unsymmetrical. Such field-controlled shape memory effect can be contributed to the driving force from the magnetic field to the twin boundaries of the variants based on the magnetic anisotropy of the martensite.

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Micromechanical and Microtribological Properties of Thin CN_x and DLC Coatings

By *Thorsten Staedler** and *Kirsten I. Schiffmann*

Diamond-like carbon (DLC) can be used as a tribological coating in mechanical engineering to reduce friction and wear (for drilling and cutting tools). This system, as well as the amorphous carbon nitride system (CN_x), is also interesting with respect to various applications in the hard-disk and microsystems industries.[1–4] The typical film thicknesses for these applications range from a few nanometers up to a couple of hundred nanometers.

The influence of the substrate in the case of a mechanical characterization of thin films is well known but not fully understood. Different approaches are described in the literature.[5–10] It is reasonable that the substrate should also have an effect on the tribological response of the film/substrate system. In this communication, examples of the influence of film thickness and substrate on the mechanical and tribological properties of thin CN_x and DLC films in the low-load regime are analyzed and discussed.

As already mentioned, DLC and CN_x are both candidates for hard-disk and microsystems industries. Both coatings are widely used today due to their high tribological potential. Therefore, these two systems were chosen for a study of the mechanical and tribological response of a film/substrate system on the nanometer scale.

The DLC films characterized in this communication were deposited via a plasma-enhanced chemical vapor deposition (PECVD) process on Si(100). Details of the deposition conditions are reported elsewhere.[11] Aside from the film thickness, the influence of bias voltage on the mechanical and tribological behavior is of interest. That is why two sample series were prepared: One with a fixed film thickness (250–350 nm) at different substrate bias voltages between 300 and 800 V, and one series at a constant bias voltage of 500 V and film thicknesses between 19 and 400 nm.

The CN_x films analyzed in this work were deposited via reactive DC-magnetron sputtering on Si(100). Details of the process conditions are reported elsewhere.[12] For the CN_x system the two parameters of interest were the nitrogen concentration of the film and the film thickness. Therefore two series were prepared. One series had different nitrogen concentrations between 0 and 20 at.-% at a constant film thickness (200–250 nm). The other series contains different film thicknesses (6–226 nm) at a constant nitrogen concentration of about 9 at.-%.

The nanomechanical properties of the substrate and the coated systems were determined by nanoindentation using a Hysitron Nanoindenter/TriboScope in combination with a Park Universal atomic force microscope (AFM). The sample surface is loaded by a diamond indenter (Berkovich indenter; 100 nm tip radius) and, after holding at a constant load, the load is reduced again. During the whole process the load and indenter position are measured resulting in a load–displacement curve. The unloading segment of these curves is analyzed with the model proposed by Oliver and Pharr in order to obtain the mechanical properties.[13] Beside these single indents multiple indents were carried out. During a multiple indentation there are unloading segments at 10, 20, 30 % of the maximum load down to a load of about 50 % of the actual load. By this means it is possible to determine the mechanical properties, hardness, and Young's modulus for various in-

[*] *T. Staedler, Dr. K. Schiffmann*
Fraunhofer Institute for Surface Engineering and Thin Films
Bienroder Weg 54E, D-38108 Braunschweig (Germany)
E-mail: staedler@ist.fhg.de

dentation depths with only one measurement. These experiments were carried out with three different final loads leading to three different loading rates, 200, 400, and 1000 μN/s respectively. The experimental results for the materials presented in this work show no significant deviation between single- and multiple indentation or different loading rates.

