

Thermal oxidation characteristics of chemical vapour deposited diamond films

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Thermal oxidation characteristics of chemical vapour deposited diamond films were studied at 973 K and at different oxygen potentials by analysing the samples before and after partial oxidation using optical and scanning electron microscopy, X-ray diffraction, and Raman and luminescence spectroscopy. On oxidation, diamond films attached to the silicon wafers undergo a colour change. Oxidation proceeds by etching pits on the diamond grains in the films. There is no evidence of any phase transformation of diamond to non-diamond carbon forms. The concentration of defects, particularly neutral vacancies, increase on oxidation. Possible routes for the reaction between diamond and oxygen are postulated.

1. Introduction

The potential applications of chemical vapour deposited (CVD) diamond films in advanced materials technology are numerous. In many of the applications, diamond-coated components are likely to be exposed to oxygen in air at elevated temperatures. Such an exposure would lead to graphitization and/or oxidation of the diamond film with associated degradation in properties followed by premature failure of the component. A study of the thermal oxidation behaviour of CVD diamond films is vital for seeking information regarding environmental limitations in terms of temperature and oxidation potential for safe use of such films in a variety of applications. During the last 2 years, several papers have been published dealing with thermal oxidation of CVD diamond films [1–8].

Optical microscopy, scanning electron microscopy, X-ray diffraction, Raman spectroscopy and luminescence spectroscopy data are presented for CVD diamond films before and after partial oxidation at 973 K and in oxygen-bearing environments containing 25–100 vol % oxygen. The objective of the study was to understand the mechanism of oxidation of CVD diamond films.

2. Experimental procedure

Diamond films were deposited on a 22 mm diameter area on 25.4 mm diameter single-crystal silicon wafers (111 orientation) from CH₄–H₂ gas mixtures by a hot filament-assisted CVD process in a bell-jar system, using tungsten ribbon filaments (0.762 mm wide, 0.0762 mm thick). All films were prepared under identical conditions: substrate temperature was 1223 K, methane content of the input gas was 0.5 vol %, system pressure was 30 torr (1 torr was 133.322 Pa), total gas flow rate was 100 standard cm³ min⁻¹, filament temperature was 2273 K, distance between filament and

substrate was 5 mm. Prior to deposition, the silicon wafers were scratched with 43 μm diamond powder. The films were grown for 20 h at an average rate of 0.32 μm h⁻¹ and had an average thickness of about 6.4 μm.

Diamond films were oxidized in a thermogravimetric system at 973 K until they lost 25 % of their initial weight. The gas phase was a mixture of UHP grade argon and oxygen. The oxygen content of various gas mixtures was 25, 50, 75 and 100 vol %. All measurements were carried out at atmospheric pressure and at a total gas flow rate of 0.0167 l s⁻¹.

3. Results and discussion

Four diamond films were studied for oxidation. The conditions under which the films were oxidized are presented in Table I. The samples are referred to in the following paragraphs by the sample numbers listed in the table.

3.1. Optical microscopy

Optical photographs of an unoxidized diamond film and of films after partial oxidation are presented in Fig. 1a–e. After oxidation, the colour of the samples changed from light grey to black. To determine whether the colour change was induced by heating

TABLE I Sample oxidation conditions

Sample	<i>T</i> (K)	O ₂ (vol %)	$F = (W_f - W_i)/W_i^a$
1	973	25	0.34
2	973	50	0.25
3	973	75	0.26
4	973	100	0.26

^a W_i , W_f are the weights of the samples before and after partial oxidation, respectively.

