Properties of Zinc-containing Diamond-like Carbon Films Prepared by Plasma Source Ion Implantation

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Zinc-containing diamond-like carbon films were prepared by a combination of magnetron sputtering of a zinc target and plasma source ion implantation and deposition in a hydrocarbon atmosphere. The effect of the preparation conditions on the film properties, such as surface morphology, film structure, Zn content, hardness and friction coefficient, was evaluated. A wide range of Zn contents can be realized, with films becoming rougher and softer with increasing Zn content. The films possess remarkable Zn-rich features as observed in SEM images. Depending on the Zn concentration, the features evolve from dots into more network-like structures.

Key words: diamond-like carbon, plasma source ion implantation, surface morphology, friction coefficient

1. INTRODUCTION
Films of diamond-like carbon possess a number of favorable properties, such as high hardness, low wear and friction coefficient, biocompatibility and chemical inertness [1]. However, some properties can be tailored by adding different elements into the film. Those are mostly light elements or transitional metals. The latter are added to reduce the internal stress of the films and thus to increase their adhesion to the substrate, to improve the wear behavior and to tune the electrical resistivity of the films [2]. Depending on the metal, bonds of carbon and metal might be formed. The size of the metal or carbide particles within the amorphous carbon matrix is usually in the range of a few to a few ten nm [3].

Zinc, however, has attracted little attention in this regard. There is only one reference to be found which deals with Zn-containing DLC (Zn-DLC) films, which were prepared by pulsed laser deposition (PLD) [4]. That study was concerned mostly with the film adhesion and the electrical properties of the films. The concentration of the Zn was limited to a maximum of 10 at.% in those experiments. Apart from that, DLC films were deposited on a Zn alloy [5] and zinc oxide nanoparticles were incorporated into DLC films [6,7]. Other investigations concerning zinc and DLC films are of a tribological nature, i.e. they examined the tribological behavior of DLC films in contact with zinc-plated steel sheets [8] or the interaction of the anti-wear additive zinc dialkyldithiophosphate (ZDDP) with DLC films [9,10]. The latter point is important because of the use of DLC films in automotive components [11]. Considering the suitability of DLC films for biomedical applications [12], zinc might be an interesting addition in this context. The biocompatibility of zinc has been demonstrated [13].

Here, results will be presented for Zn-DLC films as prepared by plasma source ion implantation and deposition (PSII&D) and magnetron sputtering. PSII&D is based on the use of positive ions from a low-pressure plasma which are accelerated towards a substrate by applying a negative voltage to the substrate [14]. For the preparation of a DLC film, a hydrocarbon gas is used as plasma gas. The metal is added by magnetron sputtering. Since the argon gas for the sputtering and the hydrocarbon gas are present in the vacuum chamber simultaneously, the setup is a reactive sputtering system, i.e. some of the hydrocarbon will deposit onto the metal sputtering target. By varying the flow rates of both gases or the power of the sputter gun, films with different compositions of carbon and metal can be realized. A wide compositional range will be covered in this study, i.e. the Zn concentration will go markedly beyond 10 at.%.

2. EXPERIMENTAL
The Zn-DLC samples were prepared by a combination of magnetron sputtering of a zinc target (99.99 %) and PSII&D. Argon was fed to the sputter source with a flow rate of 20 sccm. The RF power of the sputter source was varied between 15 and 70 W. The flow rate of the hydrocarbon gas, ethylene (C₂H₄), was varied between 0.5 and 1.125 sccm. The plasma was generated by a high voltage pulse (-10 kV, 10 µs length, 1 kHz repetition rate) applied to the sample holder, i.e. there was no additional plasma source. Films were deposited on pieces of silicon wafer with 2x2 cm² size. The process time varied between 15 and 40 min. The base pressure of the system was 3∙10⁻⁵ Pa. The distance of the substrate from the Zn sputter target was 10 cm. For a schematic of the setup see Fig. 1.

The composition of the samples was measured by X-
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3. RESULTS AND DISCUSSION

3.1 Film composition

The Zn concentration of the Zn-DLC films was in a range of 2.5 to 62.5 at.% as determined by XPS measurements. The Zn content increases with sputter power and decreases with increasing CH\textsubscript{4} flow rate. Zn can be found throughout the film, as is obvious from the SIMS depth profile in Fig. 2. Apart from some signal variation near the surface and near the interface, the carbon intensity is nearly constant within the film. That the Zn signal does not decrease immediately when the Si substrate is reached, is a consequence of the high surface roughness of the sample, see below.

![Fig. 1: Schematic of the experimental setup. (MFC=mass flow controller).](image)

![Fig. 2: SIMS depth profile of a Zn-DLC film with 55 at.% Zn.](image)

In the XPS measurements some oxygen (up to about 10 at.%) was found for the near-surface areas, with higher percentages for higher Zn contents. The inside of the film is mostly oxygen-free, however.

The film thickness is in the range of 70 to 520 nm for the majority of samples. Only samples prepared by an RF power below 45 W were thinner, with 30 to 80 nm thickness.

3.2 Film structure

The two typical features of a DLC film can be seen in the Raman spectra: the D and G peak at around 1380 and 1550 cm\textsuperscript{-1}, respectively, see Fig. 3. Starting from a value of 1.35, the intensity ratio of the respective peak areas, I\textsubscript{D}/I\textsubscript{G}, increases with Zn content, up to 2.2. Associated with this increase is a shift of the G peak position to higher values, from 1550 to about 1560 cm\textsuperscript{-1} and a decrease in its full width at half maximum, from around 160 to 130 cm\textsuperscript{-1}. This can be interpreted as an increase in sp\textsuperscript{3} hybridized C–C bonds [1]. Similar observations were reported for the addition of other metals, e.g. Ti [15,16] and Ag [17]. In the case of Ag, the sp\textsuperscript{3} content decreased with Ag content, as seen in high resolution XPS spectra [18]. Evaluating the slope of the luminescence background of the Raman spectrum [19], a hydrogen content of the Zn-DLC samples of around 25-30 at.% can be calculated, which is increasing with Zn content.

