ANALYSIS OF THE SURFACE MORPHOLOGY OF CVD-GROWN DIAMOND FILMS WITH X-RAY DIFFRACTION

M.J. Fransen$^1$, J. te Nijenhuis$^1$, J.H.A. Vasterink$^1$, R.L Stolk$^2$, and J.J. Schermer$^2$

$^1$PANalytical, Lelyweg 1, 7602 EA Almelo, The Netherlands
$^2$Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

ABSTRACT
In this study the influence of the addition of nitrogen during growth of diamond films is determined using small-spot X-ray diffraction techniques and compared with the morphological structure. Phase identification showed the presence of crystalline molybdenum carbide at the interface, as well as the incorporation of a small amount of non-diamond carbon throughout the diamond layer. The pole figures revealed a change in texture with increasing nitrogen in the gas phase. The results agree well with results obtained with scanning electron microscopy and laser reflectometry.

INTRODUCTION
Diamond is a material that has attracted the imagination of the scientists throughout the centuries, not only because of its natural beauty, but also because of its specific properties, such as its extreme hardness, and its high thermal conductivity in combination with its low electrical conductivity. It is therefore needless to say that the demonstration of the possibility to grow diamond from the gas phase using chemical vapor deposition (CVD) has been the starting point of a large number of developments in diamond crystal growth.

Amongst the new techniques for diamond growth from the gas phase, one of the most fascinating methods is combustion-flame assisted CVD, firstly reported by Hirose et al. [1]. In this method, diamond is deposited using an (commercially available) acetylene-oxygen welding torch, operating in ambient atmosphere. Despite the simplicity of this method, the results of the deposition experiments are amazing: high quality diamond films can be deposited at high growth rates [2].

In literature it has been reported that the addition of small amounts of nitrogen to the gas phase could even further increase the growth rate [3]. Furthermore, it also appeared that the presence of nitrogen clearly influences the morphology and the preferred orientation of the crystallites deposited.

In this paper we use X-ray diffraction (XRD) to investigate the effect of nitrogen addition on the phase composition and texture of diamond films. XRD is not an obvious candidate for these samples, because, as a result of the growth method, the homogeneous area in the sample is too small for conventional XRD. With the novel X-ray mono-capillary, however, sub-mm$^2$ spots can be analyzed in a reasonable time.
The big advantage of XRD, unlike Scanning Electron Microscopy (SEM) and laser reflectometry, is that it does not require the presence of crystallites with well-defined facets at the sample surface. However, on the diamond layers investigated in this particular case the well-defined faces of the diamond crystallites allow for a direct comparison of texture analysis using X-ray diffraction with the morphological structure as described earlier [3].

EXPERIMENTAL DETAILS

The diamond films investigated have been deposited onto molybdenum substrates using combustion-flame assisted chemical vapor deposition. The growth conditions are described in detail in Ref. [3]. The geometry of the samples is circularly symmetric with respect to the flame axis. The central area of these films (with a diameter of 3 mm) is homogeneous in thickness and morphology. The morphology in the outer ring differs strongly from that in the center of the film. Six samples differing by the deliberately added content of nitrogen (N₂) to the gas phase during the growth process are selected for XRD analysis.

In traditional XRD analysis, the irradiated area of the sample is typically on the order of a few cm², in order to obtain a good statistical average over the sample, as well as for speeding up the time required for data collection. In this case, however, the size of the sample is much smaller, especially if one takes into account that the irradiated area increases considerably at high tilt angles of the sample. In order to keep the data collection time reasonable, a mono-capillary was used as incident beam X-ray optical module. This module was mounted onto a Philips X'Pert PRO MPD diffractometer equipped with a vertical goniometer. The point focus of the copper X-ray tube was used. In a previous publication [4], the usefulness of the mono-capillary for XRD analysis of small spots on samples was demonstrated.

Scans of the centers of the samples were made for identifying the phases present as well as for selecting a suitable reflection for subsequent texture analysis. A mono-capillary with an inner diameter of 0.1 mm was used. As detector a scanning PSD (position-sensitive detector) has been employed. The samples were mounted onto a vertically positioned goniometer head and aligned with respect to the X-ray beam with the aid of an optical microscope which was mounted onto the diffracted beam optics position. During the measurements, the samples were spun around their surface normal. The combination of a scanning PSD, a symmetrical scanning mode and a spinning sample improves the statistical representation of the sample considerably, also under the adverse conditions of a small irradiated area and large crystallites in the sample [4].

For the pole figure measurements the spinning sample stage on the X’Pert PRO MPD system was replaced by an 1/4-circle open Eulerian cradle. As incident beam optical module a mono-capillary with an inner diameter of 0.5 mm was used, as diffracted beam module a receiving slit (set to 3 mm) together with a Xe-proportional detector. The pole figures were measured according to the Schulz reflection method [5]. The pole figures have been recorded by measuring complete circles (0° - 360°) over the rotation angle φ at fixed tilt angles ψ over a range between 0° and 90°.
PHASE IDENTIFICATION

On all samples, a symmetrical θ-2θ scan was carried out on the central area. For the phase identification, a restriction set was built which included only the elements C, H, N, O and Mo. Deleted patterns were excluded. With these restrictions, the following phases were found: Diamond (06-0675), Molybdenum (42-1120) and Molybdenum Carbide (Mo2C, 35-0787). The peak at 26º 2θ results from some other form of carbon. Several C phases (carbon, graphite) have one strong reflection in this range, while the other reflections are weak. Based on the presence of just one reflection it is not possible to decide on the exact form of this phase. In a separate experiment [6], Raman spectroscopy confirmed the presence of graphite in the samples. Finally, one can conclude that N-containing phases resulting from the addition of N2 can not be detected. In Figure 1, some of these diffractograms are shown. Note that the intensity scale of the diffractograms are not identical.