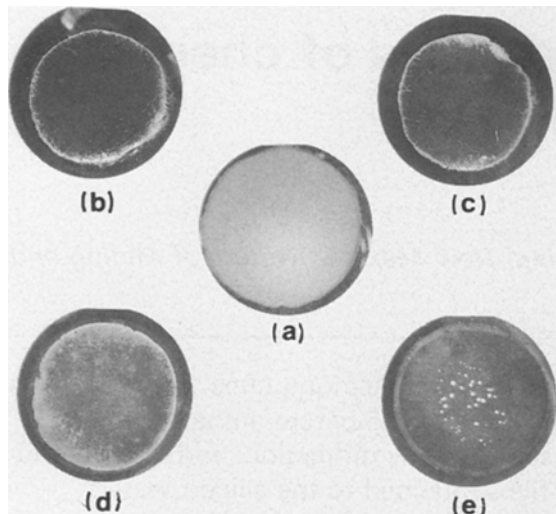


Figure 1 Optical photographs of the diamond films attached to the silicon wafers. Samples: (a) before oxidation, (b) 1, (c) 2, (d) 3, (e) 4.

alone, or whether the presence of oxygen was also necessary, a diamond film attached to the silicon wafer was heated at 973 K for 1 h in UHP grade argon flowing at 0.01671 s^{-1} . No colour change was observed, indicating that the phenomenon was not a result of simple heating: the presence of oxygen was necessary. The colour change could be the result of oxygen-assisted phase transformation of diamond to non-diamond carbon forms. To examine this possibility free standing diamond films were prepared and partially oxidized under identical conditions. Optical photographs of an unoxidized diamond film and of a film after partial oxidation in pure oxygen are presented in Fig. 2a and b. The free-standing diamond film before oxidation was pale yellow in colour but appeared light grey in the outer regions where silicon was underneath. After partial oxidation, the portion of the diamond film that was free did not undergo any colour change, while that portion of the film over the silicon changed colour from light grey to black. This observation suggests that the colour change is not a result of transformation of diamond to a non-diamond carbon form, but is rather an optical effect.

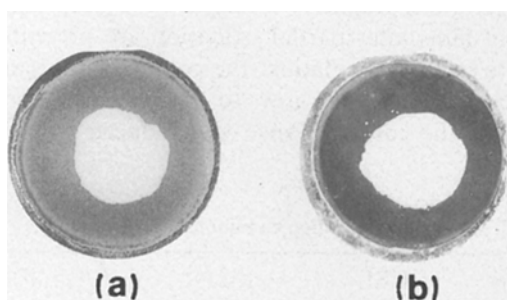


Figure 2 Optical photographs of the diamond films partially removed from the silicon wafers. Samples: (a) before oxidation, (b) after oxidation (in pure oxygen) at 973 K for 30 min.

3.2. Scanning electron microscopy

Scanning electron micrographs of the growth side of diamond films before and after partial oxidation are presented in Fig. 3a–e. Unoxidized film exhibits the typical crystalline morphology which is dominated by octahedral faces. The individual diamond crystallites range in size from 0.5–3 μm . After partial oxidation, well-faceted crystals do not exist in any of the samples. Pits of various sizes can be observed. The degree of attack seems to be the same all over (crystal edges, crystal surfaces, etc.). It is concluded that in all cases oxidation proceeds by etching pits into the film.

A comparison between the oxidation behaviour of the deposition side and substrate side of the diamond film is interesting. Scanning electron micrographs of the substrate side of diamond films before and after partial oxidation are presented in Fig. 4a and b. The

