Properties of DLC and CN_x PECVD coatings

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Carbon based thin films have been prepared by PECVD method. Silicon and steel substrates were used for thin films preparation. Deposition was carried out under various conditions. Plasma was generated by RF (13.56 MHz) discharge. Investigation of theproperties of deposited thin films has been carried out by IR spectroscopy, Raman spectroscopy, X-ray diffraction, proton scattering, scanning electron microscopy and by measurement of Vickers microhardness. Various bonds between carbon, nitrogen, hydrogen and also oxygen were observed. For all the conditions used the coatings were amorphous. In the case of thicker coatings bad adhesion was observed on both substrates.

Keywords: DLC coating; CN_x coating; PECVD method

1. Introduction

The research in the preparation of CN_x layers was started after Liu and Cohen [1,2] predicted the existence of β-C_3N_4 with a hardness exceeding that of diamond. The CN_x layers, which are prepared by several methods, also have shown very high hardness values. This work is focused on the preparation of CN_x and DLC (Diamond-like carbon) layers by the plasma enhanced chemical vapor deposition (PECVD) method and on the investigation of their properties.

2. Experimental details

CN_x and DLC thin films have been prepared on silicon and steel flat, one side polished substrates. Before deposition the substrates were ultrasonically cleaned in organic solvents and after inserting them in the reactor the samples were etched in oxygen plasma for 5 minutes. The deposition was carried out in the PECVD experimental arrangement, a schematic view is shown in Fig. 1.

The gas precursor for the preparation of DLC thin films was methane and for CN_x thin films the precursors were methane and nitrogen. The ratio of fluxes of CH_4:N_2 was changed in the range of 1:1 to 1.5:1. The substrate temperature during deposition was 280° C. Bias voltage was changed in the range of - 100 V to - 300 V. The deposit last between 5 and 20 minutes.

On several substrates a Si_3N_4 interlayer was used for adhesion improvment. This interlayer was deposited in the same reactor as a first step of the deposit process. The precursors were 1% silane SiH_4 in N_2 , and ammonia NH_3, the substrate temperature was 250°C .

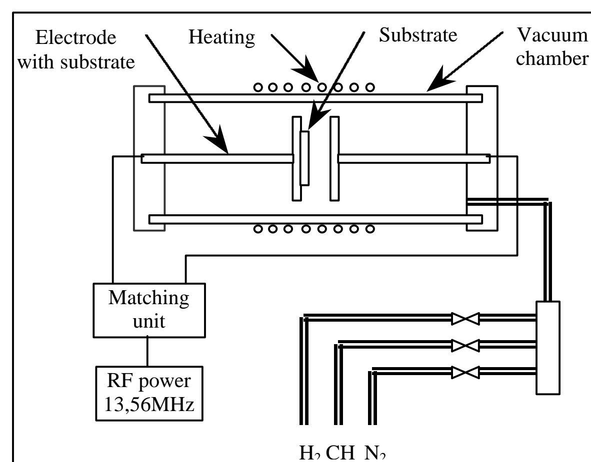

Fig. 1. Schematic view of the PECVD experimental arrangement

Electron Probe Microanalysis (EPMA) was carried out in a JEOL JXA50A microprobe using a multilayer monochromator of Ni/C (2d = 8.16 nm) for the X - rays of C, N, O. The k - ratios were determined from recordings of the C-Kα, N-Kα and O-Kα peaks emitted by standards (BN, diamond, SiO_2) and the analysed layers. EPMA in combination with STRATA software was applied to the determination of the film composition. The analysis was carried out at ACCV = 3-10 kV. The measurement of the film thickness was carried out by SEM on the fractured silicon sample at normal view. The observation of the surface quality of the film was accomplished also by SEM employing a suitable sample tilt, Vickers microhardness was measured in the load range of 50 mN to 1000 mN by means of an equipment Leitz.

Infrared (IR) absorption spectra of CN_x thin films were carried out using a NICOLET IMPACT 400 Fourier transform IR spectrophotometer taking as reference a silicon substrate. A deuterated triglicine sulphate detector was used in the 400 to 4000 cm^{-1} range at room temperature. An absorption substraction technique was applied to remove the spectral features of the Si wafers, the spectral resolution was 8 cm^{-1}.

The Raman spectra were obtained using the 532 nm line from a diode pumped laser and a SPM 2 grating monochromator. The laser power incident onto the samples was kept constant at 50 mW with a spot size of about 1 mm, the spectral resolution was 55 cm^{-1}.

