Published in Applied Physics Letters 67, issue 11, 1533-1534, 1995
which should be used for any reference to this work

X-ray photoelectron diffraction of (100)-oriented chemical vapor deposited diamond films on silicon (100)

E. Schaller,[a)] O. M. Küttel, P. Aebi, and L. Schlapbach
Institut de Physique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

(100)-oriented diamond films have been grown on silicon (100) in a microwave plasma assisted chemical vapor deposition (CVD) tubular system. X-ray photoelectron diffraction (XPD) has been used to study such oriented polycrystalline films. Comparing the diffractograms of a natural diamond (100) surface and of polycrystalline (100)-oriented CVD diamond films quite similar features are observed. XPD measurements after 8 min of bias treatment show that the tiny crystals are already preferentially oriented at deposition parameters required for (100)-oriented film growth. Our measurements indicate a strong need to control the growth parameters very carefully during the first minutes of growth to get an orientation.

Presently, polycrystalline chemical vapor deposition (CVD) diamond films oriented toward the substrate are routinely grown on silicon[1] using microwave plasma enhanced deposition. No single-crystal thin films have so far been deposited on nondiamond substrates. However, true heteroepitaxy remains as a goal for further research activities due to the expected performance of such films in electronic applications.[2] In a first step, it is important to understand the physical and chemical mechanisms which are responsible for the oriented growth on silicon. Various studies on oriented diamond films have been done using scanning and transmission electron microscopy (SEM), (TEM),[3,4] x-ray photoelectron spectroscopy (XPS),[5] or x-ray diffraction (XRD).[6,7] While most diagnostic techniques are sensitive to μm thick films only, TEM was used to reveal the structure of the silicon-diamond interface.[4] Nevertheless, there is a lack of diagnostic tools to investigate the interface in order to understand oriented growth. Moreover, it is not clear whether orientation already occurs during the first minutes of bias treatment or later during the deposition process.

In this letter, we report on x-ray induced photoelectron diffraction measurements for the characterization of the very early stage of oriented diamond growth on silicon (100). This technique was used to study diamond films after 8 min of bias treatment.

Low pressure diamond growth was performed on silicon (100) substrates via microwave plasma CVD in a tubular deposition system. Silicon substrates were cleaned in acetone, introduced in the plasma system, and the deposition was started after the pressure in the chamber reached 10^{-6} mbar. A first run during 3 min in pure hydrogen was used to remove the native oxide layer on the substrate and to adjust the deposition temperature. Nucleation was induced by applying a dc bias of -225 V to the substrate during 8 min at 810 °C and under 20 mbar of a 2% CH_4/H_2 gas mixture. The parameters for the subsequent deposition were 870 °C at 40 mbar with 1% CH_4 in H_2. High purity hydrogen was used (6.0 H_2). Figure 1 shows a 15 h deposited polycrystalline CVD diamond film with 80% of (100) oriented crystals. The tilting angle is less than 8° as measured by XRD.

XPD is a well-established technique in surface science for studying surface atomic structure of monocrystals.[8] The experiments were performed in a VG ESCALAB Mark II spectrometer modified in order to enable motorized sequential angle-scanning data acquisition,[9] equipped with low energy electron diffraction and a Mg $K\alpha$ (1253.6 eV) and a Si $K\alpha$ (1740.0 eV) twin anode. The photoelectron emission angle above the substrate is varied through sample rotation ($0° < \theta < 90°$ and $0° < \phi < 360°$).

As a reference, Fig. 2(a) shows the XPD measurement on a natural diamond (100) surface,[10] excited with Mg $K\alpha$ x-rays, at an electron kinetic energy of 964 eV. The photoelectron diffractograms obtained by this technique reflect a real space projection of the major crystalline directions of the crystal. A stereographic projection is used for the presentation. The surface normal corresponding to the [100] direction, is located in the center of the plot whereas the outer circle represents an emission angle of 90° off normal. For additional details the reader is referred to Ref. 10. The C 1*s* diffractogram shows fourfold symmetry with the [111] crystallographic directions at $\theta = 54.7°$ and the [011] directions at $\theta = 45°$ (Ref. 7) as major features. The XPD measurement on a 1 h grown CVD diamond film is represented in Fig. 2(b). The agreement with the C 1*s* diffractogram of the

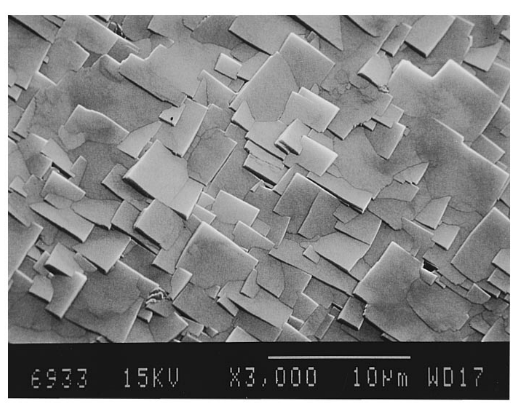

FIG. 1. SEM picture of a (100) oriented diamond film after 15 h of microwave plasma deposition.

