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Effect of substrate pretreatment on diamond deposition in a microwave plasma

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The evolution of substrate surface at an early stage of diamond formation in a microwave plasma was studied with a high-resolution scanning electron microscope. Changes in the shape, size and population of diamond particles at the same points were observed at prescribed time intervals. The substrate used was a mirror-polished Si (100) plate which was ultrasonically pretreated with diamond, c-BN or α-Al_2O_3 powders prior to the deposition. The pretreatment introduced fragments of the abrasives as well as many scratches on the substrate surface. When the diamond and c-BN abrasive were used, diamond was formed on the surface of abrasive residues. With α-Al_2O_3 abrasive powder, on the other hand, residues vanished in the plasma and no deposition was observed. These results suggest that the deposition site of diamond from the vapour phase is dependent on the type of abrasive powder used for substrate pretreatment.

1. Introduction

Diamond is one of the most promising materials because of its excellent hardness, thermal conductivity, electrical resistance, chemical stability and optical transmission [1]. Since the earliest reports on diamond formation from the vapour phase [2–4], efforts have been concentrated on the synthesis of diamond thin film, which is greatly needed in high-technology industries.

Today, diamond thin film can be synthesized by various chemical vapour deposition (CVD) methods including hot filament-enhanced CVD [5], radio-frequency (r.f.) plasma-enhanced CVD [6] and microwave plasma-enhanced CVD [7] on substrates such as diamond, Si, Mo, Ni, Cu, SiC, WC, c-BN and AlN [8–13]. It is generally recognized that the film morphology is strongly dependent on the population density of initial diamond nuclei. When an Si wafer is used as the substrate, it is treated with hard materials such as diamond and c-BN. This is an important technique for controlling the initial nucleation of diamond, but the effect of such pretreatment has not been well understood to date. Iijima *et al.* [14, 15] found that an Si wafer surface abraded with diamond powder was coated with small flakes of diamond. Then the effect of pretreatment was explained by seeding "diamond dusts" on the substrate surface. This was confirmed by clear lattice images of residues with a high-resolution TEM. However, the effect of pretreatment with non-diamond abrasive powders was still unknown.

In the present study, the time-course of a substrate surface pretreated with different abrasive powders at the early stage of diamond deposition in a microwave plasma is investigated and the effect of the substrate pretreatment is discussed.

2. Experimental procedure

The substrate was a mirror-polish n-type Si wafer, 5 mm by 10 mm in size. Pretreatment of the substrate

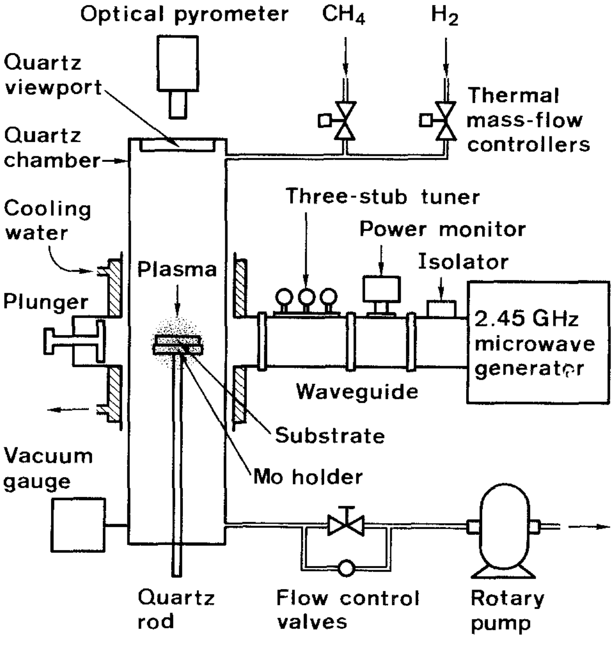

Figure 1 Schematic diagram of MPECVD apparatus used for diamond synthesis.

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was carried out in a mixture of 1.2 g abrasive powder and 12 ml acetone. The beaker was dipped in an ultrasonic water bath, and the substrate was abraded for 30–120 min. The substrate was then ultrasonically cleaned in acetone for 10 min. Diamond (8–16 μm), c-BN (8–12 μm) and α-Al_2O_3 (10–30 μm) were used as abrasive powders in the present experiments.

Prior to deposition, the surface of the pretreated substrate was observed by a high-resolution scanning electron microscope (HR-SEM, Hitachi S-900). Five points on the substrate surface were chosen as the observation targets, and the change in the surface during deposition was studied.

Some of the pretreated substrates were subjected to observation with a transmission electron microscope (TEM, Jeol JEM-200BS) by the extraction replica technique. The replica was prepared by coating the substrate with an evaporation carbon film, which was separated by dissolving the substrate in a hydrofluoric acid solution.

