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by

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INVESTIGATION OF DIAMOND HOMOEPITAXY BY *IN SITU* FIZEAU INTERFEROMETRY: THE ROLE OF OXYGEN

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ABSTRACT

Optical Fizeau interferometry has been employed as an *in situ* probe of growth rate and surface morphology in diamond homoepitaxy. The spatial fringe pattern produced by interference between HeNe laser light reflected from the front and back faces of a diamond single crystal is imaged, providing a map of the local substrate thickness. Growth causes the fringe pattern to propagate laterally, enabling *in situ* monitoring of thickness changes as small as 10 nm. We have investigated the substrate temperature dependence of [100] diamond growth in a hot-filament reactor from 0.5% CH_4 in hydrogen with and without oxygen. We obtained an apparent activation energy of 14 kcal/mol over the range 700–1000 °C for a sample grown from pure methane in hydrogen. The addition of O_2 to the reactant feedstock had pronounced effects on the growth kinetics: below 850 °C the growth rate was enhanced whereas etching was observed above 970 °C. Treatment of a polycrystalline diamond film under a hot filament with 0.25% O_2 in H_2 produced etching of both sp^3 and sp^2 carbon. These results suggest that etching of sp^3 as well as sp^2 carbon occurs in competition with growth in oxygen-containing diamond CVD environments.

INTRODUCTION

An improved understanding of the growth mechanism and the factors that determine surface morphology in diamond films grown by chemical vapor deposition is essential for optimization of the technology for specific applications. It is important to perform such studies on individual crystal faces of diamond, as the growth rates and detailed mechanisms will differ. While *ex situ* measurements of nanometer-scale morphology (1-3) and growth kinetics (4) of diamond films grown on (100), (110), and (111) natural diamond substrates have been reported recently, the tedious nature of such measurements makes systematic studies difficult. The application of optical Fizeau interferometry (5,6) provides an *in situ* growth rate monitor which greatly facilitates such investigations. The time dependence of an optical interferometric signal has been used by several authors for *in situ* measurements of growth rates (7,8), but the *spatial* fringe pattern provides a local and more sensitive monitor of growth rate and also yields direct information on morphology.

EXPERIMENTAL

We have applied optical Fizeau interferometry to the *in situ* characterization of diamond homoepitaxy in a hot-filament reactor. (100)-oriented, type IIa natural diamond substrates were held between two mullite tubes and heated by W wires embedded in the mullite. The

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sample temperature was monitored by a chromel-alumel thermocouple embedded in or cemented to the mullite support. Diamond films were grown using flow rates of 0.37–2.25 sccm CH_4 and 0–0.75 sccm O_2 in 150 sccm of hydrogen at 25 Torr. The filament comprised 2–3 0.13-mm-diameter straight W wires, positioned 5–7 mm from the substrate. The filament was held at 2300 °C, as measured using a calibrated one-color pyrometer with no emissivity correction.

Collimated, 633 nm light from a HeNe laser was reflected at near-normal incidence from the back side of the natural diamond substrate, passed through a positive lens, and impinged on a video camera CCD array detector, as shown in Fig. 1. The existence of a slight wedge angle between the back and front faces of the substrate causes interference in the light reflected from the two faces, producing a *spatial* Fizeau fringe pattern. Because the wedge angle causes the two reflected beams to separate from one another, a positive (plano-convex) lens was used to bring both beams to a focus and then diverge in order to maintain overlap between the beams and produce a magnified fringe pattern. Bright and dark fringes correspond to constructive and destructive interference, respectively, between the two reflected beams. At adjacent fringe positions the optical path length differs by one wavelength in the substrate, corresponding to a thickness difference of $\lambda / (2n \cos\theta)$, where λ is the laser wavelength, n the index of refraction (2.4 for diamond), and θ is the angle of incidence. For 633 nm light at normal incidence this path difference is 131 nm. Examples of Fizeau fringe patterns obtained from a $1.5 \times 1.5 \times 0.25$ mm^3 diamond (100) sample (9) under growth conditions are shown in Fig. 2. Uniform deposition of new diamond causes the fringe pattern to propagate laterally, shifting by one fringe for a thickness increase of 131 nm. Temperature fluctuations also cause shifts in the fringe pattern; thus, it was necessary to maintain the substrate temperature constant to within 1–2 °C. In addition to providing *in situ* growth rate information, changes in the fringe spacing or contour shape indicate changes in the surface orientation or smoothness, respectively, and therefore the method also provides a sensitive measure of the *uniformity* of growth.

