

# APPLICATIONS BULLETIN

## Mechanical properties of ultrananocrystalline diamond (UNCD) films with an influence of the nucleation density on the structure

### //// Introduction

Diamond is the hardest of all known single phase materials, with hardness values around 100 GPa, depending on the crystalline direction. The hardness values reported for polycrystalline diamond (PCD) films are in the range of 80 – 100 GPa, i.e. rather close to the single crystalline values.

The same is true even for nanocrystalline (NCD) and ultrananocrystalline diamond (UNCD) films, for which hardnesses up to 95 GPa have been reported. On the other hand, there is a considerable spread of hardness values for this type of films, but systematic studies on the influence of important deposition parameters, but also of the structure and morphology are missing.

Since UNCD films are a candidate for applications in tribology and biomedicine, it is important to know how the hardness, but also other tribological properties such as adhesion and friction depend on the deposition process and also on other film properties.

In this Application Bulletin we report on the influence of the nucleation density on the morphology of the films, on one hand, and their mechanical and tribological properties, on the other hand. By variation of the amount of ultradisperse diamond powder (3-5 nm) added to the nanocrystalline diamond powder (250 nm) used for the ultrasonic pre-treatment of the silicon substrates, the nucleation density was varied between  $1 \times 10^8$  and  $1 \times 10^{10} \text{ cm}^{-2}$ . Morphology and structure of these films were investigated by atomic force microscopy and scanning electron microscopy, the mechanical and tribological properties by Nanoindentation and Nano Scratch tests.

### //// Deposition set-up and conditions

Ultrananocrystalline diamond/amorphous carbon (UNCD/a-C) composite films were prepared by microwave plasma chemical vapor deposition (MWCVD) from 17%  $\text{CH}_4/\text{N}_2$  mixtures in a deposition set-up described in details elsewhere. The experiments were performed at a substrate temperature of 600 °C, a working pressure of 22 mbar, and a MW plasma input power of 800 W; the duration of the deposition process was 390 min. The films were grown onto monocrystalline (100) silicon wafers, etched in  $\text{NH}_4\text{F}/\text{HF}$  and then pre-treated ultrasonically in a suspension of diamond powder in n-pentane to enhance the nucleation density. The pretreatment suspension always contained 50 mg of NCD powder with a mean grain size of 250 nm, to which variable amounts (up to 80 mg) of ultradisperse diamond (UDD) powder with a mean grain size 3–5 nm were added.

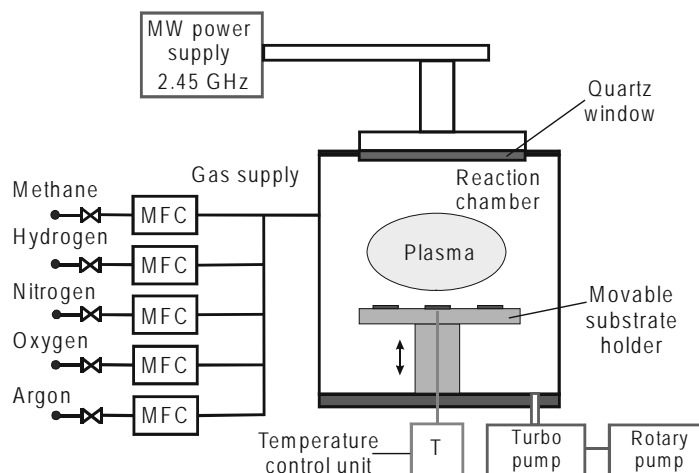


Fig. 1. Deposition principle

Working pressure: 22 mbar	$\text{CH}_4$ concentration: 17 %
Substrate temperature: 600 °C	$\text{CH}_4/\text{N}_2$ flow rate ratio: 1:5
Input MW power: 800 W	Deposition time: 390 min

### //// Morphology and Topography

The UNCD/a-C films deposited under the conditions described above have been comprehensively characterized with respect to their crystallinity, composition and bonding structure. Irrespective of their different morphology (individual nodules or closed uniform films) as discussed below, they are composed of diamond nanocrystallites with sizes of 3–5 nm as determined by XRD, which are embedded in an amorphous carbon matrix.

