Detection of Nitrogen in CVD Diamond ◇

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Nitrogen impurities in CH_4/H_2 gas mixtures influence texture and morphology of polycrystalline diamond films prepared by chemical vapour deposition (CVD). The addition of small amounts of nitrogen in the process gas can effect a transition of the surface morphology from nanocrystalline to well facetted as well as a change in the grain structure from (110) to (100) fibre texture, depending on the N/C ratio [1].

On the other hand, nitrogen impurities incorporated in diamond films have a strong influence on the optical and electrical properties of these films. E.g. nitrogen acts as a deep level donor resulting in the compensation of acceptors such as boron [2]. Furthermore, it gives rise to various optical centers due to different configurations in the diamond lattice [3], and the thermal conductivity of diamond decreases dramatically with an increasing nitrogen content in the diamond film [4].

However, there is little knowledge about the quantities of nitrogen incorporated in diamond. This is due to the fact that nitrogen is not easily detectable in diamond and, therefore, none of the common analyzation techniques has sufficient sensitivity (some 10^{-5} and lower).

Diamond films were deposited on (100) oriented crystalline silicon surfaces by microwave plasma assisted CVD from a gas mixture of 1.5% CH_4 in H_2 and a nitrogen admixture varying from 25 ppm up to 5000 ppm N_2/H_2. Thus the nitrogen to carbon ratio in the process gas was varied from 0.33% to 67%. The depositions were performed similarly to those described in Ref. [5]. The substrate was held at a temperature of 790 $°C$ during a total growth time of 900 min, which results in a film thickness of about 10 μm.

The diamond films were investigated for their nitrogen content with the arrangement for ERD analysis at the Munich tandem accelerator described in Refs. [6,7]. The Q3D magnetic spectrograph with its complex focal plane gas detector offers the possibility of multiple redundant particle identification, which is important, detecting very low nitrogen contents in a carbon matrix. Performing multiple ΔE, E_{tot} and position measurements in the focal plane of the Q3D, the mass and the nuclear charge of the detected recoil ion is determined independently several times in order to avoid any background. Hence a detection limit better than 1 ppm nitrogen in carbon can be achieved using the Q3D magnetic spectrograph with its focal plane gas detector [8].

The relationship between the nitrogen content in the diamond films c_{Dia} as measured with ERD and the nitrogen to carbon ratio c_{gas} offered in the process gas during film deposition is shown in Fig. 1. One film deposited without any nitrogen gas added intentionally showed a nitrogen content of 8 ppm. The dashed line in Fig. 1 represents a fit to the data, using a modified power law $c_{Dia} = c_0 + A \cdot c_{gas}^B$ resulting in $A = 40.9 \pm 6.5$ and $B = 0.92 \pm 0.07$ for $c_0 = 8ppm$. The fit reveals a nearly direct proportionality (B = 1) of c_{Dia} and c_{gas}. Assuming a linear dependence of c_{Dia} and c_{gas}, the incorporation probability of nitrogen from the gas phase into the diamond film can be estimated to be about 0.4% in relation to carbon over several orders of magnitude of nitrogen supplied.

The morphology and texture of the diamond films investigated as analysed by scanning electron microscopy (SEM) and X–ray diffraction analysis (XRD) was found to depend strongly on the ratio of N/C in the process gas [9]. The film deposited with a 0.33% N admixture relative to carbon atoms in the process gas showed a (110) texture with tilted (100) facettes. With increasing N/C ratio grain structure of the film shifts to a (100) fibre texture, accompanied with a well facetted surface morphology which was best for a N/C ratio of 1.3% in the process gas. A further increase in the N/C ratio in the process gas up to 67% results in a change in the film texture back to (110), and the surface morphology deteriorates showing no more crystal facetting.

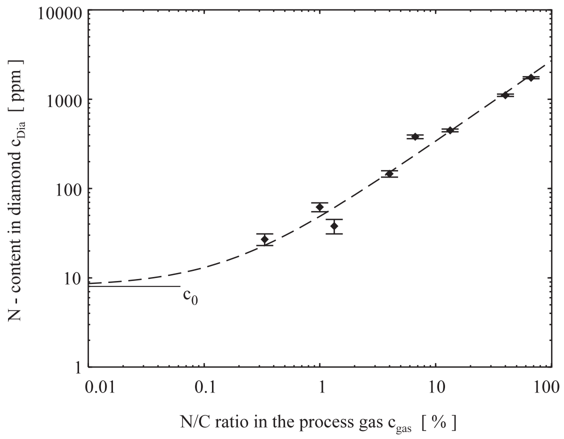

Fig. 1: The N–content in the diamond films as measured with ERD vs. the N/C ratio in the CVD process gas. The dashed line represents a fit to the data, using a modified power law. The indicated value c_0 is the nitrogen concentration measured in a diamond film deposited without adding any N_2 intentionally to the process gas.

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