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# TEM investigation of the C-Me multilayer nanocomposites deposited by Thermionic Vacuum Arc (TVA) method

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The aim of this paper is to analyze the nanostructured carbon-metal bilayers deposited by Thermionic Vacuum Arc (TVA) technology in a special two electron gun configuration. This method allows the simultaneous deposition of different materials, providing the possibility of obtaining multi-component thin films. Thin film deposition process by Thermionic Vacuum Arc (TVA) might become one of the most suitable technologies to significantly improve the quality of the surfaces covered with films in which the coating is bombarded by high energy ions of even depositing materials. The morphology of the thin films surface was examined using Transmission Electron Microscopy (TEM).

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## 1. Introduction

Since the discovery of nanocomposites [1], the understanding of the unique physical properties of wrapped graphene like materials [2–4] have attracted large attention among researchers. Nanocomposites have unique nanostructures with remarkable electronic and mechanical properties. The research communities have been focused enormous interest on their unusual electronic properties. As other useful properties have been discovered, particularly strength, interest has grown in potential applications. Nanocomposites could be used for conducting lightweight and strong materials and nanometer-sized electronics or to strengthen polymer materials [5-7]. Nanocomposites tubes are attracting interest as constituents of novel nano-scale materials, device applications, novel-mechanic, electronic, magnetic and chemical properties [8]-[9].

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 film. [15]

In recent years, multilayers composed of C coating with very thin buffer layers metals like Cu, Sn, Ag or Al become a major area of interest, especially for tribological applications. An important amount of work is presently dedicated at studying synthesis of high quality carbon films using different methods like: magnetron sputtering, Thermionic Vacuum Arc (TVA) 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. [16]

Successive deposition in vacuum of two different types of thin film materials can generate a new compound with different parameters from both used materials pure thin films. [10]-[11] It is obvious that compactness of the deposited material might be one of the main parameters. In order to ensure such materials we used as deposition method a new discharge type in pure metal and non-metal vapor plasma, namely Thermionic Vacuum Arc (TVA).[12-14]

Thermionic Vacuum Arc (TVA) has a simple construction; the cathode is a tungsten filament surrounded by a Wehnelt cylinder and the anode – an adequate crucible containing the material necessary to generate the vapors. At the application of a high dc voltage over the electrodes, the accelerated electrons incident on the anode, heats the anode material which first melts and afterwards starts to boil and evaporate. A steady state concentration of the anode material's atoms is established in the interelectrodic space. At a further increase of the applied high voltage, **in vacuum conditions,** a bright Thermionic Vacuum Arc (TVA) is established. Practically, any solid material mounted at the anode can be evaporated and transformed to bright plasma. This new technology for thin films (or even thick films) deposition has a number of sounding advantages like: -thin film is condensing exclusively from the plasma state of the material to be deposited

-during deposition, the growing thin film is bombarded by the energetic ions just of the atoms of the anode material plasma.

-the energy of the ions can be fully controlled and even changed during the deposition

-because the TVA plasma is localized around the arc electrodes, a number of independent and **simultaneous discharges** (eventually with different materials) can operate in the same time and in the same vacuum vessel in order to realize co-deposited thin films.[17]

The aim of this paper is to analyze the nanostructured carbon-metal bilayers deposited by Thermionic Vacuum Arc (TVA) technology in a special two electron gun configuration. [18-19]

The multilayer samples was investigated using Transmission Electron Microscopy (TEM) analyses were performed on a Philips CM 120 ST (120 kV) TEM provided with HR-TEM facility capable of obtaining a resolution of 1.4 Å and a magnification of 1.2 M.[20]-[22]

## 2. Experimental

By using the TVA method, the metal deposition takes place in high or ultrahigh vacuum conditions, without the presence of any gas, excepting the material evaporated at the anode. This method allows the simultaneous deposition of different materials, providing the possibility of obtaining multi-component thin films, in this particular case the C-Ag, C-Cu, Cu-Sn and Cu-Al system. The electron guns are symmetrically arranged with respect to the substrate – glass and stainless steel – mounted at a distance of 400 mm on the central line.

In order to obtain relative concentration of the C-Me elements in the prepared layers were evaporated the two elements using two independent vacuum thermionic arcs.[21] The anode temperature of the each element was adjusted in order to have comparable evaporation rates. The substrates were settled above the evaporation sources, with different relative distances from each –other as can be seen in Fig. 1.

