Ceramics International 22 (1996) 49-52

0272-8842(95)00053-4
0272-8842/96/$15 00

Cross-Sectional Scanning Force Microscopy Analysis of Arc-Discharge-Deposited Diamond-Like Carbon Films

K. A. Pischow,[a]* J. Koskinen,[b‡] M. Adamik,[b] & P. B. Barna[c]

[a]Laboratory of Processing and Heat Treatment of Materials, Helsinki University of Technology, Vuorimiehentie 2 A, FIN-02150 Espoo, Finland
[b]VTT Manufacturing Technology, FIN-02044 VTT Espoo, Finland
[c]Research Institute for Technical Physics of the Hungarian Academy of Sciences, Budapest, Hungary

(Received 9 December 1994; accepted 6 April 1995)

Abstract: The surface topography and defect structure have a fundamental effect on the tribological and corrosion properties of diamond-like carbon (DLC) films. In the arc discharge deposition of thin films the problem of particle ejection is always encountered. When diamond-like carbon films are deposited using a graphite cathode macroscopic particles and clusters are ejected along the carbon plasma plume. These particles can be filtered, e.g. by using a curved magnetic field, and the number of particles hitting the growing surface can successfully be reduced. However, due to elastic collisions to the chamber wall and other surfaces it is not possible to achieve complete filtering without also drastically reducing the deposition rate. In our previous work we studied the topography of the film using scanning force microscopy (SFM). In order to understand the observed topographical features better we used in this work cross-sectional scanning force microscopy (X-SFM) and cross-sectional transmission electron microscopy (X-TEM) to investigate the microstructure of the DLC films. In the cross-sectional micrographs nodular growth defects bisecting the film were observed. These nodular growth defects affect the surface topography of the film and thus affect the coating performance in tribological and corrosion applications. The connection between the carbon particles and the observed nodular defects is still under investigation.

1 INTRODUCTION

Tribological applications of thin hard coatings have gained an increasing industrial interest. The key factors determining the performance of the coatings in this field are the wear resistance and the low friction coefficient, which are affected by the materials properties of the applied coating as well as by the surface topography of the coating.

Diamond-like carbon (DLC) films are shown to possess several excellent mechanical and tribological properties such as, for example, high wear resistance and low friction coefficient.[1,2]

The vacuum arc-discharge method is a versatile means to deposit hydrogen-free carbon films. These diamond-like carbon (DLC) films are bonded predominantly with covalent sp^3 bonds.[3,4] One of the main problems in the deposition of the DLC films is contamination of the film from neutral particles of the cathode material. The flux of particles can be limited by deflecting the carbon plasma while neutral particles fly straight. However, a number of particles are reflected by collision with walls and objects in the vacuum chamber.

The particles and various kinds of traces of particles observed[5] in the DLC film are expected to have a strong effect on the tribological properties of the film as they have already been demonstrated to have on corrosion properties.[6]

*Present address: SURFEC, Haapatie 14D, FIN-00780, Helsinki.
‡To whom corresponsdence should be addressed.

The new local probe techniques offer good possibilities for the investigation of surface topographies of different materials.[7] However, the electric conductivity of the DLC coating is very poor and thus scanning force microscopy (SFM) is used instead of scanning tunnelling microscopy (STM).

To be able to understand and control the surface topography of the deposited DLC films the investigation of the topography itself is necessary but not sufficient, thus we have used in this work a sample preparation technique developed[8,10] for SFM allowing us to gain gross-sectional information from the films.

2 EXPERIMENTAL

2.1 Deposition method

The DLC films were deposited using a pulsed vacuum arc-discharge method equipped with a curved magnetic field to deflect the plasma. The cathode and anode electrodes were made of 99·8% pure low-porosity graphite. A 100 mF capacitor bank was charged to 400 V and discharged at a frequency of 10 Hz. During the discharge pulse the substrate sample, which is at floating potential, rises to about +30 V potential. The discharge arc was ignited by using a separate ignition electrode. The discharge current was connected through a curved solenoid coil that was used to produce the curved magnetic field for plasma deflection. According to electrostatic probe measurements the carbon ion energy in the plasma was about 60 eV (Koskinen, J., unpublished). The ambient pressure during depositions was about 500 mPa in the chamber evacuated by using a turbo molecular pump. The growth rate of the DLC film was about 1 μm/h. The substrate temperature during the deposition was lower than 60°C as measured from the back of the substrate holder.

