Ceramics International 22 (1996) 443–448

0272-8842/96 $15.00+.00
0272-8842(95)00114-X

Review Paper

Heteroepitaxy of Diamond on Silicon

Xin Jiang & Claus-Peter Klages

Fraunhofer-Institut für Schicht- und Oberflächentechnik (FhG-IST), Bienroder Weg 54 E, D-38108, Braunschweig, Germany

(Received 12 July 1995; accepted 3 August 1995)

Abstract: After the feasibility of diamond CVD growth was convincingly demonstrated by Japanese scientists about a decade ago, heteroepitaxy of diamond thin films on inexpensive single-crystalline substrates has been one of the most important research objectives of CVD diamond technology. In 1992, the controlled heteroepitaxial nucleation of diamond on 3C-SiC epitaxial films and on bare silicon wafers, respectively, was achieved independently by research groups in the USA and Germany. Although the epitaxial growth is of Volmer–Weber type in each case, i.e. polycrystalline with epitaxial orientation of individual crystallites, the physical properties of these films represent a significant improvement over the usual randomly oriented films, owing to the reduction of grain boundary angle distribution to a few degrees. This article discusses the mechanism of heteroepitaxial nucleation and growth of diamond films on silicon and reviews the results of first measurements of electrical and thermal properties. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The widespread applicability of diamond thin films in active electronics depends upon our ability to achieve heteroepitaxial growth of diamond single crystals, or the development of alternative approaches to single crystal diamond growth. After the first detailed description of CVD diamond growth in the early 1980s many research groups attempted to grow heteroepitaxial diamond on large-area economical substrates. Significant progress was made in the USA and Germany in 1992 in obtaining heterogeneous nucleation of oriented diamond crystallites on 3C-SiC epitaxial films[1] and on bare silicon wafers,[2] respectively, using bias-enhanced microwave plasma CVD processes. Today it is possible to prepare completely oriented diamond films on a 28 cm^2 silicon wafer (typical morphology see Fig. 1) and to various thicknesses depending on the deposition time, in our laboratory. A series of articles concerning the heteroepitaxial nucleation and growth of diamond films has been published, reflecting the growing interest.

In this article we report on the recent results in this area and discuss the problems to be resolved. Owing to the growing number of research groups and the rapid development in this branch only the published results will be reviewed.

2 NUCLEATION

Heteroepitaxial nucleation of diamond on Si or SiC is to date limited to microwave plasma CVD processes owing to the success of nucleation by biasing the substrate without any other *ex-situ* pretreatment. CVD diamond has been reproducibly grown on c-BN which is lattice matched, chemically compatible to diamond. On commonly used silicon, heterogeneous nucleation of the diamond phase is usually a very infrequent process. Although a continuous layer can be deposited after an *ex-situ* polish by diamond powder, only randomly distributed residues of diamond, or other carbonaceous phases are then most probably acting as the nucleation centres. A polycrystalline film with a random orientation of individual crystallites is obtained, when the diamond islands coalesce.

To create stable diamond nuclei on Si, a negative substrate bias potential is applied.[3–5] A critical kinetic energy of the species exists, which depends on the substrate bias V_b and the process gas pressure. Under conditions usually applied for diamond growth V_b is approximately -80 V.[3,5] The nucleation rate is also dependent on the substrate temperature T_s and the hydrocarbon concentration.[5] With increasing hydrocarbon (CH_4) fraction the nucleation rate increases, however the quality of the crystallites decreases. Usual hydrocarbon fractions for epitaxial nucleation are in the range of 0.5–5%. A hydrocarbon concentration

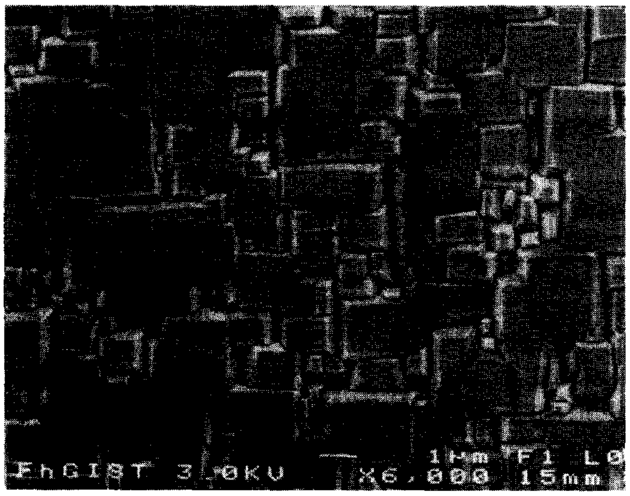

Fig. 1. An SEM image of a (100) diamond film.

which is too high leads to the loss of epitaxy. A maximum nucleation rate was found at about 850°C for $V_b = -150$ V and 4% methane. It can be explained by the opposing effects of (i) the desorption of hydrogen from the silicon surface and the sticking probability of carbon species, and (ii) etching of the diamond phase, dominating below and beyond 850°C, respectively.

