OFFICE OF NAVAL RESEARCH

Grant # N000149J1848

R&T Code 413n003

Technical Report No. 1

Low Temperature Deposition of Diamond Films for Optical Coatings

by

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Prepared for publication

in the

Applied Physics Letters

Northwestern University
Department of Materials
Science and Engineering
Evanston, IL. 60208

October 18, 1989

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report #1	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: Northwestern University R.P.H. Chang; 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION: Office of Naval Research
6c ADDRESS (City, State, and ZIP Code): Materials Science & Engineering Dept. Evanston, IL. 60208	7b ADDRESS (City, State and ZIP Code): Chemistry Division 800 N. Quincy Street Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research (partial); 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: Grant # N0001 489J1848
8c ADDRESS (City, State, and ZIP Code): Chemistry Division 800 N. Quincy Street Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO; PROJECT NO; TASK NO; WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification): Low Temperature Deposition of Diamond Films for Optical Coatings

12 PERSONAL AUTHOR(S): T.P. Ong and R.P.H. Chang

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM _____ TO _____	October 18, 1989	12

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL: Dr. Mark Ross	22b TELEPHONE (Include Area Code): (202) 696-4410; 22c OFFICE SYMBOL

DD Form 1473, JUN 86 — Previous editions are obsolete — SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

LOW TEMPERATURE DEPOSITION OF DIAMOND FILMS FOR OPTICAL COATINGS

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ABSTRACT

A low temperature (≈ 400 ^{0}C) plasma enhanced chemical vapor deposition process has been developed to grow diamond films for optical coatings application. Films with fine grains (≤ 3000 Å) have been obtained by controlling diamond nucleation. The surface roughness of the films is on the order of 50-200 Å. The optical transparency of the films is over 60 % in the range of 0.6-2 μm wavelength, which is comparable to that of type IIa natural diamond. Using a block-on ring tribotester, it is found that the diamond films adhere well to quartz substrates.

Low pressure synthesis of diamond films from a mixture of hydrocarbon and hydrogen gases has recently attracted worldwide interests[1-3] due to the many promising applications of these films. Diamond possesses exceptional mechanical, optical, physical and chemical properties.[4,5] The good optical transparency (IR-UV), combined with its high strength and chemical inertness, makes diamond film an excellent protective coating material for optical elements. A variety of chemical vapor deposition (CVD), such as microwave[6], rf[7], dc[8], and hot filament[9], has been explored to synthesize these films on different substrates at approximately 1000 ^{0}C. This high temperature process eliminates a wide range of applications. In addition, the grown films on non-diamond substrates are polycrystalline in nature and with relatively large grains (1-50 μm), resulting in rough surfaces. Hence, the films are not suitable for optical applications. The main focus of this paper is to overcome these problems by achieving the following : (a) a low temperature processing technique for depositing high optical quality (smooth and transparent) diamond films , and (b) excellent adhesion between film and substrate.

The effects of surface roughness on optical transmission spectra of a sample have been theoretically formulated by Filinski[10] based on the concept of the theory of light reflection from rough surfaces. Unlike the case for perfectly smooth surfaces, the reflected and transmitted light wavelets from rough surfaces and grain boundaries are scattered in various directions. The light scattering coefficient is found to be proportional to $(\sigma n/\lambda)^2$, where σ is the root mean squared (r.m.s.) value of surface roughness, n is the refractive index of a sample, and λ is the vacuum wavelength. Since the intensity of the transmitted beam is exponentially dependent on this scattering coefficient, it requires diamond (with a refractive index of n=2.4) films to be extremely smooth in order to minimize the incoherent light scattering which leads to surface haziness and poor transparency. Therefore, it is desirable to obtain diamond films with nanocrystallites.

In order to accomplish such a goal, one should realize the fact that the final diamond grain size is determined by the nucleation rate and the surface nucleation density. It is widely known from classical theory that there are two distinct optimum temperatures for crystal nucleation and growth.[11] The temperature for optimal nucleation is known to be lower than that for growth. By

depositing diamond at low temperatures, both the nucleation rate and the nucleation density can be optimized relative to growth. To maintain a low average substrate temperature, a plasma discharge is operated in a pulsed mode. In this way the diamond grains can be tailored to any size.