The ratio of the volume fraction of the two phases is close to unity. Investigations of the films with Raman spectroscopy, XPS and AES showed the presence of  $\text{sp}^2$ -bonded carbon atoms (up to 15 at. %). Although no  $\text{H}_2$  was added in the precursor gas mixture, the UNCD/a-C films contain about 8–9 at.% H in depth, as revealed by nuclear reaction analysis, originating from the  $\text{CH}_4$  molecules and bonded predominantly in the form of  $\text{sp}^3\text{-CH}_x$  groups.

In the present work the morphology of the UNCD/a-C films was studied by SEM. The films deposited on substrates pre-treated only with NCD powder (without UDD powder) are composed of individual nodules (Fig. 2 (a)) with a diameter of 700–800 nm, from which a nucleation density on the order of  $1\text{--}3 \times 10^8$

cm<sup>-2</sup> was determined. The addition of 25 mg UDD powder to the pretreatment suspension results in an increase of the nucleation density by more than one order of magnitude (ca. 4.5×10<sup>9</sup> cm<sup>-2</sup>). As a consequence the diameter of the nodules decreases down to 130-170 nm, the film possesses a column like structure with some voids present at the interface with the Si substrate (Fig. 2 (b)). For a mixture with 50 mg UDD powder the nucleation density increases further to about 6.5×10<sup>9</sup> cm<sup>-2</sup>; also in this case the growth has started from individual nucleation sites until the growing nodules coalesced to form a closed film leaving some voids at the interface (Fig. 2 (c)). Finally, the pretreatment with 80 mg UDD powder results in a nucleation density on the order of 1×10<sup>10</sup> cm<sup>-2</sup>, which reduces the time necessary to obtain a continuous film (Fig. 2 (d)). AFM investigations revealed that once the films are closed the topography and the rms roughness (on the order of 9-13 nm) are independent on the nucleation density. The surface consists of rounded features which in almost all cases are agglomerates of smaller substructures.

### > Morphology: Scanning Electron Microscope (SEM)

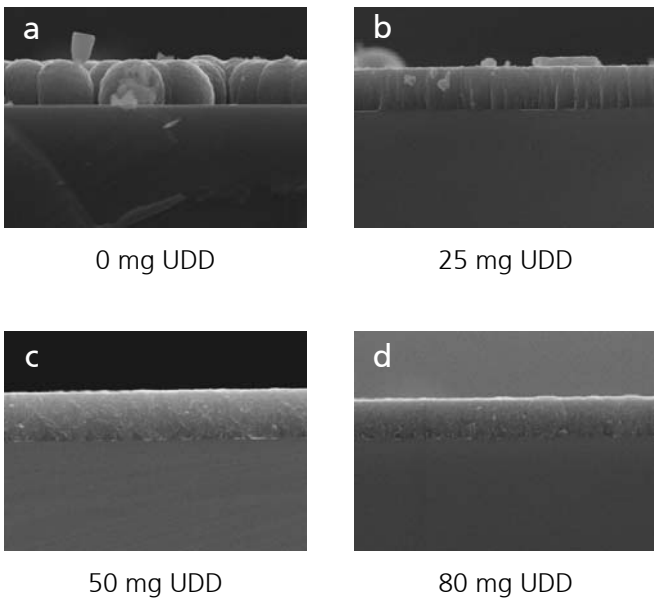
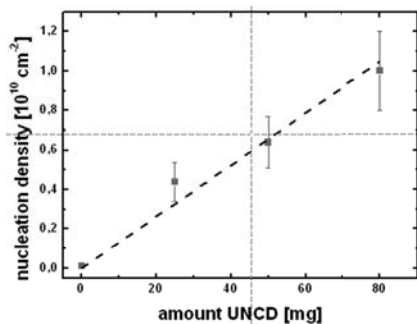
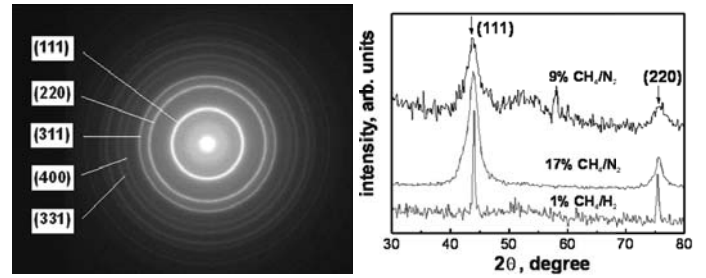