The early stage of diamond nucleation was monitored by atomic force microscopy (AFM) and reflection high energy electron diffraction (RHEED).[6] The results show that the nuclei are initially non-facetted and are of crystalline diamond structure in spite of their small size of several nanometers. This confirms the creation of the diamond nuclei by biasing the substrate, as opposed to just creating nucleation sites.

For the films with bias-enhanced nucleation a silicon carbide layer up to 10 nm was detected at the silicon/diamond interface and on the bare silicon surface using high-resolution cross-sectional transmission electron microscopy,[4] RHEED[6] and XPS, respectively.[7] For diamond CVD growth on silicon, a SiC interlayer was often, but not always, detected.[8,9] The RHEED patterns obtained for different deposition times (Fig. 2) show only spots resulting from diffraction by epitaxial cubic SiC of several monolayers for the specimens with deposition time < 6.5 min, indicating a necessary induction time of nucleation. The extended spots may be a result of the lattice strain. With a deposition time > 6.5 min, diffraction of diamond nuclei appears. It is demonstrated clearly by RHEED that the diamond nuclei formed at the beginning of the nucleation are oriented. With increasing nucleation time the density of nuclei increases drastically to about 5×10^{10} cm^{-2} (see Ref. 10) and the nuclei are then statistically randomly oriented (Fig. 2(d)). This result comfirms the importance of the control of nucleation for the epitaxial growth.

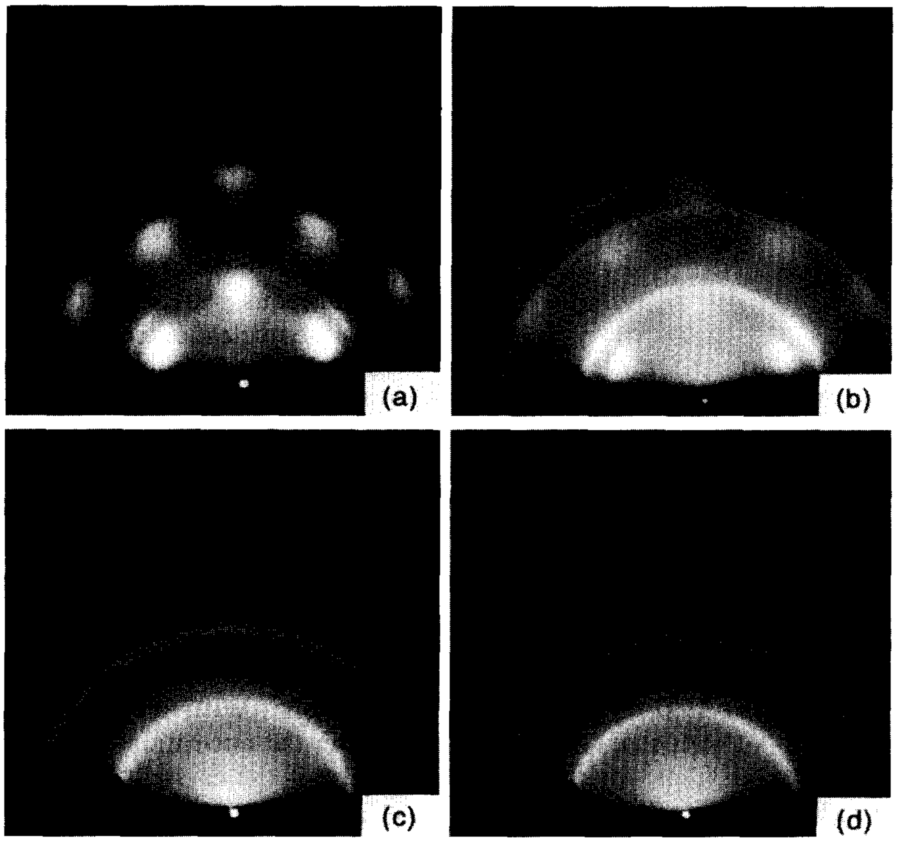

Fig. 2. RHEED patterns obtained after: (a) 7.5 min; (b) 10 min; (c) 12 min; and (d) 15 min depositions.