The fringe pattern image was projected onto a CCD video array detector and recorded on a standard videocassette recorder during growth. The analysis was performed by measuring the fringe positions as displayed on a video monitor as a function of time. Thickness changes as small as 10 nm could be resolved.

RESULTS

The dependence of the growth rate on substrate temperature, T_S, at a CH_4 concentration of 0.5% is shown in Fig. 3. A linear least-squares fit of ln(growth rate) versus $1/T_S$ over the range 700–1000 °C for the sample grown without oxygen yields an apparent activation energy of 14 kcal/mol. Addition of 0.09% O_2 enhanced the growth rate for substrate temperatures below 850 °C as compared to the sample grown with methane in hydrogen only. With oxygen present the growth rate reached a maximum near 800 °C, and *etching* was observed at substrate temperatures above 970 °C. Fizeau interferometry provides a direct indication of etching, as the fringes propagate in the opposite direction from growth.

During growth from 1.0% and 1.5% CH_4 in hydrogen the fringe pattern degraded markedly, indicating a significant change in morphology. Subsequent characterization by

scanning electron microscopy confirmed that the deposited film was polycrystalline. Raman spectroscopy showed the presence of non-diamond carbon, as shown in Fig. 4(a).

Several experiments were performed to explore the efficacy of atomic hydrogen versus H+O environments for etching of sp^2 and sp^3 carbon. A polycrystalline diamond film held at 600 °C under a filament at 2300 °C was treated for 72 hours in hydrogen at pressures ranging from 25 to 100 Torr. We estimate from scanning electron micrographs that on the order of a micron of the substrate was etched. Raman spectroscopy showed that the sp^2 carbon peak near 1580 cm^{-1} (Fig. 4(a)) was reduced but not eliminated. An identically-prepared diamond sample was treated for 20 hours using 0.25% O_2 in H_2 at 25 Torr with the filament at 2300 °C. SEM micrographs before and after this treatment, shown in Fig. 5, indicated a greater degree of etching than the treatment from hydrogen alone. The H_2+O_2 treatment eliminated the sp^2 carbon from the film, as shown by the Raman spectrum in Fig. 4(b), indicating more efficient etching of sp^2 carbon than hydrogen alone.

DISCUSSION

Fizeau interferometry provides a sensitive, *in situ* probe of growth rate and morphology in diamond homoepitaxy. Conventional growth rate studies employing *ex situ* techniques to examine thickness changes can take many months to complete (4) and are not nearly as sensitive. By contrast, the results presented here were obtained and analyzed within a matter of days. The sensitivity, ≈ 10 nm at present, is limited by fluctuations in the sample temperature which modulate both the sample thickness and the index of refraction slightly, causing a slight jitter in the fringe pattern. By improving the stability of T_S to better than 1 °C, capturing fringe images on a computer, and performing numerical analysis of the fringe intensity data, we expect to be able to measure thickness differences of ca. 1 nm. Changes in surface morphology, e.g., renucleation to form a polycrystalline film, give rise to observable changes in the Fizeau fringe image in real time. Changes in the macroscopic orientation of the substrate surface would be manifested by changes in the fringe spacing and the rate of divergence of the two reflected beams.

The growth kinetics data shown in Fig. 3 for the sample grown using 0.5% CH_4 in H_2 without oxygen are qualitatively consistent with the results reported previously (4) but exhibit some quantitative differences. The observed activation energy (14 kcal/mol) is larger than that determined by Chu *et al.* (8 kcal/mol) using 0.4 %CH_4 in hydrogen (4). Furthermore, we found no evidence for a change in activation energy at lower temperatures as was previously reported (4). The discrepancies are presumably attributable to differences in reactor conditions. Nevertheless, further experiments are needed in order to understand the factors controlling the effective activation energy for growth.

The growth rate measurements with 0.09% O_2 shown in Fig. 3 constitute the first kinetic data for the temperature dependence of diamond growth by hot-filament CVD with oxygen present, to the best of our knowledge. Oxygen clearly produces striking effects. The enhanced growth rate at lower substrate temperatures is consistent with the qualitative observations reported previously by many groups (10).

