Effect of ion irradiation
on structure and thermal evolution of the Ni-C$_{60}$ hybrid systems

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Abstract. We report on the thermal response of the transition metal/fullerene thin hybrid multilayers, pristine and ion-modified, i.e. Ni/C$_{60}$/Ni and Ni/a-C/Ni (a-C amorphous carbon), both prepared on the MgO(100) monocrystalline substrate. The multilayer sequences were gradually annealed up to the high temperatures and their structures were inspected using several analytical techniques. The inspection evidenced difference in the evolution of the virgin and ion-irradiated systems. In pristine (non-irradiated) composites (analyzed in the previous experiment) a significant part of the fullerene molecules out-
diffused during annealing < 500°C. At temperatures around (and above) 500°C fullerenes underwent (in the vicinity of Ni) massive fragmentation and conversion to a-C. Very high temperature (1000°C) annealing resulted in fabrication of an array of micrometer-sized octagonal pits and rod-type particles emerging from the encompassing a-C+Ni mixture. Ion irradiated multilayers (analyzed in the current experiment) developed in a different way. Thermal annealing < 500°C had only a minor effect on the integrity and composition of the system. Higher temperatures > 500°C, however, induced a forceful phase separation. The nominal annealing at 1000°C resulted in formation of faceted, sub-micrometer-sized (round, plate and rod-type) particles (with a Ni core and a thin a-C rind) that were spread individually (without a complex a-C+Ni matrix) on a thin a-C/MgO(100) interface. The main axes of the particles were oriented according to the crystallographic axis of the MgO(100) substrate.

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1. Introduction

The transition metal/C\(_{60}\) thin films (e.g., multilayers, co-deposited mixtures, etc.) provide a new class of materials with interesting transport, structural and other properties [1-4]. Some of them have already been utilized in practice, e.g., in electronics, see reports [5,6]. Besides their attractive properties, however, the integrated hybrid systems are considered thermodynamically and structurally unstable (due mainly to high internal stress arisen from mixing of mostly immiscible phases, and vulnerability of the C\(_{60}\)
molecule cages because of their easy photo-oxidation, polymerization or fragmentation in environment exhibiting strong catalytic properties). This makes their possible application more problematic. Obviously, various disruptive agents (such as thermal annealing, ion irradiation, laser illumination, chemical reagents, etc.) may then affect the thermodynamically-unstable systems and cause their structural changes on nanoscopic, as well as macroscopic scales. In fact, it has already been demonstrated that the transition metal/C$_{60}$ hybrids can be transformed into various ‘metal-carbon allotrope’ systems using (even only modest) energetic laser or ion beams; see, e.g., [7-9]. The input and dissipation of the energy of the external agents can trigger (in the stressed hybrid systems) processes of their rapid degradation (or transformation to arrangements exhibiting new structural parameters and properties).

Generally, ion induced disintegration of the C$_{60}$ molecules results in the modification of the hybrid nanostructures and, consequently, in a change of their properties (e.g., electric resistivity, thermal conductivity, etc.). Ion irradiation, which is a well-managed process, may, in such a way, be utilized to control and master the important hybrid systems’ properties.

The ion-induced transformation of fullerenes into other carbon allotropes (e.g., to amorphous carbon, a-C) may further affect the behavior (and evolution) of the composite systems in the post-deposition processing or exposition to various environments. Elevated temperatures (e.g., 500-1000°C) might cause a modification in nanostructures that could differ from those of the non-irradiated specimens. It is thus of interest to inspect the behavior of the transition metal/C$_{60}$ hybrid films (particularly those with high
potential applicability) exposed to such a processing, e.g., to the controlled thermal annealing in a broad temperature diapason.

Here we report on the thermal response of two thin-film hybrid packaging, i.e., as-prepared (virgin) Ni/C$_{60}$/Ni/MgO(100) and modified (ion-irradiated) Ni/a-C/Ni/MgO(100) multilayers, respectively. Both multilayer complexes were gradually annealed in a broad temperature range and their structural evolution was inspected using several techniques. The analysis showed that the C$_{60}$ – and a-C – based hybrid systems have evolved in different ways with a diversification in their nano- as well as macrostructures.

