Sputter characteristics of carbon-carbon compound material *

R. Deltschew, M. Tartz, V. Plicht, E. Hartmann, H. Neumann
Institut für Oberflächenmodifizierung e.V. (IOM)
Permoserstr. 15, D-04318 Leipzig, Germany
Tel: +49 341 235 3615 Fax: +49 341 235 2584
e-mail: deltsche@rz.uni-leipzig.de

H. J. Leiter
Astrium GmbH, Space Infrastructure,
PF 80 11 69, D-81663 München, Germany

J. Esch
Schunk Kohlenstofftechnik GmbH
Rodheimer Straße 59, D-35452 Heuchelheim, Germany

IEPC-01-118

Because of the growing interest in carbon-carbon compound materials as an extraction grid material the sputter behaviour under xenon bombardment was studied and compared with that of conventional high-density graphite. The sputter yield of carbon-carbon exceeds that of graphite, which is an effect of the pronounced macroscopic surface structure.

1. Introduction

The physico-chemical behaviour of carbon composite materials is, among others, of great relevance for spacecraft applications as a thermal shielding [1] and as an ion thrusters extraction grid material [2, 3, 4].
In gridded ion thrusters, grid eroding processes always take place leading to a gradually damage of the grids and a limited lifetime of the thruster. In addition to the primary ions neutrals can escape from the plasma chamber, providing a neutral density within the grid system. Additionally, neutrals from the residual gas in the vacuum chamber may add to this neutral density. In a charge-exchange process, a primary ion collides with a neutral, converting the ion into a neutral and the former neutral into an slow ion. If this ion is born within the grid system or in its very vicinity, it may be accelerated towards one of the grids. Because of the gained energy, the ion impact will sputter some material from the grid. A detailed investigation showed that most of the charge-exchange ions impinge on the inside of the accelerator grid holes, widening the holes during the operation [5].
Since the sputter yield of the grid material directly influences the erosion rate and, hence, the grid lifetime, it is indispensable to determine the sputter yield in dependence on the energy and angle of incidence for promising grid materials. The obtained sputter characteristics allow to assess the applicability of the respective grid material. Furthermore, on the basis of these data, the grid erosion simulation can predict reliable erosion rate and lifetime values.
The sputter yield can be simulated employing the well known formulas from Bohdansky for the energy dependence and the Yamamura formula which describes the angular dependence of the sputter yield (for a detailed description, see [5] and refs. cited therein).
Commonly, carbon and molybdenum are preferred as grid material. Carbon is widely used because of its low sputter yield and low thermal expansion coefficient. Because of the extraordinary mechanical and thermal properties the carbon-carbon composite material (CC) increasingly becomes important for ion thruster grid systems. Unfortunately, up to now only sparse sputter data are available for xenon incident on carbon. In case

* Presented as Paper IEPC-01-118 at the 27th International Electric Propulsion Conference, Pasadena, CA, 15-19 October, 2001.
Copyright © 2001 by IOM. Published by the Electric Rocket Propulsion Society with permission.

of CC no any sputter experiences have been accumulated so far.
In order to meet the conditions of thruster applications, the present paper reports on sputter yields for low energetic (≤1 keV) xenon ion impact on CC and high density graphite, which is typical for ion thruster operation. Owing to its relevance to sputter behaviour, the evolution of the surface topography was determined by SEM techniques.

2. Experimental setup

The experiments were performed within a UHV chamber which was evacuated by a turbo pump to a background pressure of less than 10^{-8} mbar. As a result of the xenon gas flow through the sputter ion source the process pressure increased up to $3*10^{-5}$ mbar. Before the experiments the chamber was baked out and the residual gas composition was permanently controlled with the aid of a mass spectrometer. During the sputtering process the oxygen partial pressure was about 7 orders of magnitude lower than that of the ion source working gas xenon. Under such conditions additional chemical etching does practically not occur.
The xenon ion beam is produced by an ISQ 40 RF ion source as developed in our institute [6]. A low divergence focusing two-grid extraction system (3 cm beam diameter) was used in order to apply a high ion current density on the target.
The sputter targets were placed in the beam centre at a distance of 10 cm from the accelerator grid. An aperture in front of the target restricted the irradiated area to 1 cm^2. The duration of the sputter experiments was between one half and 7 hours. The targets could be tilted against the beam direction. The sputter yield was estimated from the weight loss, employing a high-precision microbalance with a precision of 10 µg. Typically, the specific mass loss was larger than 0.16 mg/h so that the change in target mass could be determined with sufficient accuracy.
The roughness of the graphite samples was determined by atomic force microscopy (AFM) in contact mode. Because of irregular textures the AFM measurements failed to work for the CC samples. Therefore the surface topography of CC was studied by scanning electron microscopy (SEM).

