CSM Instruments
Advanced Mechanical Surface Testing

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 x 10^8 and 1 x 10^{10} 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% CH_4/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 NH_4F/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.

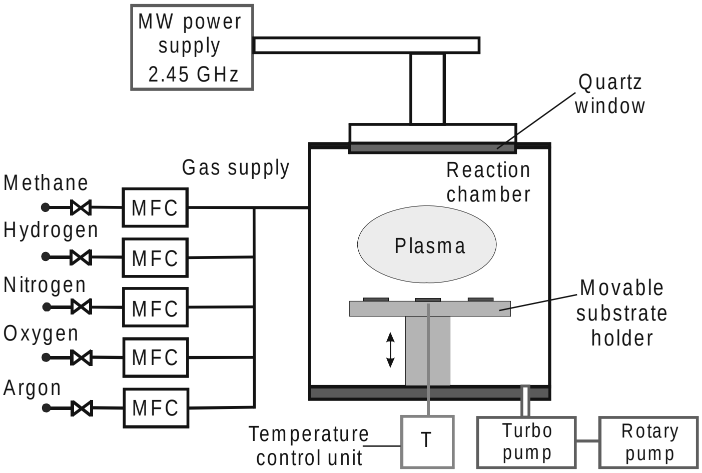


Fig. 1. Deposition principle

Working pressure: 22 mbar	CH_4 concentration: 17 %
Substrate temperature: 600 °C	CH_4/N_2 flow rate ratio: 1:5
Input MW power: 800 W	Deposition time: 390 min

//// Morphology and Topography

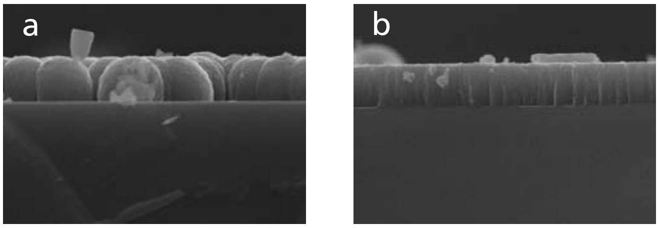
The UNCD/a-C films deposited under the conditions described above have been comprehensively characterized with respect to their crystallinity, composition and bonding structure. Irrespective of their different morphology (individual nodules or closed uniform films) as discussed below, they are composed 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 sp^2-bonded carbon atoms (up to 15 at. %). Although no 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 CH_4 molecules and bonded predominantly in the form of sp^3-CH_x groups.

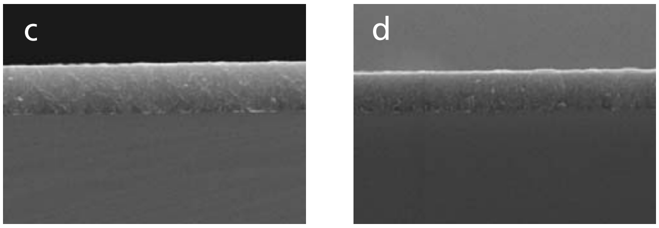
In the present work the morphology of the UNCD/a-C films was studied by SEM. The films deposited on substrates pre-treated only with NCD powder (without UDD powder) are composed of individual nodules (Fig. 2 (a)) with a diameter of 700–800 nm, from which a nucleation density on the order of 1–3×10^8

cm^{-2} 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^{9} cm^{-2}). 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^{9} cm^{-2}; 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^{10} cm^{-2}, 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)

