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Thermally stimulated exoelectronic emission of CVD diamond films

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Abstract

Exoemissive properties of several CVD diamond films (undoped or doped with nitrogen) are studied by the thermally stimulated exoelectronic emission (TSEE) method. Some experimental results are obtained after UV or X-ray irradiation. After UV irradiation, a single TSEE peak is observed at 605 or 625 K, depending upon the growth parameters. The existence of the exoemission signal is related to the surface morphology: facetted surfaces give rise to exoelectronic emission, more especially in the presence of both 111 and 100 faces, while smooth surfaces do not or only to a limit extent. A possible indication of negative electron affinity is observed at about 273 K. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Chemical vapour deposition (CVD) ; Diamond; Electronic emission; Surface morphology

1. Introduction

Because of its high thermal conductivity [1] and high carrier mobilities [1] compared with those of commonly used semiconducting materials, coupled with the recent progress in the synthesis of chemically vapour deposited (CVD) films, diamond is an attractive material in the field of high temperature electronic applications [2]. Moreover, several studies have shown that, as a function of the surface morphology, CVD diamond films may exhibit a negative electronic affinity (NEA) [3,4], increasing its exoemissive power, suggesting that this material might find some applications in cold-cathode devices such as flat panel displays [2].

The thermally stimulated exoelectronic emission (TSEE) technique is a non-destructive method which can be used for characterization of surfaces. The principle is the following: deep levels within the gap are filled with the help of an excitation source; because of the wide gap of diamond, the carriers trapped on these levels at room temperature are frozen. By heating the semiconductor, carriers can be emitted from the trap level. If the phenomena occurs near the surface, electrons can be released to the vacuum from the surface and then collected.

Numerous studies have been carried out concerning the electron field emission from CVD diamond films [5–8]. Here, we report for the first time on TSEE experimental results from CVD diamond. Results are given between 200 and 800 K after UV or X-ray irradiation.

2. Experimental details

All samples were grown by hot-filament CVD (HFCVD) on single-crystal Si (100) substrates which were abraded manually prior to deposition using 1–3 μm diamond grit. Two sets of samples, P and C, deposited in different reactors, were studied. The films of the series P (P1, P2, P3, P4, P5) were deposited in a hot filament reactor using a Ta filament operating at 2400 K. The substrate temperature was 1173 K and the process pressure was 2.63 kPa. The total gas flow of H_2/CH_4 was 200 sccm, with various ratios for the different samples. For sample P5, an amount of 0.5 sccm N_2 was added to the gas mixture to produce a technically N-doped diamond film. Because of the low percentage of N_2 in the gas phase, the doping level was extremely low and it had only a minor effect; the main consequence of nitrogen incorporation was the change in morphology and defects of the film [9,10]. For the series C (C1, C2, C3), the films were deposited in another HFCVD reactor where the Ta filament was maintained at 2500 K and the substrate at 1173 K. The total pressure was 2.63 kPa. The total gas flow

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was 120 sccm (1% vol. methane in hydrogen). Different concentrations of N_2 were injected in the gas mixture for C2 (200 ppm) and C3 (5000 ppm), resulting in as-deposited 'N-doped diamond films' (see remark above). These samples were characterized by Raman spectroscopy and scanning electron microscopy and the detailed results are described elsewhere [9]. A brief description of the morphology of the films is given in Table 1.

TSEE measurements were obtained with the help of a CH_4 gas flow multineedle counter [11] with a voltage of 2450 V; the method is based on proportional or Geiger–Müller counter principles. The heating rate was programmed at 1 K/s from 300 to 800 K. After the measurements, the cooling of the samples took place in ambient air. Each sample was subjected to different irradiations: low-pressure mercury lamp (253.7 nm line mainly) or X-ray source (W-target, 45 kV). Both irradiations were performed in air at 300 K. The UV irradiation time was 1 min for series P and 5 min for series C. The X-ray air kerma was 62.4 Gy for samples P1, P2 and P4, 166.2 Gy for P5 and 4 kGy for P3; it was 333.2 Gy for C1, C2 and C3.