The diamond synthesis was performed by microwave plasma-enhanced chemical vapour deposition (MPECVD). A schematic diagram of the MPECVD apparatus is shown in Fig. 1. Microwave radiation of 2.45 GHz was introduced through a waveguide into a quartz-tube reaction chamber of 43 mm inner diameter. The source gases were CH_4 and H_2, and their flow rates were controlled with thermal mass-flow

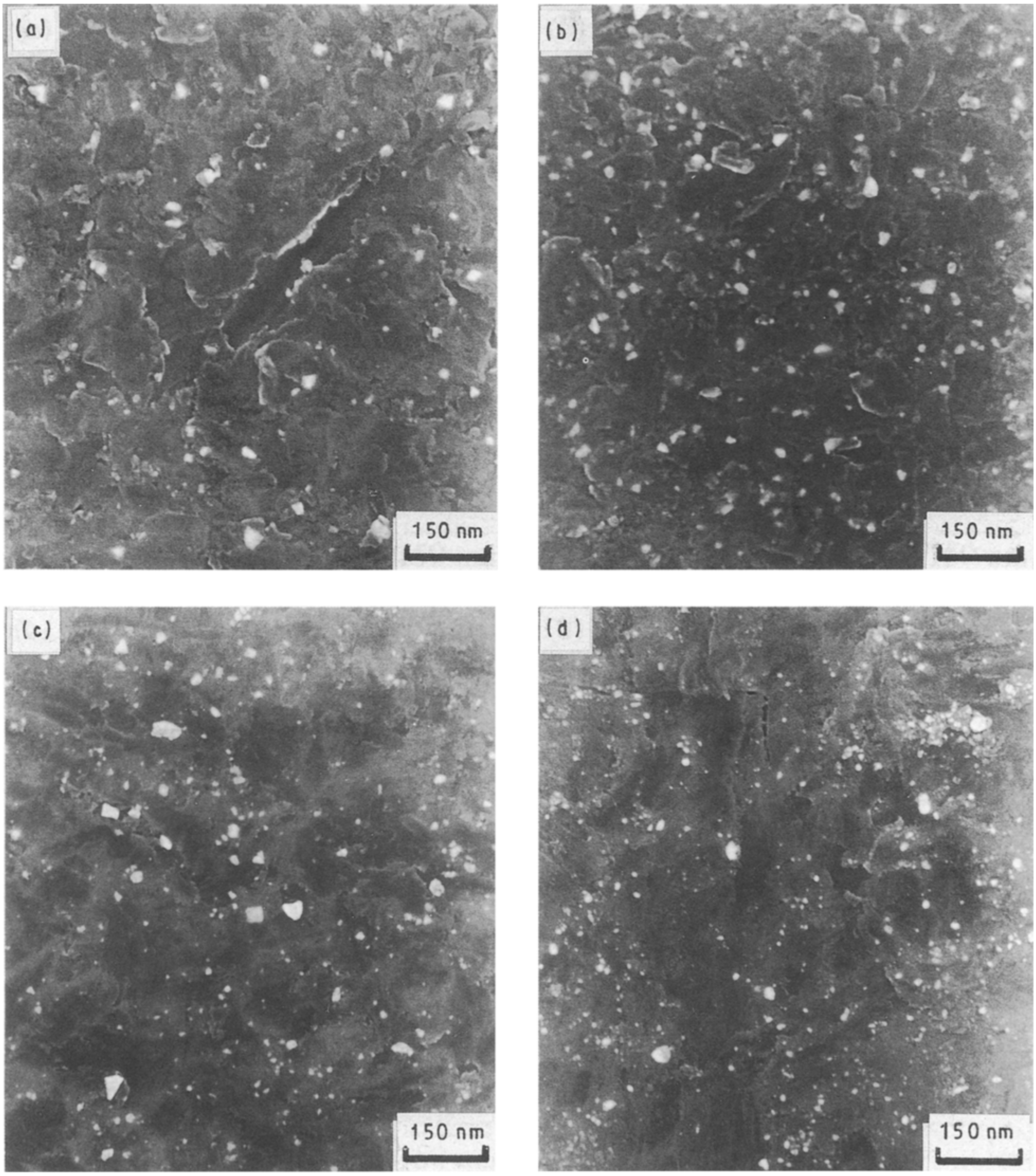

Figure 2 Silicon substrate surfaces pretreated with (a) diamond abrasive for 60 min, (b) diamond abrasive for 120 min, (c) c-BN abrasive for 60 min and (d) α-Al_2O_3 abrasive for 30 min.

controllers. The substrate was placed in the microwave cavity, and the surface temperature was measured by an optical pyrometer assuming an emissivity of unity. In this experiment, the substrate temperature was maintained at 810–820°C.

After evacuating the quartz chamber, 0.5 ml min^{-1} of CH_4 and 100 ml min^{-1} of H_2 at ambient temperature and pressure were introduced into the chamber and then a mixed gas plasma was generated at a microwave power of 200 W. The total gas pressure was kept at 5.3 kPa (40 torr).

The MPECVD was repeated at prescribed time intervals, and the substrate surface was investigated by HR-SEM observation without coating. The final product was characterized by X-ray diffraction (XRD) and Raman spectroscopy.

