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# Properties of the carbon thin films deposited by thermionic vacuum arc

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The aim of the present paper is to investigate the properties of the Diamond Like Carbon (DLC) film condensation from the carbon plasma generated by Thermionic Vacuum Arc (TVA) method. The carbon film is bombarded during its deposition by energetic carbon ions with established value of directed energy. Because this system can heat at elevated temperature any material, it is one of the most adequate technologies for the deposition of refractory metals with high melting points (over 3000 K), Raman spectra were analysed to identify the C phase of the deposited films and SEM (Scanning Electron Microscope) used after the nanoindentation print of different loads. Mechanical tests were carried on deposited carbon film using a Fischerscope depth sensing indentation tester. The hardness of the deposited films was found in the range of 10 to 14 GPa, typical values for DLC films and the elastic modulus was found in the range from 100 to 125 GPa.

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*Keywords*: DLC, Mechanical properties, Thermionic Vacuum Arc

## 1. Introduction

DLC thin films have a wide range of applications in such branches as nanoelectronics, novel optical devices, integrated digital circuits and protective coatings [1,2]. From all of these, DLC thin films used as protective coatings cause a growing interest for many areas as: compact disks, optical windows (glasses), optical fibers, magnetic storage disks, micro-electromechanical devices (MEMs), biomedical coatings, PET bottles and also recently in preventing blocked arteries, due to their excellent properties. Especially for the mechanical and tribological applications significant consideration needs to be given to the effect of intrinsic and extrinsic stresses on the adherence between carbon films and all kind of substrate material. In this paper we present the results of depth sensing indentation tests made on carbon films H30 and H31 deposited on glass and silicon substrates by Thermionic Vacuum Arc method, in different working conditions. TVA method generates hydrogen-free DLC thin films. Comparing with hydrogenated DLC, hydrogen free DLC films show advantages such as higher hardness and elastic modulus, lower coefficient of friction in humid environment and also higher thermal stability [3].

## 2. Experimental details and coating characterization

The method used for carbon thin film deposition was Thermionic Vacuum Arc (TVA) technology. The carbon film is bombarded during its deposition by energetic carbon ions with established value of directed energy. Because this system can heat any material at elevated temperature, it is one of the most adequate technologies for the deposition of refractory metals with high melting points (over 3000 K).

TVA is an externally heated cathode arc, which can be established, in high vacuum conditions, in vapors of the anode material [4,5]. Thermionic Vacuum Arc is ignited between a heated cathode surrounded by an electron-focusing Wehnelt cylinder and an anode, in our case a carbon rod, which would be deposited.

The substrates for the deposition were Si and glass for each of both working conditions presented in Table 1. The pressure for arc discharge inside of the vacuum vessel was maintained around $10^{-6}$ mbar.

*Table 1. Experimental parameters for samples H30 and H31.*

| SAMPLE | H30 | H31 |
|---|---|---|
| The intensity of the arc current (A) | 1.5 | 1.8 |
| The intensity of the heating current of the filament (A) | 90 | 98 |
| Applied voltage (V) | 900 | 930 |
| Sample-anode distance (cm) | 14 | 17 |

For a certain value of the discharge current, the discharge voltage applied was found to be directly proportional to distance between anode and cathode. As the interelectrodic distance, this parameter could not be greater than 4 mm due to the instabilities, an accurate increment of its value was not possible. Therefore, the variation of this parameter was undertaken via variation of discharge voltage

The indentation tests were performed using the Fischerscope H100 DSI tester equipped with Vickers indenter. The applied load $L$ ranges from 0.4mN to 1N and the accuracy of the depth measurement is of about ±1nm.

The SEM images were made using a JEOL JSM 6460 apparatus with an accelerating voltage of 20kV.

Raman measurements were performed with a "JOBIN YVON/SPEC/DILOR" device, supplied by He-Ne laser at 632.817 nm wavelength. The LabRam system is a fully integrated package designed to perform the measurements. Also, the LabRam system has a completely stigmatic spectrograph with two interchangeable gratings for variable spectral resolution**.** The sample was placed on a stage driven with step motors capable of 0.5μm movement in the X and Y directions**.**

### 3. Results and discussion

The Ficherscope tester enables to register the indentation depth as a function of the applied load during both the loading and unloading part of the indentation tests.