In our experiments, a 2.45 GHz microwave plasma CVD apparatus[12] is used to deposit the diamond films. Clean fused quartz slides (2 cm x 2 cm) are used as substrates. The substrates are first polished with 1/2 - 1 μm diamond powder, and then ultrasonically cleaned with acetone, methanol and deionized water for approximately 1/2 hour. Typical deposition conditions are : gas mixture, $CH_4 : H_2 : O_2 = 0.3 : 99.5 : 0.2$; total flow rate = 100 sccm; pressure = 40 mbar; microwave power = 400 W. The substrate is inductively heated by the incident microwave. No external heating source is provided.

The hydrocarbon gas mixture is fed into the reactor a few seconds after the plasma is turned on. The discharge is maintained for a certain time interval until the substrate temperature (T_f) reaches 500-800 ^{0}C , and then the plasma is immediately turned off. The substrate is cooled down to room temperature (which takes about 10 minutes) before another similar cycle is initiated. This process is repeated until a continuous film is obtained. The time duration of each cycle (Δt) and T_f can be varied to change the diamond grain size. It is found that the grain size increases with Δt and T_f, as shown in Figure 1. For a given Δt, the total number of cycles used to form an uniform and continuous film is different. More process cycles are needed for the case of smaller Δt to cover the substrate surface with a continuous diamond film. In addition, the average temperature (T_{avg}) over one process cycle is lower as Δt is reduced. The T_{avg} is obtained by using :

$$T_{avg} = \left[\int_0^{t_f} T(t)\, dt \right] / t_f \quad , \qquad (1)$$

where T_{avg} is the average temperature, T(t) is the instantaneous temperature, t is the time , and t_f is the time to reach the T_f. The variable t does not include the time when the plasma is off for cooling the substrate. Since nucleation process is constantly occurring during each process cycle, diamond films with higher nucleation density and smaller final average grain size are obtained as we reduce Δt (Figure 1a,b). By reducing T_f and Δt further, the average temperature can be substantially lowered. This results in films with much finer grains, as shown in Figure 1c with T_f and Δt equal

to 600 ^{0}C and 45 sec respectively. The surface roughness of the films is measured by a Tencor Alpha Stepper profilometer, and taken as the r.m.s. of the peak to valley profile of the film surfaces. As clearly indicated in the Figure 1c, the film with the finest grain size (sample c) has the smoothest texture (r.m.s. = 100 Å). No preferred orientation of crystals is observed in the obtained films for all cases. The lowest average temperature is about 400 ^{0}C in our experiments. The growth rate has been measured based on total integrated time. It is found to be approximately 1.2 - 1.5 μm/hr.

The crystalline structure of the films is confirmed by a Hitachi H-700 transmission electron microscope (TEM). The bright-field image of the film, as shown in Figure 2, indicates the distinct diamond crystal habit. The sharp continuous rings in the diffraction pattern confirm the polycrystalline nature of the film. Table I shows the crystallographic plane spacings (d) measured from the diffraction rings. The tabulated values are in excellent agreement with the corresponding values for natural diamond (ASTM 6-675) and not graphite-2H(ASTM 23-64), which has values for d spacings closest to that of diamond.The films are also characterized by Raman spectroscopy . The presence of the phonon peak at 1332 cm^{-1} corresponds to that of the diamond phase.