Fig. 2. Cross-section SEM images of UNCD/a-C films on Si substrates pre-treated without (a) or with the addition of (b) 25 mg UDD powder, (c) 50 mg UDD powder, and (d) 80 mg UDD powder.

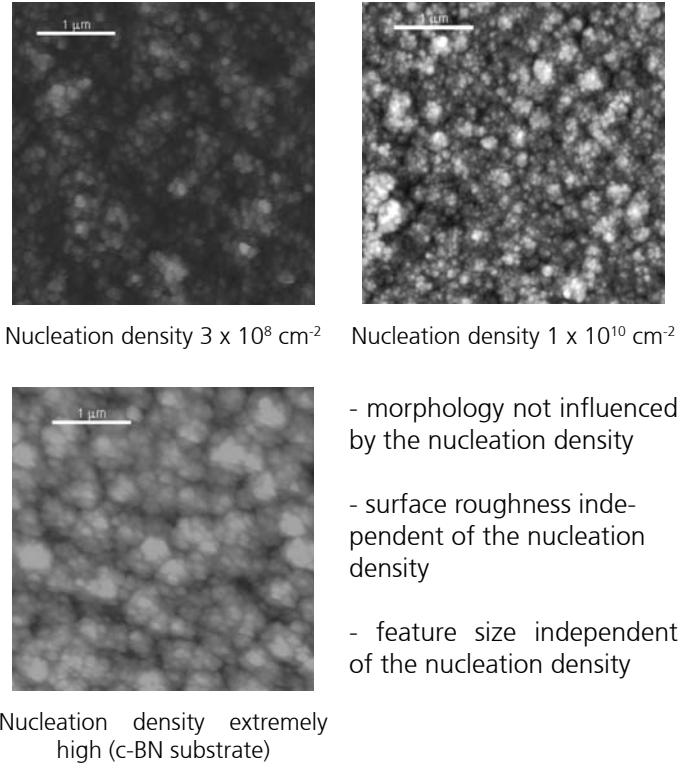


- nucleation density increases with the amount of UDD powder
- development from individual nodules to closed films
- the higher the nucleation density the sooner the films are closed
- in all cases voids present at interface

### > Crystallinity



### > Topography: Atomic force microscopy (AFM)



- morphology not influenced by the nucleation density
- surface roughness independent of the nucleation density
- feature size independent of the nucleation density

### //// CSM Nano Platform

To perform all mechanical measurements we use the CSM Nano Platform. (Open platform with Nano Scratch head, Nanoindentation module, Atomic Force Microscope and High Quality Optical Microscope (Fig. 3)).

Multiple testing and imaging modules are installed together on the same platform. All measurement and imaging modules are "Positionally Synchronised" to each other, the optical microscope being included as a standard module on the platform.

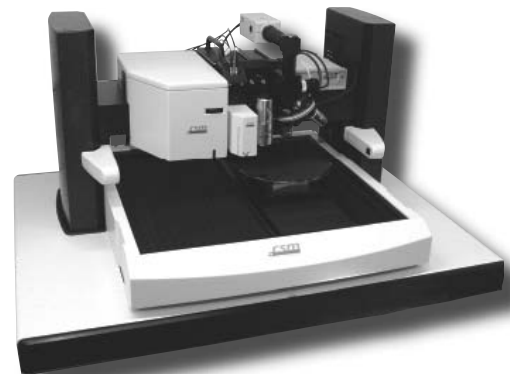


Fig. 3. CSM Nano Platform

## //// Advanced Mechanical Testing

Our previous mechanical studies with UNCD/a-C films with a nodule structure deposited at a higher substrate temperature (770 °C) showed that the interaction of the indenter with the film in most of the cases resulted in removal of individual nodules due to the discontinuous morphology. On the other hand when the indenter is directed to the top of the nodules, the mechanical properties determined are very similar to those of the closed films. In the present investigation only the closed UNCD (25), UNCD (50) and UNCD (80) films were subjected to mechanical measurements with respect to their nanoindentation and adhesion.