For film thicknesses below 100 nm and a typical influence of the tip radius (100 nm) up to indentation depth of about 15–20 nm the substrate should have a significant influence on the measured hardness and Young's modulus of the film/substrate systems. To take this effect into account the film hardness is calculated according to Equation 1. This equation follows a proposal given earlier[9] and is modified to satisfy the case of a hard film on a soft substrate. It is therefore similar to the basic approach given for the substrate influence on the measured Young's modulus.[10] H_{measured}, $H_{\text{substrate}}$, and H_{film} are the measured, the substrate, and the film hardness respectively; $\varphi = h_c/d_{\text{film}}$ is the ratio of contact depth h_c to film thickness d_{film}; α is a fitting parameter.

$$H_{\text{measured}} = H_{film} + (H_{\text{substrate}} - H_{\text{film}})e^{-\alpha\varphi} \quad (1)$$

The Young's modulus is calculated via an empirical approach based on the model of Doerner and Nix[14]: Equation 2. E_{measured}, $E_{\text{substrate}}$, and E_{film} are the measured, the substrate, and the film Young's modulus respectively.

$$(1/E_{\text{measured}}) = (1/E_{\text{substrate}}) + [(1/E_{\text{film}}) - (1/E_{\text{substrate}})]e^{-\alpha\varphi} \quad (2)$$

For both models a hardness of 12 GPa and a Young's modulus of 160 GPa is assumed for Si(100). These values result from measurements of uncoated Si(100) substrates and are constant in the contact depth regime of 20–120 nm.

The results of the film thickness variation are presented in Figure 1. In good agreement with the Bückle law a significant influence of the substrate on the measured hardness for contact depth exceeding 10 % of the film thickness is observed.[15] The measured values are well described by Equation 1. As the absolute contact depth of all indentations range somewhere between 20 and 120 nm the regime of larger ratios, φ represents measurements taken on thinner films and the regime of small φ values corresponds to indentation measurements of thicker coatings. The existence of one fitting curve for all samples and measurements is interpreted as a homogeneous hardness over the considered film thickness range of 19–400 nm. The hardness of the DLC layers deposited at 500 V substrate bias is 27 ± 1 GPa.

The fact of a substrate influence also applies to the Young's modulus. The measured values of Young's modulus are well described by Equation 2. An analysis of samples from the bias voltage variation shows only a very small influence on the mechanical properties in the considered bias range of 300–800 V. Hardness and Young's modulus both have a slight maximum at 500 V bias: 27 and 260 GPa respectively. These results are in good agreement with other reported hardness values of PECVD DLC coatings (for an overview see Bhushan[16]).

Recent publications[17] show that it is difficult to describe load–displacement curves of CN_x by a power law like the Oliver and Pharr model due to the very strong elastic recovery of these films. In this case it is convenient to introduce a recovery $R = (h_{\max} - h_f)/h_{\max}$ to compare different CN_x coatings:[18,19] $h_{\max}$ and h_f are the maximum displacement under load and the final displacement after unloading respectively. Our samples with a relatively low nitrogen concentration of 9 at.-% (for the film thickness variation) show no fullerene-like phase and provide a recovery of about 74 % compared to 84 and 90 % reported elsewhere.[18,19] Therefore problems of the Oliver–Pharr model associated with the strong elastic recovery do not have a significant influence on the analysis here and all experimental data are well described by the model.

The measured hardness of the CN_x samples treated in this work shows an unusual behavior (Fig. 2) with respect to the ratio of contact depth to film thickness. At first, as in the case of the DLC coatings, the measured hardness increases with decreasing φ: a behavior expected for a coating being harder then the substrate material underneath. Thereafter the measured hardness decreases with decreasing φ (φ < 0.5). This behavior could be taken as a non-homogeneous hardness distribution with film thickness but a closer look at the topography around the indents reveals pile-up. This material behavior is described in the literature[8] and in this case occurs because of a confinement of the plastic zone inside the film because of the larger Young's modulus of the silicon substrate compared to CN_x.