In examining the effect of film surface roughness on optical transmission properties, transmission measurements from 0.2 to 2 μm wavelength region are carried out on two diamond film coated quartz substrates which differ in surface roughness due to different average grain size. The optical transmission study is carried out using a double-beam Perkin Elmer 330 UV/Visible/near IR spectrometer. Tungsten and deuterium light sources are used, from which the light wave is sent from the quartz substrate side at normal incidence angle. The film transmittance versus wavelength in μm is plotted in Figure 3. The transmission of the rough film (sample d; r.m.s. = 2000Å) is lower than that of the smooth film (sample b; r.m.s. = 200 Å) of equivalent thickness by as much as 20 %. The effect of surface irregularities on the transparency of the films is clearly significant. The optical absorption edge for both films is at 0.225 μm, similar to the type IIa diamond. The observed tailing near the absorption edge for both type of films is believed to be from the structural imperfection and impurities in the film (such as a-C, graphite, and sputtered Si from quartz), as well as the internal light scattering at the grain boundaries. The degradation of the film transparency near the absorption edge can also be accounted by the enhanced incoherent light

scattering from the rough surfaces as σ is approaching the wavelength of incident light. However, the 60+% optical transparency from 0.6 - 2 μm wavelength is sufficiently high for most practical applications. The oscillations in the transmission spectra are due to Fresnel interference phenomena of the thin film .

In order to evaluate the adhesion property of the diamond films to the quartz substrate, we have used a block-on-ring tribotester.[14] Experiments are performed on bare and ~ 0.4 μm diamond coated quartz by applying a constant load of 18.13 lb force on the sample against a 52100 steel (62 C Rockwell) rotating with a speed of 1 m/sec. It is constantly lubricated by a jet of mineral oil. The total sliding distance is 1.8 km. The friction force at the contact area is recorded through a load cell from which the calibrated change in resistance is converted into force. The friction coefficient, f, can then be evaluated by dividing the friction force with applied normal force.

As shown in Figure 4a, the optical micrograph clearly depicts the significant amount of materials wear for the bare quartz, and this is further substantiated by the measured surface profile across the grinding track (Figure 4b). The diamond film coated quartz, however, is completely intact after being tested under the same condition. In fact, some materials from the bearing part are transferred onto the film with rough surface. This is shown in the optical micrograph by the white striations along the direction of the grinding (Figure 4c). This finding implies that the diamond film adheres extremely well to the quartz substrate. The coefficient of friction for the coated and uncoated quartz has been evaluated to be 0.047 and 0.09 respectively.

In conclusion, we have demonstrated that a low temperature microwave plasma enhanced CVD technique has been developed to deposit diamond films. The technique enables us to control diamond nucleation to achieve films with fine grain size for optical applications. Smooth, transparent and good adherent films have been obtained on quartz substrates.

This work is sponsored by Department of Energy Basic Energy Science Division and the Office of Naval Research. We gratefully acknowledge the technical assistance of Dr. W.A. Chiou, Dr. M.S. Wong, Dr. K.C. Sheng, and Mr. R. Meilunas. We also thank Professor H.S. Cheng of the Center for Engineering Tribology at Northwestern University for the use of the facilities.

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Table I. Transmission electron diffraction data for CVD diamond film, the reported values of natural cubic diamond (ASTM 6-675) and hexagonal graphite-2H (ASTM 23-64). (Hitachi H-700, 200 kV)

Observed		Reported (ASTM 6-675)		Graphite-2H (ASTM 23-64)		% Deviation of the observed spacings from	
Ring no.	d (Å)	hkl	d_{hkl} (Å)	hkl	d_{hkl} (Å)	ASTM 6-675	ASTM 23-64
1	2.06	111	2.059	101	2.033	+0.048	+1.32
2	1.266	220	1.261	110	1.232	+0.39	+2.76
3	1.082	311	1.075	200	1.067	+0.67	+1.40
4	1.032	222[a]	1.030[b]	201	1.053	+0.19	-1.99
5	0.891	400	0.8917	204	0.9002	-0.078	-1.02
6	0.816	331	0.8183	210	0.8062	-0.28	+1.21
7	0.723	422	0.7281[b]	300	0.7110	-0.70	+1.69
8	0.6806	511/333	0.6865[b]	118	0.6935	-0.86	-1.86

[a] Due to second order diffraction

[b] Calculated values based on lattice constant = 3.5667 A^0

LIST OF FIGURE CAPTIONS

Fig. 1 The dependence of average diamond grain size on the process cycle time interval (Δt) and the final temperature (T_f) when the plasma is turned off.