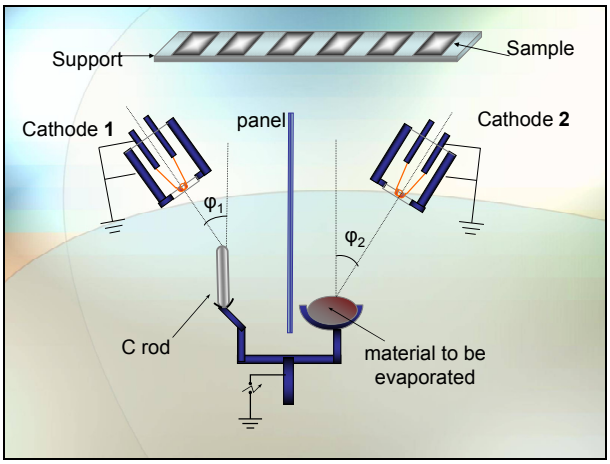


*Fig. 1. Electrodes set-up for simultaneous deposition of two materials on the same sample.*

In this case, due to the deposition rate that decreases with the square of the anode-substrate distance, we can expect that the samples situated close to the C anode to contain higher C concentration relative to the Cu. The same experimental arrangement was used for the C-Ag, C-Sn and C-Al layer preparation.

The intensity of the heating filament was $I_f$ = 48 A. at a deposition rate of 3Å/s. The pressure during the discharge process was about 1.5x10$^{-5}$Torr~7.5x10$^{-6}$Torr.

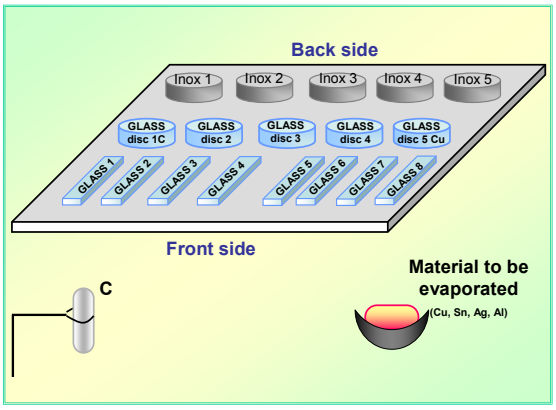


*Fig. 2 Sample position on holder for C-Ag discharge.*

The deposition was made on stainless steel discs and glass. In Fig. 2 are presented the sample position on the holder, we can observe 5 pieces of stainless steel discs, 5 pieces of optical glass and 8 pieces of glass.

## 3. Results and discussion

The elementary composition of the obtained carbon multilayers were investigated by mean of Transmission Electron Microscopy (TEM) analyses were performed on a Philips CM 120 STEM.

The samples of deposited C- Cu films (deposited on glass and stainless steel discs) have been solved in water before TEM examination. They have shown nanostructure films. Fig. 3 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.

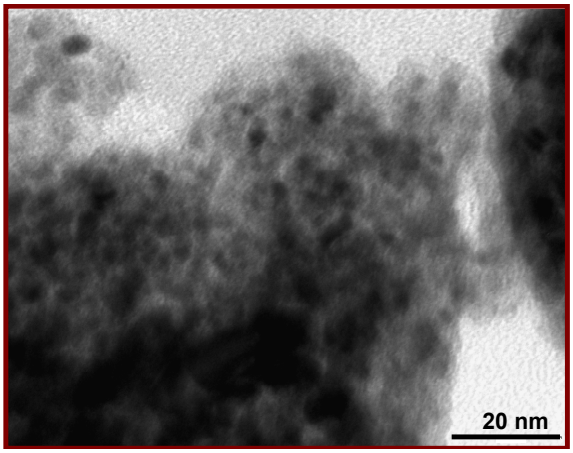


*Fig.3 C-Cu nanocomposite film at 20 nm scale.*

In Fig. 4 we can observed at the same scale (20nm) report of the grains obtained, with maximum frequency corresponding at 4, 69 nm mean diameter

