Ultra nanocrystalline diamond (UNCD) films feature crystallites smaller than 10 nm and a smooth surface; thus, they represent a homogeneous and isotropic material (Fig. 1) [1]. Furthermore, both p- and n-type doped UNCD films are available with high carrier concentrations, a requirement for applications in sensing-devices based, for instance, on electrochemistry. UNCD films are grown in a chemical vapour deposition process with a high secondary nucleation rate. The obtained films are composed of separated single crystal diamond grains with rounded shapes which are embedded randomly oriented in an amorphous carbon-hydrogen matrix. To obtain information about the grain size and the distance of the grains in the matrix, UNCD films are usually studied by transmission electron microscopy (TEM), which, however requires a highly sophisticated preparation. An alternative method to obtain information about the structural film properties is grazing-incidence small-angle X-ray scattering (GISAXS). This technique allows the determination of the shape of the grains, their size and size distribution as well as the distances between the grains without any sample preparation. Furthermore, due to the much larger probe area defined by the spot size of the X-rays on the sample surface, the data have excellent sampling statistics, and we thus studied UNCD films with GISAXS [2]. For the analysis of the GISAXS data, information about the scattering length density (SLD) and the surface roughness of the UNCD film are required. Both parameters were determined independently by X-ray reflectometry (XRR) measurements.

An undoped UNCD film with homogeneous film thickness of 3.8 µm was deposited on pre-cleaned (2 cm × 3 cm) cm² Si(001) substrates by using a modified hot filament technique with a precursor gas mixture of pure CH₄ and H₂. To obtain a plane sample, the substrate temperature had to remain in the range of 760-770°C all along the diamond growth process. XRR measurements were carried out using a D5000 diffractometer (Siemens). The XRR curve was fitted with a model of a homogeneous film on a substrate. This way, the surface roughness as well as the scattering length density and the absorption of the film were determined. GISAXS measurements were performed at beamlines BW4 and P03, both at HASYLAB, DESY, Hamburg. As detectors, a MarCCD camera or PILATUS 300k were used. Incident angles αᵣ were chosen both below and above the critical angles of the UNCD film. All measurements were taken at pristine spots to avoid potential effects of beam damage. The GISAXS images were modelled using the FitGISAXS software [3] which is based on the distorted-wave Born approximation. The scattering length densities and the absorption values measured by XRR were used as input parameters. The diamond nanoparticles were modeled.
as monodisperse spheres of diameter $D$ (Fig. 1). Their correlation within the film plane was approximated as a two-dimensional liquid. As a fitting parameter, the ratio of the centre-to-centre distance between the spheres, $D_{HS}$, and $D$, was used. The hard-sphere volume fraction, $\eta_{HS}$, was fixed at 0.1. Since the refractive index values of all layers are similar, the model "Buried layer" was used, i.e. the spheres are homogeneously distributed between the film surface and a depth of 3 µm, and the refractive index of the matrix of the film matrix was assumed to be equal to the one of the substrate.

Figure 2. (a) Measured GISAXS images at the incident wave vectors having a $z$-component $k_z = 0.239$ nm$^{-1}$. The blue lines parallel to $q_y$ denote the regions over which was integrated to obtain the profiles in (c). (b) Corresponding simulated image and (c) intensity profile (black circles) and model curve (red line).

A representative 2D image is shown in Fig. 2a. Intensity maxima are visible at $q_y = 0.28$-0.36 nm$^{-1}$ which have a round shape and extend from the horizon to higher $q_z$ values. Their intensity decays towards high $q_z$ values due to the scattering geometry in grazing incidence. These maxima are caused by the scattering from the diamond nanocrystallites which have an electron density different from the surrounding amorphous matrix and a certain average distance from each other. The model resulted consistently in the 2D image showing scattering of similar shape as the experimental one (Fig. 2b). The sphere diameter, $D$, and the average centre-to-centre distance of the spheres, $D_{HS}$, were determined from 1D line profiles summed over a stripe narrow in $q_z$ and extending along $q_y$ (Fig. 2c). It is positioned such that it includes the region of strong intensity at $q_z = 0.4$-0.5 nm$^{-1}$, depending on $k_z$. In these profiles, the $q_y$ positions and the peak heights were matched by varying the parameters. At this, the increasing intensity towards $q_y = 0$ was not taken into account. Then, the 2D GISAXS image was generated and the overall shape of the intensity maxima in the 2D images was verified. This procedure resulted for all images in $D = 8.0$-8.5 nm and $D_{HS} = 10.4$-11.9 nm. With these values, the model used describes the 2D images in a satisfactory way. Only at high $q_y$ values (above ca. 0.5 nm$^{-1}$), the model curve decays too steeply. This may be due to the monodisperse approximation. Moreover, the TEM images from similar UNCD samples suggest that the crystallites are slightly elongated with a random orientational distribution. Such a distribution can, however, not be modelled in the present version of the FitGISAXS software.

We conclude that the diamond crystallites are close to spherical and do not touch each other but there is a minimum distance between them of 2-4 nm. GISAXS gave statistically relevant information in a non-destructive way.

References