3. Results and discussion

3.1. Surface conditions of the pretreated substrate

Fig. 2 shows high-resolution images of the substrate surface pretreated with diamond abrasive for 60 min (Fig. 2a), diamond abrasive for 120 min (Fig. 2b), c-BN abrasive for 60 min (Fig. 2c) and α-Al_2O_3 abrasive for 30 min (Fig. 2d). All the pictures show that many scratches are introduced by the pretreatment. Furthermore, bright irregular particles ranging in size from a few to a few tens of nanometres are formed densely and increase with increasing pretreatment time. Fig. 3a and b show TEM images of the replica films prepared from the substrates pretreated for 60 min with diamond and c-BN abrasive powder, respectively. The replica films have inclusions which are similar in shape and size to the particles observed on the pretreated surface by HR-SEM. Electron diffraction (ED) patterns obtained from these inclusions are shown in Fig. 4a and b. Each pattern of spots is in agreement with that of the crystal used as the abrasive powder. The results of ED suggest that the bright particles shown in Fig. 2 are residues of the abrasive powder used for pretreatment. A series of TEM observations led to the conclusion that an important role of substrate pretreatment is to introduce abrasive residues on the substrate surface. The reason that the residues were observed as "bright particles" by HR-SEM is the charge-up phenomenon caused by the high

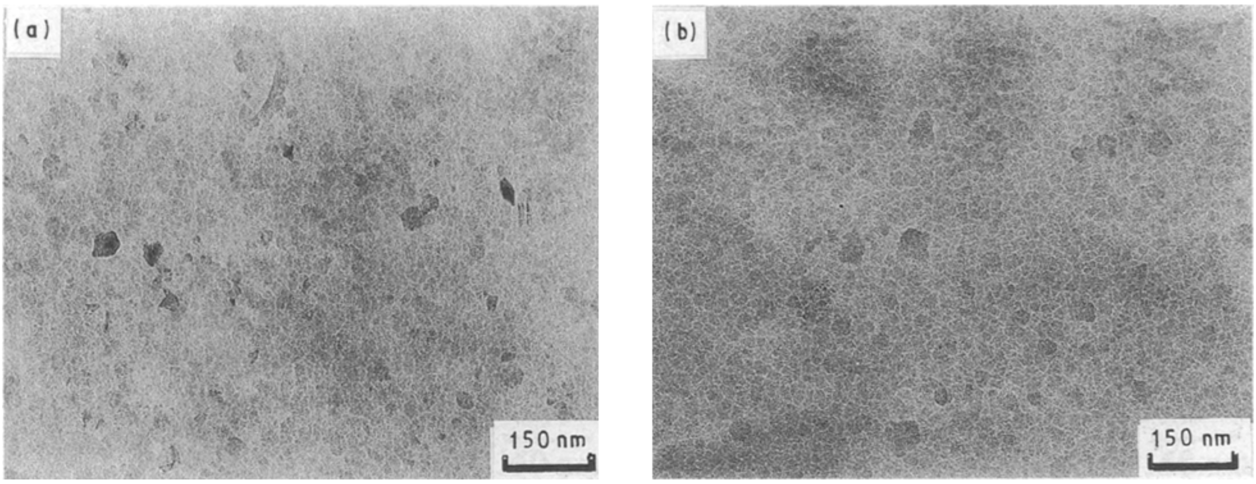

Figure 3 TEM images of replica films recovered from substrate pretreated for 60 min with (a) diamond abrasive and (b) c-BN abrasive