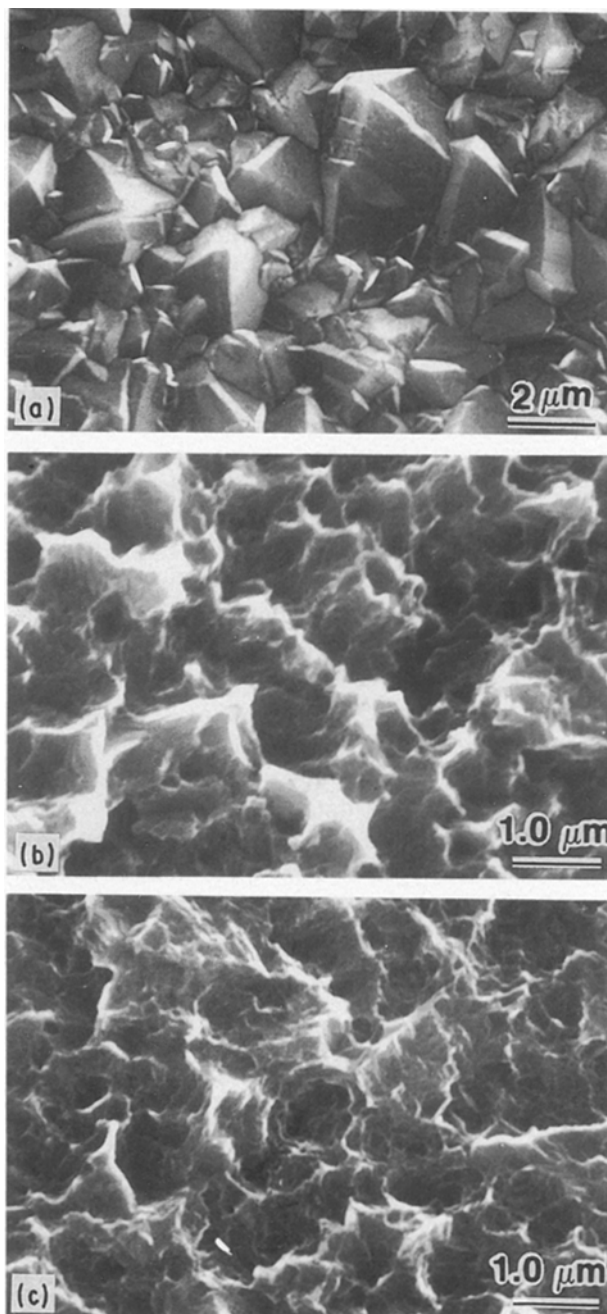


Figure 3 Scanning electron micrographs of the diamond films attached to the silicon wafers. Samples: (a) before oxidation, (b) 1, (c) 2, (d) 3, (e) 4.

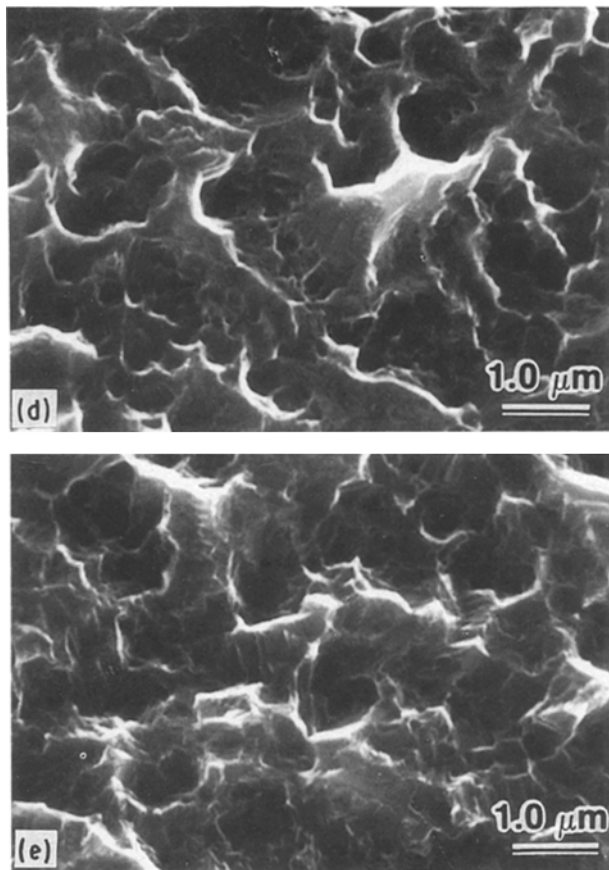


Figure 3 continued.