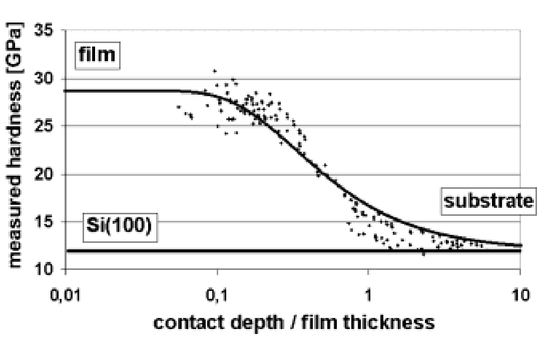


Fig. 1. Hardness results of nanoindentation measurements of DLC films on Si(100) (sample series of film thickness variation) are well described by Equation 1.

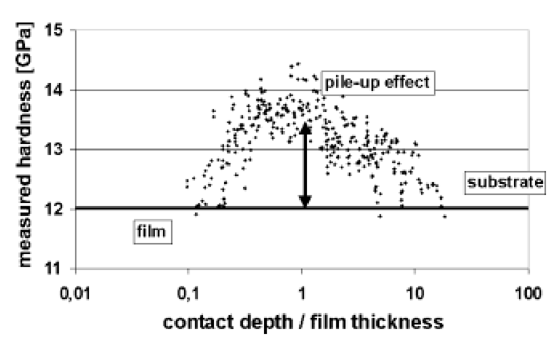


Fig. 2. Unusual behavior of the measured hardness (nanoindentation) for the CN_x thickness variation (for details see text).

As this pile-up is not taken into account by the evaluation of the Oliver and Pharr model the estimated contact area is smaller then the actual one leading to an over-rated hardness. In this special case (9 at.-% nitrogen films) the error is about 0.8 GPa. In the further treatment this effect was taken into account.

An analysis of the CN_x sample series shows a significant influence of the nitrogen concentration on the mechanical properties. The hardness decreases in a linear way from 16 to 10 GPa with increasing nitrogen concentration (0–20 at.-%). Analogously the Young's modulus also decreases with increasing nitrogen concentration (140–90 GPa). These observations are in good agreement with values reported by Li et al.[4]

The tribological tests were performed with the same experimental setup as in the case of the nanomechanical measurements. The only exception is the conical diamond indenter (cone angle 90°, tip radius 560 nm) used here instead of the Berkovich diamond. Two different methods were used. On the one hand a single scratch with linear increasing load over a length of 10 μm was applied to study the load dependence of the friction coefficient (final loads 0.5, 1, and 5 mN, scratch velocity 0.67 μm/s). On the other hand an oscillating wear test over a length of 4 μm at a constant load was used to analyze the time dependence (1, 2, 3, 4, 5, 10, and 25 cycles) of wear at different loads (0.5, 1, and 3 mN) at a scratch velocity of 4 μm/s. In both tests the topography of the scratched surface was mapped with the same tip before (pre-scan) and after loading (post-scan) at a contact load of 20 μN. The difference between these two topographic measurements leads to an information about the remaining wear depth after the test.

The microtribological tests (single scratch and oscillating test) were carried out with two samples of the CN_x series at 9 at.-% nitrogen concentration (226 and 14 nm film thickness) and the DLC series of film thickness variation.

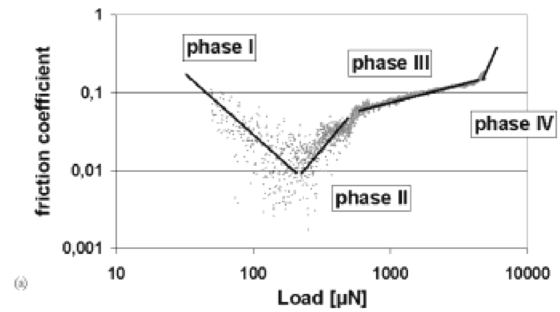
Depending on the mechanical properties and the film thickness of the coated samples as well as the final load, two or more phases are observed during one single scratch. In the case of the softer CN_x system, four different scratch phases could be found, which are particularly pronounced in the friction signal. In Figure 3a the friction coefficient μ during the scratch of the 14 nm thick CN_x film on Si(100) is plotted against the applied normal load.