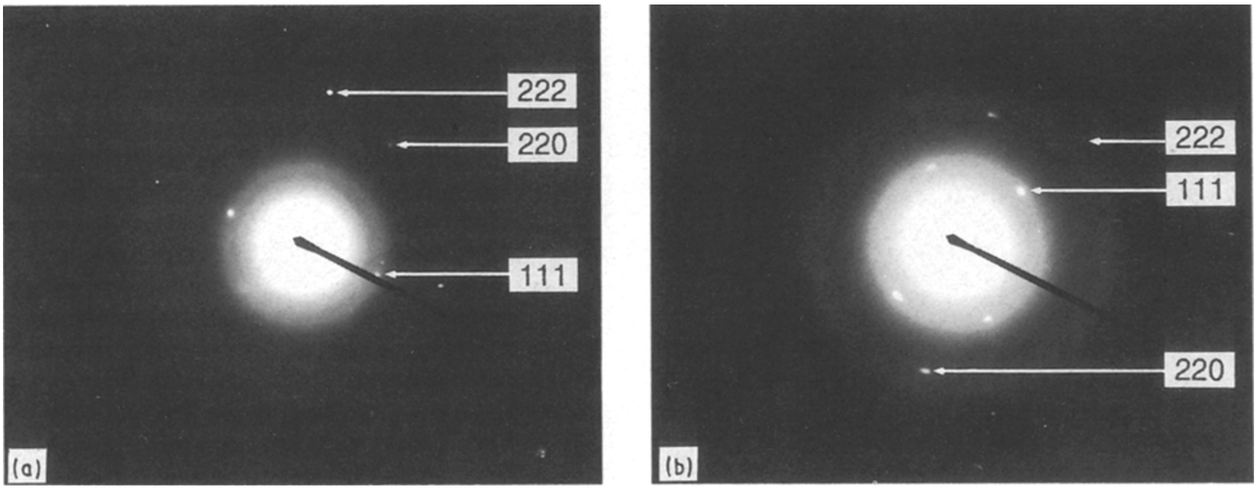

Figure 4 Electron diffraction patterns of inclusions in replica films obtained from substrate pretreated with (a) diamond abrasive and (b) c-BN abrasive. Each pattern of spots is in agreement with that of the crystal used as abrasive.

electrical resistivity of the abrasive powders used in this research.

3.2. Evolution of surface conditions during MPECVD

Figs 5 and 6 show the time evolution of the substrate surface pretreated with diamond abrasive powder. Fig. 6 is a higher-magnification view. Most of the residues changed in morphology from an irregular shape to an angular one within 5 min, and some of them had already grown to faceted diamonds a few times larger than the residues. An important phenomenon at this stage is that diamond deposition from the vapour phase occurs only on the residue particles as shown in Figs 5 and 6. This agrees with the conclusion of Iijima *et al.* [14, 15] that the diamond residues act as seeds for crystal growth in CVD film formation.

In the present experiments, the diamond residue particles were stable in the plasma atmosphere and all the residues grew to finally coalesce with each other. Figs 5 and 6 also show that the deposition rate differs among residue particles. This difference seems to be dependent on the crystallinity of the residue particles and on their orientation to the substrate, because no relation was found between the deposition rate and the apparent shape of the residue particles.