Although SiC is detected at the silicon growth surface, it results in no nucleation enhancement. The final SiC layer thickness is achieved in a very short time (only about 2 min[11]), however the diamond nucleation occurs later (6.5 min in Fig. 2), which indicates that the delay caused by the carbide formation is not equal to the whole induction time of nucleation. Therefore the carbide formation is not a sufficient condition, if it is necessary, for subsequent diamond growth. A direct lattice observation of the interface between silicon and an epitaxially grown diamond was not yet performed successfully. It needs further investigations to decide whether the diamond nuclei are grown on the thin epitaxial SiC "transition" layer, or are in direct contact with the silicon substrates.

To understand the nucleation mechanism one must know what role the substrate bias potential plays. It has been shown that, in physical vapour deposition (PVD) or plasma assisted chemical vapour deposition (CVD) processes, the application of a negative substrate potential is an effective way to increase the energy of ionic particles bombarding the substrate surface. The film nucleation and growth is therefore influenced greatly.

Based on the experimental surface analysis data, we propose, analogous to the steps for film growth from hyperthermal particles,[12] the following growth model for the heteroepitaxial diamond nucleation:

1. Due to the negative electrical potential positively charged carbon and hydrocarbon ions will be accelerated towards the substrate, the high energy part of CH_x ions (>50 eV) is able to penetrate the surface of silicon to a depth of typically one or several monolayers, depending on the kinetic energy and mass of the charged species.
2. The penetrated carbon occupies a site in the host lattice, resulting in a compressive stress around the site and therefore an increase of the surface energy and reactivity. With increasing the carbon concentration in the host matrix a carbon cluster will be formed with sp^3 bonding because of the compressive stress. This cluster serves then as a nucleation centre for further diamond growth.
3. Epitaxial diamond nucleation is then realized by the subsequent surface diffusion of the adsorbed precursors. The attraction of the positively charged carbon containing species produces a carbon supersaturation at the substrate surface and the ion bombardment increases the adatom mobility, favouring the probability of the adatoms and the nucleation centres meeting each other and forming stable nuclei. A recent observation[10] of the nearest neighbouring distance enlargement of the diamond nuclei compared to a statistical distribution provides strong evidence for the surface diffusion of adsorbed precursors.
4. The orientation of the diamond nuclei is influenced by the host crystalline environment on the crystallization of a collection of injected carbon atoms, for example, by the angular dependence of the displacement probability due to the different displacement energies for recoil along different crystal directions.

The thermal diffusion of carbon adatoms results in a possible formation of an epitaxial SiC. The formation of SiC layer would also be favoured by ion mixing effect or secondary deposition from the sputtered/etched silicon. This however does not influence the establishment of the model. In fact, the previously observed SiC layer has a thickness of 50–100 Å. If the SiC is formed prior to the diamond nucleation, i.e. the diamond is not in direct contact with silicon, one need only take the SiC layer as the host matrix.

It cannot be excluded that the gas phase chemistry in the plasma will be modified because of the biasing potential of the substrate, which might also play a role in increasing the formation probability of the substrate-oriented nuclei. The selective nucleation, which has been recently achieved[13,14] (and will be described afterwards), demonstrates the importance of ion bombardment of the substrate surface.

3 GROWTH AND FILM STRUCTURE

As already mentioned, a precise control of the nucleation is necessary to obtain oriented nuclei. This control is in practice not always easy, because the nucleation density increases drastically once the nucleation begins. If the nuclei are not oriented completely, textured growth after nucleation can be applied to obtain completely (100%) epitaxially oriented films. Textured growth utilizes an "evolutionary selection" if the growth process proceeds to a large thickness, and only allows the crystallites which have the fastest growing direction approximately parallel to the general growth direction to grow further. Such an approach was used to prepare both textured and epitaxially oriented films.[15–18]

Owing to the relatively low substrate surface energy the growth of diamond crystallites on silicon