(a) Δt=60 min, T_f = 800 ^{0}C , T_{avg} = 800 ^{0}C; SEM picture (after 1 cycle)

(b) Δt=4 min, T_f=800 ^{0}C , T_{avg} = 600^{0}C; SEM picture (after 4 cycles)

(c) Δt=45 sec, T_f=600 ^{0}C, T_{avg} = 415 ^{0}C; SEM picture (after 16 cycles)

Fig. 2 (a) Transmission electron micrograph of the diamond film (bright field, 200 kV).

(b) The corresponding transmission electron diffraction.

Fig. 3 Transmission spectra of: (a) 1mm thick quartz ; (b) 0.92 μm diamond coated quartz (r.m.s.= 200 Å), (c) 1mm thick type IIa natural diamond (from ref. 13) ; (d) 1.25 μm diamond coated quartz (r.m.s. = 2000 Å)

Fig. 4 Results of block-on-ring tribotest on bare and diamond coated quartz

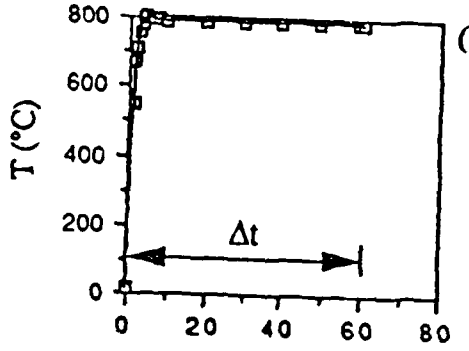
(a) Optical micrograph of the grinding track on bare quartz.

(b) Surface profile across the grinding track of sample (a).

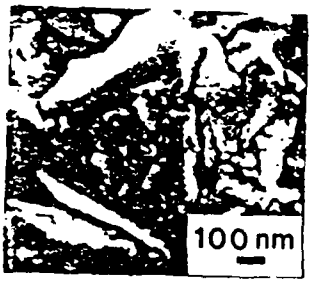
(c) Optical micrograph of the grinding track on 0.35 μm diamond coated quartz.

(d) Surface profile across the grinding track of sample (b).

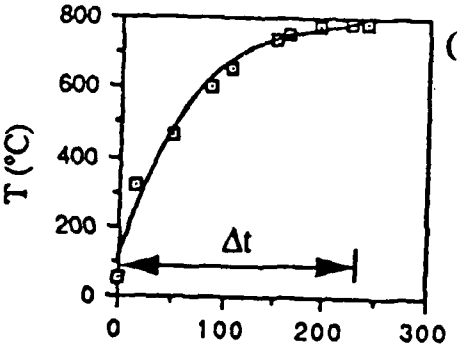
The big arrows indicate the direction of the grinding. The small arrow indicates the materials transferred from the steel bearing.



(a)



r.m.s. = 1600 Å



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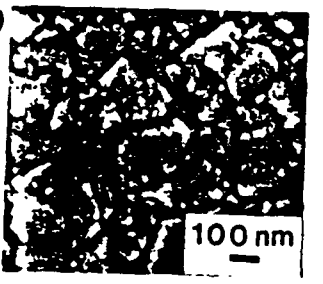
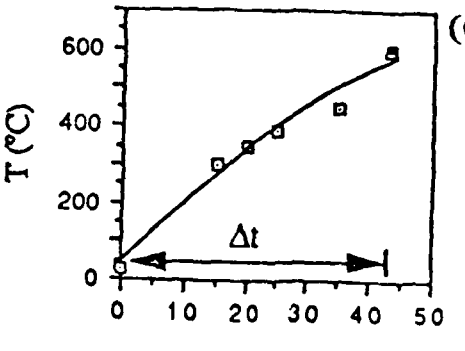
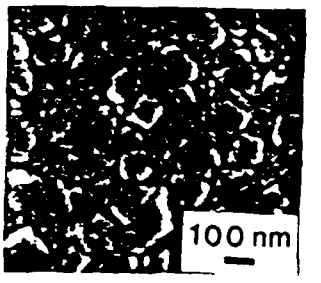