Under hot-filament conditions the oxygen in dilute mixtures with hydrogen should be converted almost completely to water (11), together with much smaller concentrations of OH radicals. Struck and D'Evelyn recently observed the relatively facile dissociative adsorption of water on diamond (100) (12), indicating that modification of CVD surface

chemistry could occur by adsorption of H_2O or, presumably, of OH radicals. CO desorbs from diamond at mild temperatures (13,14), providing a facile etching channel. Etching of CVD diamond films at 800 °C in 360 Torr of water vapor (15) reduced the amount of sp^2 carbon in the film and produced a morphology very similar to that shown in Fig. 5(b), which suggests that diamond is etched concurrently with sp^2 carbon by either treatment.

We believe this to be the first report of a transition from growth to etching of diamond with substrate temperature. This result demonstrates unequivocally that etching of diamond can take place under conditions similar to that which produce growth. In addition, it suggests that competing growth and etching processes take place in parallel over the entire temperature range but have different effective activation energies so that growth prevails at low temperatures but etching dominates at high temperatures. Our results are also consistent with the proposition that high quality diamond homoepitaxy requires simultaneous growth and etching (16) and suggest that the beneficial effects of oxygen in diamond CVD at low temperatures are due in part to enhanced etching, relative to atomic hydrogen, of both sp^2 and sp^3 carbon.

Further experiments are underway in our laboratory to understand the factors controlling the homoepitaxial growth kinetics of diamond in more detail, particularly the effects of oxygen.

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REFERENCES

1. T. Tsuno, T. Imai, Y. Nichibayashi, K. Hamada, and N. Fujimori, Jpn. J. Appl. Phys. **30**, 1063 (1991).
2. L. F. Sutcu, C. J. Chu, M. S. Thompson, R. H. Hauge, J. L. Margrave, and M. P. D'Evelyn, J. Appl. Phys. **71**, 5930 (1992).
3. H. G. Maguire, M. Kamo, H. P. Lang, E. Meyer, K. Weissendanger, and H. -J. Guntherodt, Dia. Rel. Mater. **1**, 634 (1992).
4. C. J. Chu, R. H. Hauge, J. L. Margrave, and M. P. D'Evelyn, Appl. Phys. Lett. **61**, 1393 (1992).
5. S. Tolansky, An Introduction to Interferometry, Longman Press, London, 1973.
6. P. Hariharan, Optical Interferometry, Academic Press, 1985.
7. B. R. Stoner, B. E. Williams, S. D. Wolter, K. Nishimura, and J. T. Glass, J. Mater. Res. **7**, 257 (1992).
8. K. A. Snail and C. M. Marks, Appl. Phys. Lett. **60**, 3135 (1992).
9. Dubbeldee Harris Diamond Corp., Mt. Arlington, New Jersey, USA.
10. Y. Hirose and Y. Terasawa, Jpn. J. Appl. Phys. **25**, 519 (1986); C.-P. Chang, D. L. Flamm, D. E. Ibbotson, and J. A. Mucha, J. Appl. Phys. **63**, 1744 (1988); Y. Saito, K. Sato, H. Tanaka, K. Fujita, and S. Matsuda, J. Mater. Sci. **23**, 842 (1988); Y. Liou, A. Inspektor, R. Weimer, D. Knight, and R. Messier, J. Mater. Res. **5**, 2305 (1990); J. Wei, H. Kawarada, J. Suzuki, and A. Hiraki, J. Cryst. Growth **99**, 1201 (1990); R. A. Rudder, G. C. Hudson, J. B. Posthill, R. E. Thomas, R. C. Hendry, D. P. Malta, R. J. Markunas, T. P. Humphreys, and R. J. Nemanich, Appl. Phys. Lett. **60**, 329 (1992).
11. W. A. Weimer, F. M. Cerio, and C. E. Johnson, J. Mater. Res. **6**, 2134 (1991).

12. L. M. Struck and M. P. D'Evelyn, "Infrared spectroscopy of hydrogen and water on diamond (100)," these *Proceedings* and J. Vac. Sci. Technol. A **11** (in press).
13. S. Matsumoto, H. Kanda, Y. Sato, and N. Setaka, Carbon **15**, 299 (1977); S. Matsumoto and N. Setaka, Carbon **17**, 485 (1979).
14. R. E. Thomas, R. A. Rudder, and R. J. Markunas, J. Vac. Sci. Technol. A **10**, 2451 (1992).
15. N. Uchida, T. Kurita, H. Ohkoshi, K. Uematsu, and K. Saito, J. Cryst. Growth **114**, 565 (1991).
16. M. Zhu, R. H. Hauge, J. L. Margrave, and M. P. D'Evelyn, "Mechanism for diamond growth on flat and stepped diamond (100) surfaces," these *Proceedings*.