3. Sputter Materials

There are two basic modifications of carbon [7]. Diamond (sp^3 hybridisation) has a tetrahedral arrangement of the carbon atoms and, therefore, features an extreme hardness. The graphite (sp^2 hybridisation) modification consists of layers of hexagonal packed carbon atoms. This modification possesses a low thermal expansion, good corrosion stability and a low well-defined mass density of 2.2 g/cm^3.
Carbon black may be formed by incomplete burning of carbon-containing substances. It is polycrystalline with very irregular substructures.
Outstanding properties of materials like high stiffness and flexibility over large areas with low specific weight and high thermal stability cannot be reached by a homogeneous material. Instead, this may be attained in composite materials where small particles of a hard material are embedded within a matrix which do not react to one homogeneous phase.
The mechanical properties are determined from both components. The small particles mainly define the solidity and stiffness of the compound material, the matrix gives its elasticity and the thermal and electric conductivity. Furthermore, the matrix protects the framework against damage.
While graphite due to its low sputter yield is now a well-approved material for ion extraction grids, the interest in CC composites is continuously growing in recent

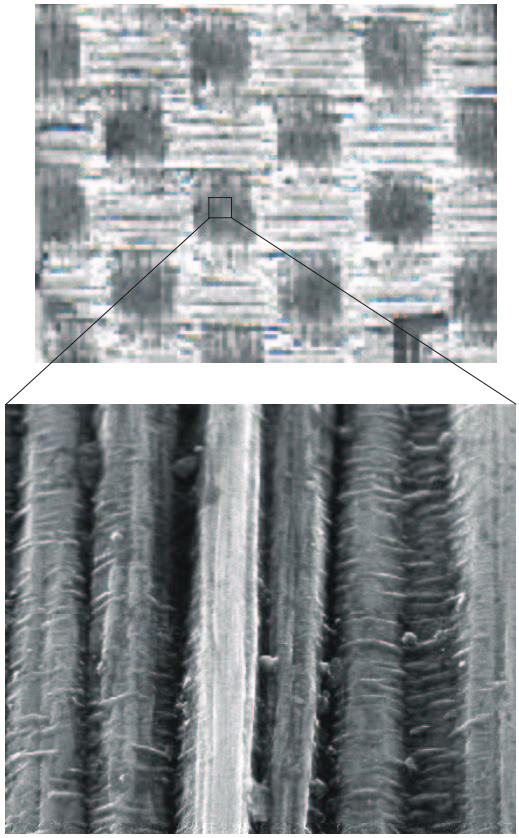

Figure 1. Surface topography of the Carbon-Carbon samples.

years. That is why both materials were considered in this study.
The graphite sputter targets were prepared from high-density graphite PT 2120 (Carbone Lorraine) with a purity better than 5 ppm.
In the CC material (Schunk Kohlenstofftechnik GmbH) which was used in this study, carbon fibres based on PAN (polyacrylnitrile) are embedded in a reinforced amorphous carbon matrix. The textile carbon structures, consisting of about 3000 filaments, are biaxial woven (Satin-1.4) (see figure 1). Therefore, the CC surface shows a regular structure of parallel fibre bundles. The carbon material undergoes a final high-temperature treatment above 2500°C. The purity is better than 5 ppm. The CC samples were used as received from the fabrication without any further processing.