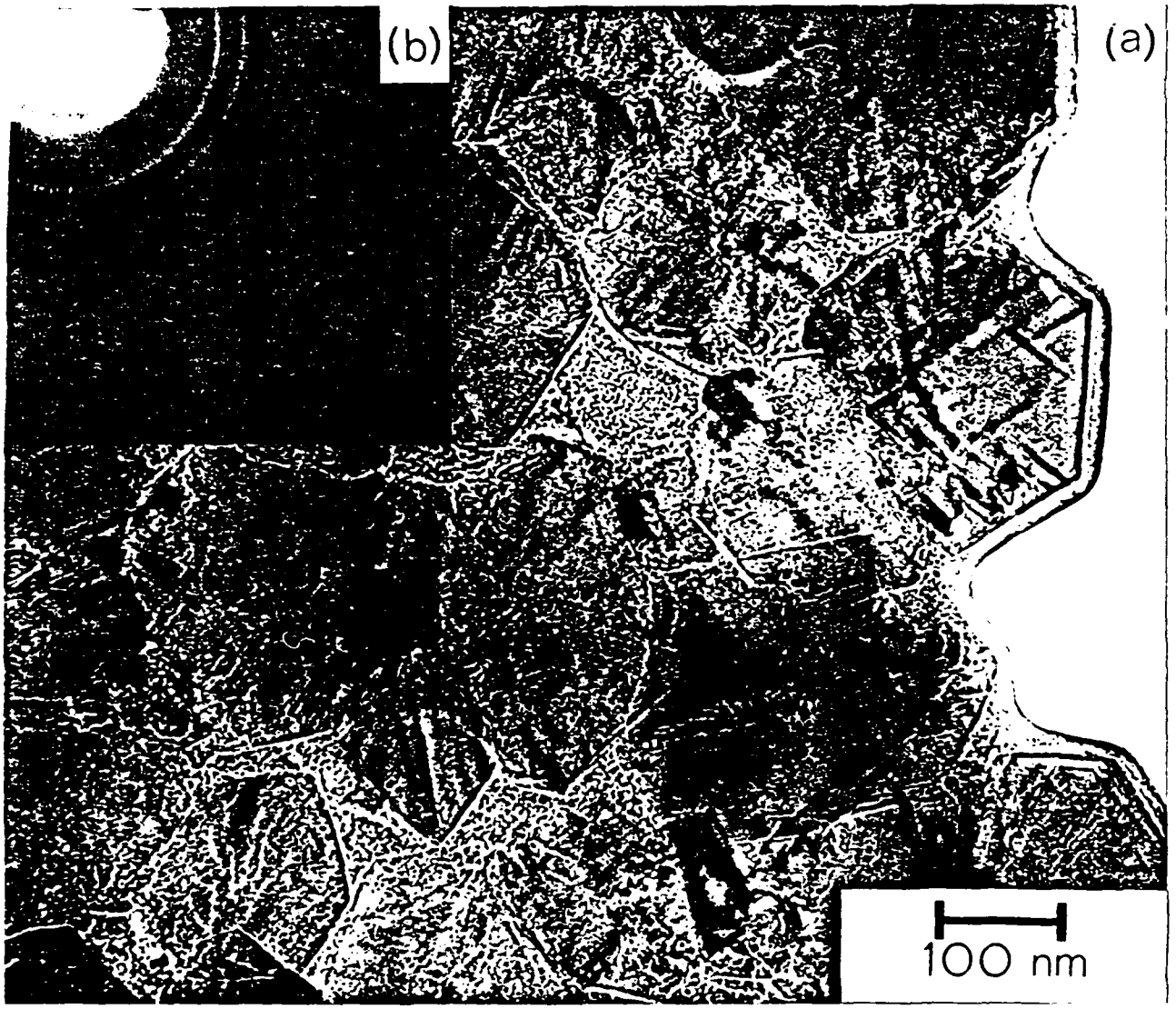
r.m.s. = 150 Å