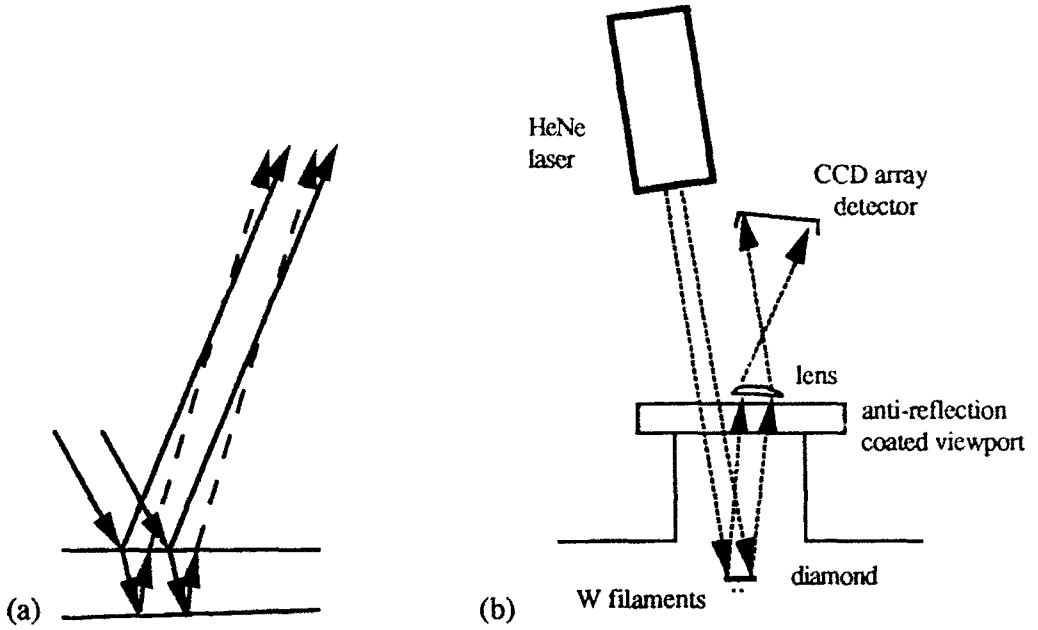


Fig. 1. Schematic of experimental setup for *in situ* Fizeau interferometry: (a) basis for interferometric fringes; (b) optical layout.

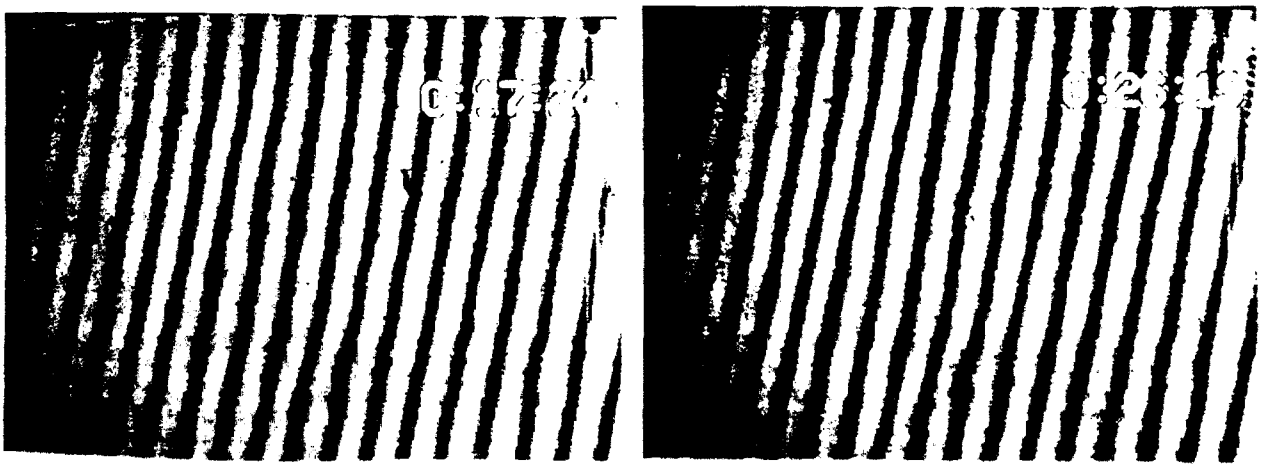


Fig. 2. Images of Fizeau fringe patterns propagating laterally during growth of diamond(100) at 850°C.