At low loads (Phase I) there is pure elastic deformation of the sample surface. In this case the friction coefficient decreases according to Equation 3, which is derived from Hertzian contact theory.[20,21] F_{load} and F_{friction} are the normal load and friction force respectively.

$$F_{\mathrm{friction}} \propto F_{\mathrm{load}}^{2/3}$$

$$\mu = F_{\mathrm{friction}}/F_{\mathrm{load}} \propto F_{\mathrm{load}}^{-1/3} \tag{3}$$

If the load exceeds a critical value there is an onset of irreversible deformation underneath the indenter (Phase II). This



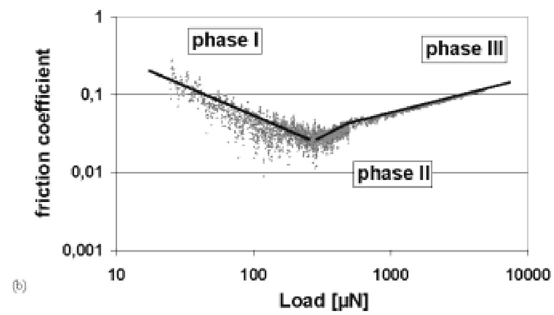


Fig. 3. Different phases during a single scratch test of a thin film: a) 14 nm CN_x, b) 19 nm DLC film on Si(100) (details are given in the text).

irreversible deformation may occur in form of film cracking, material compression, or yield, whereas it is difficult to distinguish between those forms by measurements on the nanometer scale. Due to an increased growth of the contact area between indenter and surface the friction coefficient rises during this phase (Phase II). The main change compared to Phase I is the additional contact area component perpendicular to the scratch direction, which adds a new (ploughing) term to the lateral force.[22] This evolution proceeds until the indenter contacts the substrate. The different slopes of Phase II and Phase III are due to a friction contrast between film and substrate material. During Phase III a gradually increasing pressure is induced into the film substrate interface until finally complete film failure occurs (Phase IV).

For the single scratch test of the 19 nm thick DLC coating on Si(100) only three different phases are observed (see Fig. 3b). The maximum scratch load of 5 mN is not enough to lead to a complete failure of the film. Possibly this behavior is caused by the so-called plate bending effect described elsewhere.[23] The floes of the cracked hard film on the softer substrate still function as a kind of protective quasi-coating.

It is obvious that aside from the absolute values of the friction coefficient the different transition loads between the single scratch phases are particularly suitable to describe the scratch process of the coated substrates. In Figure 4 the critical load of the transition between Phase I and II is plotted versus actual film thickness. A significant influence of the substrate on the critical load is observed. The critical load decreases with decreasing film thickness from the value of quasi-bulk DLC (film thickness > 250 nm) to the value obtained for the uncoated silicon substrate, 595 and 170 μN respectively. A similar behavior was reported for much thinner films.[3] In the case of the thinner DLC films the onset of

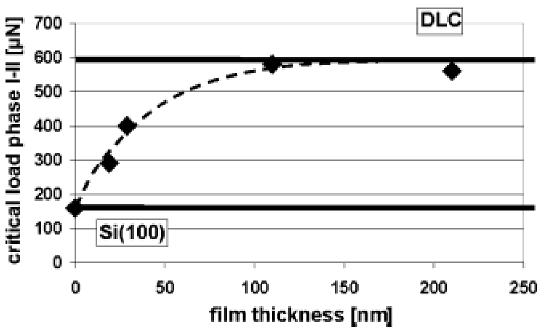


Fig. 4. Dependence of the critical load for a transition between scratch Phase I and II (elastic to non-elastic contact) during a single scratch test of a DLC film on Si(100) substrate with respect to the film thickness (for details see text).

irreversible deformation starts underneath the film in the substrate resulting in the decrease of the critical load of transition from Phase I to II with decreasing film thickness.