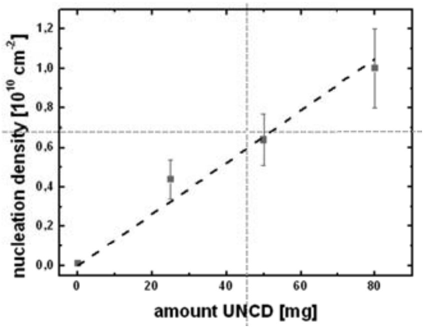


0 mg UDD 25 mg UDD



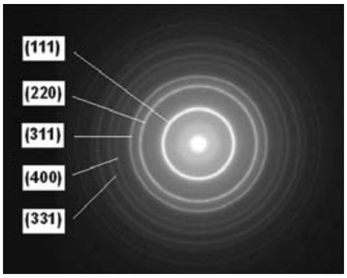
50 mg UDD 80 mg UDD

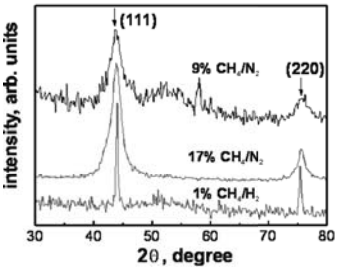
Fig. 2. Cross-section SEM images of UNCD/a-C films on Si substrates pre-treated without (a) or with the addition of (b) 25 mg UDD powder, (c) 50 mg UDD powder, and (d) 80 mg UDD powder.



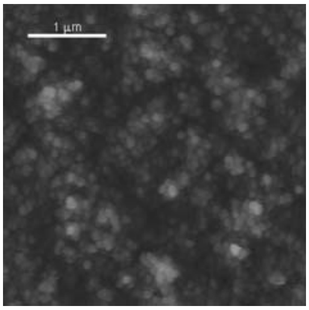
- nucleation density increases with the amount of UDD powder
- development from individual nodules to closed films
- the higher the nucleation density the sooner the films are closed
- in all cases voids present at interface

> Crystallinity

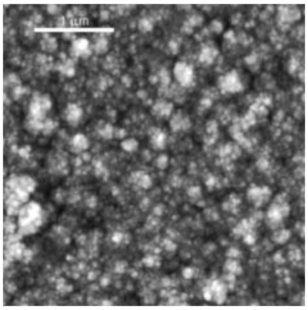




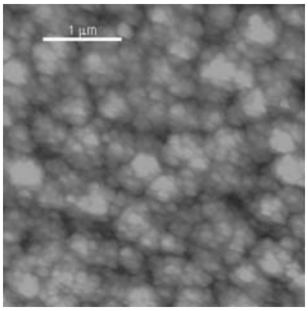
> Topography: Atomic force microscopy (AFM)



Nucleation density 3 x 10^{8} cm^{-2}



Nucleation density 1 x 10^{10} cm^{-2}



Nucleation density extremely high (c-BN substrate)

- 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.

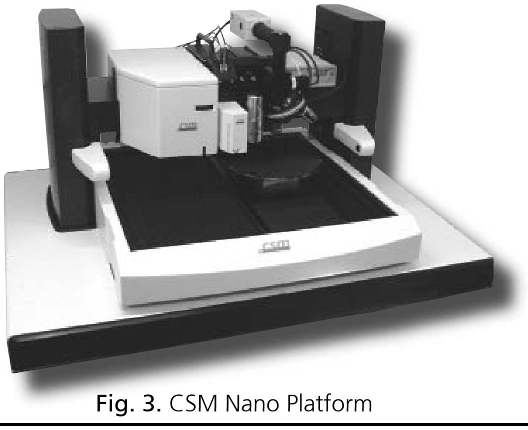


Fig. 3. CSM Nano Platform

//// 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.

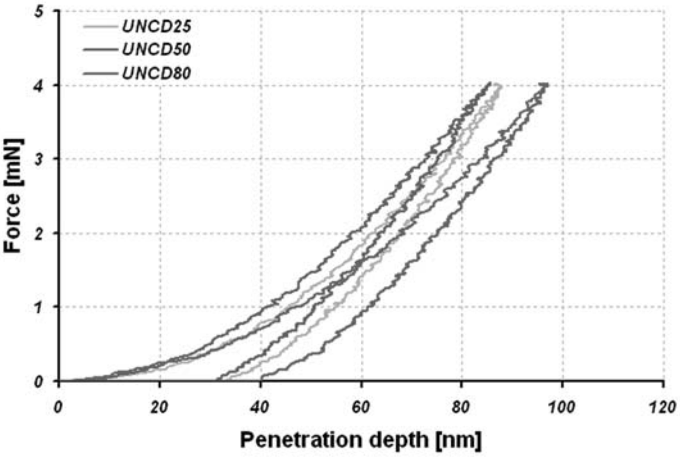


Fig. 4. Typical load/displacement curves of UNCD/a-C films on Si substrates pre-treated with different amounts of UDD powder.

In all measurements the penetration depth was limited at 4 mN (approximatively 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 loosing 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 µm instead of 4 µm) may also have contributed to this decrease of H_{IT} and E_{IT}.

