Analele Universităţii de Vest din Timişoara
Vol. XLVIII, 2006
Seria Fizică

THIN FILMS DEPOSITED BY THERMIONIC VACCUM ARC METHOD

V. Ciupina[1], R. Vladoiu[1], C. P. Lungu[2], I Mustata[2], G. Prodan[1], V. Bursikova[3], G. Musa[1]

[1]*Department of Physics, Ovidius University, Mamaia 124, Constanta, Romania,*

[2]*National Institute of Plasma Physics and Laser Radiation, Bucharest-Magurele, Romania*

[3]*Masaryk University, Brno,Kotlarska 2, Czech Republic,*

Abstract
In this paper we are promoting a novel technique called Thermoionic Vacuum Arc (TVA) for deposition of thin films. This type of arc ignites in high vacuum conditions in the vapors of the anode material, continuously generated by the electron bombardment of the anode. The TVA method is characterized by producing plasma in the pure vapors of the metal to be deposited (C or W) without using any buffer gas.
Keywords: thermionic vacuum arc, carbon thin films, tungsten thin films.

1. Introduction

The continuous development of technology is based on new materials with improved properties used in highly performing devices. One of the most interesting materials nowadays is metal-carbon (carbon) film used for Micro-Electro-Mechanical-Systems (MEMS) applications. MEMS is about 80% based on Si. Even Si can be used in many applications; its usage is limited due to the low mechanical and high wear resistances and high coefficient of friction between Si and SiO_2. These problems can be solved by using new materials with enhanced tribological properties [1-2] ensuring lubrication and hydrofobicity to prevent adhesion.

Research on developing new carbon films production technologies is still undergoing, as adhesion failure (due to the residual stress during deposition), the impossibility of uniform deposition of carbon film on large areas and the high production costs are the most important factors limiting the performance of these films.

An important amount of work is presently dedicated to study synthesis of high quality carbon films using different methods like: magnetron sputtering, chemical and plasma vapor deposition (CVD and PACVD, respectively), electron cyclotron resonance (ECR), filtered cathodic vacuum arc (FCVA), ion beam sputtering, pulsed laser deposition (PLD), ion beam sputtering etc.

The aim of this paper is to present and to characterize a new technique called thermionic vacuum arc (TVA) for deposition of unstress, smooth, thin, high sp^3 content metal-carbon (carbon) nanostructured coatings compatible with silicon processing technologies.

2. Experimental arrangement

The TVA discharge can be established in vacuum between a heated cathode and an anode mounted at a small distance in front of cathode. The external heated cathode (W + 0.2%Th filament) produces thermally emitted electrons of about 100 mA. These electrons are accelerated and focused by a Whenelt cylinder to the anode which is biased to high voltage (1 – 6 kV). The cathode filament was made by thoriated tungsten wire with 1,5 mm diameter, three times wounded and heated by a current of 100 A.

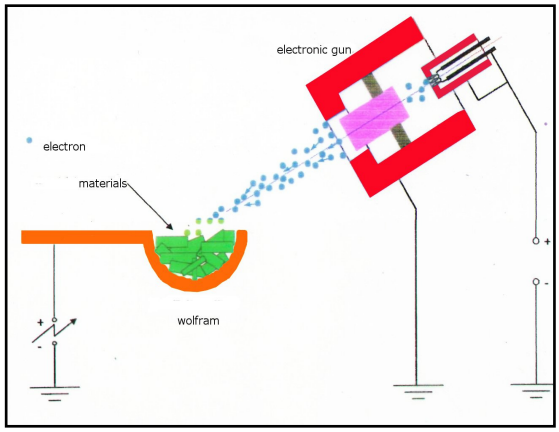

Figure 1. *TVA experimental arrangement.*

In vacuum, a steady state density of the metal vapors appears in the interelectrodic gap. The value of the equivalent pressure of the metal vapors depends mainly on the power of the accelerated electron beam from the cathode. At further increase of the applied high voltage, suddenly a bright discharge appears in the interelectrodic space in the vapors of the anode material (Figure 2) with a simultaneous decrease of the voltage drop over the electrodes and with a significant increase of the current. During the carbon discharge arc running the anode was continuously rotating with a speed of 6 rotation/minute. Moreover, the cathode-anode distance was adjusted each time when the arc current was decreasing more than 10%. The schematic view of the experimental arrangement for carbon film evaporation is shown in Figure 3. For carbon film deposition using TVA technology the main working parameters are presented in Table 1.