In Figure 5 results of the oscillating wear tests for four samples are presented, two CN_x films (14 and 226 nm film thickness) and two DLC coatings (19 and 210 nm film thickness). In this illustration the remaining wear depth (the difference between pre- and post-scan topography) is plotted versus the cycle number. For the thicker films of both systems the wear behavior of CN_x and DLC is observed. In contrast to this behavior the two thin films show fatigue and a complete film failure after a certain number of cycle. The critical number of cycles to film failure at a given load of 1 mN is smaller for the thin CN_x film due the poorer mechanical properties compared to DLC. But aside from this both materials show interesting features in their wear behavior.

In Figure 5a, the CN_x films, the remaining wear depth at low cycle numbers is smaller for the thinner film compared to

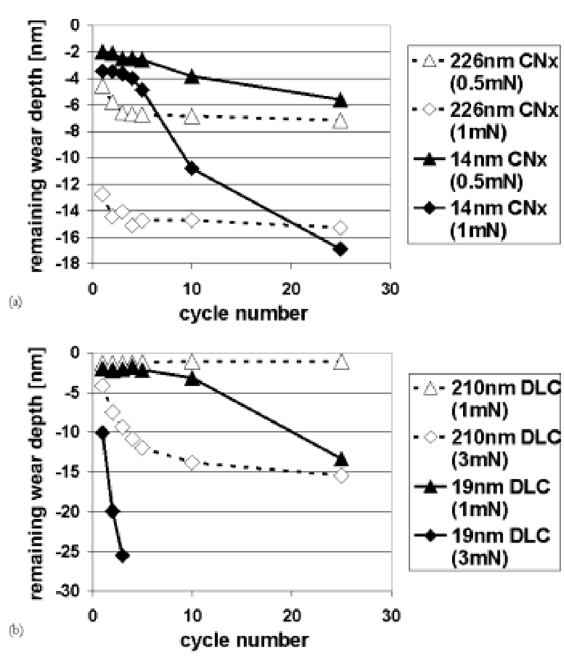


Fig. 5. Results of oscillating wear tests: Comparison of the wear behavior of: a) thin and thick CN_x (normal load 0.5 and 1 mN); b) DLC films (normal load 1 and 3 mN) with respect to cycle number.

that of the thick one. This corresponds to the pile-up effect on the measured hardness reported above. In Figure 5b the time dependence of wear is shown for the 19 and 210 nm thick DLC coatings. The remaining wear depth of the 210 nm thick film at 1 mN is almost neglectable. This is not true for the 19 nm thick film. The remaining wear depth for this thinner film starts at the same small values at low cycle numbers (cycle number < 5), but afterwards there is a significant onset of wear leading finally to a complete film failure. This behavior is possibly caused by fatigue due to a bending of the hard film on the softer Si(100) substrate. In this case the substrate acts like a soft spring underneath the hard coating and tensile stress is induced in the film leading to cracks.

The results reported here show the influence of the mechanical properties of the film (CN_x and DLC) on the nanotribological behavior of a film/substrate system. Due to the poorer mechanical properties of CN_x the critical number of cycles for film failure (oscillating wear test/load 1 mN) is smaller compared to the DLC coating. For the single scratch test the sample coated with 14 nm CN_x shows a complete film failure at a load of 5 mN whereas the sample coated with 19 nm DLC shows no failure at all.

Besides the influence of the film material it was shown that the film thickness has also a significant influence on the tribological response of the film/substrate system. At a given load a decreasing film thickness leads to a growing influence of the substrate on the mechanical and tribological response of the system. The critical load for a transition between elastic and non-elastic phase of a single scratch test is significantly influenced by the substrate. For a hard DLC coating on a Si(100) substrate a decreasing critical load with decreasing film thickness is observed. This behavior indicates an onset of non-elastic processes inside the substrate underneath the film at smaller film thicknesses.

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