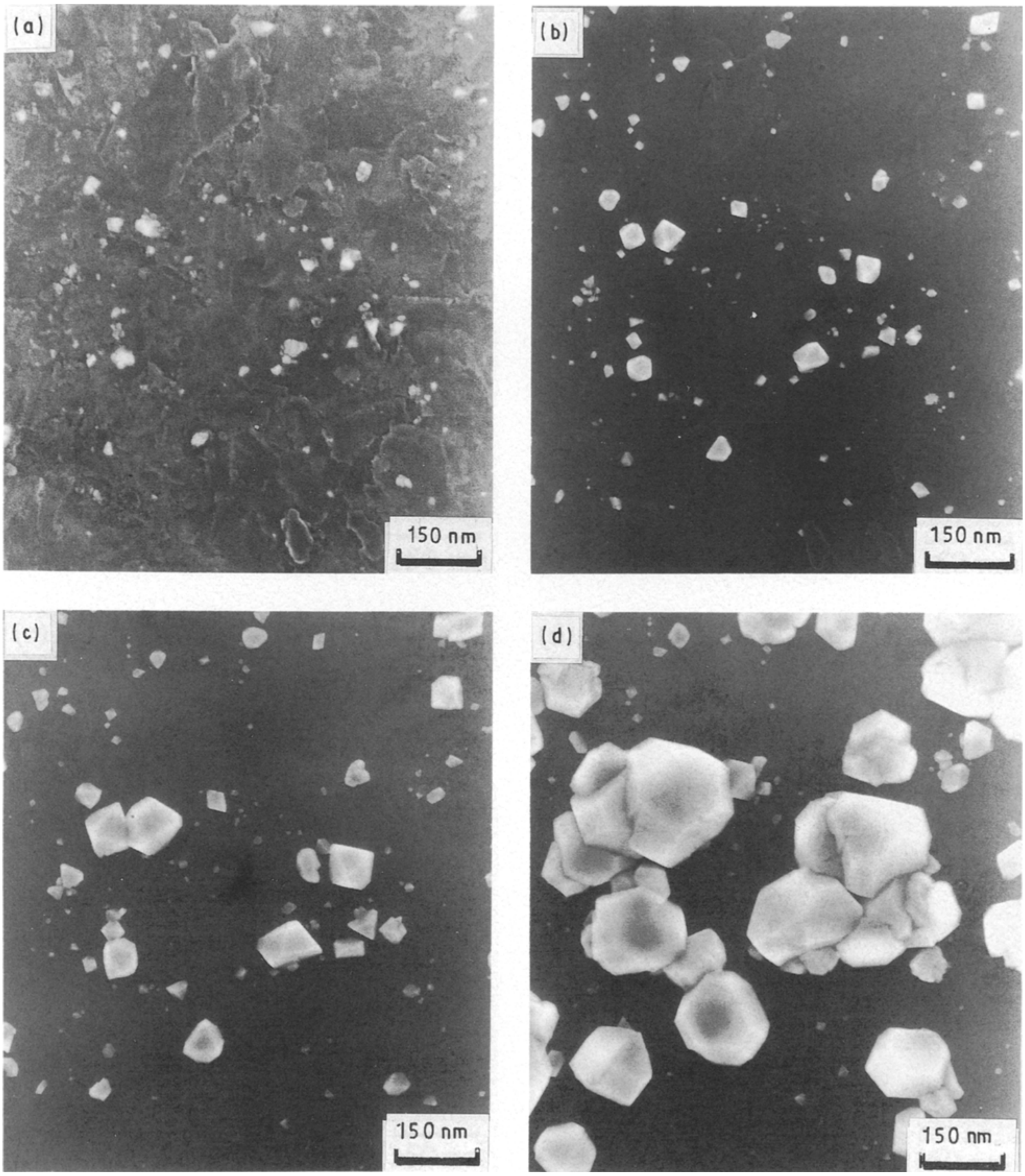

Figure 5 Time evolution of substrate surface pretreated with diamond abrasive. MPECVD for (a) 0 min (initial state), (b) 5 min, (c) 15 min and (d) 30 min.

A similar experiment was performed for the substrate treated with c-BN abrasive powder. The time evolution of the substrate surface is shown in Fig. 7, and indicates that the surface of the c-BN residue particles, like that of diamond abrasive powder, acted as the deposition site of diamond from the vapour phase. Most c-BN residues, however, disappeared in an early period and only a small number of them, approximately 1% in this experiment, survived to contribute to diamond deposition. This behaviour seems to reflect difficulty in the nucleation of diamond on a c-BN surface compared with a diamond surface. If the MPECVD conditions change, the fraction of the residues that contributes to diamond deposition may change to some extent. It was very difficult to distinguish any differences in the contribution of residue particles to the nucleation resulting from their shape or size.

Fig. 8 shows time-dependent changes in the substrate surface pretreated with the α-Al_2O_3 abrasive powder. Bright particles observed on the initial surface rapidly decreased within 5 min, and all of the α-Al_2O_3 residues vanished after 60 min of MPECVD. As a result, no deposition from the vapour phase was