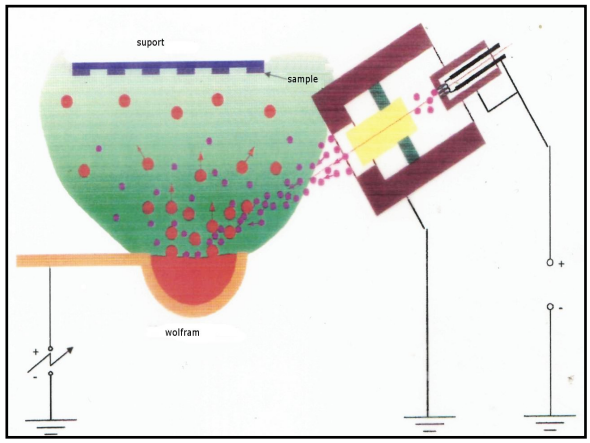

Figure 2. *The bright discharge in the interelectrodic space.*

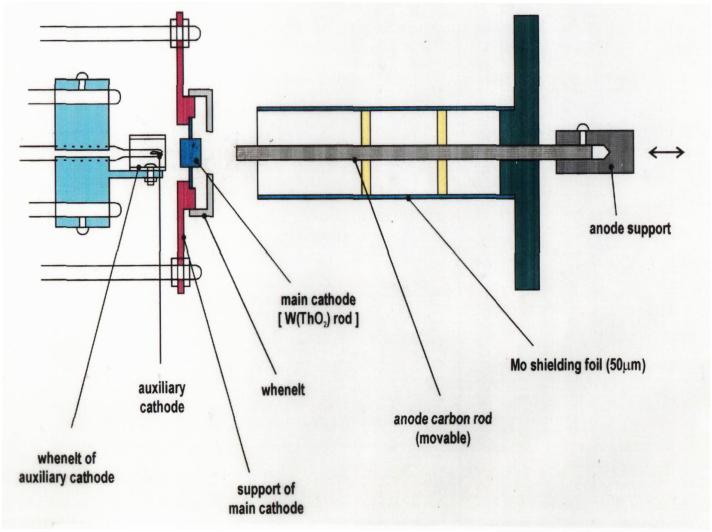

Figure 3. *Schematic view of the experimental arrangement for carbon film evaporation*

Table 1. *The main working parameters for TVA technology.*

Parameters	**Value**
Anode carbon rod diameter (mm)	10
Anode carbon rod length (mm)	15
Interelectrodic distance (mm)	2
Intensity of the arc current (mA)	270
Applied high voltage (kV)	1.8
Working pressure (torr)	5×10^{-5}
Time of deposition (s)	150
Deposition rate (Å /s)	2
Thickness of the film (nm)	30

3. Results and discussions

The deposited C films were studied using TEM electronic microscopy with a magnification of 1.4 M and a resolution of 1.4 Å. The samples of deposited carbon films (deposited on NaCl or KCl monocrystals) have been solved in water before TEM examination. They reveal nanostructured films.