4. Results

4.1 Normal incidence

Figure 2 depicts the energy dependent sputter yield at normal ion incidence in comparison with available experimental [8, 9] and theoretical data [5]. While the sputter yield of graphite is in a rather good agreement with the reference data, the sputter yield of CC always exceeds that of graphite by a factor up to 2. This difference is higher at lower ion energy.
This difference can be traced back to the regular macroscopic structure of the CC samples. Approximately, the surface consists of numerous parallel cylinders. Figure 3 shows the actual distribution of the angle of incidence at normal ion impact, with the mean angle amounting 47°. By integrating the angular distribution with the theoretical angular dependence of the sputter yield (see [5]), the resulting sputter yield of the "cylindrical" surface should be greater than that of a plane surface by a factor of 3.1 at 500 eV. This factor decreases with growing ion energy up to 2.3 at 1000 eV in a good agreement with the measured data. The observed difference between the two samples is smaller mainly for three reasons. (i) The used graphite surface is not ideally polished, but has a surface roughness of about 20 nm (for an representative area of 4x4 μm^2) which is quite similar to the micro-roughness of the CC samples. However, the graphite surface does not possess such a pronounced macro-structure as CC. (ii) The CC surface does not represent an ideal cylinder structure but shows flat regions between some of the fibres. Several fibres are deeper embedded in the matrix than others. (iii) The surface structure changes its shape during sputtering and, therefore, the sputter yield will do it in the same manner. The latter aspect will be discussed now in more detail.
Figure 4 demonstrates for a representative structure the evolution of two typical features with the sputter time in accordance with the experiences in ion beam etching [10]. First, the cylindrical structure with circular cross section evolves into a triangular cross section (prism-like shape, see white arrows at bottom of figure 4) as has been simulated in figure 5. Between the fibres a chain of spikes is growing with a width of 1 μm (see the black arrow at bottom of figure 4). Because of the very oblique incidence in this trench the sputter yield tends to fall below its maximum. The direction of the sputtered particles at oblique incidence is not normal to the surface at this point but is tilted in the plane of incidence vector and surface normal [11]. Therefore, the sputtered particles cannot leave the sample when sputtered from the slope of the cylinder, and are deposited between the fibres. Both effects tend to slow down the erosion.

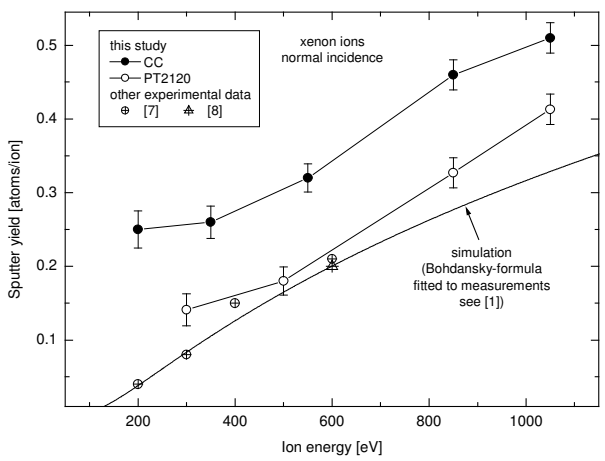

Figure 2. Energy dependence of the sputter yield of Carbon-Carbon and Graphite in comparison to literature data and simulation.

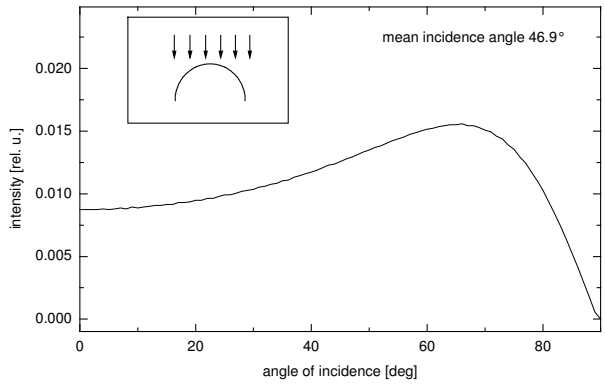

Figure 3: Distribution of the angle of incidence on a cylindrical surface at normal incidence.