Immediately prior to the deposition, the samples were sputter-cleaned with an Ar ion beam (750 eV, 1 mA/cm^2) by using a 3-cm Kaufman ion source, and after the sputter cleaning a few nm-thick SiC layer was sputtered on the substrate as an intermediate layer.

DLC films were deposited on Si(100) wafers. No surface cleaning was performed prior to mounting the sample into the vacuum chamber.

2.2 Sample preparation for X-SFM analysis

The sample preparation is based on the hypothesis of producing first a completely smooth surface by polishing and secondly etching this to a topography reflecting the underlying bulk microstructure.

The details of the sample preparation technique are given elsewhere.[7–11] It should only be mentioned here that the ion beam polishing was carried out by TELETWIN ion guns with an Ar+ ion beam. In the first step two ion guns were applied at 10 keV ion energy and 3 mA ion current. The incidence angle of the ion beams measured from the surface plane was 3° and the sample was rotated at 2 rpm. The polishing time at this stage was about 60 min. In the second step one ion gun was used at 10 kV and 3 mA, and the sample was rocked ± 45° measured from the normal to the TiN coating. The ion bombardment occurred from the silicon wafer side in order to push the smooth Si surface morphology onto the TiN layer. When an appropriately smooth surface was achieved on the area containing the TiN layer, the polishing was finished. A final polishing was applied by one ion gun working at 2·5 kV and 1 mA for 10 min, while the sample was rocked in the same way as before. The chamber vacuum was all the time better than 2·5 × 10^{-3} Pa.

Ion beam etching was applied to develop a surface topography reflecting the bulk structure of the sample. One ion gun was applied at 2 kV ion energy and 0·5 mA ion beam intensity. The incidence angle of the ion beam was 25° measured from the surface plane. The sample was rotated during the 2·5-minute etching time.

2.3 Tribological tests

Tribological tests were carried out by using a pin-on-disc apparatus. A steel pin (RB6RS SKF) slid against the DLC-coated silicon sample at a sliding velocity of 10 mm/s. The diameter of the wear track was 4 mm and the sliding distance was 200 m.

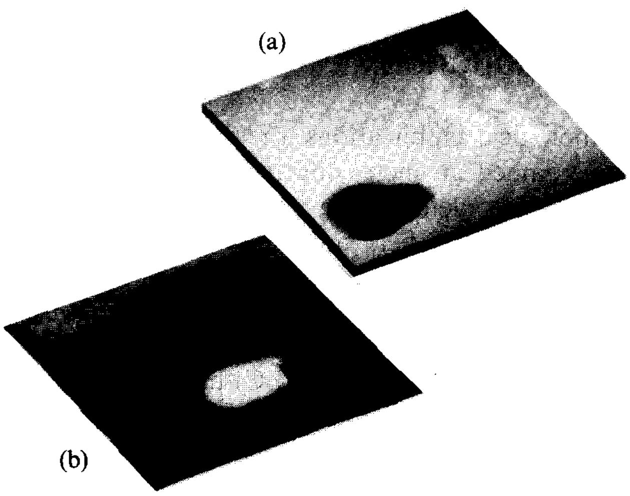


Fig. 1. Three-dimensional SFM scans of the DLC film after a pin-on-disc test. Scanning areas 1500 nm × 1500 nm. (a) A particle on the wear track. (b) A hole on the wear track and at the right part of the picture loose particles, which have ploughed during a scan on a smaller area.

The normal force was 2·2 N and the frictional forces were monitored constantly by a load cell. The tests were done at 22°C temperature and 50 % relative humidity.