A second experimental set-up was used, permitting to achieve experiments under an ultra-high vacuum (UHV) of about 2×10^{-6} Pa. In this case, TSEE and thermally stimulated luminescence (TSL) signals can be recorded simultaneously. The TSL is the emission of photons which can occur when the trapped carriers are thermally emitted from the trap level to the valence or the conduction band and then retrapped on another level. The exoelectrons were detected by a channel electron multiplier (CEM) operating in the pulse-counting mode whereas the photons were led to a photomultiplier tube (PMT) using optic fibre bundles followed by a focusing lens. The chosen silica optical fibres are UHV-resistant and have a good UV transmission. In order to eliminate the infrared emission produced by the heating holder, appropriate optical filters were used. After they were recovered and shaped, the PMT and CEM information – transformed into TTL signals – were driven to a pulse counter and recorded simultaneously with the sample temperature. A more complete description of the apparatus is given elsewhere [12].

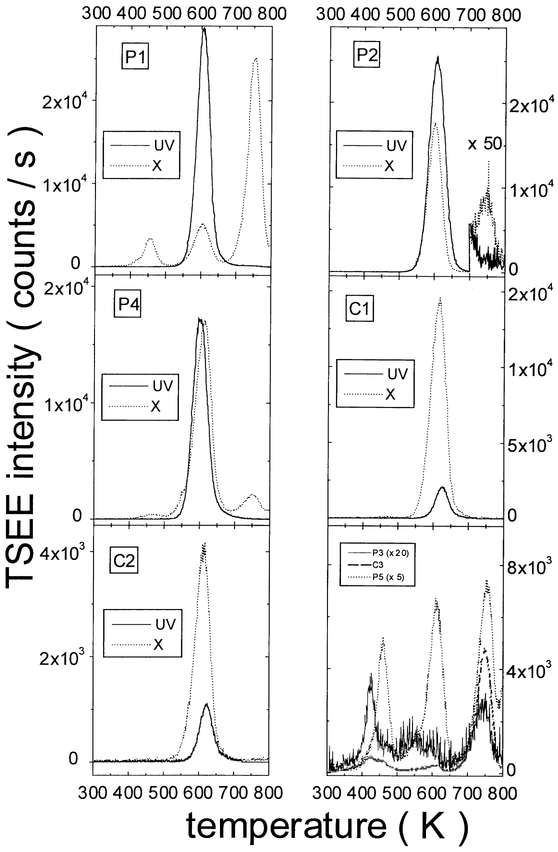

Fig. 1. TSEE glow curves of the CVD diamond films after UV and X-ray irradiations. For the samples P3, P5 and C3, only TSEE curves after X-ray irradiation are represented since TSEE peaks were not observed after UV exposure.

3. Results and discussion

Fig. 1 shows the characteristic glow curves of TSEE. For

Table 1
Description of the CVD films

Sample	% CH_4	%N_2	Structural description	Thickness (μm)	Mean grain size (μm)
P1 [13]	0.5	0	Polycrystalline, mixture of 111 and 100 grains	2–3	1
P2 [13]	1	0	Polycrystalline, mixture of 111 and 100 grains	3–4	0.5
P3 [13]	3	0	Nanocrystalline, smooth	3–4	0.01
P4 [13]	0.4	0	Polycrystalline, mixture of 111 and 100 grains	2	1
P5 [13]	0.4	0.25	Polycrystalline, mainly 100 grains	4	1.5–2.0
C1 [14]	1	0	Polycrystalline, mixture of 111 and 100 grains	4	1.5–2.0
C2 [14]	1	0.02	Polycrystalline, mixture of 111 and 100 grains	10–11	2.0–2.5
C3 [14]	1	0.05	Nanocrystalline, smooth	8–9	0.02

the films P3, P5 and C3, TSEE peaks are observed only after X-ray irradiation. A preliminary study showed that wavelength excitation is higher than 230 nm, i.e. 5.4 eV, which is about the value for the bandgap of diamond, giving evidence that the excitation mechanism is a band-to-band transition.