In this context it should be noted that for a 1 µm thick UNCD/a-C film deposited onto a polycrystalline diamond film at 600 °C higher values of H_{IT}=33.7±4.1 GPa and E_{IT}=362±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 ± 1.7 GPa, very close to the theoretical value of 72 ± 2 GPa.

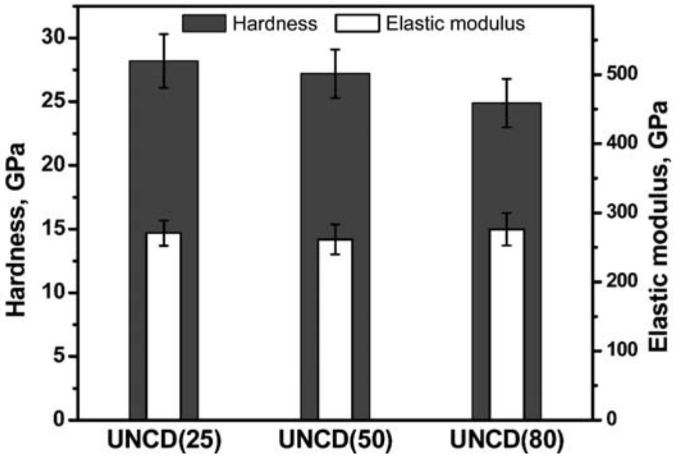


Fig. 5. Hardness and elastic modulus of UNCD/a-C films on Si substrates pre-treated with different amounts of UDD powder.

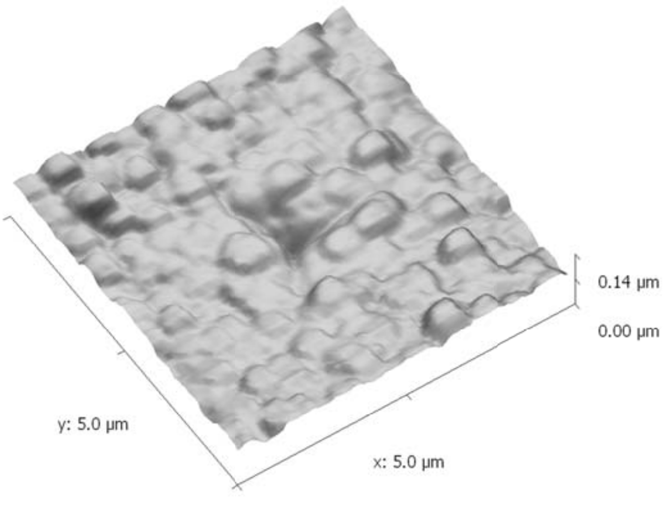
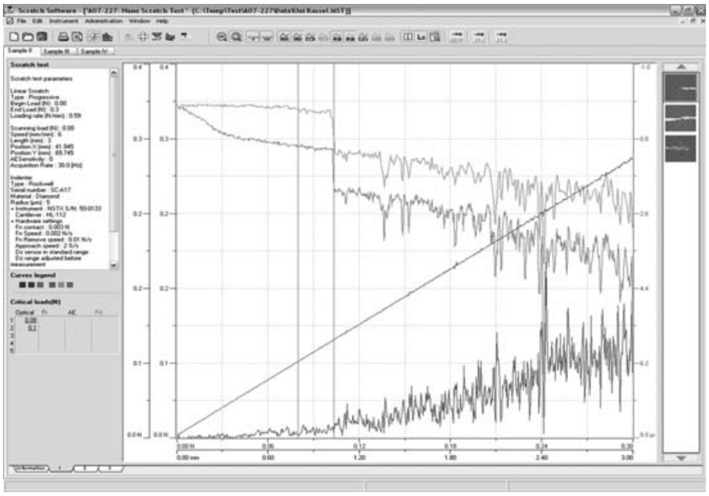


Fig. 6. AFM image of Nanoindentation on UNCD 25 sample.

> Scratch Testing

For the Nano Scratch Tests (NST, CSM Instruments), a sphero-conical scratch indenter with a radius of 5 µm 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).