2.4 Investigation methods

SFM analyses were performed using a DME Rasterscope 4000 equipped with both STM and SFM facilities. In the SFM work a micro-fabricated cantilever with a spring constant of 0·02 N/m was used and the applied force was from 0·5 nN to 2·0 nN. Contact mode was used in this work.

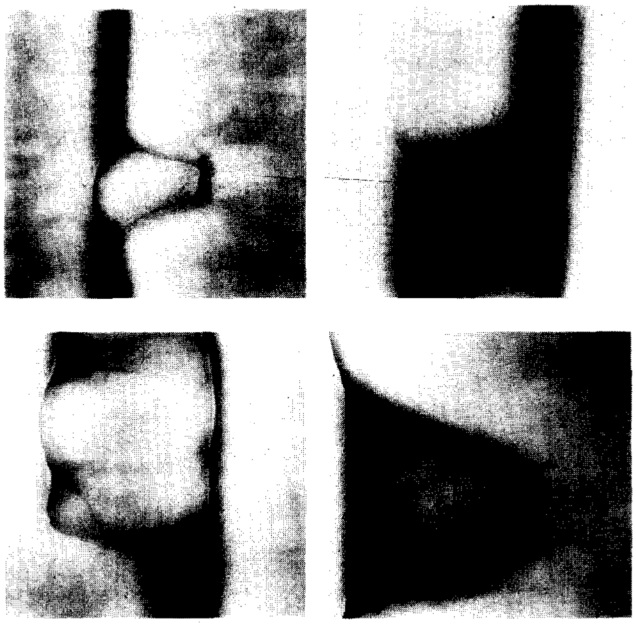
X-TEM analysis of the samples was carried out by applying Phillips CM20 transmission electron microscopy.

3 RESULTS

The coefficient of friction was initially about 0·4 but after a few hundred revolutions it reduced to a value of 0·1.

The SFM analysis of the pin-on-disc wear track on the DLC surface is shown in Fig. 1. The wear track is at this stage of test still very low; however, three features should be considered. Firstly, particles having dimensions in the range of some hundred nanometers, Fig. 1(a), which show a lesser wear than the surroundings can be found on the wear track. Secondly, holes (Fig. 1(b)) having roughly the same dimensions as the aforementioned particles can be found on some places of the wear track. Thirdly, fine-grained loose particles, which will be ploughed to the right side of the scanned area, Fig. 1(b), occur on the whole area of the wear track.

(a) (b)



(c) (d)

Fig. 2. X-SFM scans of the DLC film. (a) Scan of a 1000 nm × 1000 nm area showing the glue on the left, DLC coating on the right and in the middle of the picture a grain growing out of the film surface. (b)–(c) Scans of a 1000 nm × 1000 nm area showing the glue on the right and DLC coating on the left and a bigger cluster of several grains on the middle. (d) Scan of a 750 nm × 750 nm area showing a small cluster which has not reached the level of the surrounding matrix.

Fig. 3. X-TEM micrograph showing the DLC film in the middle and a layered intermediate layer in the lower part of the figure. The bright area on top of the DLC is glue. Two grains starting almost from the bottom of the DLC coating and rising above the coating surface can be seen.

X-SFM analysis of the DLC film is shown in Fig. 2. The overall structure of the film is smooth, and at the magnification used it looks featureless. However, about every five microns, grain-like features, which look like single grains rising over the coating surface (Fig. 2(a)); seem to be composed of several grains rising over the coating surface (Fig. 2(b,c)), or have not reached the level of the surrounding matrix (Fig. 2(d)), can be found.

X-TEM analysis of the film also showed same kind of features (Fig. 3). At this place the grains seem to be bigger and start closer to the coating interlayer interface.