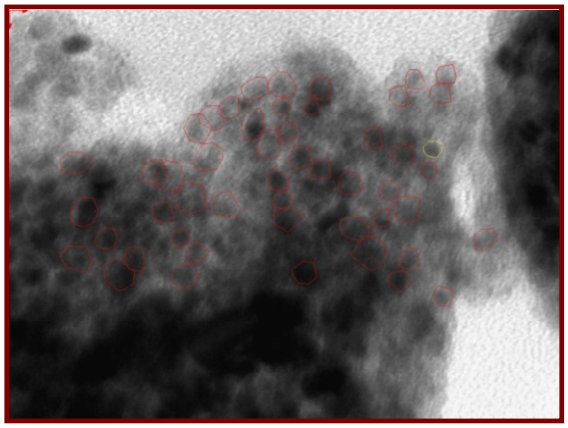

*Fig. 4 TEM image with grains distribution (20nm).*

Fig. 5 and Fig. 6 present a complex morphology of the film deposited by Thermionic Vacuum Arc method. The film is compound by Sn nanoparticles; the existence of these nanoparticles indicated the presence of the defined rings by electron diffraction. The diameter of the Sn nanoparticles varied between 10-30 nm.

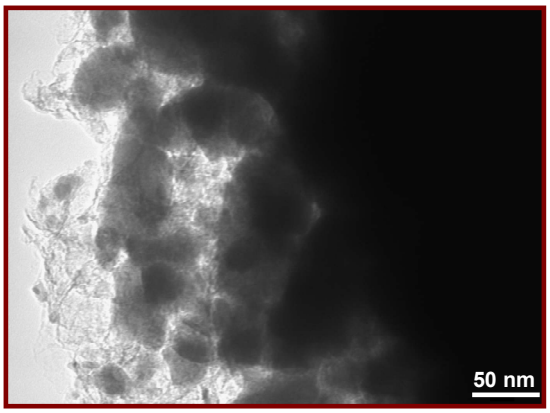


*Fig.5 TEM image for C-Sn nanocomposite film at 50 nm scale obtained of the out edge of deposition film.*

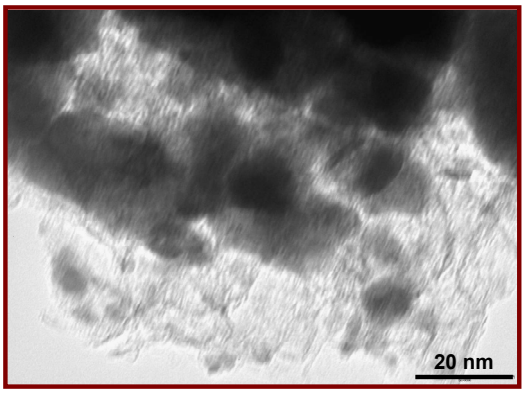


*Fig. 6 TEM images obtained for C-Sn on the boundary film (20 nm).*

Electron diffraction pattern for as deposited C-Sn film (10nm) shows the contrast fringes given by complex crystalline particles included in the carbon amorphous film. (Fig. 3)

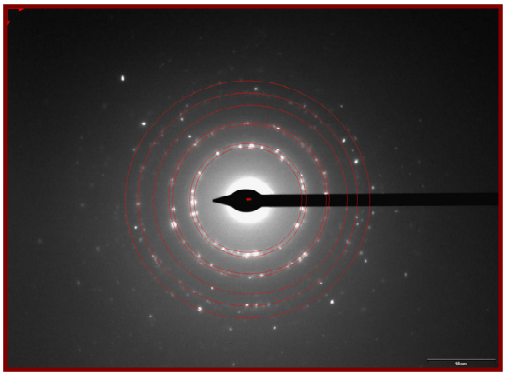

*Fig. 7 Electron diffraction pattern for as deposited C-Sn film (10nm).*

Also, in the case of C-Ag film we can observe Ag nanoparticles included in the carbon amorphous film. (Fig. 8), the presents of this are confirmed by electron diffraction.