After the UV irradiation, a single peak was observed. It was centred around 605 K for the series P and 625 K for the series C. X-ray irradiation induced one or several TSEE peaks, depending on the samples. The peak revealed by UV excitation was also present and centred in the same temperature range for the series P but at a lower position (618 K) for the series C. Currently, we have no explanation for this shift. Some other peaks appeared, centred around 455 and 750 K. These peaks were well resolved for samples P1 and P4, but they were observed for P5 and P3 only after a higher X-ray irradiation dose, especially for the latter sample. No supplementary peaks were observed after X-ray irradiation for the samples of the series C, except for C3, for which a signal around 455 K was measured, as well as the peak at 750 K.

It is noteworthy that UV irradiation induces a single peak at 605 or 625 K only for films having a polycrystalline structure, i.e. with a large grain size and a facetted surface. The layers with nanocrystalline grains and a smoother surface did not give rise to the exoemission signal after UV irradiation. Therefore, we think that the defects related to this peak are surface defects show up only when the surface is well faceted. However, sample P5, which is polycrystalline and has a mean grain size of 1.5–2 μm, does not give the 605 K TSEE peak after UV irradiation, although this peak exists after X-ray exposure. Contrary to other samples, which exhibit this peak after UV excitation and are mainly constituted of both 111 and 100 grains, P5 is 100-textured. It appears then that the simultaneous presence of 111 and 100 faces at the diamond surface creates a more favourable condition to TSEE than the presence of 100 faces alone.

An additional experiment of simultaneous detection of thermally stimulated luminescence (TSL) and TSEE was carried out on sample P1 using the apparatus described in Section 2. In this case, the sample was irradiated at 77 K with an UV deuterium lamp and the heating rate was 0.25 K/s. The results are reported in Fig. 2. Two TSEE peaks were observed: the main one corresponded to the single peak at 605 K observed in the previous experiment. A second much weaker peak was located at 273 K and was close to a TSL peak observed around 283 K. Since TSL is related to bulk defects whereas TSEE probes the surface, this suggests that at this temperature TSL and TSEE are probably linked to the same kind of defects. Moreover, the maximum of this TSEE peak is at a lower position than the maximum of the TSL peak. A recent model to estimate the effective electron affinity from the simultaneous detection of TSL and TSEE has been developed [15]. It has been shown that a TSEE peak, correlated with a TSL peak and measured at a lower temperature, could indicate a negative electron affinity (NEA). This then suggests that the CVD diamond film of the sample P1 may exhibit a NEA.

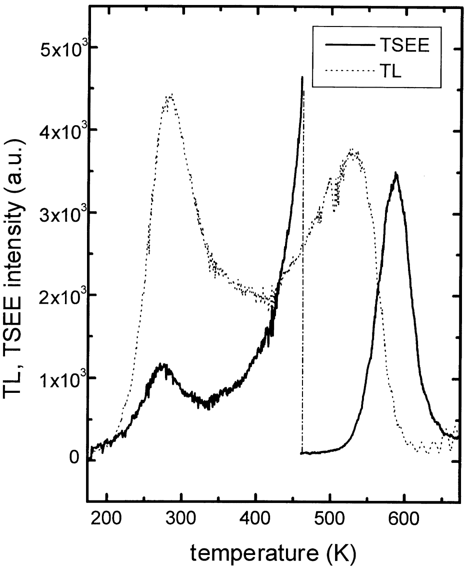

Fig. 2. Simultaneous detection of TL and TSEE under vacuum. The TSEE glow curve was obtained with two different UV exposure procedures: below and above 460 K, the energetic fluence was adjusted by a suitable interferential filter during irradiation and by changing the time of UV irradiation through the filter.

4. Conclusion

We have shown that CVD diamond films give TSEE signals after UV or X-ray irradiation provided that the crystal facetting is not affected by the growth conditions. This effect is improved with the simultaneous presence of 111 and 100 faces at the diamond surface. Moreover, a simultaneous detection of TSL and TSEE indicates the assumption of NEA, making this material interesting in the field of cold-cathode devices.

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