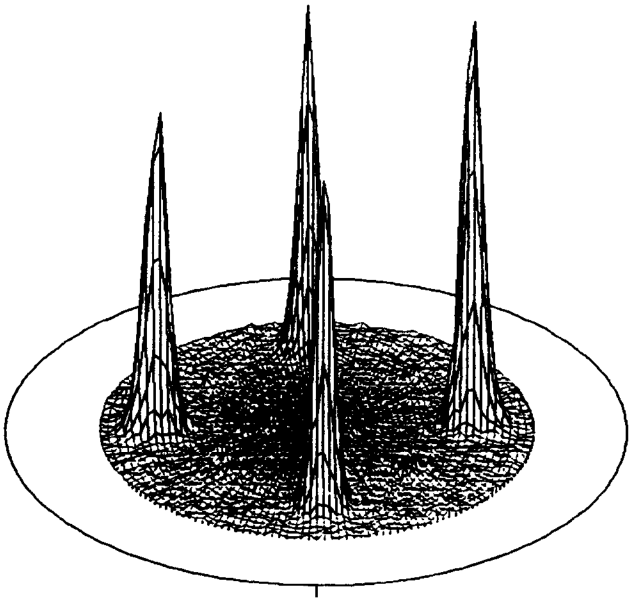

Fig. 3. {111} X-ray pole figure of a (100)-oriented diamond film.

is Volmer–Weber type, i.e. 3-D island growth. A result of this type of growth is the slight orientation deviation of the crystallites with respect to the substrate. The deviation of the crystal orientation up to a few degrees was determined by X-ray pole figure analysis and by quantitative image analysis of atomic force microscopy.[2,17,19] A typical {111} diamond pole figure obtained from a 6 μm thick (100) oriented film is depicted in Fig. 3. The FWHMs in the polar and azimuthal angles are approximately 8°. With increasing film thickness smaller FWHM values have been found.[17] Smaller average tilting angles of the crystallites have been found for (111) epitaxial diamond films on silicon.[17,20]

Both X-ray and AFM analyses show no preferential tilt direction. The interpretation of the crystal tilting in heteroepitaxial grown diamond films without having a lattice image of the interface is difficult. Crystal lattice mismatch compensation, suggested[21] for the diamond/SiC epitaxial system, cannot explain the statistical tilting angle distribution reported in the diamond/silicon system. In fact, a crystal tilting up to several degrees is often found for epitaxial systems with a relatively large lattice mismatch. In this case the interface energy is high, largely because of the lattice strain, and no significant energy change of the system will occur if the grown crystallites are slightly tilted. In fact, by optimizing the process conditions (better base vacuum in the reactor, precise control of the nucleation) a minimization of the tilting angle has been achieved.[19] Therefore the tilting seems to be caused not only by the interface mismatch, but the crystal imperfection at the interface has also to be taken into consideration.

The grain boundary between two highly oriented diamond grains was imaged by TEM.[22] The slight orientation deviation between the grains was again confirmed. Along the grain boundary a network of parallel dislocations is formed, which is characteristic of a low angle grain boundary where an array of periodic dislocations forms to accommodate the slight orientation deviation.

4 SELECTIVE NUCLEATION AND EPITAXY

Excellent patterning and epitaxial growth of diamond films are two requirements for realizing their electronic and micromechanic applications. Selective deposition of synthetic diamond has become significantly important in the fabrication of diamond devices. Recently an approach of selective nucleation and epitaxy (Sentaxy) of diamond films