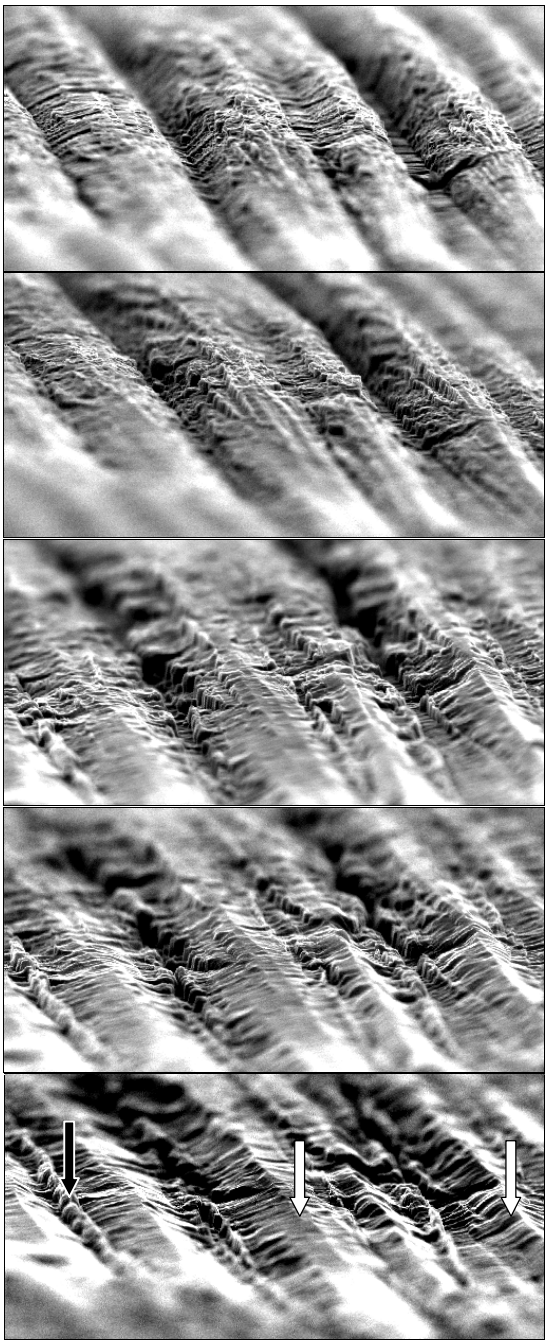

Figure 4: Evolution of the CC surface studied by SEM. Sputter time from top: 0.5 h, 1 h, 1.5 h, 2 h, 2.75 h. Parameter: xenon ion energy 500 eV, normal incidence.

Figure 5 depicts in the bottom the surface after a 4 hours sputtering. The resulting surface structure proves stable until the top fibre layer is largely removed which did not occur on the time scale of the present study. However, the angular distribution of normally incidence ions will retain over a long period, and the sputter yield will remain greater than that of graphite.