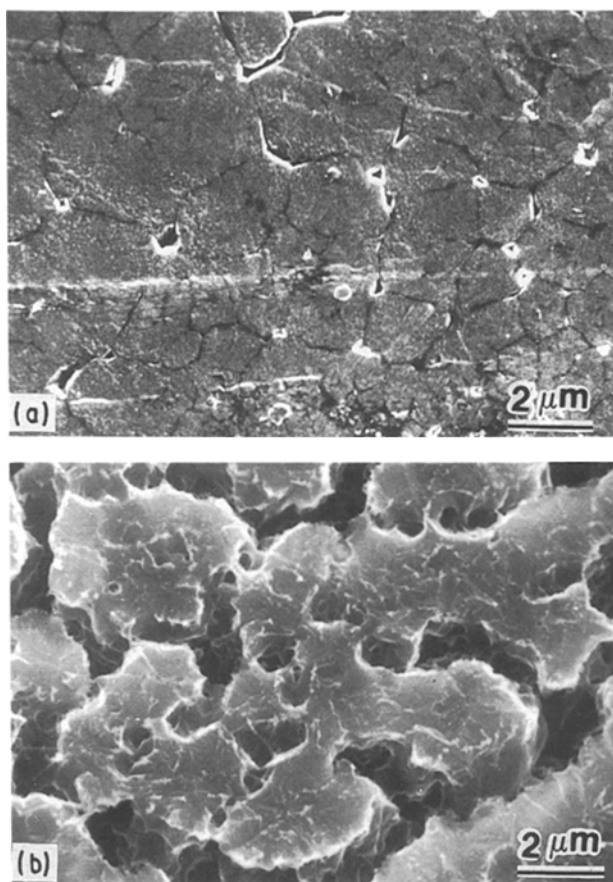


Figure 4 Scanning electron micrographs of the substrate side of the diamond films. Samples: (a) before oxidation, (b) after oxidation at 973 K, $F = 0.25$.

sample was oxidized in pure oxygen. Comparison of Figs 3a and 4a indicates that the substrate side of the diamond film is very smooth, compared to the deposition side. On the substrate side, the boundaries between the grains are clearly visible. Void spaces can also be seen which are a result of nucleation and subsequent growth behaviour. Comparison of Figs 3e and 4b indicates that on the substrate side, the degree of attack is somewhat less; however, grain boundaries are etched more severely, compared to the grains.

3.3. X-ray diffraction

X-ray diffraction (XRD) measurements were carried out to identify transformation of diamond in the films to crystalline non-diamond carbon forms upon oxidation. The XRD patterns of unoxidized and partially oxidized diamond films are presented in Fig. 5a–e. The unoxidized diamond film shows all three diamond peaks, (1 1 1), (2 2 0) and (3 1 1), in the 2θ range scanned (20° – 100°). The other reflections are characteristic of the silicon wafer. In samples partially oxidized at 973 K in various oxygen-bearing gases, the three diamond peaks are still present despite the loss of well-faceted crystalline morphology as evinced by SEM. Signals from crystalline non-diamond carbon forms were not observed. XRD studies, therefore, suggest that oxidation of CVD diamond films up to 973 K in gas mixtures containing from 25–100 vol % oxygen–balance argon is not accompanied by phase transformation of diamond to crystalline non-diamond carbon forms (graphite, chaoite, lonsdaleite, carbynes, etc.). However, these studies do not rule out the possibility of phase transformation of diamond to amorphous non-diamond carbon forms.

3.4. Raman spectroscopy

As mentioned above, XRD provides no information regarding the presence of amorphous carbon phases, even if they dominate the deposits. Raman spectroscopy is a much more sensitive technique for the identification of amorphous carbon phases. Therefore, Raman spectroscopy was performed to identify the transformation of diamond to amorphous carbon forms during oxidation. The Raman spectra of unoxidized and partially oxidized diamond films are presented in Fig. 6a–c. In all cases, sharp peaks at 520 and 1332 cm^{-1} , and the broad maximum centred around 1550 cm^{-1} are attributed to silicon wafer, diamond and a highly disordered carbon phase consisting of both sp^3 and sp^2 hybridized carbon that is amorphous in nature, respectively. The intensity of the diamond Raman band relative to the silicon Raman band is a measure of the amount of film assuming that the accompanying “diamond-like carbon” is not absorbing too much light. On oxidation, the above-mentioned ratio decreases as expected, indicating a decrease in film thickness. The only exception is the sample oxidized at 973 K in pure oxygen (Fig. 6e). The stronger diamond peak relative to silicon in this sample has been explained previously in terms of preferential oxidation of (1 1 1) planes of diamond [3].