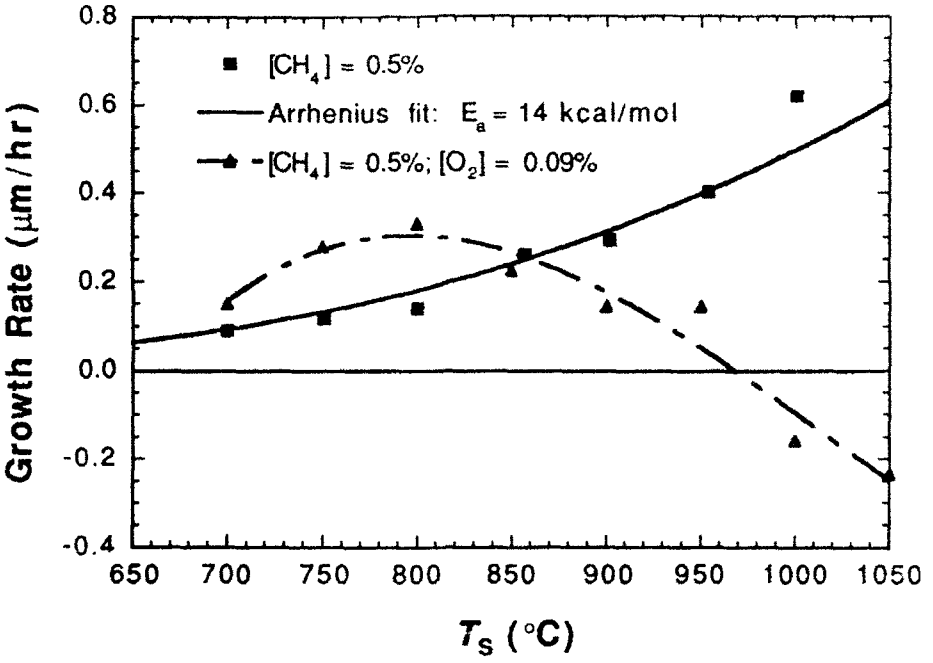


Fig. 3. Dependence of homoepitaxial [100] growth/etch rate on substrate temperature.

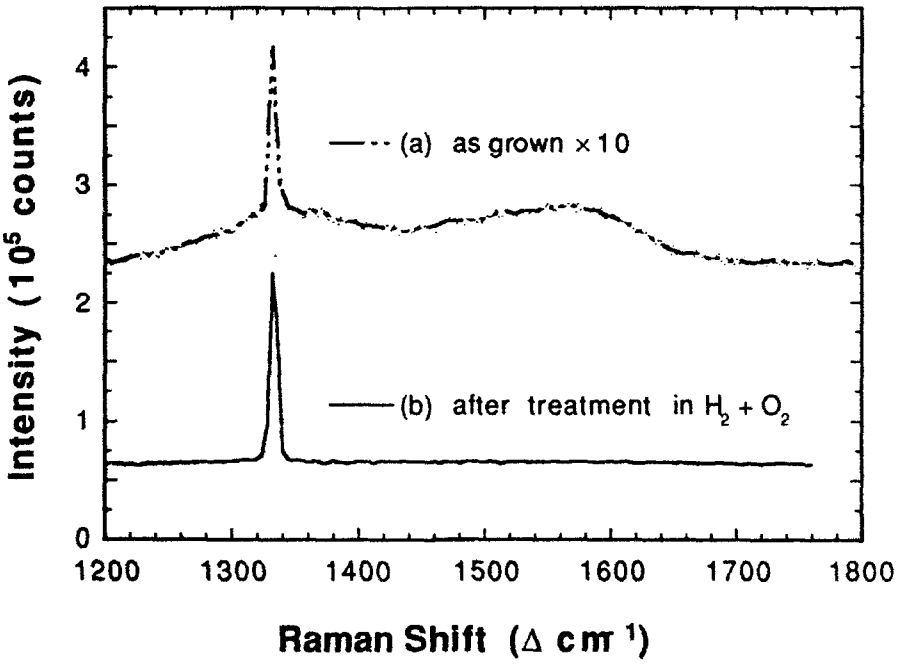
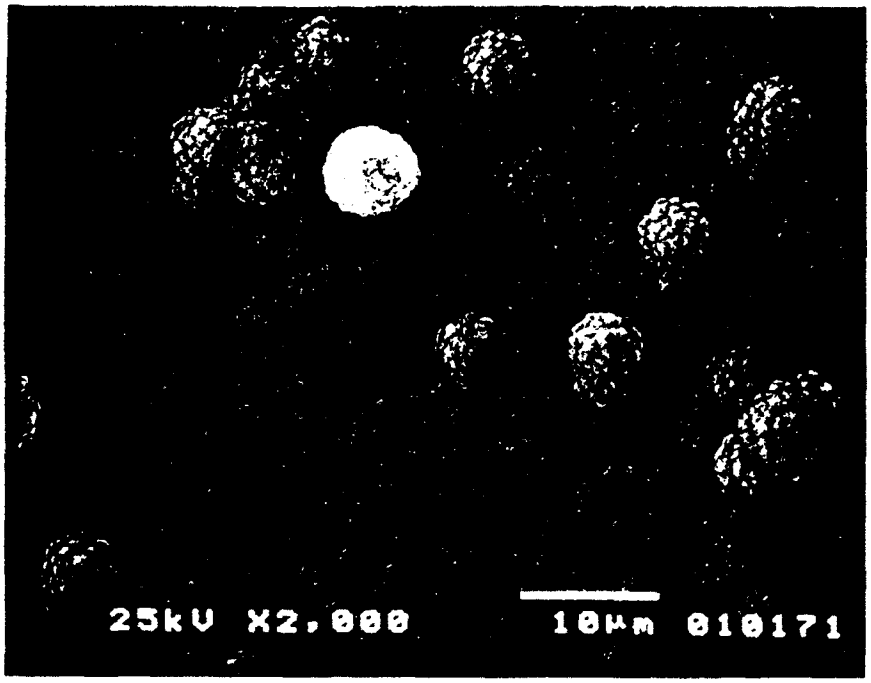


