

Morphology and electronic structure of nanostructured carbon films embedding transition metal nanoparticles

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Abstract. Inclusions of metals in the growth process of carbon cluster assembled materials (ns-C) induce modifications in the structural and electronic properties of the material. A novel pulsed microplasma cluster source (PMCS) is able to deliver highly intense, collimated and stable beams suitable for producing bulk quantities of cluster-assembled nanocomposite films. Loading of metal nanoparticles into carbon cluster based films is obtained either by mixing a gas phase metallorganic compound with the carrier gas (He) before entering into the source (for example molybdenum (V) isopropoxide), or by using a double component sputtering target (metal (Ti, Ni)/graphite). The study of film morphology on nanometer scale, carried out by transmission electron microscopy (TEM), reveals the dispersion in a ns-C matrix of metallic particles and, in the case of molybdenum containing films, also of carbide particles. Spatially resolved ultraviolet photoemission spectroscopy confirms the segregation of metal particles and exhibits evident anisotropy in the Mo:ns-C films, mainly ascribable to the formation of carbide nanoparticles.

PACS. 81.05.Uw Carbon, diamond, graphite – 81.05.Zx New materials: theory, design, and fabrication – 68.37.Lp Transmission electron microscopy (TEM) (including STEM, HRTEM, etc.) – 79.60.Dp Adsorbed layers and thin films

1 Introduction

Supersonic cluster beam deposition is a viable technique for the synthesis of nanostructured films where the structural and functional properties of the material are influenced by the mean size of the clusters [1]. A precise control on the cluster beam is fundamental for obtaining deposits with tailored properties [2]. Intense and stable cluster sources are then needed. The Pulsed Microplasma Cluster Source (PMCS) [3] satisfied this requirements, yielding it suitable for producing bulk quantities of cluster-assembled films of various materials.

In this paper we present a study on the structural and electronic properties of nanostructured carbon (ns-C) films embedding transition metals grown by using PMCS. The inclusion of metals is expected to induce modifications in the structural and electronic properties of the material. For example it has been demonstrated that ns-C films show a very large surface available for electrochemical reactions [4]. The dispersion of metal nanoparticles into ns-C films could built up a highly efficient catalyst. Moreover formation of carbide nanoparticles can improve the

mechanical properties of the material, such as hardness and wear resistance. The metals used in the source have been molybdenum *via* gas-phase, nickel and titanium from solid phase. Film morphology, characterized on micrometer length scale by scanning electron microscopy (SEM), does not seem to be affected by metal particle inclusions. Likewise backscattered electron images do not show regions with different atomic weight, that is metal particles appear to be uniformly dispersed. A detailed investigation at nanoscale by transmission electron microscopy (TEM) reveals the dispersion in a ns-C matrix of metallic nanoparticles and in the case of molybdenum also the presence of MoC nanoparticles. Spatially resolved ultraviolet photoemission spectroscopy has been utilized for mapping the spectral features of the valence bands. This technique has highlighted a large anisotropy in the Mo:ns-C film due to the local formation of molybdenum carbide.

2 Experimental

The cluster beam deposition apparatus is equipped with a pulsed microplasma cluster source (PMCS), in detail described in reference [3]. Briefly, the apparatus consists

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of three differentially pumped chambers, separated by electroformed skimmers, and operates in the high vacuum regime, with a base pressure of 1×10^{-7} Torr. The PMCS source is hosted in the first chamber, in which the mean pressure during the deposition is maintained between 2×10^{-5} and 2×10^{-4} Torr. In the second chamber a manipulator for intercepting the seeded beam and a quartz microbalance for the beam intensity monitoring are housed. The third chamber hosts a linear time of flight mass spectrometer (TOF/MS), which is mounted collinear to the beam axis in order to achieve the best transmission. In the PMCS a helium pulse is injected into the reaction chamber and ionized by an intense pulsed electric discharge between the two electrodes. The vaporized atoms produced by localized ion sputtering are quenched by He and then condense in clusters. These are carried by helium through the PMCS nozzle to form a seeded supersonic beam. By placing substrates on the beam trajectory, cluster assembled films can be grown [5].