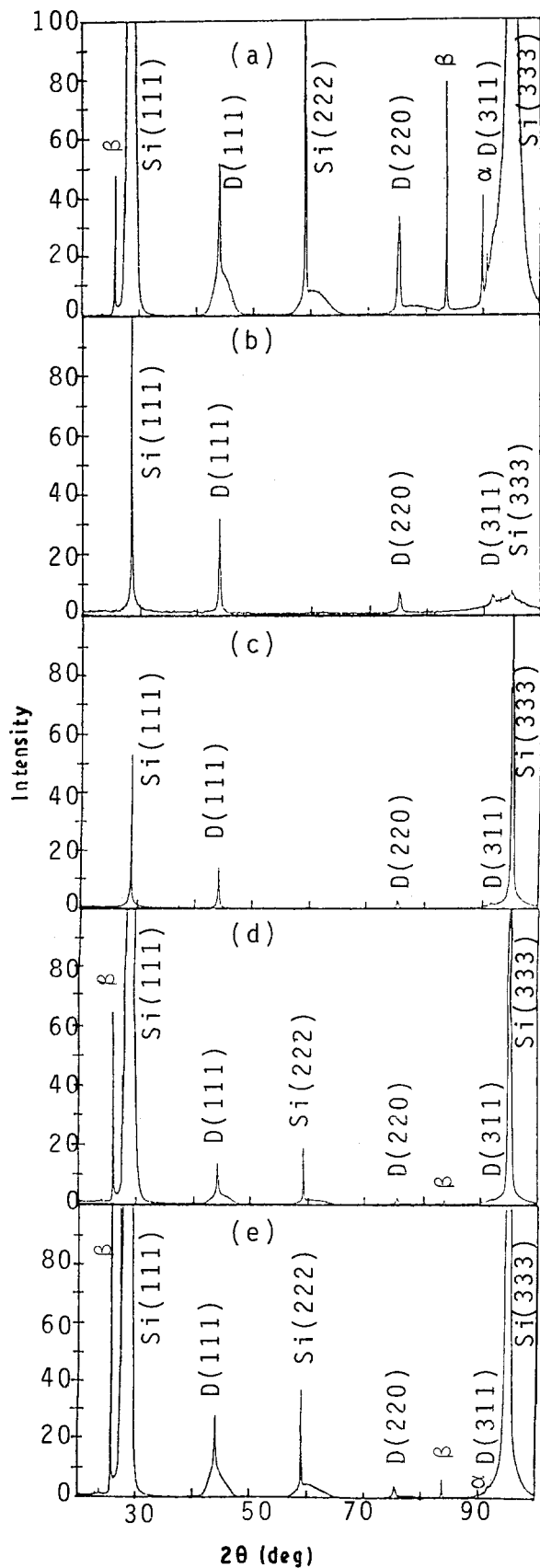


Figure 5 X-ray diffraction patterns of the diamond films. Samples: (a) before oxidation, (b) 1, (c) 2, (d) 3, (e) 4.