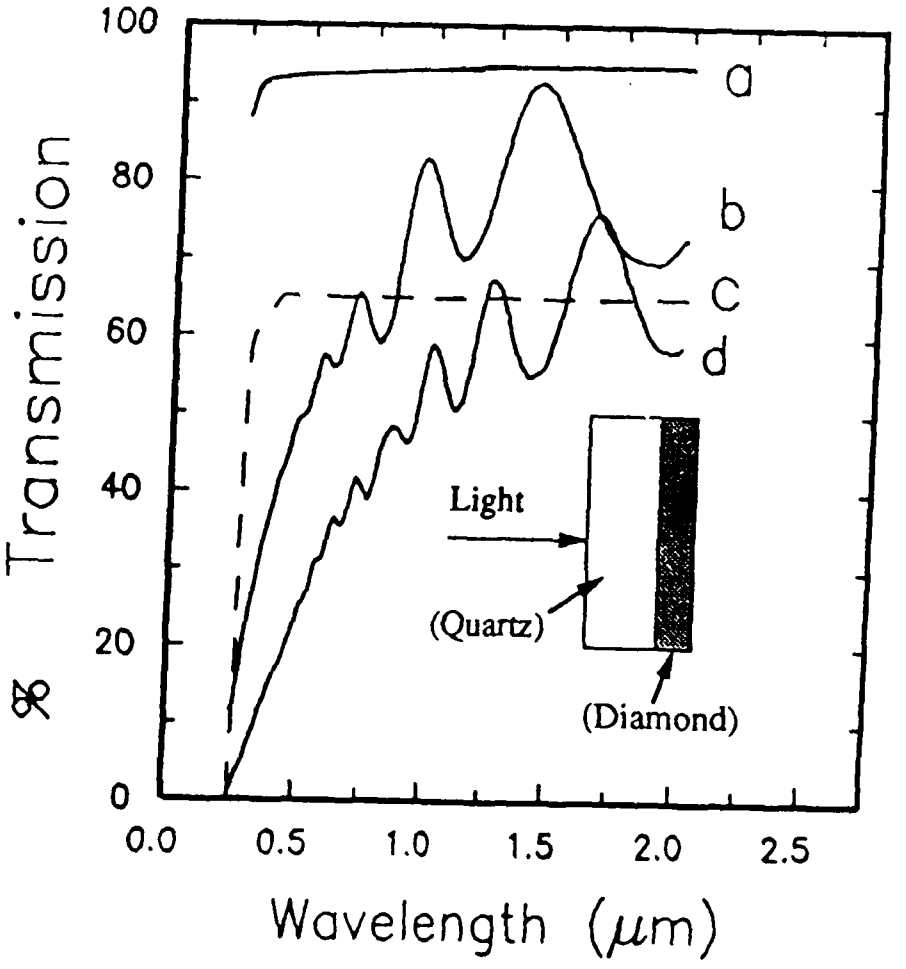


(c)