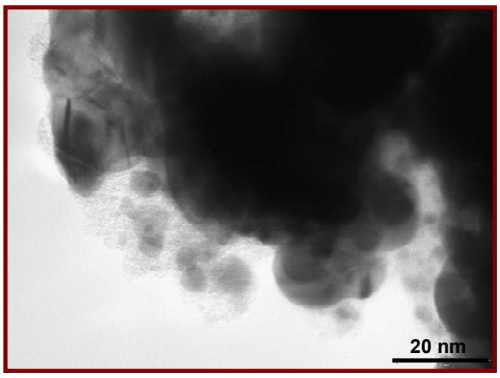


*Fig. 8 High-resolution TEM image of the C-Ag film deposited using TVA (20 nm).*

Electron diffraction performed on the silver nanostructures indicated the presence of the well- defined rings, the diameters is 10 nm. (Fig. 9)

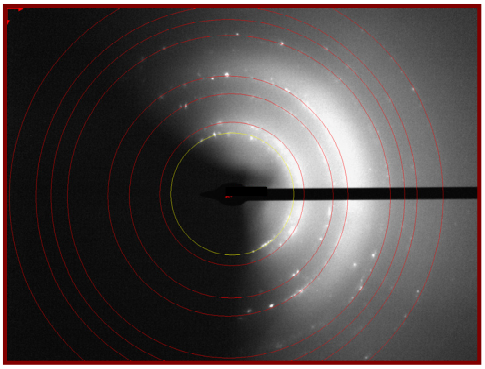

***Fig. 9*** *Electron diffraction pattern for as deposited C-Ag film (10nm).*

The complex morphology of the thin film can be observed from the following figures (Fig. 10 and Fig. 11). The thin film is composed by $Al_4C_3$ grains that are confirmed by the electron diffraction. On the other hand, we indentified Al by the electron diffraction.

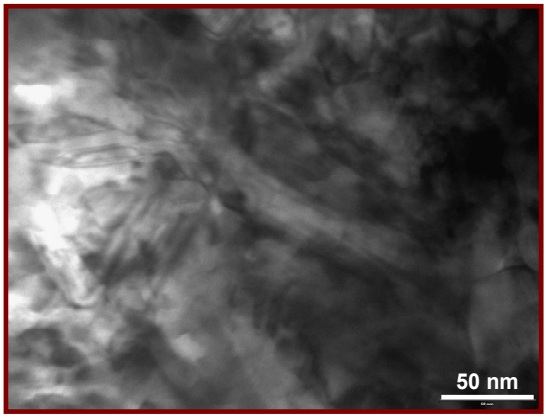


*Fig. 10 TEM images obtained for C-Al on the boundary film (50 nm) for observed structural and morphology details.*

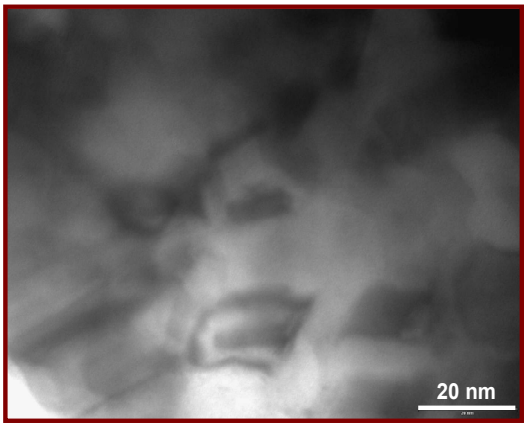


*Fig. 11 TEM images obtained for C-Al on the boundary film (20 nm).*

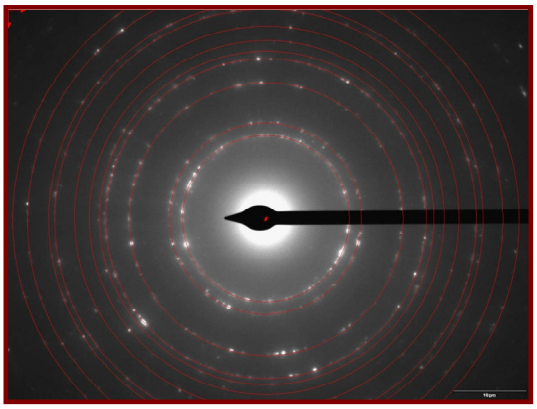

*Fig. 12 Electron diffraction pattern for as deposited C-Al film.*

Electron diffraction performed on the Al nanostructures indicated the presence of the very well-defined rings. C-Al film with a d-spacing corresponding to a rhomboedral structure space group R-3m with a = 0.333 nm and c = 2.49 nm (Fig.12)

## 3. Conclusions

We used a new technique, Thermionic Vacuum Arc, for depositing multilayer nanocomposite thin films. TVA discharges were generated using carbon and metals (Cu, Sn, Ag, Al) as anode materials. It was presented the method of as a very suitable procedure for obtaining multilayers films of a controlled quality.