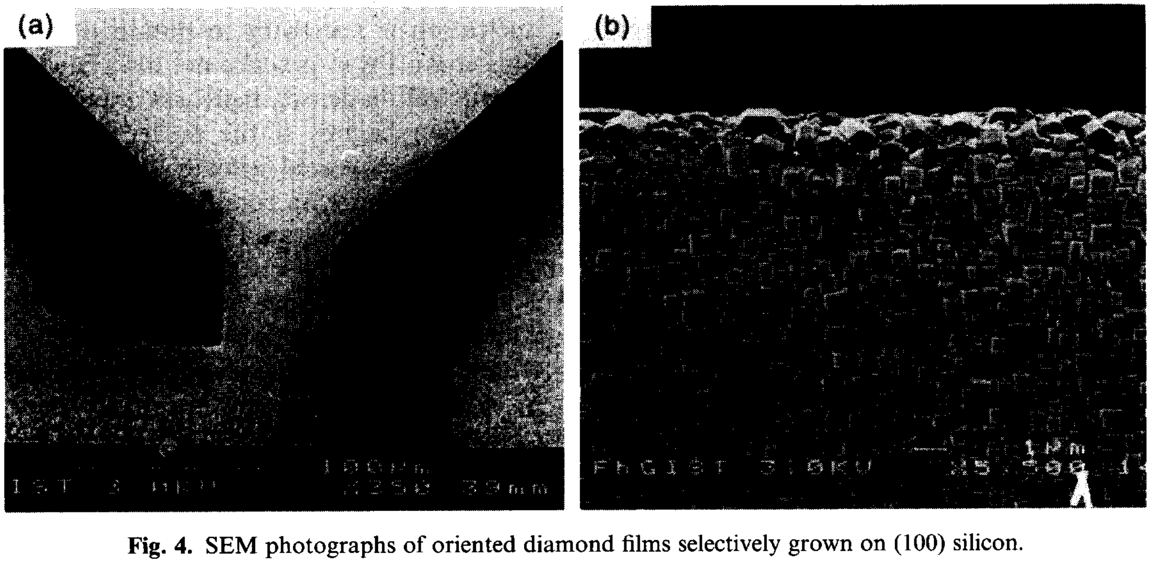

Fig. 4. SEM photographs of oriented diamond films selectively grown on (100) silicon.

on (100) Si was performed.[14] The selectively deposited diamond films on the SiO_2-patterned silicon follow the defined pattern very closely (Fig. 4(a)). The selectivity of diamond forming on the desired area and not forming on the area covered with SiO_2 is higher than 200.[13] In Fig. 4(b) a patterned diamond film is shown, demonstrating crystallites with lateral sizes of about $2{\times}2\ \mu m^2$ with well-developed (001) surfaces. A major portion of the crystallites is grown epitaxially, showing their (001) surfaces parallel to the substrate.

The high selectivity of diamond nucleation is clearly caused by the different electrical conductivities of silicon and SiO_2, respectively. For a substrate temperature of over 800°C during nucleation the silicon conducts well, and the negative d.c. potential can be applied, whereas the SiO_2 retains its insulating properties.

5 PROPERTIES

It is recognized that the grain boundaries, through charge trapping and carrier depletion, dominate the electrical properties and limit the benefits of diamond in electronic applications. The orientation deviation between the crystallites generates a dislocation network that traps carriers at the grain boundary. The trapped carriers may produce a potential barrier and impede carrier transport. It was therefore expected that an increase in carrier transport properties of the diamond films will be obtained if the orientation deviation angle of the grains decreases. Fox *et al.* studied the transport properties of highly oriented B-doped diamond films.[22] The presence of low angle grain boundaries in the highly oriented film reduced the density of interfacial traps by 50% over randomly oriented polycrystalline films and improved the mobility by almost a factor of three over the polycrystalline film. Hole mobility of 278 cm^2/Vs was recently reported, which is nearly a ten-fold increase of hole mobilites, compared with the best reported values for random films, in spite of the still imperfect alignment of the diamond crystallites with respect to the underlying substrate lattice.[23]

Homogenous films with high crystalline quality and low grain boundary density are necessary to come close to the thermal diffusivity of natural diamond. Therefore epitaxial diamond films are also expected to have higher thermal diffusivities than non-oriented diamond films. The thermal diffusivity of heteroepitaxially grown diamond films on silicon were recently investigated.[24] Lateral thermal diffusivities, measured in thick diamond films 70–90 μm from the film/substrate interface, were found to improve from 5–6 cm^2/s in fibre-textured samples to between 8 and 11 cm^2/s in (100) oriented heteroepitaxial films, fairly close to the bulk thermal diffusivity of 12 cm^2/s of natural type IIa diamond.

6 CONCLUSIONS

Significant progress towards heteroepitaxial growth of diamond on silicon has been achieved. High quality, large area, highly oriented films can be deposited, which show an approach to the physical properties of a single crystalline diamond. A number of investigations have been performed to understand the nucleation mechanism and the diamond/silicon interface. The main problem remaining is the reduction of the deviation of the crystal orientation. The question of whether a real single crystalline diamond film will be able to be prepared on silicon is still open.

ACKNOWLEDGEMENTS

The work is financially supported by BMFT under grant No. 03M2727B4 and by Daimler Benz AG. The authors wish to thank Mrs A. Westphal for the RHEED and Mrs M. Heinau for the X-ray analysis.