Fig. 4. Raman spectra of polycrystalline diamond film (a) before; and (b) after treatment at 600 °C with 0.25% O_2 in H_2 at 25 Torr under a hot filament.

(a)



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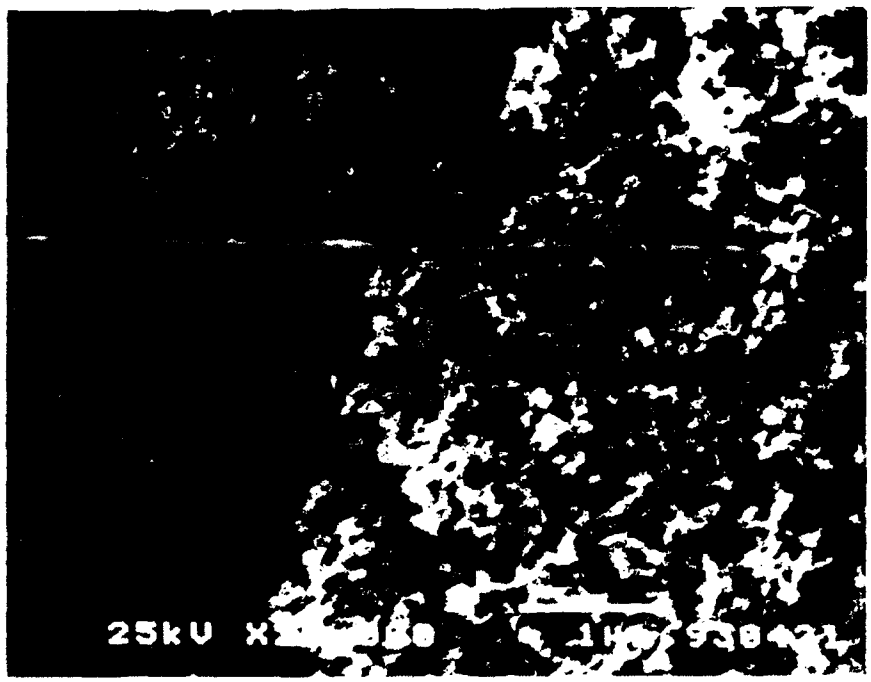

Fig. 5. Scanning electron micrographs of polycrystalline diamond film (a) before; and (b) after treatment at 600 °C with 0.25% O_2 in H_2 at 25 Torr under a hot filament.