2. Experimental

The Ni/C$_{60}$/Ni/MgO(100) sandwich multilayers were prepared by alternating vapor deposition of the Ni or C$_{60}$ components under the background pressure ~ 10$^{-7}$ Torr. Vaporization of Ni and C$_{60}$ was accomplished either by electron bombardment of the Ni pellets (99.9 %) or resistive filament heating (400-500°C) of the C$_{60}$ powder (99.9%). In order to specify the Ni/C$_{60}$/Ni sandwich structure better, the multilayers were synthesized with an epitaxially grown buffer Ni and intermediate C$_{60}$ layers. To do so, following deposition kinetics was applied: deposition rates of Ni and C$_{60}$ were < 1 Å/s, temperature of the substrate was kept at 500°C (for the buffer Ni layer) or 120°C (for the C$_{60}$ interlayer; the Ni covering lid was deposited at the same temperature, in order not to disrupt the fullerite under-layer), and the thickness of each layer was selected the same - of about 300 nm. After deposition, a part of the samples were irradiated with the 7 MeV $^{12}$C$^+$ ions up to a dose 10$^{16}$ cm$^{-2}$ in order to induce fragmentation of the C$_{60}$ cages and
conversion of the fragments to a-C (the 7 MeV energy allowed the $^{12}\text{C}^+$ ions to pass through the whole multilayer sequence; the range of the 7 MeV ions in Ni itself is, according to the SRIM 2008 code, of about 2.8 µm). Both types of the samples (virgin and ion-modified) were gradually annealed in the Ar (+3% H$_2$) flow atmosphere up to the temperature 500°C (the irradiated sample was annealed also at 1000°C). All systems were analyzed before annealing and after each annealing step by a variety of methods, i.e., X-ray diffraction using the Xpert MRD diffractometer (for the $\Theta$-2$\Theta$ scans and texture analysis), RBS / Channeling (using 2 MeV $^4\text{He}$ ions with an intensity 10 nA and fluence 5 µC), and scanning electron microscopy SEM-EDS JEOL (operating at the energy 1 keV in order not to induce fragmentation of the fullerenes during measurement). Several measurements were also done using the µ-Raman Renishaw 2000 spectrometer.

3. Results and discussion

Fig. 1 shows the typical $\Theta$–2$\Theta$ scans of the Ni/C$_{60}$/Ni/MgO(100) multilayer: (i) as deposited, (ii) after irradiation with 7 MeV $^{12}\text{C}^+$ ions up to the fluence $10^{16}$ cm$^{-2}$, and (iii) after irradiation and thermal annealing at 500°C for 1 hr. The $\Theta$–2$\Theta$ scan of the as-prepared multilayer system (Fig. 1, full curve) indicates the Ni(200) and C$_{60}$(111) reflections, which confirm that in the Ni/C$_{60}$/Ni/MgO(100) sequence the buffer Ni and the buried C$_{60}$ layers were grown epitaxially; the RBS/Channeling examination however excluded that the upper Ni layer was also grown epitaxially. The broad peak at the position ~ 21º belongs to the forbidden reflection from MgO indicating that the selected substrate was not a perfect monocystal. The XRD analyses evidenced: (i) cube-on-cube texturing of the Ni(100)/MgO(100) interface (see the inset in the Fig. 1), and (ii) growth
of the (111) oriented C$_{60}$ crystallites. The misfit between the lattice constant of the Ni(100) layer and separation between the rows in the fcc C$_{60}$ crystallites (in the (111) plane) is large – of about 23%, but it obviously has only a limited influence on the epitaxial growth of the C$_{60}$ film [4].