We developed two methods for loading metal nanoparticles into the reaction chamber of the source: one is based on gas phase injection, where a metallorganic compound is mixed to helium at the back of the pulsed valve; the other one is based on solid phase injection, where the sputtered target is a double component rod (metal-graphite). The gas mixture is prepared in a bubbler, a 75 cm^3 stainless steel cylinder, containing a liquid solution of the metallorganic compound. A high pressure helium line enters the bubbler and flushes the gas into the liquid; a second line exits the bubbler and carries the helium-metallorganic vapor mixture to PMCS. Inside the reaction chamber of the source, the electric discharge ionizes the helium and induces the cracking of the metallorganic compound, furnishing metal atoms and highly reactive radicals to the condensing carbon vapor. This method allows a careful control of the amount of the injected metallorganic precursor by acting on the bubbler temperature, according to the relation

$$\log p = \left(-0.2185 \frac{A}{T} \right) + B$$

where p is the vapor pressure of the solution (in Torr), T is the temperature (in K), A and B are parameters related to the organic chemical species used as solvent of metallorganic compounds. For example, we used isopropanol, that has $A = 10063.5$ and $B = 8.996156$, and validity range for the above formula from -26.1 to 232.0 °C [6]. In order to prevent the condense of the metallorganic component of the gas outcoming from the bubbler, temperature is maintained at a lower value than room temperature. In this way the partial pressure of the metallorganic compound is limited to less than 1%. To inject a higher quantity of metal it is necessary to use a solid phase precursor. We have assembled a target rod with a copper stand, which holds in sequence: a graphite cylinder, a metal disk and a graphite cap. As reported in reference [3], the target erosion process is highly localized, thus we can sputter the metal-graphite border region eroding at the same time carbon and metal. In the experiments presented in this work we have used

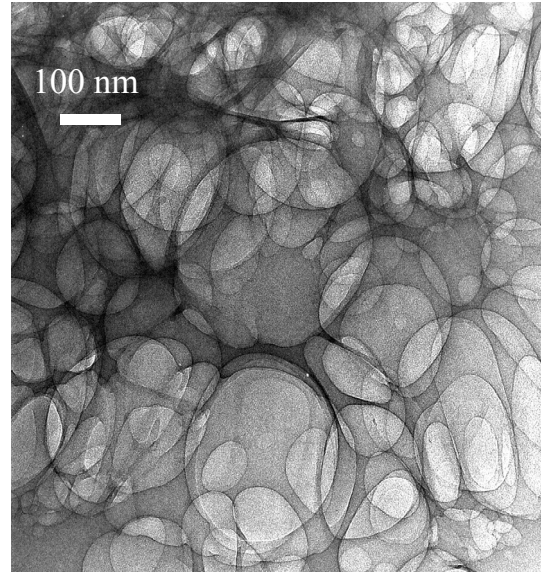


Fig. 1. TEM picture of foam-like carbon obtained by adding metallorganic molybdenum.

molybdenum in gas phase ($\text{Mo}(\text{OC}_3\text{H}_7)_5$), nickel and titanium in solid phase (purity 99.99%).

Thin films have been characterized by transmission electron microscopy (TEM) with a microscope JEOL JEM-4000EX (400 kV, spatial resolution 0.2 nm).

Spatially resolved photoemission spectroscopy has been performed at the Spectromicroscopy beamline at ELETTRA synchrotron light source [7]. The scanning photoemission microscope is based on a multilayer-coated Schwarzschild objective suitable for focusing X-ray radiation. The lateral resolution is $0.5 \mu\text{m}$. The energy resolution ranges between 0.1 to 0.2 eV depending on the analyzer pass energy. The study of the electronic features of the metal containing ns-C film has been carried out using a photon energy at 95.0 eV.

3 Results and discussion

3.1 Morphology

TEM analysis shows the existence of ordered nanostructures: (i) nanosized metal and/or carbide particles; (ii) graphitic-like structures, such as fullerenes and onions; (iii) distorted graphene sheets. All of those structures are embedded in an amorphous carbon matrix. In the case of molybdenum including samples, the structure exhibits unique foam-like features never observed till now [8]. As shown in Figure 1, the film appears to have a low density due to a light skeleton that marks out spheroid voids, whose dimensions are of the order of 100 nm. The metal and/or carbide particles have a typical diameter of about 10 nm and appear to be uniformly dispersed into the material. We regard the foam-like carbon structures as the result of a sort of catalytically driven aggregation process in which a small amount of molybdenum plays a crucial