### > Nanoindentation

All nanoindentation measurements yielded reproducible and comparable results with typical load/displacement curves as shown in Fig. 4.

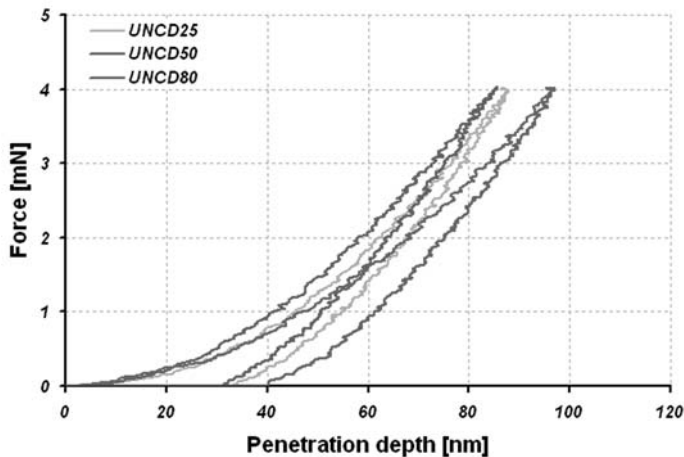


Fig. 4. Typical load/displacement curves of UNCD/a-C films on Si substrates pre-treated with different amounts of UDD powder.

In all measurements the penetration depth was limited at 4 mN (approximately 90 nm of penetration) to minimize the influence of the substrate. The Instrumented Hardness  $H_{IT}$  and the Elastic modulus  $E_{IT}$  were calculated using the Oliver & Pharr method; for all UNCD/a-C films under investigation they were in the ranges of 25–28 GPa and 262–271 GPa, respectively (Fig. 5). The elastic recovery was estimated from the maximum and the residual penetration depths to be on the order of 62–65%. On a first view the values of  $H_{IT}$  and  $E_{IT}$  found for our UNCD/a-C films seem to be rather low in comparison not only with diamond, but also with PCD, NCD and other UNCD films.

These results can only be explained by the presence of the amorphous carbon matrix, which forms roughly one half of the material. On the other hand, for many mechanical or tribological applications not the hardness but rather the toughness is decisive. It has been shown that nanocomposites consisting of a hard or superhard nanocrystallites embedded in an amorphous matrix can add considerable toughness without losing too much of the hard character. The values of  $H_{IT}$  and  $E_{IT}$  for UNCD/a-C films under investigation deposited at 600 °C are a little bit lower than those of the films prepared at 770 °C.

This may be caused by the slightly increased fraction of the matrix and reduced density due to the lower deposition temperature. But the reduced film thickness (1  $\mu\text{m}$  instead of 4  $\mu\text{m}$ ) may also have contributed to this decrease of  $H_{IT}$  and  $E_{IT}$ .

In this context it should be noted that for a 1  $\mu\text{m}$  thick UNCD/a-C film deposited onto a polycrystalline diamond film at 600 °C higher values of  $H_{IT}=33.7\pm 4.1$  GPa and  $E_{IT}=362\pm 49$  GPa have been observed.

The Nanoindentation Tester was verified according to the ISO 14577 by measurements on fused silica; the elastic modulus determined was  $71.3 \pm 1.7$  GPa, very close to the theoretical value of  $72 \pm 2$  GPa.