The composition of the prepared CN_x thin films was also investigated by resonant scattering of protons of 2.38 MeV of energy.

3. Results

The compositions of the prepared CN_x layers measured by means of STRATA software were in the ranges of 60.7 to 85.9 at.% C and 5.5 to 30.7 at.% N. In many samples a great oxygen contamination was revealed (up to 17.5 at.%). Similar results for the composition were obtained by resonant scattering of protons. The analytical methods employed could not detect hydrogen, which surely was presented in the layers. The thickness of the layers was in the range of 100 nm to 500 nm depending on the deposit duration. An example of the layer cross section is shown in Fig. 2 while Fig. 3 shown the CN_x layer with the Si_3N_4 interlayer employed for adhesion improvement. Notice the good quality of the CN_x surface layer.

Fig. 2. Typical layer cross section.

The IR spectra of CN_x thin films are shown in Fig. 4. The main asymmetric broad absorption band in the range of 1100-1700 cm^{-1} displays a high frequency band near 1300 cm^{-1}. This spectral profile corresponds to the Raman active G and D bands, observed at 1550 and 1360 cm^{-1}, respectively, of pure amorphous carbon [3]. The presence of an amorphous phase in the CN_x thin films was also confirmed by X-ray difraction. The presence of the G and D bands are due to scattering from graphite-like (G) and

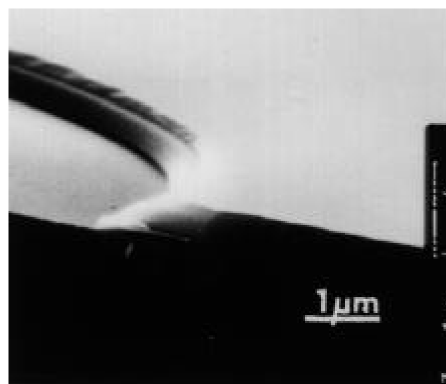

Fig. 3. CN_x layer deposited on a Si_3N_4 interlayer, the substrate employed was silicon.

disordered (D) forms of sp^2-bonded carbon. The breaking of symmetry due to incorporation of nitrogen atoms into the carbon network turns these into IR active bands. The observed structure in the IR absorption spectrum in the range from 1600 to 1690 cm^{-1} is probably due to an overlap of the C=C and C=N stretching vibrations. The weak broad band in the range of 2800-3000 cm^{-1} is attributed to the stretching vibrations of CH_n groups due to contamination of samples while the weak band around 3365 cm^{-1} could be originated from the presence of OH groups.

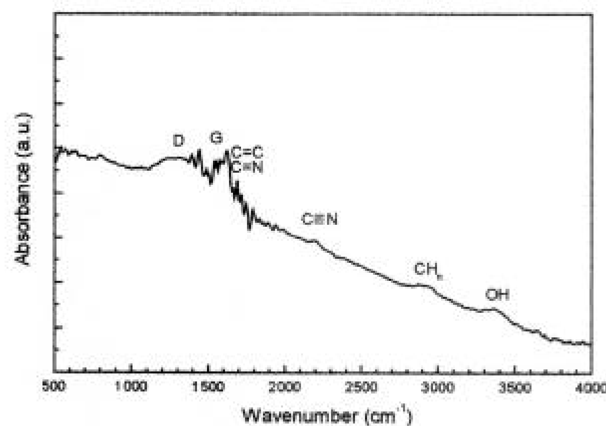

Fig. 4. Representative IR absorbance spectrum of CN_x thin films prepared by the PECVD method

The Raman spectra of samples are displayed in Fig. 5. Two good pronounced Raman active modes are centered at 1368 cm^{-1} (D band) and 1564 cm^{-1} (G band). The position of these bands was obtained by a non-linear fitting of the measured spectra employing two Gaussians. These bands are characteristic of a mixture of disordered and graphite-like sp^2-bonded carbon. As compared with the position of the G peak in amorphous carbon, the position of the G peak in our films shows a red shift of around 5 cm^{-1}. This fact is interpreted as a result of the downsizing of the sp^2 domains in our films. The other bands are less pronounced. A very weak band around 2200 cm^{-1} is supposed to be due to Raman active C-N triple bond vibrations of CH_n groups.