r.m.s. = 100 Å


(b)
(a)
100 nm



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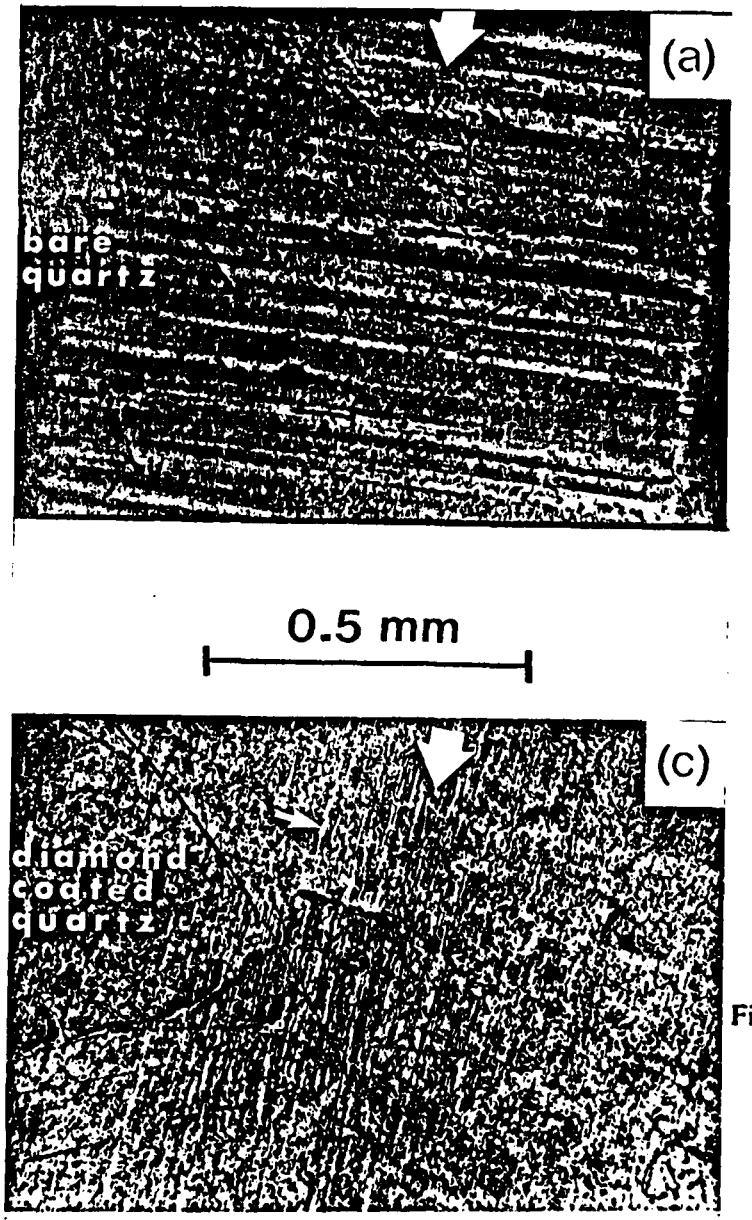

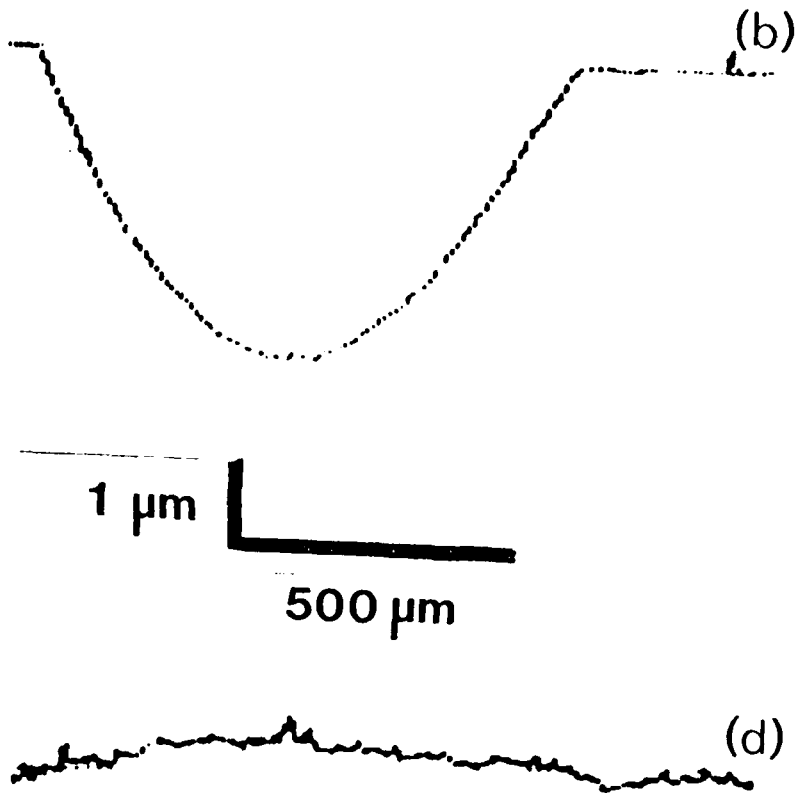

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