REFERENCES

1. STONER, B. R. & GLASS, J. T., *Appl. Phys. Lett.*, **60** (1992) 698.
2. (a) JIANG, X. & KLAGES, C.-P., *Diamond Rel. Mater.*, **2** (1993) 1112; (b) JIANG, X., KLAGES, C.-P., ZACHAI, R., HARTWEG M. & FÜßER, H.-J., *Appl. Phys. Lett.*, **62** (1993) 3438.
3. YUGO, S., KANAI, T., KIMURA, T. & MUTO, T., *Appl. Phys. Lett.*, **58** (1991) 1036.
4. STONER, B. R., MA, G.-H. M., WOLTER, S. D. & GLASS, J. T., *Phys. Rev.*, **B45** (1992) 11067.
5. JIANG, X., KLAGES, C.-P., ZACHAI, R., HARTWEG, M. & FÜßER, H.-J., *Diamond Rel. Mater.*, **2** (1993) 407.
6. JIANG, X., SCHIFFMANN, K., WESTPHAL, A. & KLAGES, C.-P., *Appl. Phys. Lett.*, **63** (1993) 1203.
7. YUGO, S., KIMURA, T. & KANAI, T., *Diamond Rel. Mater.*, **2** (1993) 328.
8. WILLIAMS, B. E. & GLASS, J. T., *J. Mater. Res.*, **4** (1989) 373.
9. MEILUNAS, R., WONG, M. S., SHENG, K. C., CHANG, R. P. H. & VAN DUYNE, R. P., *Appl. Phys. Lett.*, **54** (1989) 2204.
10. JIANG, X., SCHIFFMANN, K. & KLAGES, C.-P., *Phys. Rev.*, **B50** (1994) 8402.
11. COLLINS, R. W., CONG, Y., KIM, Y.-T., VEDAM, K. & LIOU, Y., *Thin Solid Films*, **181** (1989) 565.
12. LIFSHITZ, Y., KASI, S. R. & RABALAIS, J. W., *Phys. Rev. Lett.*, **62** (1988) 1290.

13. KATSUMATA, S. & YUGO, S., *Diamond Rel. Mater.*, **2** (1993) 1490.
14. JIANG, X., BOETTGER, E., PAUL, M. & KLAGES, C.-P., *Appl. Phys. Lett.*, **65** (1994) 1519.
15. CLAUSING, R. E., HEATHERLY, L., SPECHT, E. D. & MOORE, K. L., In *New Diamond Science and Technology*, ed. R. Messier, J. T. Glass, J. E. Butler & R. Roy. Mater. Res. Soc. Symp. Int. Proc. NDSST-2, Pittsburgh, PA, 1991, p. 575.
16. WILD, C., HERRES, N. & KOIDL, P., *J. Appl. Phys.*, **68** (1990) 973.
17. JIANG, X., KLAGES, C.-P., RÖSLER, M., ZACHAI, R., HARTWEG, M. & FÜßER, H. J., *Appl. Phys.*, **A57** (1993) 483.
18. STONER, B. R., SAHAIDA, S. R., BADE, J. P., SOUTHWORTH, P. & ELLIS, P. J., *J. Mater. Res.*, **8** (1993) 1334.
19. SCHIFFMANN, K. & JIANG, X., *Appl. Phys.*, **A59** (1994) 17.
20. SCHRECK, M., HESSMER, R., GEIER, S., RAUSCHENBACH, B. & STRITZKER, B., *Diamond Rel. Mater.*, **3** (1994) 510.
21. ZHU, W., WANG, X. H., STONER, B. R., KONG, H. S., BRAUN, M., MA, G.-H. M. & GLASS, J. T., *Phys. Rev.*, **B47** (1993) 6529.
22. FOX, B. A., STONER, B. R., MALTA, D. M., ELLIS, P. J., GLASS, R. C. & SIVAZLIAN, F. R., *Diamond Rel. Mater.*, **3** (1994) 382.
23. GLASS, J. T., Presentation of *Gorham's Conference on CVD Diamond and Diamond-like Carbon Coating Technology*, Orlando, FL, 6–8 March, 1994.
24. KÄKING, O. W., RÖSLER, M., ZACHAI, R. & FÜßER, H.-J., *Diamond Rel. Mater.*, **3** (1994) 1178.