role. The corresponding diffraction pattern shows several spots laying on circles, indicating the presence of sub-micrometer sized particles. However no conclusive evaluation of the lattice parameters can be extracted and those particles can not be definitely identified as pure metal or carbide. In the case of Ni:ns-C and Ti:ns-C films, no indication about the presence of carbides arises from TEM characterization, nor metallic lattice distortions, ascribable to the presence of interstitial carbon atoms, are visible. This is expected in the case of Ni. In fact, if a nickel-carbon mixture could even exist at high temperature, it immediately undergoes a segregation phenomenon when temperature decreases. On the other hand, the absence of composites is somehow surprising in the case of Ti, whose tendency to form carbides is well-known. The amount of graphitic nanostructures appears to be related to the metal species. In the case of the Ni:ns-C films, they look more uniformly and densely distributed than in the case of the titanium containing films. Moreover they are more rich in fullerenes and onion-like structures. On the contrary, Ti containing films are poor in these structures and show, as predominant form of carbon allotropes, a large fraction of amorphous material together with highly distorted graphene sheets. Ni particles appear in spheroidal shape, essentially monodisperse with size in the range 2–7 nm, and uniformly spread across the sample. Most of these particles are covered by several graphitic shells. Ti particles have a more spread size distribution than in the case of Ni, ranging up to about 50 nm; moreover, they are not uniformly spread at the nanoscale. Ti particles are always covered by 1 or 2 graphitic layers. The recognized differences in the carbon nanostructures can be driven by the higher catalytic activity of nickel in promoting graphitization with respect that one of the titanium.

3.2 UPS characterization

The UPS spectra of a pristine nanostructured carbon film have been acquired in different zones of the sample for investigating the presence of possible anisotropies detectable in the spectral features. Since no meaningful differences appear among the spectra, the average spectrum can be adopted for a reliable picture of the DOS features of the pure ns-C films (see Fig. 2). The spectrum is dominated by an intense peak at a binding energy of 7.0 eV, relative to the p - σ band. The p - π states appear as a shoulder at around 3.5 eV. On the high energy side, two additional features are distinguishable: a broad peak at 17.3 eV and a shoulder at 13.2 eV attributable to $2s$ and sp bands respectively. Also the UPS spectra of metal containing ns-C films have been worked out as the mean of spectra collected in various zones of the samples. The obtained VB spectra are shown in Figure 2. It appears evident that the inclusion of Ti, Ni, and Mo in the ns-C film growth process induce a presence of metal containing clusters which manifest themselves in the VB photoemission spectra. The contribution of the metal related components can be studied due to their larger photoemission cross-sections comparing to the carbon's one. Actually the calculated photoemission cross-section of the VB electrons for Ni, Ti and Mo at a photon energy of 95 eV is 8.7, 3.25 and 0.9 Mbarn respectively, whereas for C is 0.65 Mbarn [9]. A metal inclusion should also induce an increment of the density of states close to the Fermi level, however the metal containing cluster are simply embedded in a ns-C matrix (*i.e.* they are not surely interconnected). We cannot distinguish between a spectral modification at the Fermi level related to the metal containing cluster signal or to a modification of the ns-C VB. In order to examine more deeply these results, we tried to identify the existence of spectral differences in photoemission maps and correlate them to an anisotropic distribution of the metal inclusions. The Ni:ns-C and Ti:ns-C maps do not show any position-related spectral anisotropy whereas the photoelectron map of Mo:ns-C show a quite large spectral anisotropy. In Figure 3b we report the spectra recorded in position 1 and 2 as labeled in the photoelectron map, shown in Figure 3a. The difference spectrum, displayed in the bottom panel, exhibits a peak at 3.3 eV, an intensity increase in the 0.0–5.5 eV range and a depletion in the 5.5–11.0 eV range. Comparing this result with the calculated DOS of metallic Mo, MoC and MoO [10] and photoemissions studies [11], we find a strict correspondence of the difference spectrum features with those of the MoC DOS, where the peak at 3.3 eV is related to a single narrow feature of $4d$ electrons. Moreover the Mo $4d$ electrons show a distributed intensity in the 0.0–5.5 eV range in

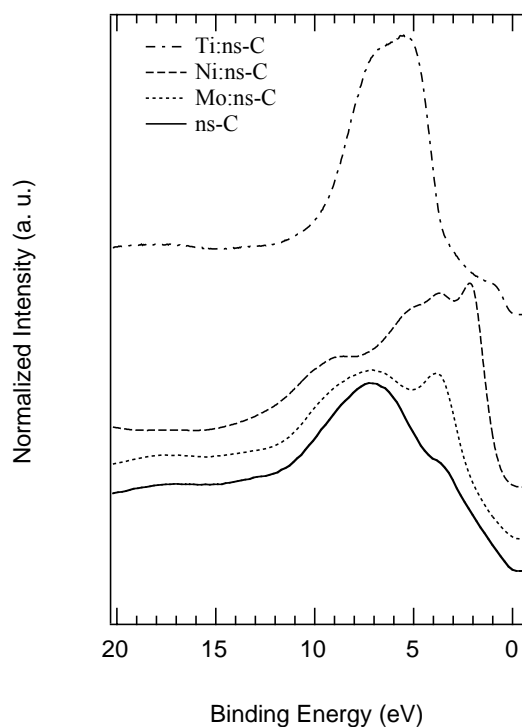


Fig. 2. UPS spectra of ns-C, ns-C:Ti, ns-C:Ni, ns-C:Mo. The presence of d -electrons from the valence bands of the included metals induces notable differences in the lineshapes. All the metal containing films show an increment of the density of states near the Fermi level, more prominent in the case of ns-C:Ni deposits.