The irradiation of the hybrid multilayer with the energetic $^{12}$C$^+$ ions had a fatal effect on the crystallographic arrangement of both buried epilayers. After 7 MeV $^{12}$C$^+$ ion irradiation (with the fluence $10^{16}$ cm$^{-2}$), the epitaxial fullerite layer disappeared (see Fig. 1, dash curve), and the epitaxy of the buffer Ni layer was dramatically reduced to about one third (the area of the Ni(200), and reflection dropped significantly down, i.e., Ni(200)$_{\text{ion-irradiated}}$/Ni(200)$_{\text{as-deposited}}$ = 0.36). Clearly, the irradiation with carbon ions induced a massive disarray of the epitaxially grown Ni crystallites and created various structural alterations and defects (amorphization, intermixing of layers, etc). The epitaxy of the film (by ion beam bombardment) was critically disrupted (a part of the Ni crystallites however kept their fcc form). Interestingly, the subsequent thermal annealing at elevated temperatures led to a reconstruction of the buffer Ni epitaxy. A significant effect was mainly observed at the nominal temperature 1000ºC: after 1 hour of thermal annealing the Ni(200)$_{\text{ion-irradiated}}$ reflection rapidly increased (see Fig. 1, dot curve), i.e., Ni(200)$_{\text{annealed}}$/Ni(200)$_{\text{as-iron-irradiated}}$ = 7.7. Obviously, the thermal processing brought about recrystallization of the Ni layers that resulted in the improved epitaxy. The epitaxial recrystallization mainly regarded the buffer Ni (as was proved also by RBS/Channeling), the top Ni lid contained, even after irradiation, scattered a-C structures (measured by the Raman spectroscopy) that prevented the Ni matrix to be (even at 1000ºC) efficiently epitaxially recrystallized.
Fig. 2 shows a series of the RBS spectra of both (virgin and processed) multilayers (i.e., as deposited and annealed, ion-irradiated and annealed). The spectra illustrate an alteration of the original multilayer composition Ni/C$_{60}$/Ni (as imply the XRD scans) after ion beam bombardment, and, as well, the difference in the thermal response of the virgin and transformed structures. The RBS spectra of the multilayers measured after the ion-beam irradiation (with the 7 MeV $^{12}$C$^+$ ions with the fluence $10^{16}$ cm$^{-2}$) did not indicate any difference from the RBS pattern of the virgin system. Apparently, the profile structure of the ion-treated multilayer remained basically unchanged (contrary to the observed alteration in the epitaxy of the intermediate C$_{60}$ and buffer Ni layers). The ion beam bombardment caused destruction of the fullerene cages (and consequently, their crystallographic arrangement was also destroyed), and partial incorporation of the fragments (due to the knock-in process) from the C$_{60}$/Ni interfaces into the buffer Ni films. The depth profiles, however, remained practically unchanged. Concerning the thermal evolution of the system, one can see (Fig. 2) that a large portion of the C$_{60}$ molecules escaped during annealing from the non-irradiated sample (see the decrease of the dip separating the upper and buffer Ni layer signals), in the irradiated sample almost all of the transformed a-C substance remained. This gives evidence for (i) the considerable diffusivity of the C$_{60}$ molecules through the upper Ni polycrystalline film (one should also expect, however, diffusion through the buffer Ni film towards the Ni/MgO interface), and (ii), contrary, very limited mobility of the a-C species through the encompassed Ni matrix. The diffusion paths of the C$_{60}$ molecules might be identified with the porous grain boundaries existing in the polycrystalline Ni layer, as was suggested in [3]. Fig. 3a and 3b represent the evaluation (using the SIMNRA 6.04 code)
of the RBS patterns. They show in detail the C and Ni depth profiles (in form of relative concentrations). One can see that annealing of the non-irradiated multilayer induces diffusion of C (C<sub>60</sub>) not only out of the system, but also towards the Ni/MgO interface. This has been observed earlier in [4, 10]. The part of C that has indiffused towards the interface is almost one third of the original C mass, a part that has escaped from the multilayer is estimated to about 25%. For the irradiated and annealed hybrid sample only a slight outdiffusion of C has been found, the estimation is about 8% of the original amount.

Annealing at elevated temperatures dramatically diversifies the development of the systems. It has been found (by Raman spectroscopy) that during diffusion (induced at temperatures < 500°C) a part of the C<sub>60</sub> molecules decay and remain dispersed in the Ni matrix (after transformation) as a-C substance (the fragmentation of C<sub>60</sub> is mainly due to the strong catalytic properties of Ni). The fragmentation of the fullerene molecules (diffusing through the Ni matrix) depends on the parameters of the thermal processing (i.e., on the temperature and time of annealing). For higher temperatures (though < 500°C) the fragmentation rate is high, and a longer time of annealing causes decay of more fullerenes. At temperatures around and above 500°C the fullerene molecules fully dissociate and the fragments convert to a-C (creation of other carbon allotropes cannot be, however, excluded). The structural evolution of the hybrid multilayers induced by subsequent thermal annealing > 500°C strongly depends on the presence of the a-C allotropes that resides in the Ni layers. It has been observed that the high temperature (~1000°C) thermal annealing of the non-irradiated samples led to the formation of the various peculiar nano- and microstructures, such as rectangular ‘footprints’ with a-C
based central area, or rod-type particles coated with a thin a-C rind that were emerged in a surrounding complex a-C+Ni mixture [3]. Thermal annealing of the irradiated multilayers (Ni/a-C/Ni) should however proceed in a different way. The multilayers contain a larger amount of C (in form of a-C) that behaves differently than highly mobile and diffusive fullerenes. Due to the low miscibility of Ni and a-C and limited diffusivity of the a-C clusters, the thermal annealing at very high temperatures would lead to a more dramatic phase separation than in the case of the non-irradiated systems. One can expect that after high temperature annealing (e.g., at 1000°C), the Ni and a-C components would separate forcefully, and in case of long annealing they would form separated Ni and a-C zones. Fig. 4 (SEM micrograph) represents the results of the high temperature (1000°C / 1 hr) annealing of the ion-irradiated (7 MeV \(^{12}\text{C}^+\), \(10^{16}\ \text{cm}^{-2}\)) Ni/a-C/Ni/MgO(100) sequence. One can see that the annealing resulted in the production of the sub-micrometer-sized (spherical-like or plate and rod-type) particles with a Ni crystalline core and a thin a-C covering rind (as was indicated by the micro-Raman inspection). The particles are (contrary to observation in [3]) individually spread without any encompassing a-C+Ni complexes. Similar to [3] the crystalline particles are facetted and their main axes are oriented according to the crystallographic axis of the MgO(100) substrate. The particles were found to be supported by a continuous a-C layer that forms a thin platform covering the underlying substrate.