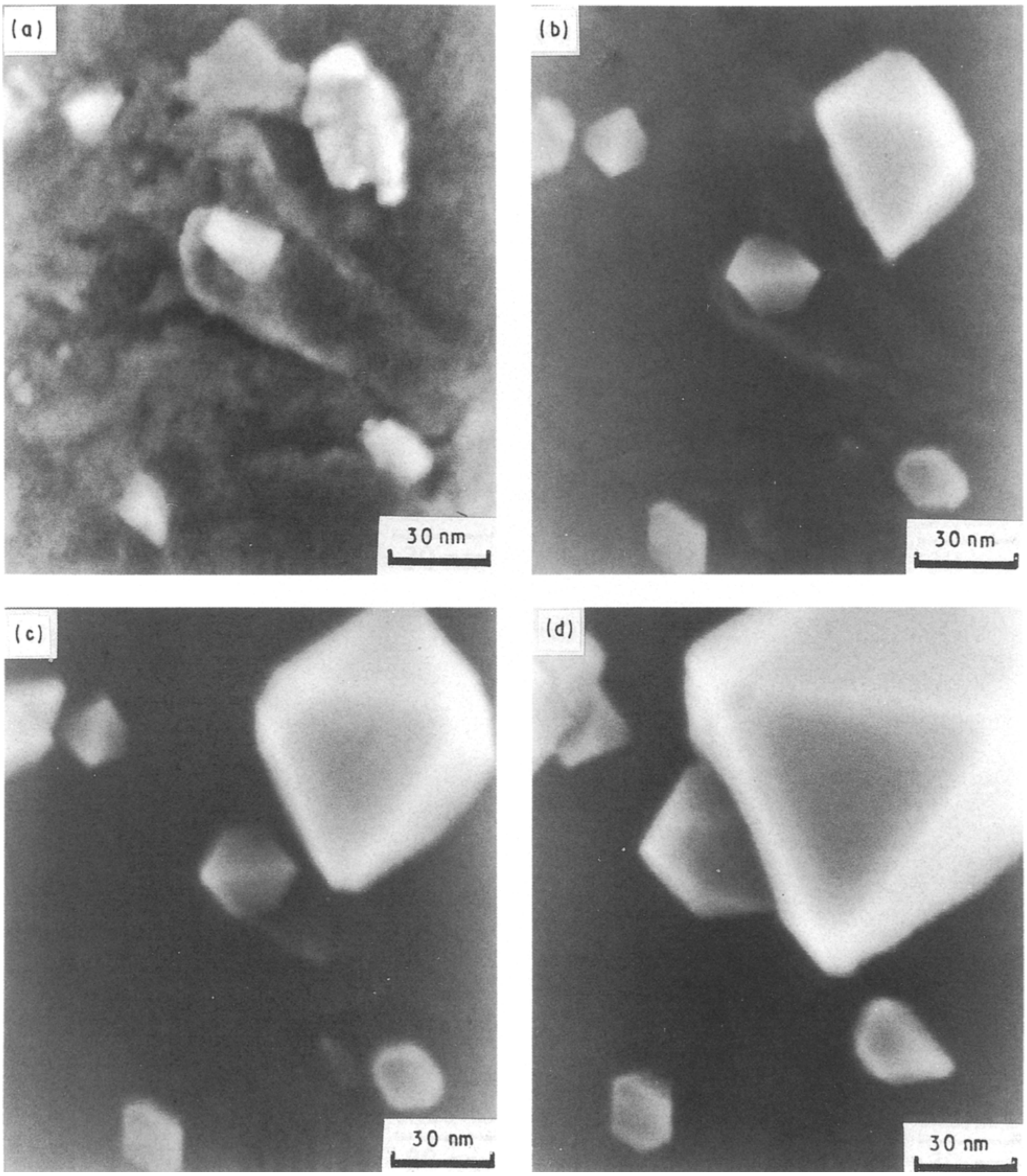

Figure 6 Higher-magnification view of time evolution of substrate surface pretreated with diamond abrasive. MPECVD for (a) 0 min (initial state), (b) 5 min, (c) 10 min and (d) 20 min.

observed within 60 min. After a long-time deposition of 10 h, however, nucleation enhancement by the α-Al_2O_3 abrasive pretreatment was clearly recognized, as shown in Fig. 9, although the effect was much weaker than that of the diamond or c-BN abrasive. These results suggest that the α-Al_2O_3 abrasive powder does not contribute directly to diamond deposition and that the mechanism of nucleation enhancement is different from that with diamond or c-BN abrasive powder.

Cullis and Booker [16] reported that when Si films were deposited on sapphire substrate at 900 °C, a reaction product remained at the interface between Si and sapphire. This suggests that the dimly bright parts clearly observed on the substrate after 45 min MPECVD in the present experiment are products produced by the reaction between Si substrate and α-Al_2O_3 abrasive powder.

Fig. 9 shows the film morphology after 10 h MPECVD. All the products shown in Fig. 9 were identified as cubic diamond by XRD and Raman spectroscopy measurements.

The final morphology of diamond film deposited from the vapour phase is strongly influenced by the