Figure 4 shows the contrast fringes given by complex crystalline particles included in the amorphous film. The arrows indicate the interplanar distance corresponding to the crystalline structures. Particles are embedded in the film with graphite zone that covers the particles

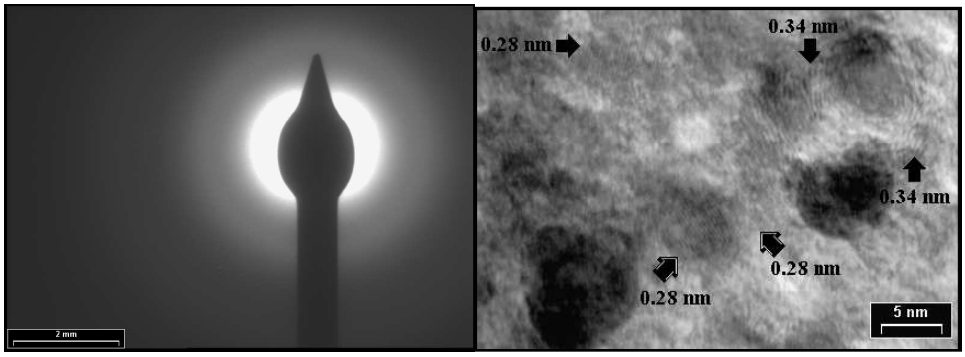

Figure 4. *TEM image of carbon thin film.*

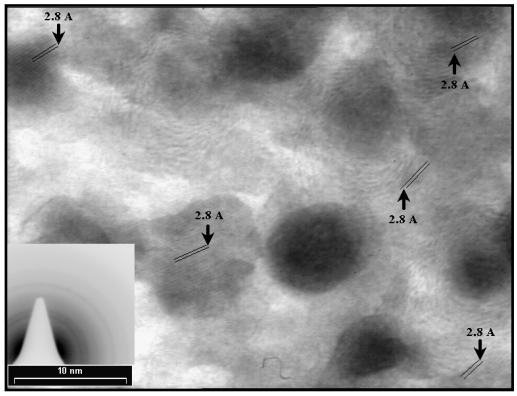

Figure 5. *HRTEM Image of carbon thin film and electron diffraction.*

High resolution transmission electron microscopy (HRTEM) images analysis shows the interference fringes given by the complex crystallites included into the amorphous carbon (Figure 6). The arrows show the interplanar distances corresponding to the crystalline structure. The pictures present the lattice plane from nano-crystal obtained for different position and orientation of substrate (NaCl, KCl).

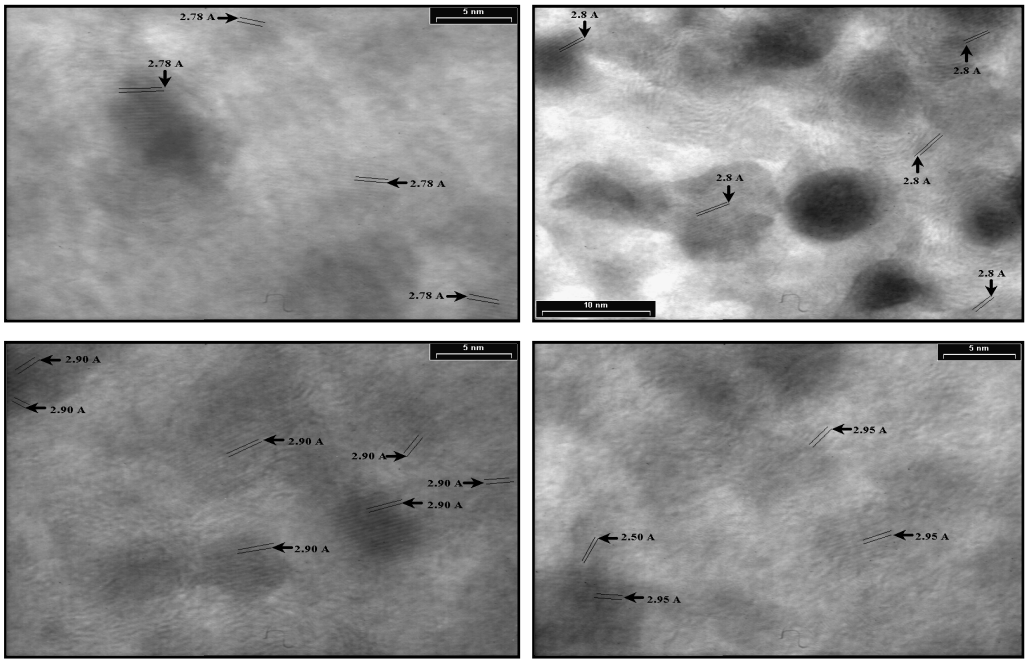

Figure 6. *HRTEM pictures of the lattice plane obtained for different position and orientation of substrate (NaCl, KCl).*

A rhomboidal structure with lattice parameters: a = 0.25221 nm, c = 4.3245nm (ASTM pattern: 79 - 1473) of diamond/carbon [3] has been obtained from electron diffraction pattern. In Figure 7 it can be observed SAED pattern obtained from carbon thin film deposited by TVA method using indirect by heated cathode.