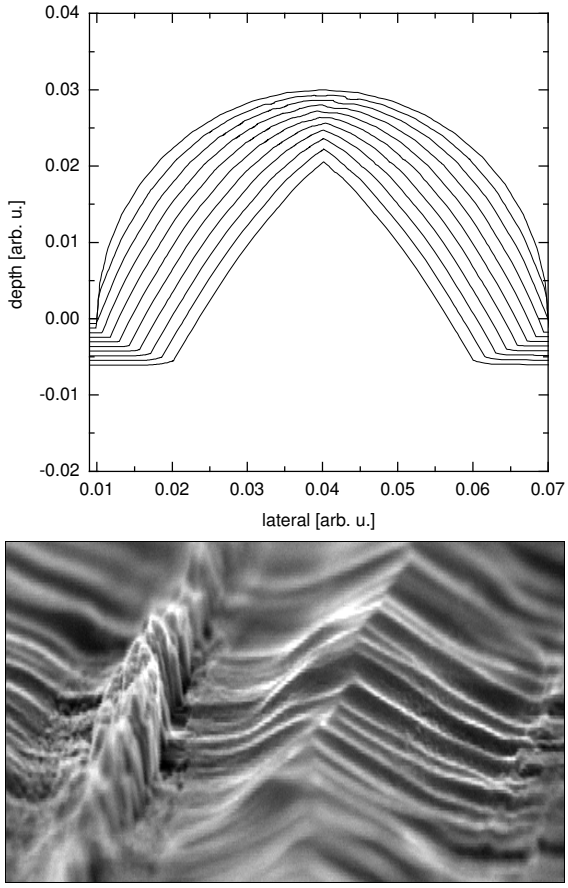

Figure 5 top: Simulation of the evolution of a cylindrical shaped surface following the "method of characteristics" approach by Arnold [10]. Bottom: The structure of a CC-fiber after a 4 hours sputtering at normal incidence with 500 eV xenon ion energy (SEM) showing resulting prism-like structure and spikes between fibers.

In the course of studying the surface evolution the sputter yield was also determined at every break of the sputter experiments. Figure 6 shows the sputter yield of this series of experiments (i.e. the sputter yield obtained from break to break, respectively) in comparison with the yields as determined from continuos sputter experiments without breaks. The rather high sputter yield within the first hour indicates a pronounced influence of oxygen and water which is deposited on the samples during exposure to the atmosphere. Although the layer of water on carbon should be very thin and removed within a few minutes, the porous structure of the CC samples allows water and oxygen to intrude in lower parts, which requires more time to gets removed by desorption. In order to improve the sputter experiment the samples were heated up to 120°C for a half hour before the sputter bombardment started. This leads to a

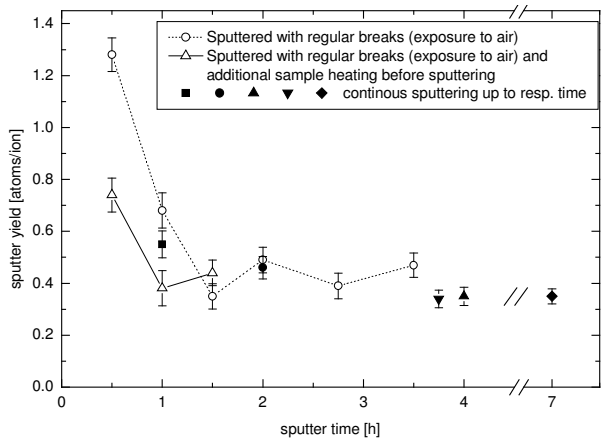

Figure 6: Time-dependence of the sputter yield with and without access to atmosphere.

removal of surface and volume contamination which results in lower sputter yield for this particular short-time experiments (see figure 6). The remaining decrease of the sputter yield during the first hour is traced back to the evolution of the surface structure as discussed above.

As a consequence for the determination of sputter yield a sputter time of more than 4 hours is required to suppress the influence of the run-in phase and desorption. After this time the measured sputter yield is considered as an time-averaged value.

4.2 Oblique incidence

Figures 7 shows the dependence of the sputter yield of CC and graphite on the ion beam incidence angle. Neither for carbon nor for CC angular dependent sputter

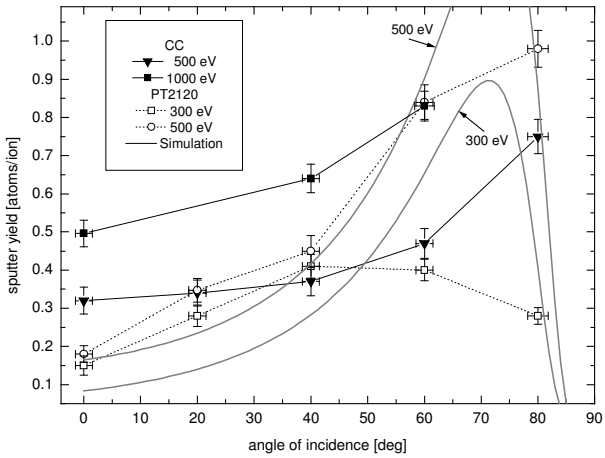

Figure 7: Angle of incidence dependent sputter yield of Carbon-Carbon and Graphite in comparison to simulated data (see [5]).