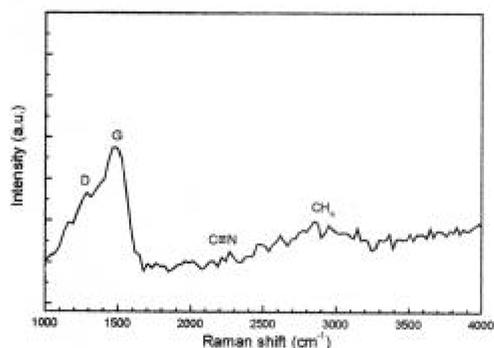

Fig. 5. Typical Raman spectrum of CN_x thin films prepared by the PECVD method

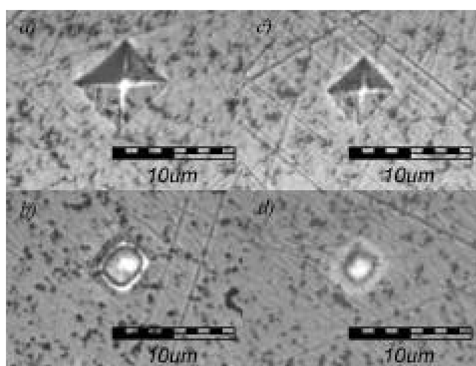

Fig. 6. Micrographs of indentation pattern made by a Vickers indenter. a) load 10 g, steel substrate, b) load 10 g, steel substrate with DLC thin film, c) load 5 g, steel substrate only, d) load 5 g, steel substrate with DLC thin film

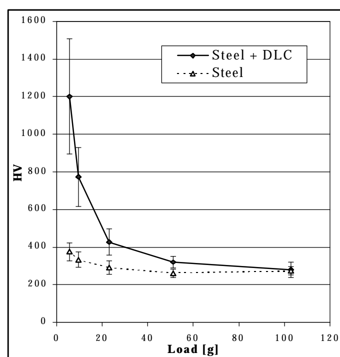

Fig. 7. Measured values of integral Vickers microhardness of steel substrate and DLC thin film system, corresponding to figure 6. For comparison the microhardness of steel substrates is also presented. The measurement was carried out at 5 values of load of 5 to 100 g (the curve is only an eye guides)

The results of the microhardness investigation of the CN_x and DLC thin films are shown in Figs. 6-9.

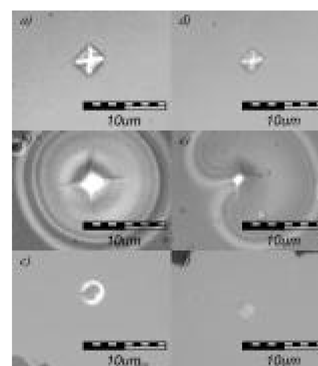

Fig. 8. Micrographs of the indentation patterns made by a Vickers indenter, a) load 10 g, silicon substrate only, b) load 10 g, silicon substrate with CNx thin film, c) load 10 g, silicon substrate surface after removing of CNx thin film, d) load 5 g, silicon substrate only, e) load 5g, silicon substrate with CNx thin film, f) load 5 g, silicon substrate surface after removing of CNx thin film

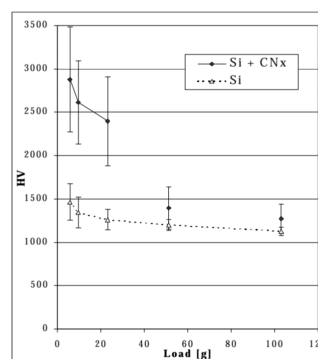

Fig. 9. Measured values of integral Vickers microhardness of silicon substrate and CN_x thin film system, corresponding to figure 8.

4. Conclusions

The CN_x and DLC layers were prepared by PACVD method. Composition of layers was examined by EPMA and by resonant scattering of protons, a great oxygen contamination was detected. The film thickness and morphology was investigated by SEM, the thickness of the films was in the range of 100 to 500 nm. Surface quality of CN_x layers was acceptable. The analyses of IR and Raman spectra of the PECVD prepared films confirmed the fact that the structure of our CN_x films was very similar to that of amorphous carbon. It suggested that carbon and nitrogen atoms were chemically bonded in the films studied. High values of Vickers microhardness were measured on some samples with CN_x and DLC films.

Acknowledgements

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References

[1] A. Y. Liu, M. L. Cohen, Science **245**, 841 (1989).
[2] A. Y. Liu, M. L. Cohen, Phys. Rev. B 41, 10727(1990).
[3] R. O. Dilon, J. A. Woollam, V. Katkanant, Phys. Rev. B **29**, 3482(1984).