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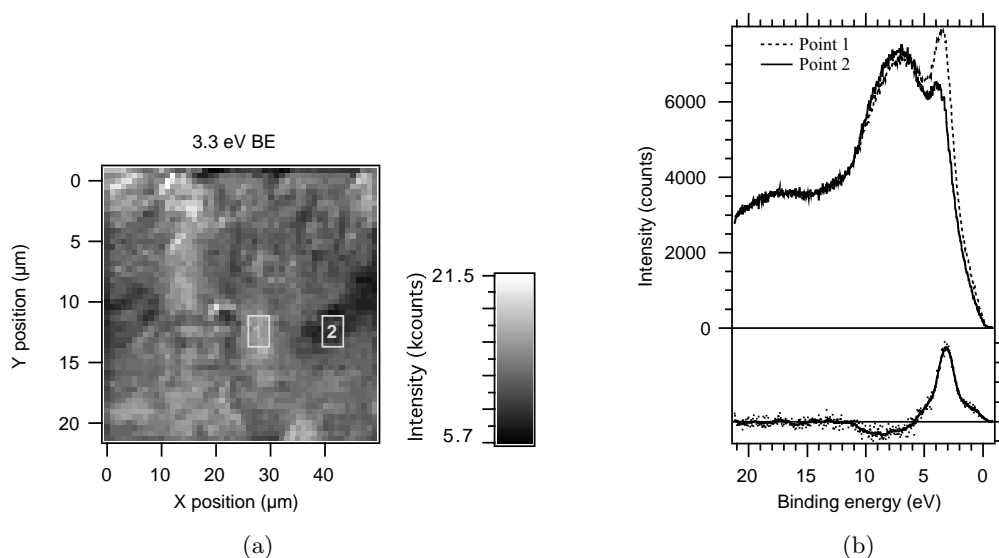


Fig. 3. (a) Photoelectron map of the ns-C:Mo at 3.3 eV. (b) Top panel: UPS spectra in the points labeled 1 and 2. Bottom panel: difference spectrum. The principal feature is related to the anisotropy of the film surface.

good agreement with the difference spectrum. Due to the difference in photoemission cross-section, the spectral signature of Mo 5s and C 2s and 2p are much less intense. Thus we expect that their relative peaks, placed at 5.5 and 10.0 eV, are responsible of faint features in the measured spectra. The comparison of spectral features of Ti:ns-C film with calculated DOS of metal carbide and oxide suggests the formation of TiO_x . The VB spectrum Ni:ns-C is very structured showing a sequence of peaks up to a binding energy of 10 eV. No clear assignments of these features can be done. In fact on one hand Ni and NiO calculated DOS show less structured profiles [10], while on the other NiC calculated DOS [10] present a series of peaks whose positions cover a 11 eV-wide range and seem to better resemble the revealed features. Nevertheless no unerring indication of carbide formation arises from these spectroscopic measurements.

4 Conclusions

The use of metallorganic compounds or of solid phase metals in a supersonic cluster deposition apparatus by using the PMCS source has been demonstrated to be a viable technique for the synthesis of nanostructured carbon films embedding transition metals. We have verified that the film morphology on nanometer scale depends on the metal species, in particular

- (i) molybdenum favors the formation of foam-like features of the assembled carbon;
- (ii) nickel promotes more efficiently the graphitization with respect to titanium;
- (iii) the embedded nanoparticles are mainly metallic in nature.

Spatially resolved UPS has shown the absence of anisotropy in nickel and titanium containing films, while in molybdenum including film a large anisotropy can be

detected. This effect has been attributed to the formation of MoC, not excluded in TEM analysis, but not unequivocally revealed. The assignment has been operated by means the comparison of the VB spectra with calculated DOS of corresponding pure metal, oxide and carbide. From an analog analysis for titanium and nickel, the oxidation of titanium and a probable formation of nickel carbide have been identified.

These first results on metal-carbon films grown by cluster assembling are very promising for the synthesis of materials with tailored functional properties.

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