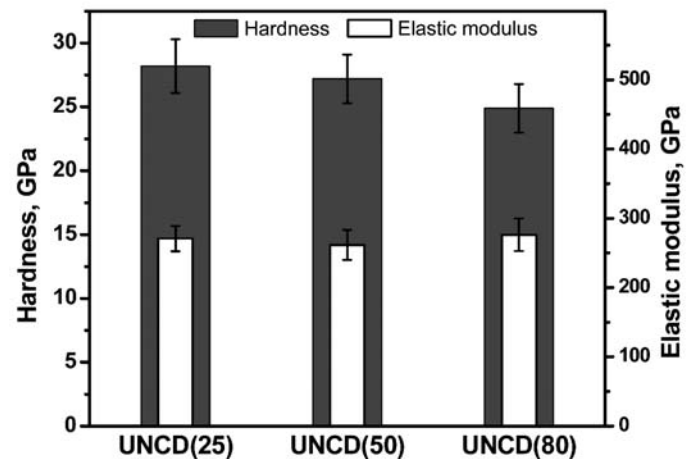


Fig. 5. Hardness and elastic modulus of UNCD/a-C films on Si substrates pre-treated with different amounts of UDD powder.

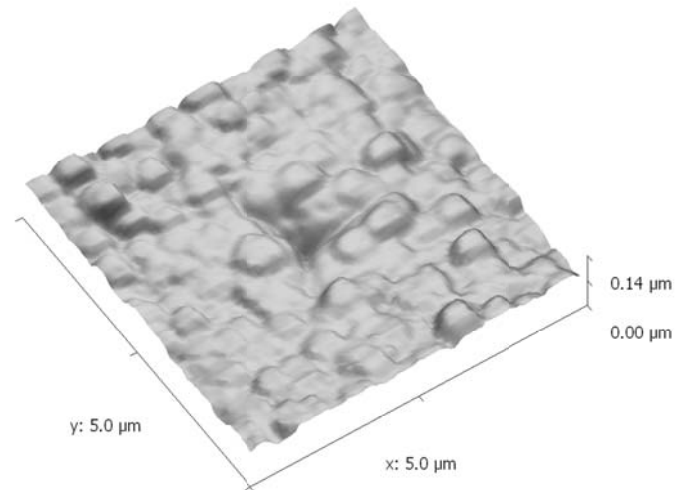


Fig. 6. AFM image of Nanoindentation on UNCD 25 sample.

### > Scratch Testing

For the Nano Scratch Tests (NST, CSM Instruments), a spheroconical scratch indenter with a radius of 5  $\mu\text{m}$  and an angle of 90° was used. Three scratch tests on each sample were performed from 0.05 mN to 300 mN with a 6 mm scratch length, the loading rate was 600 mN/min at a scanning speed 6 mm/min.

The critical loads for full delamination were determined from the recorded normal force, frictional force and penetration depth curves along the scratch; the respective images have also been taken (Figs. 7-9).

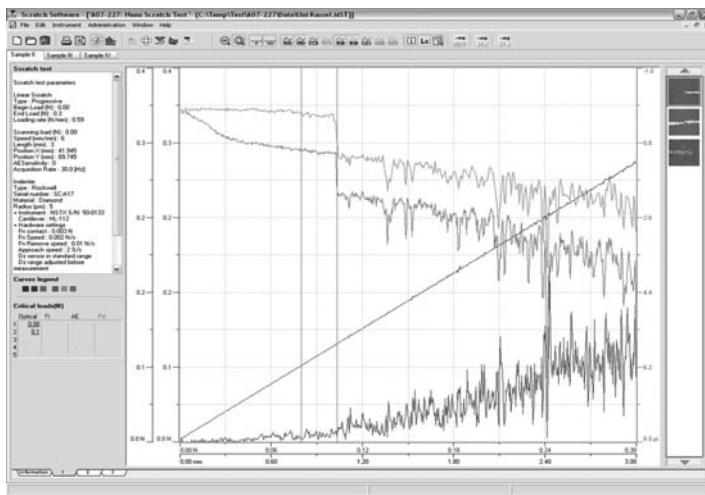


Fig. 7. Nano Scratch datas of UNCD 25 sample.