On the basis of this method material parameters such as universal hardness *HU* (DIN50359-1), plastic hardness $HU_{\mathrm{pl}}$ and effective elastic modulus $Y_{\mathrm{HU}}$ may be determined. The relations are:

$$HU = \frac{L}{26.43h^2} \quad , \qquad HU_{\mathrm{pl}} = \frac{L_{\max}}{26.43h_r} \tag{1}$$

$$Y = \frac{1}{\dfrac{4\tan(\alpha/2)h_r}{\sqrt{\pi}dL/dh(_{h\max})} - \dfrac{1-\nu^2{}_{Dia}}{E_{Dia}}} \tag{2}$$

In these relations:

- *HU* is the universal hardness (resistance against elastic and plastic deformation),

$L$ is the applied load, $h$ indentation depth, 26.43 – geometric factor, $\alpha$=136° is the angle between two faces of the Vickers indenter,

- $HU_{\mathrm{pl}}$ is the plastic hardness (resistance against plastic deformation), $h_{\max}$ is the maximum indentation depth at given maximum load $L_{\max,}$
- $Y = E/(1\text{-}\nu^2)$ is the so called indentation modulus ($E$ is the Young's modulus and ν is the Poisson's ratio, abbreviation Dia refers to the material parameters of the diamond indenter), $dL/dh(_{hmax})$ is slope to the unloading curve at maximum indentation depth, $h_r$ the intercept of the slope to the unloading curve with the indentation depth axis at L=0.

A number of increasing loads ranging from 1 to 1000 mN were applied to each sample to obtain the hardness and elastic modulus as a functions of load and indentation depth (see Figs. 1 and 2.) This enabled us to study the influence of the substrate on the measured material parameters. The loading time was 20 s. The maximum load was kept constant 5s. The subsequent unloading part lasted 20 s. Each indentation test was repeated at least nine times, the results of the hardness and elastic modulus were averaged calculated and the 95% confidence level was determined. In case of the indentation testing of thin films, the measured properties depend on the indentation depth due to combined response of the coating and the substrate. The thickness of studied films was too low to obtain the so-called critical indentation depth, where the substrate influence may be neglected. Therefore, the measured elastic modulus and hardness values were corrected for the substrate influence.

The combined effect of the film and substrate on the measured values of composite hardness $H_{\mathrm{c}}$ was modelled according to Battacharya and Nix [7] by

$$H_c = H_s + \left(H_f - H_s\right)\exp\left[-\alpha_n\left(\frac{h}{t}\right)^n\right] \tag{3}$$

where $h$ is the indentation depth and $t$ is the film thickness, $\alpha_n$, and $n$ are fitting parameters. The film hardness is marked with suffix f and the substrate hardness is marked with suffix s. The relationship (4) is purely empirical, however it was found to correlate well with finite element simulations [7]. The Marquart-Levenberg algorithm was used for fitting the function (3) to the experimental data to determine unknown parameters in the model. The calculated film hardness $H_f$ was 13.4±0.4 GPa for film H31 and 11.5±0.5 GPa for film H30. The obtained hardness values indicate suitable values for data storage applications [8,9]. The fitting parameter n was found to be in the range from 0.93 to 0.98, which is in good agreement with the value n=1 proposed for hard coatings on soft substrates [7].

Both films exhibited indentation induced delamination at higher loads (~500mN). The relationship (3) does not take the influence of the fracture into account, so the experimental data were fitted only up to 500 mN, where the interfacial fracture and delamination begun.

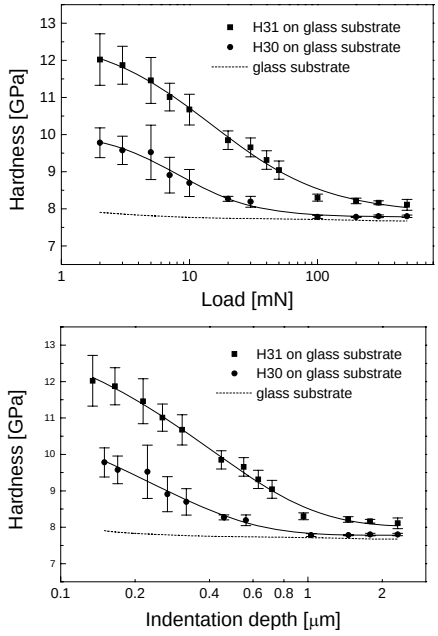


*Fig.1. The composite hardness of the film-substrate systems (H31 on glass, H30 on glass) and the hardness of the glass substrate as a function of the load (left) and of the indentation depth (right).*

