component zero. The validity of this assumption will be checked in further work with the tilted backscattered Raman technique. If the stress is equal biaxial in form then the first order Raman peak in diamond will be split into a singlet and a doublet. The singlet will be the LO phonon that is observed. After a review of the elastic constants of diamond the dependence of the position of this singlet peak on the magnitude of the biaxial stress was determined. The stress could therefore be found from

$$\sigma(\text{GPa}) = 0.552 \times \Delta\omega(\text{cm}^{-1}).$$

Raman spectra were obtained from Facet A at various positions and depths below the surface. The depth of the readings was adjusted to account for the refractive index of diamond. The stresses deduced from these Raman spectra are plotted against depth in Fig. 2. The stresses calculated from this technique at all points on the facet all levelled out at stress levels of approximately 1 GPa at depths below approximately 50 μm.

5. Finite element analysis

Finite element analysis (FEA) was undertaken using the ABAQUS suite of programs on the University of Bristol's mainframe silicon graphics computer "zeus". It has been shown that the finite element method originally developed for working on macroscopic engineering structures can be successfully applied to microstructures [10,11]. A four thousand node model was constructed to represent one quarter of the diamond crystallite and surrounding film. The dimensions were approximately scaled to those of Facet A. The stress in the film was simulated by applying displacements to the outer edges of the model. The amount of these displacements was varied to obtain stresses in the model that were quantitatively similar to those observed in the bulk of the film. The program then found the equilibrium stress state of the system by successive numerical iterations involving matrix decomposition. Fig. 3 shows the patterns of σ_{xx} stress observed in a section through the crystallite taken in the ⟨100⟩ direction. This diagram shows the in-plane stress becoming more positive and therefore more compressive with depth in the crystallite. The out-of-plane stress was predicted from the finite element models to be zero at the surface of the facet and at least an order of magnitude less than the in-plane stress throughout the analytically significant areas of the model.

Fig. 4 shows a comparison of the stress calculated from Raman spectroscopy measurements to that calculated from CL measurements on the splitting of the 575 nm ZPL below point b which lies towards the corner of Facet A. Also shown is the variation of one component of in-plane stress with depth predicted by FEA below an equivalent point on an appropriately scaled model.

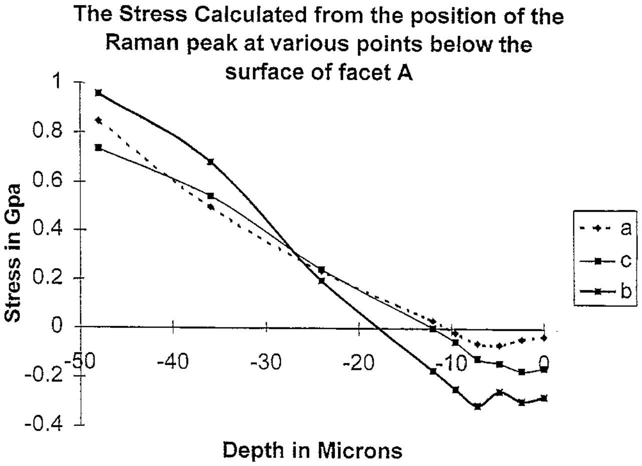

Fig. 2. A comparison of the stresses calculated from the position of the first order diamond Raman line in spectra taken with the confocal volume focused at different depths in the crystal for three positions on Facet A. The positions a, b and c are those indicated on Fig. 1.

6. Discussion

All three results shown in Fig. 4 appear to be in qualitative agreement. The quantitative disagreement between the CL and Raman results as to the magnitude of the tensile stress at the surface might be explained by a number of factors. Firstly, the assumptions that were made about the nature of the stress in both cases were too simplistic. Examination of the full tensor nature of the stress at these particular positions in the diamond crystal may lead to a reappraisal of the assumptions made here and a better quantitative agreement. Such an investigation is currently under way involving the use of polarisers to determine the full stress tensor from both techniques. Secondly, the Raman spectra may be affected by the position of the confocal volume with respect to the surface. This may cause additional effects on the peak shift that are not accounted for in the present investigation. Lastly, it is possible that the conditions under which the defect that causes the 575 nm line is created in CVD diamond growth may lead to additional stresses. Local stresses caused by clusters of