In conclusion, the heavy \(^{12}\text{C}^+\) ion irradiation has a strong effect on the structure of the inspected Ni/C\(_{60}\)/Ni hybrid system. It results in the formation of structures that differ from the original (as-deposited). The intermediate fullerene layer is converted to a-C that exhibits different structural and other properties. The thermal processing leads to
structures that are different for the non-irradiated and irradiated composites. The different evolution is related to the various content of a-C in the hybrid systems. The high temperature annealing (at 1000°C) of the irradiated multilayers leads to the fabrication of the individual (separated) sub-micrometer sized particles (with a Ni crystalline core and a thin a-C rind) that are weakly bounded to an a-C platform on the MgO substrate. The particles are facetted and oriented according to the crystallographic axis of MgO(100).

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References


**Figure caption**

Fig. 1.

The Θ–2Θ scans of the Ni/C$_{60}$/Ni/MgO(100) system as deposited (full curve), after irradiation with 7 MeV $^{12}$C$^+$ ions up to the fluence $10^{16}$ cm$^{-2}$ (dash curve), and after irradiation and thermal annealing at 1000ºC (dot curve). The buffer Ni and C$_{60}$ layers were grown epitaxially, the top Ni layer was polycrystalline. The 7 MeV $^{12}$C$^+$ ion irradiation resulted in a destruction of the fullerite (and partially also of the buffer Ni) layer epitaxy. Thermal annealing led to recrystallization and restoration of the Ni epitaxy.
Fig. 2.
The 2 MeV $\alpha$-particle RBS spectra for the Ni/C$_{60}$/Ni/MgO(100) multilayer: (i) as deposited, (ii) after annealing at 500°C for 1 hr, and (iii) after irradiation with 7 MeV $^{12}$C$^+$ ions (up to the fluence of $10^{16}$ cm$^{-2}$) and successive annealing at 500°C for 1 hr.

Fig. 3a, b.
The C (a) and Ni (b) depth profiles (in form of relative concentrations) evaluated using the SIMNRA 6.04 code. The annealing of the non-irradiated multilayer induces diffusion of C out of the system and towards the Ni/MgO interface. For the irradiated and annealed multilayer a slight outdiffusion of C has been observed.

Fig. 4.
SEM micrographs of the Ni/C$_{60}$/Ni/MgO(100) multilayer irradiated with the 7 MeV $^{12}$C$^+$ ions up to the fluence of $10^{16}$ cm$^{-2}$ and annealed up to 1000°C. The multilayer system metamorphosed into a complex Ni – a-C structure. After the high temperature annealing the sub-micrometer-sized particles (with a Ni crystalline core and a-C thin rind) were formed.
Fig. 1.
Fig. 2.
C depth profiling

- ● as deposited
- □ annealed at 500°C / 1 hr
- △ irradiated with 7 MeV C⁺ 10¹⁶ cm⁻² and annealed at 500°C / 1 hr

C relative concentration (%)

Thickness (1E15 atoms/cm²)

Fig. 3a.
Ni depth profiling

- ● as deposited
- □ annealed at 500°C / 1 hr
- △ irradiated with 7 MeV C⁺ 10¹⁶ cm⁻² and annealed at 500°C / 1 hr

Ni relative concentration (%)

Thickness (1E15 atoms/cm²)

Fig. 3b.