4 DISCUSSION

X-SFM analysis of the arc-deposited amorphous DLC films showed nodular grain-like defects occurring evenly distributed, so that a 5-mm long cross-section contained on average one defect. The observations of these nodules at the wear track indicate that the nodules are mechanically hard. This fact and the cross-sectional images (Figs 2 and 3) seem to rule out the possibility that the nodules are particles which are ejected from the cathode spots. If such hard particles had originated from the cathode one would expect to observe voids under the particles or nodules. Since the carbon material surrounds the nodule with no such voids there would have to be a very high mobility of the carbon atoms in the film-growing process which is in contradiction to the models and experiments that have been reported of the film growth.[12]

Molecular dynamic simulations of the growth of the carbon film from energetic ion beams indicate that an amorphous film structure is obtained. However, the existence of hard nodules embedded in the smooth carbon film has not been previously reported. Investigations are under way to characterize the microstructure of the nodules and to explain the growth of these nodules in the film. The growth could be initiated by several factors that are specifically inherent to the pulsed vacuum arc deposition: cathode particle bombardment, high plasma current pulses, surface charging of the growing film.

The growth of the nodules seems in all samples analyzed to start only after a few hundred nanometers have been coated. This could point to a strain-induced process. Since the vacuum-arc-deposited carbon films have a several GPa compressive stress it is probable that the nodules can nucleate only at a sufficiently high compressive stress of the carbon matrix. However, in the X-TEM micrograph both defects start very close to the coating multilayer interface. This is in contradiction to the hypothesis that these defects would be strain-induced, because the X-ray rocking curve measurements have clearly shown that the strains are released by these TiMo multilayers.

5 CONCLUSIONS

In the cross-sectional micrographs nodular growth defects bisecting the film were observed. These nodular growth defects affect the surface topography of the film and thus affect the coating performance in tribological and corrosion applications. Observations of the nodules at the wear track after the tribological test indicate that the nodules are harder than the surrounding carbon material. The connection between the carbon particles and the observed nodular defects is still under investigation.

REFERENCES

1. HIRVONEN, J.-P., KOSKINEN, J., LAPPALAINEN, R. & ANTTILA, A., *Materials Science Forum,* **52&53**, *Trans Tech Publications*, ed. J. J. Pouch & A. Alterovitz. Zürich, 1990, pp. 197–216.
2. KOSKINEN, J., ANTTILA, A. & HIRVONEN, J.-P., *J. Surf. and Coat. Techn.*, **47** (1991) 180–7.
3. GREEN, D. C., McKENZIE, D. R. & LUKINS, P. B., *Materials Science Forum,* **52&53**, *Trans Tech Publications*, ed. J. J. Pouch & A. Alterovitz, Zürich, 1990, pp. 103–24.
4. FALLON, P. J., VEERASAMY, V. S., DAVIS, C. D., ROBERTSON, J., AMARATUNGA, G. A. J., MILNE, W. I. & KOSKINEN, J., *Phys. Rev. B.*, **48** (1993) 4777–82.
5. PISCHOW, K. A. & KOSKINEN, J., Presented at *AVS-93*, Orlando 1993.
6. KOSKINEN, J., EHRNSTÉN, U., MAHIOUT, A., LAHTINEN, R., HIRVONEN, J.-P. & HANNULA, S. P., *J. Surf. and Coat. Techn.*, **62** (1993) 1329–36.
7. PISCHOW, K. A., RISTOLAINEN, E. O. & KORHONEN, A. S., In *Proceedings of AMPT'93*, ed. M. S. J. Hashmi. Dublin, 1993, pp. 1887–995.
8. PISCHOW, K. A., KORHONEN, A. S., ADAMIK, M. & BARNA, P. B., *J. Surf. and Coat. Techn.*, in press.
9. PISCHOW, K. A., ADAMIK, M., BARNA, P. B. & KORHONEN, A. S., *J. Vac. Sci. Techn. B.*, **12** (1994) 1716–21.
10. PISCHOW, K. A., *Tribologia,* **12** (4) (1993) 20–32.
11. PISCHOW, K. A., KORHONEN, A. S., ADAMIK, M. & BARNA, P. B., *J. Vac. Sci. B.*, in press.
12. KAUKONEN, H. P. & NIEMIENEN, R. M., *Phys. Rev. Lett.* **68** (1992) 620.