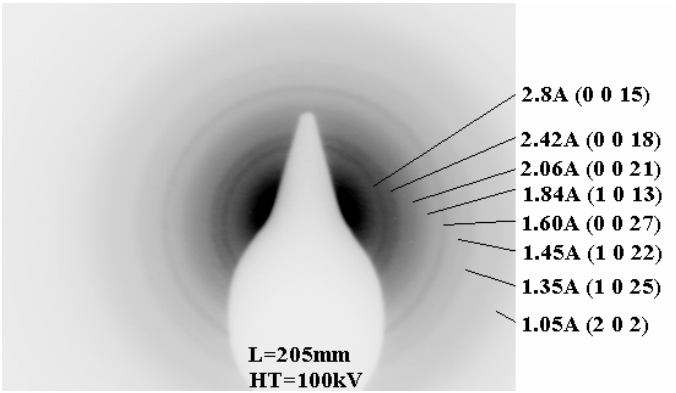

Figure 7. *SAED pattern obtained from carbon thin film.*

Raman spectroscopy was used to identify the carbon phase of the deposited films. Raman spectra were obtained in a back-scattering configuration using the 514.5 nm line of an Ar^+ laser

with 5 mW power and 50 mm spot diameter. The signal was detected with a photomultiplier using a standard photon counting system with the acquisition time of 60 s.

Figure 8 shows the Raman spectrum of a film grown in conditions presented above. One can clearly observe two asymmetric bands. For deeper analysis this spectrum was fitted with gaussian functions using a commercial fitting computing program. The fitted peak shape, have their maximum value at 1416 cm^{-1} and at 1577 cm^{-1} and correspond to D and G bands respectively [6].

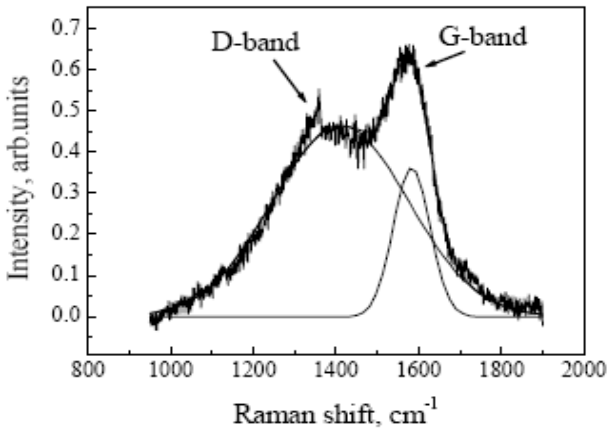

Figure 8. *Raman spectrum of a carbon film.*

An important characteristic appearing in carbon coatings is those of the film adhesion. The adhesion of the film to the substrate is very close related on the stress magnitude and the micro-structural defects at the interface film-substrate, appearing particularly at high temperature depositions [5]. A general conclusion on the stress level of the coatings prepared by different methods shows that by chemical vapor deposition (CVD) techniques the stress levels are larger compared with that of the coatings prepared by physical vapor depositions (PVD). This is because the substrate is heated when are using CVD methods.

Thermal stress appears just after the deposition, during cooling, when the thermal expansion coefficient is very much different from those of the substrate. The stress can be of tensile or compression type. The former can be generated by small holes, pores in substrate and the latter, found particularly to the PVD coatings, can be produced by the high energy of the particles bombarding the film during deposition. Lowering of the compression stress can be achieved by using deposition methods where the working pressure is as low as possible. The TVA method has a high potential to obtain films with very low stress because do not use any

buffer gas and the processing pressure is at the order of 10^{-4} Pa. Internal stress is an important parameter due to the fact that the maximum admissible thickness depends on it.