Scratch test

Scratch test parameters

Linear Scratch
Type : Progressive
Begin Load (N) : 0.00
End Load (N) : 0.3
Loading rate (N/min) : 0.59

Scanning load (N) : 0.00
Speed (mm/min) : 6
Length (mm) : 3
Position X (mm) : 41.945
Position Y (mm) : 89.745
AE Sensitivity : 0
Acquisition Rate : 30.0 [Hz]

Indenter
Type : Rockwell
Serial number : SC-A17
Material : Diamond
Radius (µm) : 5
+ Instrument : NSTX S/N: 50-0133
Cantilever : HL-112
+ Hardware settings
Fn contact : 0.003 N
Fn Speed : 0.002 N/s
Fn Remove speed : 0.01 N/s
Approach speed : 2 %/s
Dz sensor in standard range
Dz range adjusted before measurement

Critical loads(N)

	Optical	Ft	AE	Fn
1	0.00			
2	0.2			
3				
4				
5				

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

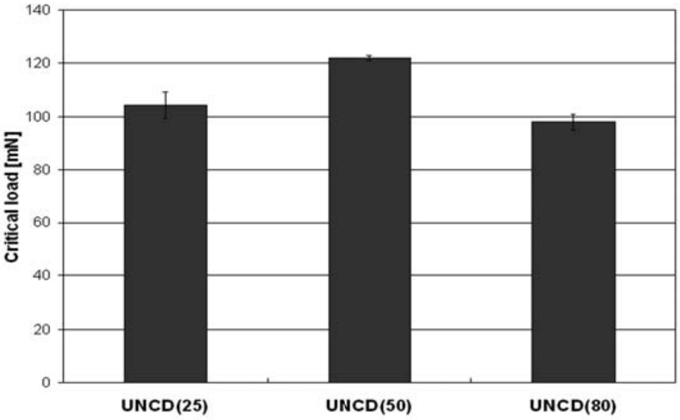


Fig. 8. Critical forces for delamination of UNCD/a-C films on Si substrates pre-treated with different amounts of UDD powder.

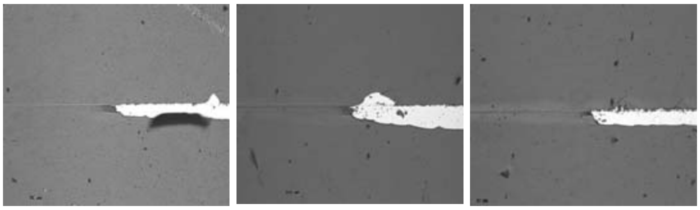

UNCD(25) UNCD(50) UNCD(80)

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 underlaying silicon substrate is severely damaged, proving the protecting nature of the UNCD/a-C coatings.

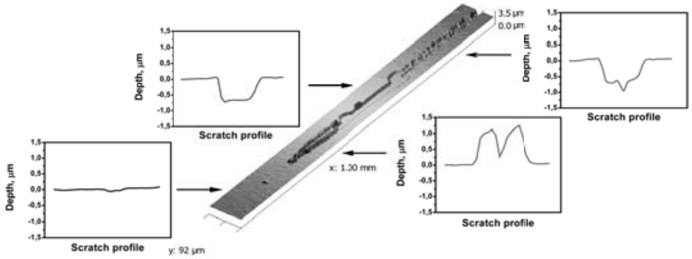


Fig. 10. 3-D image of a 1 mm long scratch on UNCD/a-C film created with a nanoscratch tester. The profiles correspond to the four cases described in the text.

//// Conclusions

Ultrananocrystalline diamond / amorphous carbon composite films were prepared by MWCVD from CH_4/N_2 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 underlaying substrate.

//// Acknowledgments

The authors wish to express their sincere gratitude to:

Dr. W. Kulisch (European Commission Joint Research Centre, Institute for Health and Consumer Protection, Ispra, Italy)

Prof. J.P. Reithmaier (Institute of Nanostructure Technologies and Analytics, University of Kassel, Germany)

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

Editor Dr. Cyril POPOV (University of Kassel, Germany)
M. Gregory FAVARO (CSM Instruments SA)

Should you require further information, please contact:

CSM Instruments
Rue de la Gare 4
CH-2034 Peseux
Switzerland

Tel: + 41 32 557 5600
Fax: +41 32 557 5610
info@csm-instruments.com
www.csm-instruments.com

621011.08 v1 CSM Instruments / Printed in Switzerland