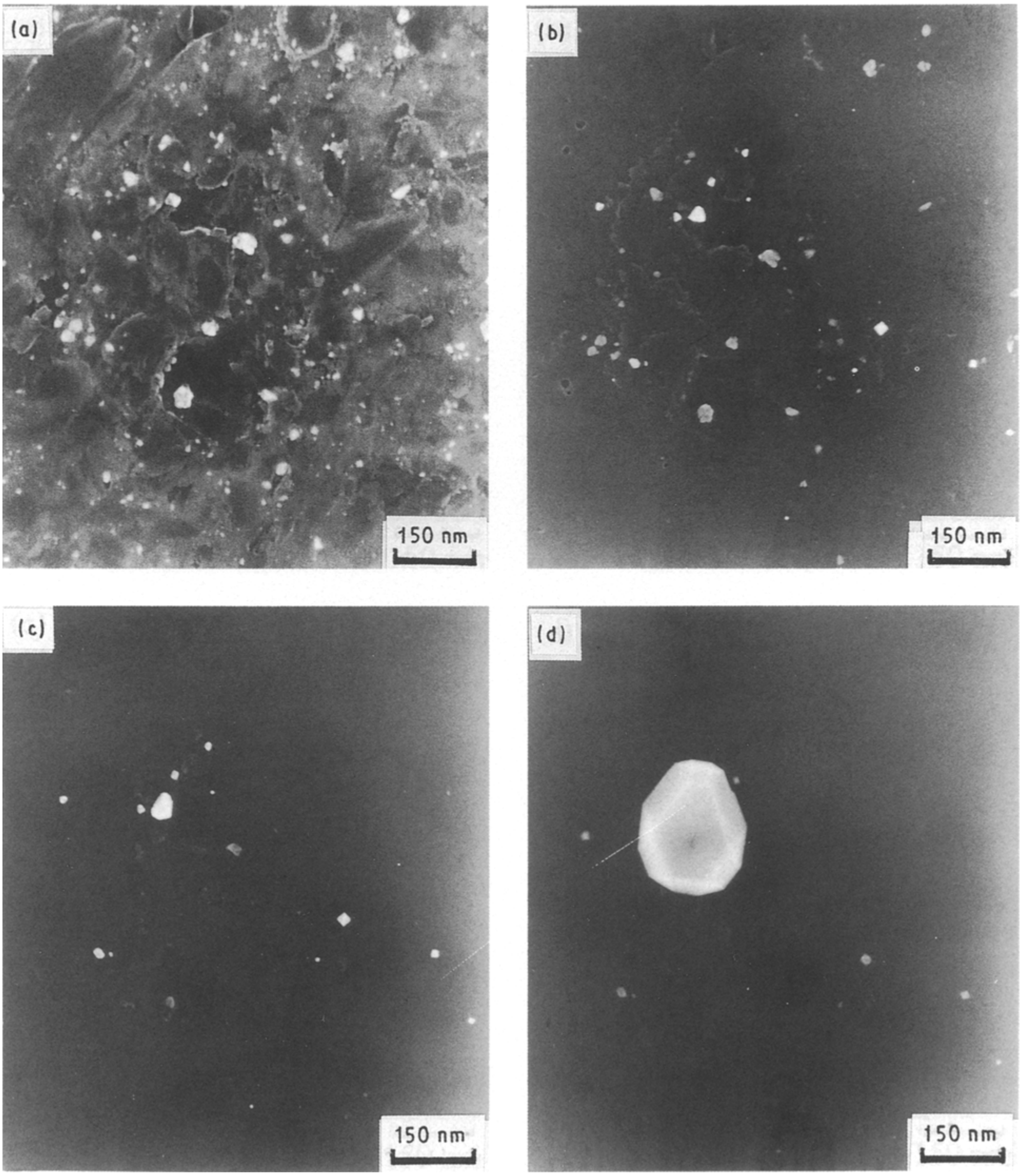

Figure 7 Time evolution of substrate surface pretreated with c-BN abrasive. MPECVD for (a) 0 min (initial state), (b) 5 min, (c) 15 min and (d) 45 min.

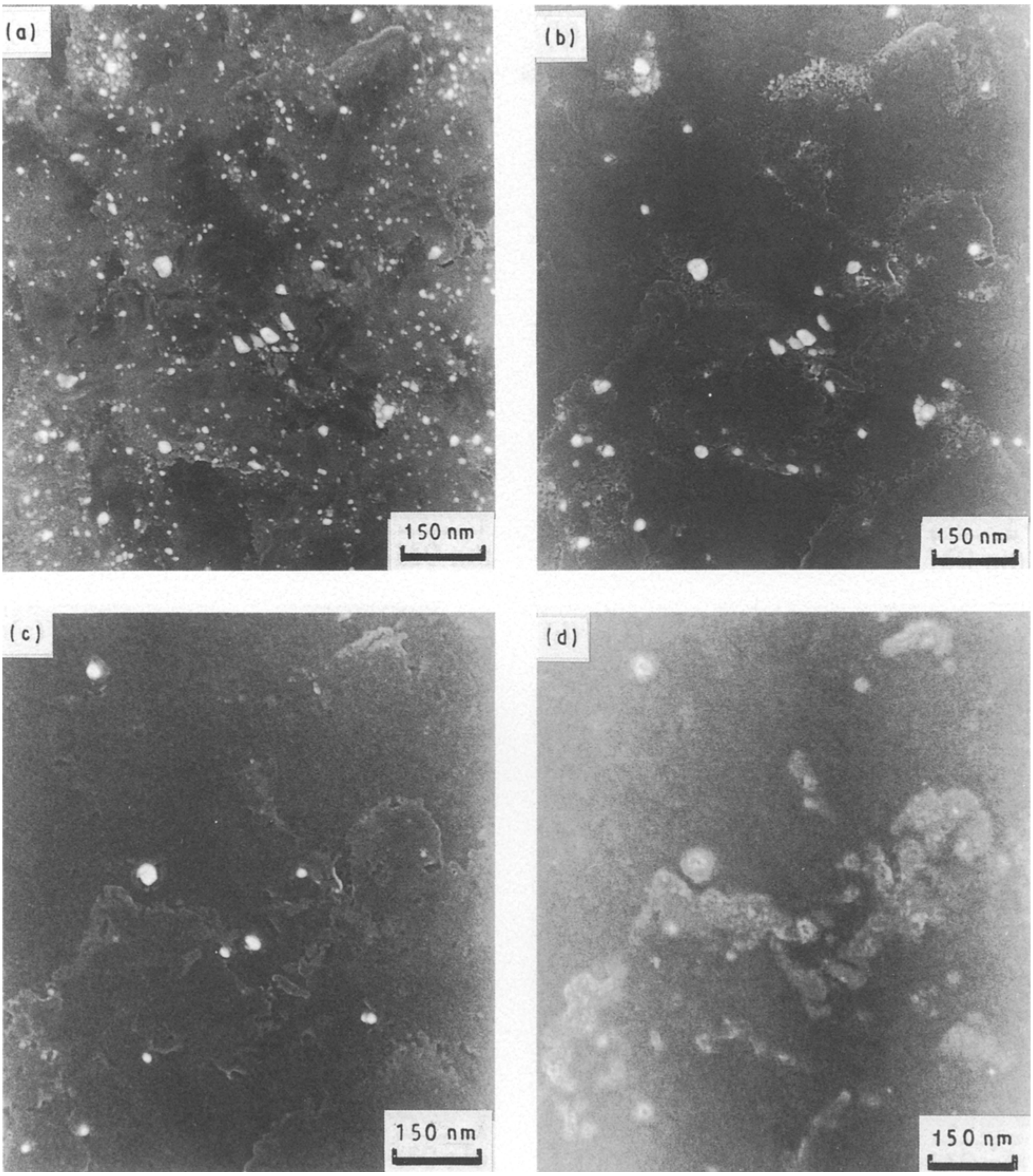

Figure 8 Time evolution of substrate surface pretreated with α-Al_2O_3 abrasive. MPECVD for (a) 0 min (initial state), (b) 5 min, (c) 15 min and (d) 45 min.

population density of the residues that can contribute to diamond deposition, and by the type of abrasive powder used for the substrate pretreatment.