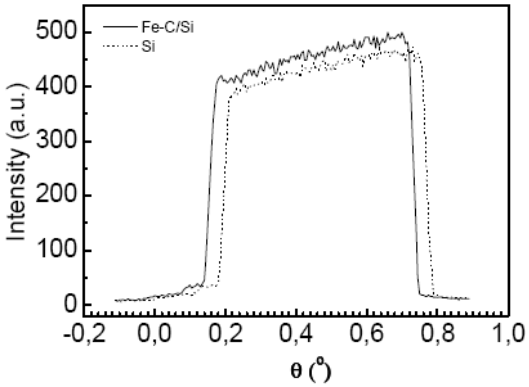

Figure 9. *XRD peaks of the residual stress of the carbon film made by TVA.*

This is important for avoiding the peeling of the deposited layer. Measurement of the residual stress can be made using X-ray techniques in the frame of the $\sin^2 y$ method based on the study of the crystallographic planes. Another technique is based on the study of the full width at high maximum (FWHM) of the XRD peaks, Figure 9.

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.

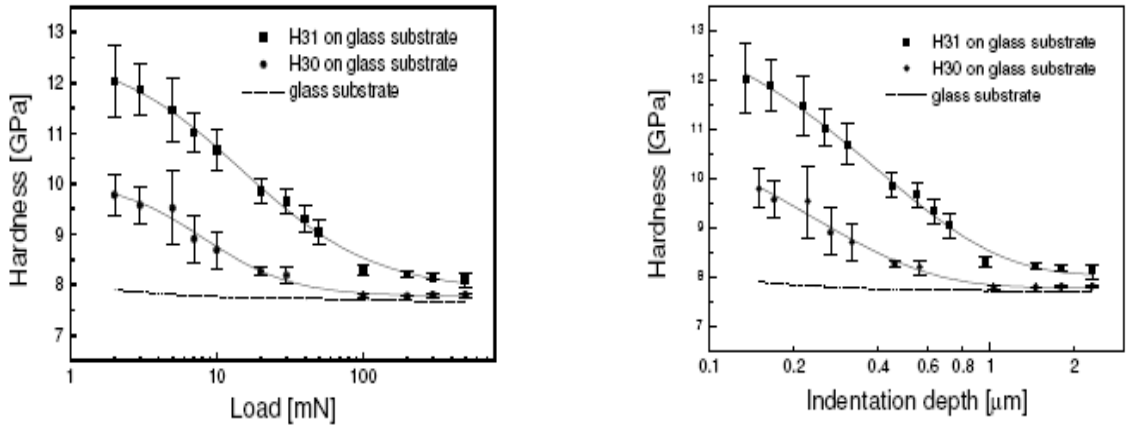

Figure 10. *The composite hardness of the film-substrate systems (H31 on glass, H30 on glass) and the hardness of the glass substrate as a function of the load (left) and of the indentation depth (right).*

A number of increasing loads ranging from 1 to 1000 mN were applied to each sample to obtain the hardness [4] and elastic modulus as a function of load and indentation depth (Figure 10). This enabled us to study the influence of the substrate on the measured material parameters.