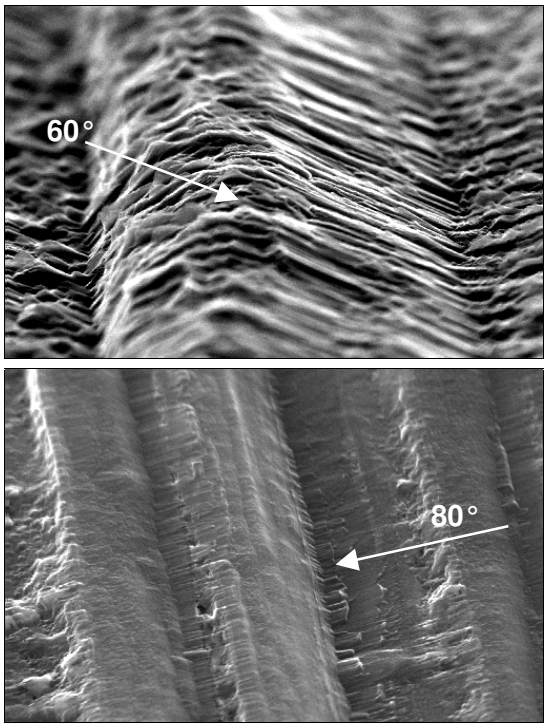

Figure 8: Surface structure of CC under oblique incidence. Parameter: xenon ion energy 500 eV, ion incidence perpendicular to the fibre direction, sputter time 4 hours.

data with xenon ions is available so far to which one can compare the results.

In contrast to the normal incidence, in case of CC the azimuthal incidence angle has now to be taken into account. In all measurements the CC sample was adjusted with respect to the beam so, that the projection of the ion impact vector on the target is either parallel to the cylinder axis or perpendicular to it.

Because of the macroscopic structure of CC the observed angular sputter yield dependence is different to the theoretical sputter yield and that of graphite (PT2120) as shown in figure 7. With varying ion beam incidence angle also the distribution of the target surface incidence angle and the characteristics of redeposition and self-shadowing change.

The surface evolution is strongly affected by the incidence angle, so the resulting stable surface structure depends on the sputter conditions. Figure 8 exemplifies the resulting shapes of single fibres for various ion beam incidence angles in the cross section plane. If the oblique ion impingement is directed parallel to the fibre axis the resulting shapes of the fibres (see figure 9) are similar to that at normal incidence, slightly modified by the addition of the azimuth angle.

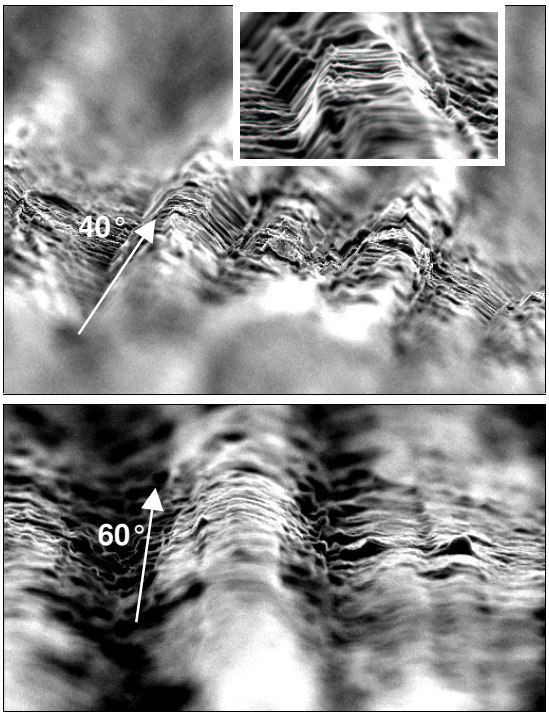

Figure 9: Surface structure of CC under oblique incidence. Parameter: xenon ion energy 500 eV, ion incidence parallel to the fibre direction.

In case of oblique incidence the redeposition rate in the trench between fibres is drastically reduced, and the spikes between the fibres no longer built up.
For oblique incidence the time evolution of the sputter yield has been studied at 500 eV and various incidence angles (figure 10). After the starting phase is over, no significant change in the sputter yield with time could be found. The strong variations of the sputter yield at 80° reflect the rather large effects of measurement errors (low current density and mass, large sensitivity on incidence angle) under these particular conditions.