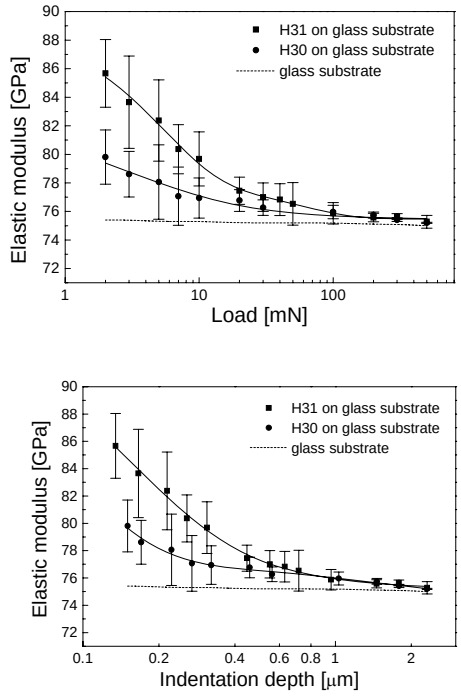


*Fig. 2. The effective elastic modulus of the film-substrate systems (H31 on glass, H30 on glass) and the glass substrate as a function of the load (left) and the indentation depth (right).*

The combined influence of the film and substrate on the apparent indentation modulus $Y_a$ could be described according to following relationship

$$\frac{1}{Y_a} = \left(\frac{\Theta(h/t)}{Y_f}\right) + \left(\frac{1-\Theta(h/t)}{Y_s}\right) + \frac{1}{Y_i} \qquad (4)$$

where $Y_f$ ,$Y_s$ and $Y_i$ is the film, the substrate and the diamond indentation modulus ( $Y = \frac{E}{1-\nu^2}$ , where ν is the Poisson's ratio) respectively and Θ is a complicated function of the indentation depth $h$ and may be fitted by the following simplified relation [10]

$$\Theta = 1 - \exp(-\beta \frac{t}{h}), \qquad (5)$$

where $\beta$ is a constant. The calculated elastic modulus for film H31 was $Y_f$ = 128±4 GPa and for the film H30 was $Y_f$ = 100±2 GPa.

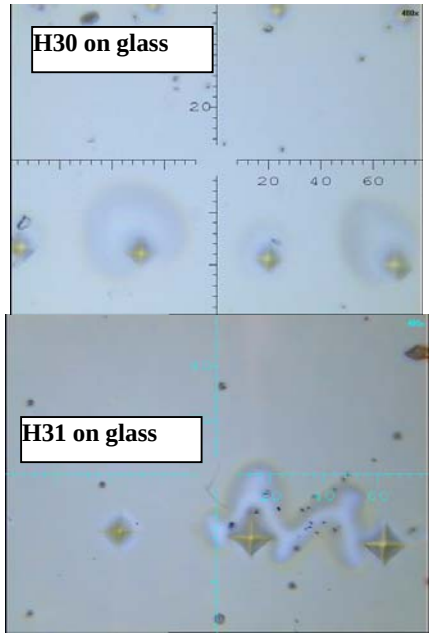


*Fig. 3. Images of the indentation prints film after indentations using maximum loads of 500 mN in case of film H30 (left) and 1N in case of film H31 (right) on glass substrate.(The scales are in micrometers.)*

In case of film H30 the indentation induced film delamination from glass substrate begun at lower loads (see indentation induced formation of blisters around the indentation prints on the left side of Fig. 3.) than in case of film H31 on the glass substrate. In case of film H31 the buckling begun at loads higher than 750 mN. As it is shown at the right side of Fig. 3, the delamination had the so-called telephone-cord character. The resistance against delamination for both of films H30 and H31 on silicon substrate was very low comparing to the same films deposited on glass substrate. The comparison of

indentation prints is shown on SEM images in Fig. 4. While the indentation print made in film H30 deposited on glass substrate did not show cracking or delamination even at 300 mN (on the left), in case of silicon substrate formation of buckling and radial cracking was observed already from 20 mN.