At a first glance, the patterns are largely similar and indeed all phases are present in all diffractograms. Upon closer inspection, however, one can see that the diamond (004) reflection close to 120º is much higher in intensity in the samples grown with a low N2 addition. In the reference pattern for diamond, however, the (004) reflection is lower in intensity than the neighbouring (311) and (331) reflections. This indicates already a preferred orientation in the [001] direction for the first three samples. Also the intensity of the Mo reflections is varying, which could be due to varying film thicknesses for the different nitrogen additions. Even within one scan, however, the ratio between the different Mo reflections is varying, indicating some preferred orientation of the Mo substrate.

In order to check the position of the various phases in the layer system, one of the samples was also measured with fixed angles of incidence of 2º, 3º, 4º and 5º, respectively. Upon comparison of these scans, only the diamond reflections increase in intensity for decreasing angle of incidence. The small carbon reflection at 26.1º 2θ stays fairly constant, indicating that a small amount of graphitic carbon is incorporated throughout the diamond layer. The Mo2C and Mo signals decrease upon decrease of the angle of incidence, which confirms that these phases is present only deeper in the material. The Mo2C signal is much stronger than the Mo signal in the grazing incidence scans, indicating that the latter phase is below the former, as expected. In fact, only the Mo reflections at larger 2θ angles can be found in the grazing incidence diffractograms. It is known from literature [7] that diamond growth on metallic surfaces proceeds by the formation of an intermediate carbide layer. From a comparison of the symmetrical and the grazing incidence scans it can be concluded that this carbide layer is indeed present at the interface and, moreover, that this layer consists of polycrystalline Mo2C.

In the grazing incidence measurements a small feature on the left-hand side of the (111) diamond reflection at 43.9º 2θ can be observed. This reflection is an indication of the presence of stacking faults in the diamond [8].
Figure 1. Diffractograms from five of the samples recorded with symmetrical \(\theta/2\theta\) scans (upper plot), stick patterns of the four identified phases (middle plot) and grazing incidence scans with varying angle of incidence, together with symmetrical scan as recorded on the sample grown with 100 sccm N\(_2\) added (lower plot).
POLE FIGURE MEASUREMENTS

From the scans used for phase identification it turned out that only the diamond \{111\} reflection at a 2θ angle of 43.9° was useful for preferred orientation analysis. Other possible candidates are much lower in intensity and/or overlap with reflections from other phases. Figure 2 shows six pole figures measured on samples deposited with an increasing nitrogen addition to the gas phase ranging from 15 to 100 sccm.

It appears that these pole figures show an axial sample symmetry (fiber texture), which is in accordance with the geometrical symmetry of the experimental set-up of the growth process. A clear change in the texture can be observed. The upper pole figures, corresponding to N₂ additions of 15 sccm, 20 sccm and 40 sccm, respectively, reveal that the maximum intensities of the reflections are located around ψ = 55°. This indicates clearly that the diamond film has a fiber texture in the [001] direction.

When the N₂ concentration is increased further from 60 sccm through 80 sccm to 100 sccm (see also Fig. 2d-f), the morphology of the film changes: the preferred orientation almost disappears. The decrease in intensity in all the pole figures at high ψ-tilt angles (above 80°) is due to the defocusing effect.

From the limited number of spots in the ring on the pole figures in the lower range (see Fig. 2a-c) it can be concluded that the crystallites are fairly large. These rings become much smoother with increasing nitrogen addition (Fig. 2d-f) indicating that the crystallites decrease in size.
DISCUSSION

The XRD pole figure measurements clearly reveal a change in the preferred orientation with increasing nitrogen content of the gas phase. Therefore the results described above can be compared with the morphological observations of Schermer and de Theije [3]. In the lower range of nitrogen addition, the SEM images [3] show a layer with large crystallites having \{100\} facets at their tops. These large crystallites are represented by the spikes around $\psi = 55^\circ$ in the upper pole figures in Figure 2. With higher nitrogen additions, it can be seen in the SEM images that the size of the crystallites decreases. Furthermore, the faceting is not observed anymore. The fact that the spikes have disappeared from the pole figures of the samples with high N$_2$ addition corresponds well to the observed reduction in average crystallite size. XRD also shows that these smaller crystallites loose their preferred orientation: the lower pole figures in Figure 2 evolve to a random texture.

In a separate publication [9], these results are discussed in more detail; a simple crystal growth model is proposed there which qualitatively explains the changes in film morphology upon addition of nitrogen.

CONCLUSION

In this paper we have discussed the results of a study on the evolution of the texture in diamond films as a function of the amount of nitrogen added to the gas phase during the deposition process.

It was shown that powder XRD, although generally considered as a large-area technique, can also give useful results on small samples within a reasonable time, especially when advanced X-ray optical modules such as mono-capillaries are being used.

Phase identification revealed the presence of crystalline molybdenum carbide (Mo$_2$C) at the interface and showed that a small amount of graphitic carbon is incorporated throughout the layer.

Pole figure measurements showed a change in the texture of the diamond films grown with increasing nitrogen addition to the gas phase. These results have been compared with a direct observation of the surface morphology using Scanning Electron Microscopy. From this comparison, it can be concluded that for these samples, both methods give the same results. XRD, however, can also be used in situations when the crystallites do not show well-defined facets.

ACKNOWLEDGEMENT

The authors like to thank Dr. Stefan Wienströer (Thyssen Krupp Steel, Germany) and Dr. Paul Schields (XOS, USA) for helpful comments to this work.
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