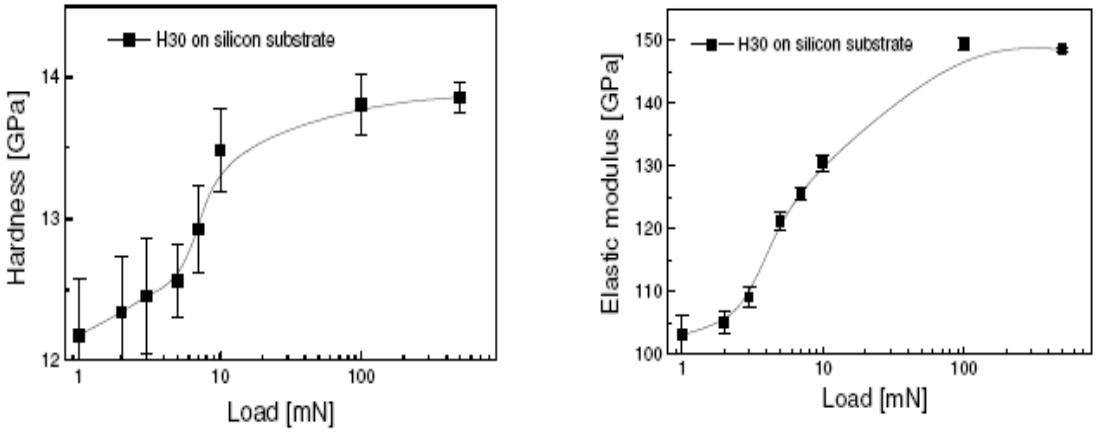

Figure 11. *Hardness and elastic modulus of the H_30 film on silicon substrate.*

The film H_30 had lower hardness and elastic modulus than the silicon substrate, so the measured composite hardness and effective elastic modulus increased with increasing load (figure). In Figure 11 it can be observed an abrupt drop in both graphs due to cracking and delamination effects when the applied load of 10 mN was exceeded.

4. Conclusions

TVA method can be used successfully for preparation of zero stress metal-carbon films for MEMS applications. High resolution TEM images of the prepared films using TVA method reveal nanostructured particles with 3-11 nm diameter size, embedded in the amorphous carbon film. The obtained films are smooth with an average roughness of 2-3 nm. The unstressed films revealed by a XRD method were obtained using metal (Fe, Cr, Ni, Al) as dopants. The Fe-C films exhibited higher resistance to some chemical agents used in microelectronics technologies and the electric resistance was found to decrease with the atomic number of the metal additive.

One concludes that TVA method can be used successfully for preparation of unstressed metal-carbon films for MEMS applications.

High resolution TEM images of the prepared films using TVA method reveal nano-structured particles with 3-11 nm diameter size, embedded in the amorphous carbon film.

The obtained films are smooth with an average roughness of 2-3 nm. The unstressed films revealed by a XRD method were obtained using metal (Fe, Cr, Ni, Al) as dopants.

References

[1] „ Nanostructured carbon thin films deposition using Thermionic Vacuum Arc (TVA) technology", G. Musa, I. Mustata, M. Blideran, V.Ciupina, R. Vlădoiu, G. Prodan, E. Vasile, J Optoelectron Adv M, vol. 5, No.1,(2003) 667-673

[2] „Diamond like nanostructured carbon film deposition using Thermionic Vacuum Arc", G. Musa, I. Mustata, V. Ciupina, R. Vlădoiu, G. Prodan, E. Vasile, H.Ehrich, Diamond and Related Materials, vol.13 (2004) 1398-1401

[3] „Thermionic Vacuum Arc (TVA) new technique for high purity carbon thin film deposition", G. Musa, I . Mustata, M. Blideran V. Ciupina, R. Vlădoiu, G. Prodan, E. Vasile, H Ehrich, Acta Physica Slovaka ,vol 55, no 4,(2005) 417-421

[4] "Unstressed carbon-metal films deposited by thermionic vacuum arc method", C. P. Lungu, I. Mustata, G. Musa, A. M. Lungu, O. Brinza, C. Moldovan, C. Rotaru, R. Iosub, F. Sava, M. Popescu, R. Vlădoiu, V. Ciupina, G. Prodan, N. Apetroaei, J Optoelectron Adv M, vol. 8, no1 (2006) 74-78

[5] "Handbook of carbon, graphite, diamond and fullerenes", Hugh O. Piearson, Noyes Publications, New Jersey, USA, (1993)

[6] "Raman spectra of carbon thin films", G. Musa, R. Vlădoiu, V. Ciupina, J. Janik, J Optoelectron Adv M, vol 8, no 2 (2006) 621-624