Again the intensity of the broad maximum relative to the diamond Raman band can be used to guesstimate the volume fraction of non-diamond carbon in the film. In all cases, the above-mentioned intensity ratio decreases, suggesting preferential etching of non-dia-

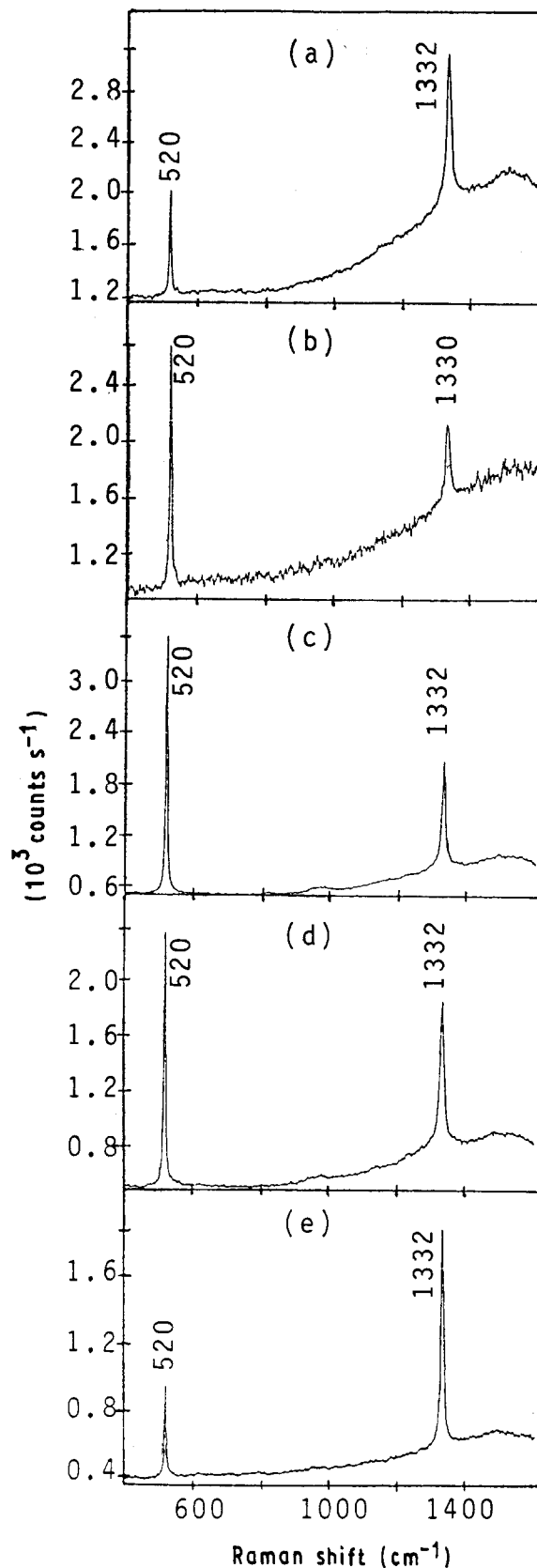


Figure 6 Raman spectra of the diamond films. Samples: (a) before oxidation, (b) 1, (c) 2, (d) 3, (e) 4.

mond carbon in the film upon oxidation. Raman spectroscopy failed to identify the transformation of diamond in the films to amorphous carbon forms. However, the possibility of phase transformation is not completely ruled out. Preferential etching of

amorphous non-diamond carbon does not allow Raman spectroscopy to detect a build-up in the concentration of non-diamond carbon on oxidation.

3.5. Luminescence spectroscopy

Luminescence spectroscopy is a powerful tool to examine defect concentrations in diamond films. Luminescence spectra were obtained to see if the data could be used to characterize oxidized versus unoxidized samples. Spectra from unoxidized and several oxidized diamond films are presented in Fig. 7a–c. Both unoxidized and oxidized diamond films contain a number of optical centres which produce a series of features. In each spectra, the sharp peak at about 5800 cm^{-1} is interesting. This spectral feature has previously been attributed to the neutral vacancy [8]. The intensity of this peak relative to the diamond peak is indicative of the vacancy concentration in the film. The intensity ratio increases with increasing oxygen content of the gas phase, indicating a concomitant increase in the vacancy concentration. The significant differences in the fluorescence of unoxidized and

oxidized diamond films can be used as an indicator of film degradation by oxidation.