4. Conclusion

The early stage of diamond film formation from the vapour phase was investigated in detail, mainly by means of high-resolution SEM and TEM. Observation of exactly the same parts of the substrates suggested different mechanisms for the formation and growth of diamond particles according to the abrasive used. When diamond abrasive particles were used, all the residues, which were implanted diamond fragments, survived. With c-BN abrasive particles, some residues disappeared in the plasma. This suggests that growth and disappearance of seeds occurred competitively. The role of α-Al_2O_3 seeds was different from that of diamond and c-BN residues.

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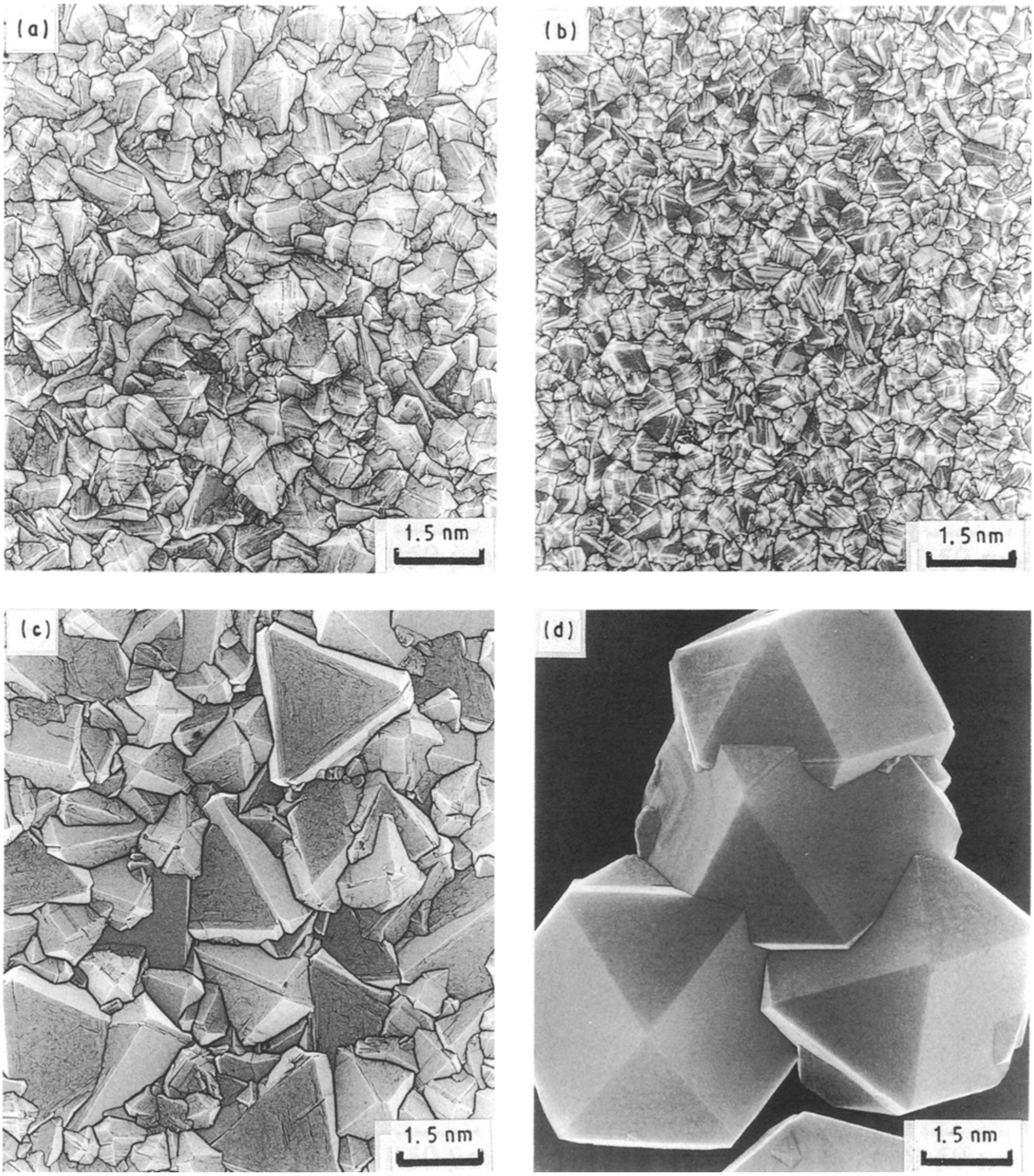

Figure 9 Products after 10 h deposition on substrate pretreated with (a) diamond abrasive for 60 min, (b) diamond abrasive for 120 min, (c) c-BN abrasive for 60 min and (d) α-Al_2O_3 abrasive for 30 min.

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