The structure of the films have been characterized using Transmission Electron Microscopy (TEM) performed on a Phylips CM 120 ST (120 kV) TEM with a resolution point of 1,4 Å and a magnification of 1,2 million times. The results obtained for the multilayer films were between 20 – 50 nm.

## References

[1] S. Ijima, Nature London **354**, 56, (1991).
[2] J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, C. Dekker, Nature ~London **391**, 59 (1998).
[3] O. M. Kuttel, O. Groening, C. Emmenegger, L. Schlapbach, Appl. Phys. Lett. **73**, 2113, (1998).
[4] F. Okuyama, T. Hayashi, and Y. Fujimoto, Journal Appl. Phys. **84**, 1626 (1998).
[5] V. Ciupina, C. Baban, A. Petcu, L. Petcu, P. Rambu, G. Prodan, G. I. Rusu, J. Optoelectron Adv. Mater. **10**(3), 665 (2008).
[6] C. Prados, P. Crespo, J. M. Gonza´lez, A. Herna´ndo,
[7] J. F. Marco,R. Gancedo, N. Grobert, M. Terrones, R. W. Walton, H. W. Kroto, Phys. Rev. B **65**, 113405, (2002).
[8] F. U. Naab, O. W. Holland, J. L. Duggan, F. D. McDaniel, J. Phys. Chem. B **109**, 1415 (2005).
[9] H. Khodja, M. Pinault, M. Mayne-L'Hermite, C. Reynaud, Nucl. Instr. and Meth. in Phys. Res. B **249**, 523 (2006).
[10] G. Musa, R. Vladoiu, V. Ciupina, C. P. Lungu, I. Mustata, S.Pat, T. Akan and N. Ekem, J. Optoelectron. Adv. Mater. **8**(2), 617, (2006).
[11] T. Akan, G. Musa, Balkan Physics Letters, **13**(2), 57 (2005).
[12] C. Mathew Mate, Tribology on the small scale, Oxford University Press, 2008.
[13] R. Vladoiu, V. Ciupina, A. Mandes, V. Dinca, M. Contulov, G. Prodan, G. Musa, J. Optoelectron. Adv. Mater. **10**(3), 723 (2008).
[14] T. Akan, N. Ekem, S. Pat, R. Vladoiu, G. Musa, J. Optoelectron. Adv. Mater. **7**, 2489 (2005).
[15] C. P. Lungu, I. Mustata, A. M. Lungu, O. Brinza, V. Zaroschi, V. Kuncser, G. Filoti, L. Ion, J. Optoelectron. Adv. Mater. **5**(4), 2507 (2005).

[16] C. P. Lungu I. Mustata, A. M. Lungu, O. Brinza, C. Moldovan, C. Rotaru, R. Iosub, F. Sava, M. Popescu, R. Vladoiu, V. Ciupina, G. Prodan, N. Apretroaei, J. Optoelectron. Adv. Mater. **8**(1), 74 (2006).
[17] G. Musa, C. Surdu-Bob, C. P. Lungu, V. Ciupina, R. Vladoiu, J. Optoelectron. Adv. Mater. **9**(4), 867 (2007).
[18] G. Musa, I. Mustata, V. Ciupina, R. Vlădoiu, G. Prodan, E Vasile, H. Ehrich, Diamond and Related Materials **13**, 1398 (2004).
[19] R. Vlădoiu, V. Ciupină, C. Surdu-Bob, C. P. Lungu, J. Janik, J. D. Skalny, V. Bursikova, J. Bursik, G. Musa, J. Optoelectron. Adv. Mater. **9**(4), 862 (2007).
[20] C. Farcau, V. Canpean, M. Gabor, T. Petrisor Jr., S. Astilean, J. Optoelectron. Adv. Mater. **10**(4), 809, (2008).
[21] R. Vladoiu, C. P.Lungu, I. Mustata, V. Bursikova, J. Bursik, J. Optoelectron. Adv. Mater. **9**(4), 1087 (2007).
[22] F. Piazza, D. Grambole, L. Zhou, F. Talke, C. Casiraghi, A. C. Ferrari, J. Robertson, Diamond and Related Materials **13**, 1505 (2004).

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