3.6. Oxidation mechanism

Both XRD and Raman spectroscopy failed to identify any phase transformation of diamond in the CVD films to non-diamond carbon forms. However, the possibility of phase transformation cannot be ruled out. Oxidation of diamond can, therefore, proceed in two ways:

1. direct reaction of diamond with oxygen to form CO and/or CO_2 ;

2. transformation of diamond to non-diamond carbon, followed by reaction of non-diamond carbon with oxygen to form CO and/or CO_2 . If the oxidation proceeds by this mechanism then the rate of reaction of the non-diamond carbon with oxygen is higher than the rate of its formation (otherwise the transformed phase would have been detected) suggesting that the overall oxidation rate is limited by the rate of transformation of diamond to non-diamond carbon.

Of course, oxidation can proceed by both the routes.

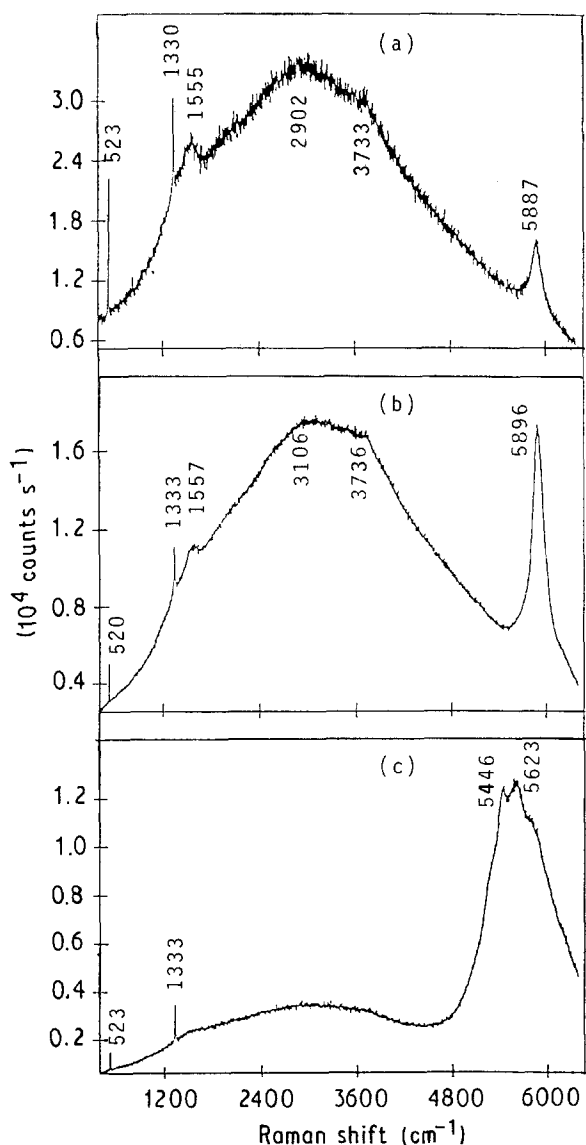


Figure 7 Luminescence spectra of the diamond films. Samples: (a) before oxidation, (b) 1, (c) 4.

4. Conclusions

Thermal oxidation behaviour of synthetic diamond films prepared by hot filament-assisted CVD process was investigated at 973 K and at different oxygen partial pressures in the gas phase. Oxidation proceeds by etching pits in the film and there is significant difference in the oxidation behaviour of the free surface and substrate side of the film. The quality of the film deteriorates rapidly as the defect concentration increases (neutral vacancies) rapidly, as oxidation occurs. X-ray diffraction and Raman spectroscopy failed to identify transformation of diamond to crystalline or amorphous non-diamond carbon forms. However, the possibility of phase transformation cannot be ruled out. Perhaps the films oxidize by direct reaction between diamond and oxygen. If, however, oxidation occurs via an intermediate, the rate of oxidation of the intermediate phase is higher than the rate of its formation from diamond.

Acknowledgement

This work was supported by the National Association of Corrosion Engineers under the seed grant programme.

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*Received 2 September 1991
and accepted 4 February 1992*