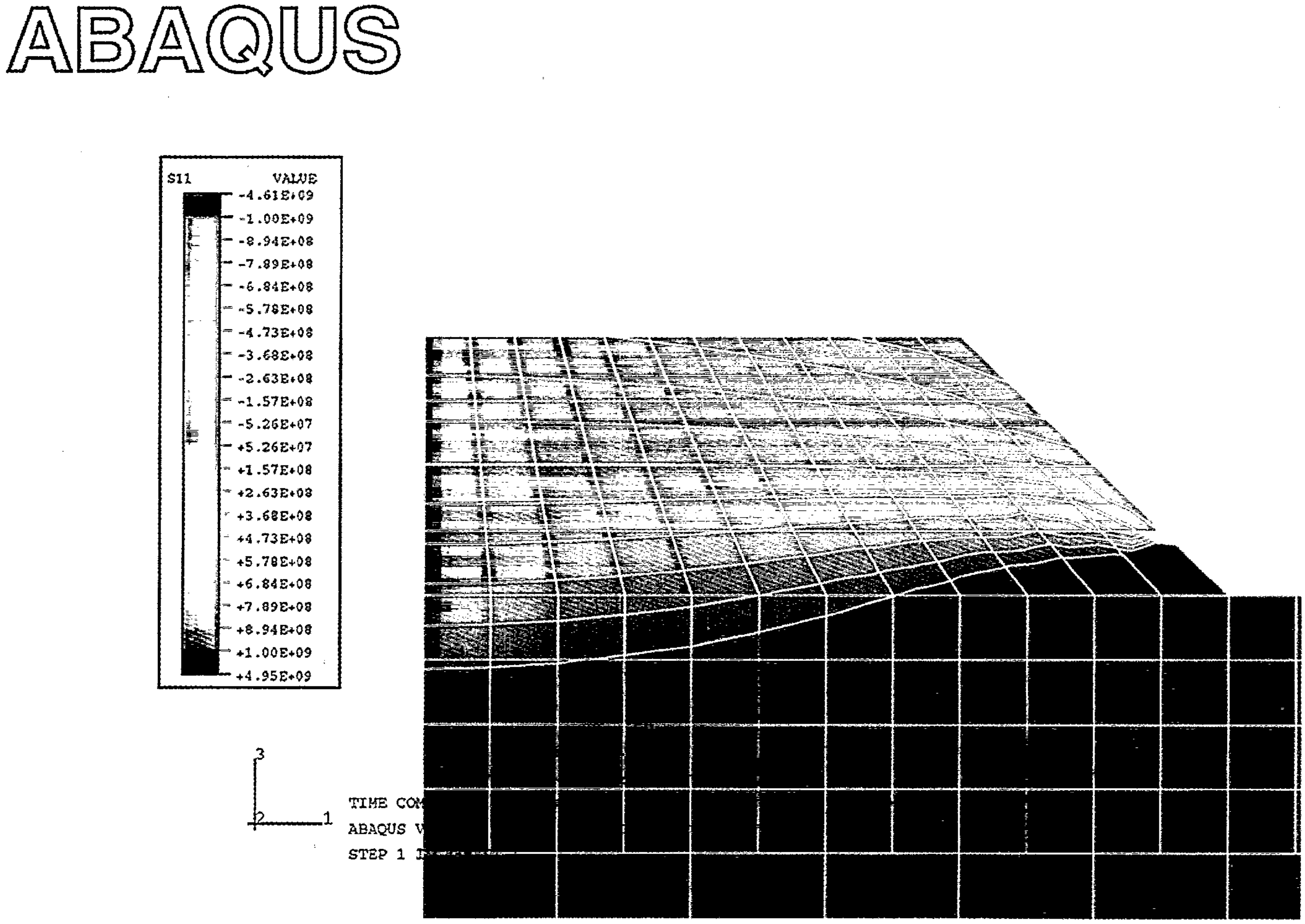

Fig. 3. The patterns of σ_{xx} stress calculated by finite element analysis in a section through the crystallite taken in the ⟨100⟩ direction. Note that the stresses are given in terms of the engineering stresses S_{11} and are hence in the opposite sense to those used elsewhere (positive stresses are tensile).

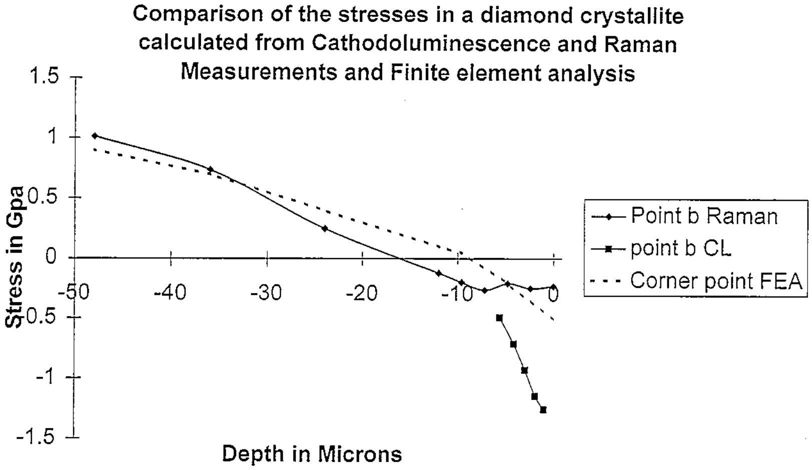

Fig. 4. A comparison of the stresses calculated from cathodoluminescence and Raman spectroscopy measurements below point b at the corner of Facet A to one of the components of the in-plane stress calculated by finite element analysis at an equivalent point on an appropriately scaled model.

vacancies or microvoids might explain the additional tensile stresses and the difference between the two results. Investigations into the validity of these factors are planned.

7. Conclusions

Finite element analysis has been shown to be a useful tool in the modelling of the stresses present within diamond crystallites. It has been shown that a very good qualitative agreement exists between the stresses predicted by this technique and those measured by the two different experimental techniques. It is clear from all the techniques that the stresses in diamond films can be quite inhomogeneous. Although the equilibrium of microstresses will allow for such distributions it is noted that techniques that only measure the stress at one point, particularly at the surface of the films may present an incomplete picture of the stress state of the films.

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