[a)]Electronic mail: eliane.schaller@unifr.ch

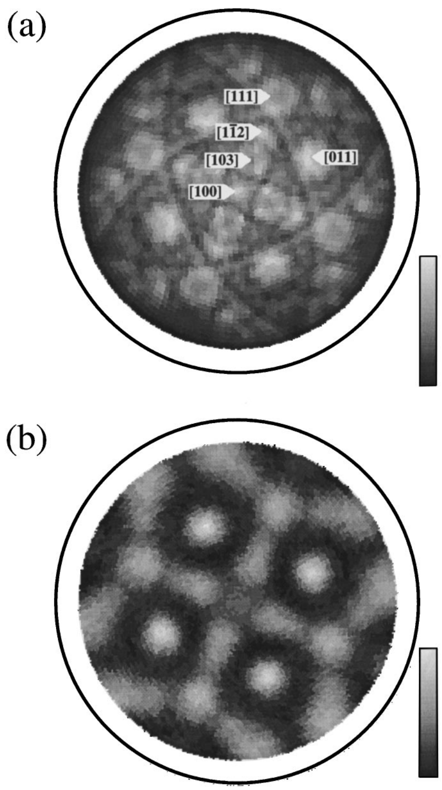

FIG. 2. Stereographic projection of the C 1s XPD intensities at 964 eV induced by Mg $K\alpha$ radiation of (a) a natural diamond (100) surface and (b) a CVD (100) surface after 1 h of growth. Low index directions are labeled.

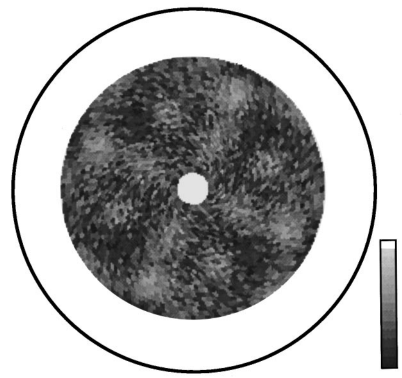

FIG. 3. C 1s diffractogram at 964 eV of a diamond layer after 8 min of bias treatment, showing a preferential orientation of the crystals (has not been measured up to the normal).

(100) natural diamond surface is striking: clear spots in the [111] and the [011] directions are observed and all the other maxima are visible too. However, the overall fine structure of the CVD diamond film diffractogram is more fuzzy and partly lost. This can be explained in terms of a superposition of the diffractograms from different, slightly misaligned microcrystals. Keeping in mind that XPD collects electrons from the top 30 Å of the surface and of an area of 1 mm^2, our results confirm the presence of a high grade (100)-oriented CVD diamond film after 1 h.

Since XPD is very surface sensitive, investigations have been made after the first minutes of an oriented CVD diamond film deposition. After 3 min of deposition (bias treatment), the C 1s diffractogram already shows the four [111] maxima at θ=54.7° (not shown). Figure 3 shows the fitted C–C component diffractogram of the C 1s photoemission signal of a (100)-oriented CVD layer after 8 min of bias treatment. As measured by atomic force microscopy, at this time, the diamond layer is not complete and is between 50 and 100 nm thick. The diffractogram detail structure is not obvious (for example, we cannot distinguish the [103] from the [112] maxima around θ=40°), but the four [111] maxima at θ=54.7° and the four [011] maxima at θ=45° are clearly visible. This proves that the growing film is oriented diamond which is formed from the beginning of the deposition on. However, the detailed structure is weak or missing due to the slightly preferential orientation of the diamond crystals at such an early stage. Our measurements clearly indicate that the orientation is determined within the first minutes of bias treatment. Therefore, it is primordial to choose and control very precisely the deposition parameters.

(100) oriented diamond films have been grown in a microwave plasma assisted CVD tubular deposition system. SEM and XRD show a good layer quality and XPD shows a preferential orientation of the tiny crystals after 8 min of deposition. Further experiments using XPD will be undertaken, focusing especially on the presence and the orientation of a SiC interface between the diamond nuclei and the silicon substrate.

This work forms part of a joint project with CSEM in Neuchâtel and EMPA in Dübendorf. The authors gratefully acknowledge financial support by the Swiss National Science Foundation. It was carried out under the auspices of the trinational ''D-A-CH'' cooperation of Germany, Austria, and Switzerland, on the ''Synthesis of Superhard Materials.''

[1] S. D. Wolter, B. R. Stoner, J. T. Glass, P. J. Ellis, D. S. Buhaenko, C. E. Jenkins, and P. Southworth, Appl. Phys. Lett. **62**, 1215 (1993).
[2] W. A. Yarbrough and R. Messier, Science **39**, 1 (1989).
[3] B. R. Stoner and J. T. Glass, Appl. Phys. Lett. **60**, 698 (1993).
[4] B. R. Stoner, G. H. Ma, S. D. Wolter, W. Zhu, Y. C. Wang, R. F. Davis, and J. G. Glass, Diam. Relat. Mater. **2**, 142 (1993).
[5] S. Yugo, T. Kanai, and T. Kimura, Diam. Relat. Mater. **1**, 388 (1992).
[6] R. Kohl, C. Wild, N. Herres, P. Koidl, B. R. Stoner, and J. T. Glass, Appl. Phys. Lett. **63**, 1792 (1993).
[7] R. Hessmer, M. Schreck, S. Geier, B. Rauschenbach, and B. Stritzker, Diam. Relat. Mater. **4**, 410 (1995).
[8] C. S. Fadley, in *Synchrotron Radiation Research: Advances in Surface Science*, edited by R. Z. Bachrach (Plenum, New York, 1992), Chap. 11.
[9] J. Osterwalder, T. Greber, A. Stuck, and L. Schlapbach, Phys. Rev. B **44**, 13764 (1991).
[10] O. M. Küttel, R. G. Agostino, R. Fasel, J. Osterwalder, and L. Schlapbach, Surf. Sci. **312**, 131 (1994).