![Fig. 3: Raman spectrum of a Zn-DLC film with 22 at.% Zn after background correction.](image)

3.3 Hardness

The hardness of the films decreases with Zn content. Starting at a value of 15 GPa for a pure DLC film, the hardness decreases already to 9.5 GPa for a 2.5 at.% Zn-DLC film and to 8.8 GPa for a 3.8 at.% Zn-DLC film. Nanoindentation of films with higher Zn contents could not be performed because of their roughness. Those films are probably softer as is evident from their susceptibility to scratching. The low hardness is a result of the addition of the relatively soft Zn and the reduction in sp\textsuperscript{3} bondings.

For films containing up to 10 at.% ZnO particles the hardness was reported to be below 5 GPa [7]. The addition of silver to DLC films lowers the hardness, too [18,20].

3.4 Surface morphology

Zn-containing films tend to be rough, as can be seen already with the SEM. Not only that, but the films also exhibit a peculiar surface morphology. In Fig. 4 the surface of a film with about 10 at.% Zn can be seen. The light grey areas represent the zinc-rich areas, while the darker areas are carbon-rich. This becomes even more
obvious when switching to the detection of backscattered electrons because of the involved atomic number contrast. The zinc-rich areas consist of dot-like features with up to 100 nm diameter. In some cases, those features are elongated in one direction. They are not necessarily straight; they can change direction or split into branches.

Fig. 4: SEM image of a Zn-DLC film with about 10 at.% Zn (the scale bar is 1 µm wide).

Fig. 5: SEM image of a Zn-DLC film with about 40 at.% Zn (the scale bar is 1 µm wide).

Fig. 6: SEM images of Zn-DLC films (the scale bar is 1 µm wide) with 6, 25, 47 and 62.5 at.% Zn, respectively.

The important point here is that the structures are limited in size in one dimension. With a higher Zn concentration, see Fig. 5, the grey Zn-rich areas are more frequent, but they do not coalesce.

Depending on the preparation conditions, sometimes a few bigger particles can be found, but again there are always distinct Zn-rich areas. Fig. 6 gives a few more examples for four samples with increasing Zn concentrations.

This surface morphology has not been described before for Zn-DLC films. May it be that those structures do not form when the samples are prepared by PLD or that the recording of AFM images with dimensions of 1x1 µm² [4] was a too extreme limitation of measurement area to be able to spot those structures.

Comparing the morphology of Zn-DLC films with those of Ag-DLC films [20,21], it can be noted that higher concentrations of Ag also lead to a rougher surface, but with globular features of various sizes. Although Ag and Zn are both rather soft and do generally not form carbides, the resulting surface structures are different.

The roughness of the samples was evaluated with a confocal laser scanning microscope. The values for the average roughness, Ra, increase with Zn content. For low Zn content samples Ra is in the range of 20 nm – it should be remembered, though, that the height resolution of the instrument is not better than 10 nm, i.e. the actual value of the roughness might be smaller. The average roughness increases to around 80 nm for higher Zn contents of 50 at.% and above. While the earlier study [4] also found an increase in roughness, its reported values were much lower. This might have to do with the much lower film thickness, the different preparation process and the limited measurement area as mentioned above.

3.5 Friction coefficient

The friction coefficient of a pure DLC film is below 0.1, see Fig. 7. The inclusion of Zn, even in low concentrations of 2 at.%, leads to a distinctly higher friction coefficient of about 0.3 after 2500 rotations. With 25 at.% Zn it is already at a value of 0.6 after 1000 rotations. The considerable increase of friction coefficient for small additions of the metal is in contrast to the findings for some metals other than Zn. With Ag it was noted that the addition of 1.8 at.% Ag reduced the friction coefficient as compared to the one of a pure DLC film [21]. For Mo, a larger percentage (11 at.%) is effective in reducing the friction coefficient [22].

Fig. 7: Friction coefficient as a number of rotations for a pure DLC film and two Zn-DLC films with different Zn content.
The reason for the higher friction coefficient of the Zn-DLC films is the combination of higher surface roughness with the lower hardness of the film. As a result, there is considerably more debris to be found on the ball from the ball-on-disk test. Fig. 8 shows microscope images of a ball after a test of a pure DLC film with nearly no debris visible after 5000 rotations and a ball after a test of a 25 at.% Zn-DLC film after 1000 rotations.

Correspondingly, the wear tracks differ as shown in Fig. 9. On the pure DLC film the wear track is hardly visible. With 2 at.% Zn there is a noticeable wear track and with 25 at.% the film has been removed on a width of about 240 µm.

The earlier investigation [4] found no change of friction coefficient with the addition of Zn. As mentioned above, thickness, roughness and preparation conditions were different. Furthermore, in that investigation the evaluation of the friction coefficient was done from the data of a scratch test. Here, the more direct approach of a ball-on-disk test was chosen.

4. CONCLUSION

The Zn-DLC films exhibit a unique surface morphology. Zn-rich areas are visible, whose extent is limited in one dimension. With increasing Zn content, the number of Zn-rich areas increases and the morphology changes from occasional spots to a more network-like arrangement. Zn-rich films are soft and rough; as a consequence, the friction coefficient is markedly higher than the one of a pure DLC film, even for low Zn concentrations.

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References


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