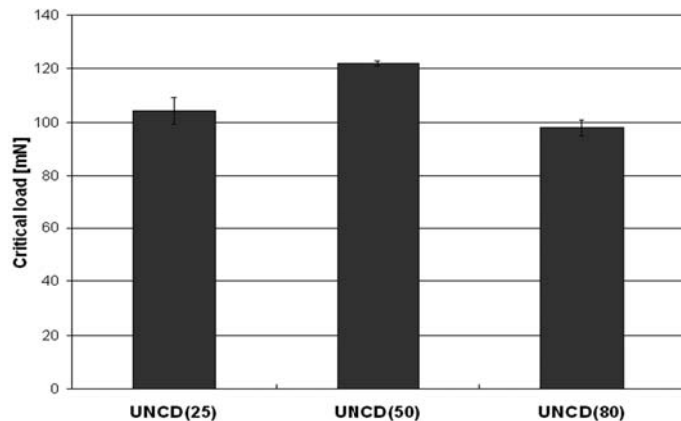


Fig. 8. Critical forces for delamination of UNCD/a-C films on Si substrates pre-treated with different amounts of UDD powder.

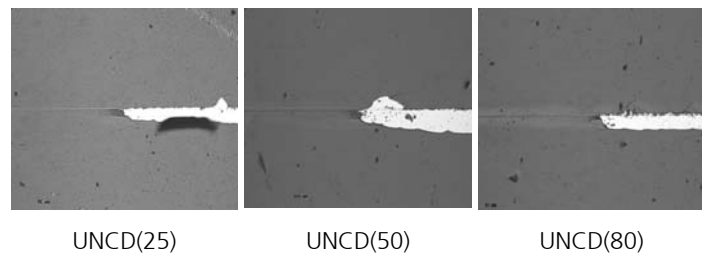


Fig. 9. Comparison of the optical critical load.

A typical 3-D image of the resulting scratch is shown in Fig. 10. Four different parts can be distinguished alongside the scratch: (i) no penetration of the indenter in the UNCD/a-C film, (ii) increase of the penetration depth and beginning of the delamination, (iii) full delamination of the films, and (iv) damage of the silicon substrate.

Once it occurred, the delamination is not restricted to the width of the scratch, but took place in larger areas with a semicircular shape with a diameter of over 20 µm. For all samples the normal load at which the full delamination takes place, i.e. the critical force, was determined (Fig. 8). As can be seen from the figure, no distinct influence of the nucleation density on the adhesion of the closed UNCD/a-C films on Si could be observed.

However, in all case in those areas where full delamination had occurred, the underlying silicon substrate is severely damaged, proving the protecting nature of the UNCD/a-C coatings.

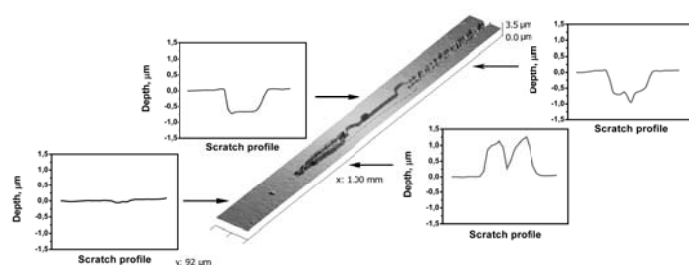


Fig. 10. 3-D image of a 1 mm long scratch on UNCD/a-C film created with a nanoscratch tester. The profiles correspond to the four cases described in the text.

### /// Conclusions

Ultrananocrystalline diamond / amorphous carbon composite films were prepared by MWCVD from CH<sub>4</sub>/N<sub>2</sub> mixtures on silicon substrates after different pre-treatments. The addition of ultradisperse diamond powder to the pre-treatment suspension increases the nucleation density by two orders of magnitude. As a result the morphology of the coatings changes from individual nodules to closed and uniform films.

The nucleation density, however, has no distinct influence on the mechanical properties, like microhardness, elastic modulus and adhesion, of the closed films. The presence of amorphous matrix in the composite films although reducing the hardness may be of advantage by improving their toughness and can help to prevent fatal brittle failure. The results of the nano scratch tests reveal the protecting nature of the coatings on the underlying substrate.

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This Applications Bulletin is published quarterly and features interesting studies, new developments and other applications for our full range of mechanical surface testing instruments.

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