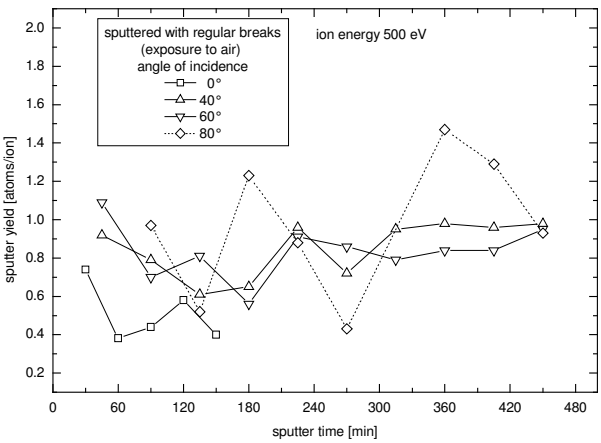

Figure 10: Time-dependence of the sputter yield at oblique incidence.

More effort has to be invested towards a comprehensive sputter characteristics of CC particularly under oblique incidence.

4.3 The hole interior surface

Having in mind that grid erosion occurs preferentially on the inner hole surfaces, the edgewise surfaces of the CC material are actually of greater interest than the top surface. Obviously, the investigation of the edge surface is much more complicated.
Small stripes of CC were slit from the CC sample by laser cutting, which may be one of the suitable processes for drilling the grid holes. Figure 11 shows in the two upper pictures the surface topography before treatment. It consists of cut bundles of fibres and fibres which were cut parallel to their direction. Due to the cutting the surface has partly melted (right in this figure). However, the hole surface will consist of unregular cone structures (i.e. the cut bundles, see top of figure 11) and parts whose structure is similar to that of the sample surface. Therefore, the sputter yield of the hole surface will not significantly differ from that of the sample top surface as discussed before.
For a rough estimation of the sputter yield of the interior surface, the face of the stripe was exposed to the ion beam. Due to the small area, the experimental error is rather large. However, the sputter yield at ion energy of 500 eV and normal incidence was found to be about $0.4 \pm 35\%$ atoms/ion, which is in a good agreement with the data from the sample top surface (figure 2).
The right SEM plot in figure 11 shows the sputtered surface. The "cylinder" area reveals a similar erosion pattern as the sample top surface. However, from the cut fibres surfaces cones develop. Probably, this structure will not be formed at oblique incidence.
Owing the complex sample structure, up to now no prediction can be made on the equilibrium topography of the inner hole surface, particularly not on the observed cones. Furthermore, the required time to reach this equilibrium has to be studied. More experimental effort will be necessary.

6. Conclusions

The sputter behaviour of carbon-carbon composite material has been studied for xenon ion impact energies up to 1 keV at normal and oblique incidence. The sputter yield was found to be greater than that of graphite, which is the result of the pronounced surface structure