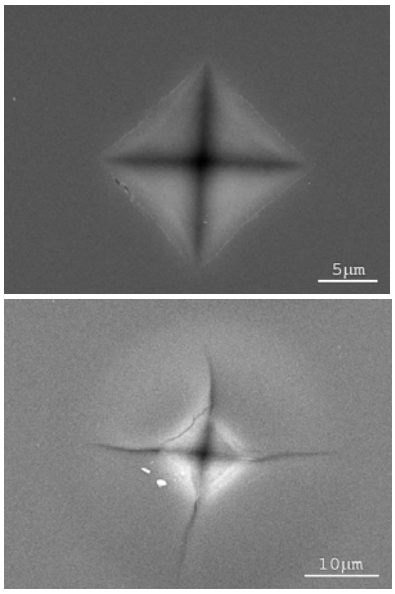


*Fig. 4. SEM images of the indentation print after Vickers intendations on glass (left) and on Si (right).*

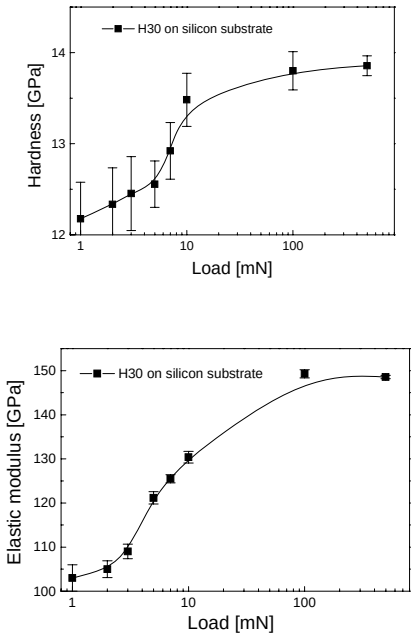


*Fig. 5. The composite hardness (left) and elastic modulus (right) for the film-substrate system H30 on silicon substrate as a function of applied load.*

The film H30 had lower hardness and elastic modulus than the silicon substrate, so the measured composite hardness and effective elastic modulus increased with increasing load (Fig. 5). There was observed an abrupt drop in both graphs due to cracking and delamination effects when the applied load of 10 mN was exceeded. Fitting of the functions in Fig. 5 according to models (2) and (3) provided for film H30 the same results in the range of the experimental errors as above in the case of glass substrate. The film H31 on the silicon substrate showed almost complete delamination, therefore it was not possible to obtain nanoindentation data on this film/substrate system.

All the Raman spectra obtained on films H30 and H31 were broad and consisted of peaks centered around 1331 $cm^{-1}$ (diamond peak) and 1560 $cm^{-1}$ (graphite peak). These spectra clearly showed that the carbon bonding states present in the deposited films are $sp^2$ and $sp^3$ [6].

An additional peak on films H31 and H30 deposited on Si was also observed in the Raman spectra at about 1070 $cm^{-1}$. This was due to the second order peak of the Si substrate.

## 4. Conclusion

Amorphous diamond-like carbon films were deposited on glass and single crystal silicon substrates using thermionic vacuum arc method. Mechanichal tests, SEM investigation of the film surface after nanoindentation test and Raman spectra were used for characterization of the amorphous carbon thin films. The hardness of the deposited films was found in the range from 10 to 14 GPa and the elastic modulus was found in the range from 100 to 125 GPa [9,10]. The operating parameters such as the arc current, the intensity of the heating current of the filament, the applied voltage and the sample-anode distance were higher in case of the film H31 than in case of film H30. Film H31 showed higher hardness and elastic modulus, than film H30, however its adhesion especially to silicon substrate was worse than in case of film H30. Nanometer-sized diamond crystallites were found on all samples, with high $sp^3$ content and relatively low growth stress. The results show that TVA has been proved to be a very suitable method for the preparation of diamond like nanostructured coatings, as well as other types of coatings.

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