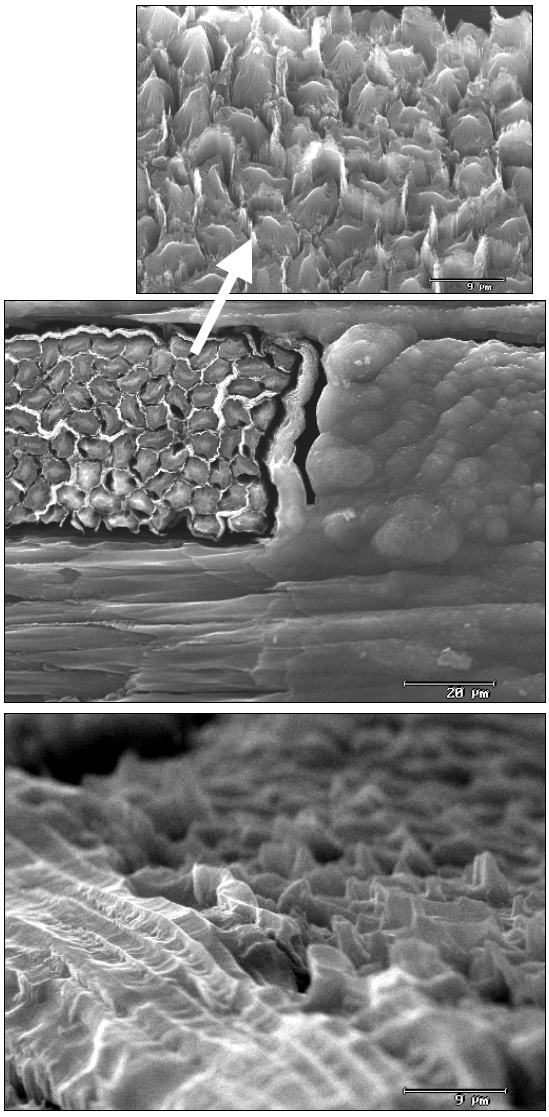

Figure 11: The evolution of the surface topography of the "hole surface" before (left) and after sputtering at normal incidence with 500 eV ion energy.

of CC. The evolution of the surface structure determines the time dependence of the sputter yield.
In order to come to a comprehensive sputter characteristics of CC, some more effort has to be invested to determine the equilibrium surface structure particularly at oblique ion incidence.
Generally, the topography of the surface affects the sputter behaviour to a large extend. Therefore, similar studies have to be undertaken for other promising grid materials.

Acknowledgements

The authors thank Ms. U. Gleisberg for performing the SEM investigations.
Financial support by the DLR (*Deutsches Zentrum für Luft- und Raumfahrt*) is gratefully acknowledged.

References

[1] T. Paulmier, M. Balat-Pichelin, D. Le Quéau, R. Berjoan, J.F. Robert, *Physico-chemical behavior of carbon materials under high temperature and ion irradiation,* Applied Surface Science 180 (2001) 227-245.

[2] M. Patterson et.al., *Ion propulsion development activities at NASA Glenn Research Center,* Paper No. AIAA 2000-3810, 36th Joint Propulsion Conference, Huntsville, July 17-19, 2000.

[3] J. Mueller, J. Brophy, D. Brown, *Design, Fabrication and testing of 30 cm diameter dished Carbon-Carbon ion engine grid*s, AIAA Paper No. 96-3204, 32. Joint Propulsion Conference, Lake Buena Vista, 1996.

[4] H. J. Leiter, H. W. Loeb, K. H. Schartner, *RIT15S and RIT15LP - the development of high performance mission optimised ion thrusters*, AIAA Paper No. AIAA 99-2444, 35. Joint Propulsion Conference, 1999.

[5] M. Tartz, E. Hartmann, R. Deltschew, H. Neumann, *Experimental validation of a grid erosion simulation,* Paper AIAA 99-2860, 35. Joint Propulsion Conference, Los Angeles, June 20-24, 1999.

[6] M. Zeuner, F. Scholze, H. Neumann, R. Deltschew, *Optimisation and characterisation of a tcp type rf broad beam ion source*, Surf. Coat. Technol., in press.

[7] W.Göpel, Chr.Ziegler, *Einführung in die Materialwissenschaften*, Teubner, Stuttgart-Leipzig, 1996.

[8] D. Rosenberg, G. K. Wehner, J. Appl. Phys. 33 (1962) 1842.

[9] W. Eckstein, C. Garcia-Rosales, J. Roth, W. Ottenberger, *Sputtering data*, Max-Planck-Institut für Plasmaphysik Report IPP 9/82 (1993).

[10] J. C. Arnold, H. H. Sawin, M. Dalvie, S. Hamaguchi, *Simulation of surface topography evolution during plasma etching by the method of characteristics*, J. Vac. Sci. Technol. A 12 (1994) 620-35.

[11] R. Deltschew, M. Tartz, S. Jankuhn, E. Hartmann, H. Neumann, *Redeposition of sputtered material on ion thruster grids*, Paper No. AIAA 2000-3665, 36th Joint Propulsion Conference, Huntsville, July 17-19, 2000.