Spontaneous Partitioning of the Ni+C\textsubscript{60} Thin Film Grown at RT

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Abstract

We report on the pattern formation in the thin film of Ni+C\textsubscript{60} mixture deposited on the MgO(100) substrate at RT. Using magnetic force microscopy a periodic array of the magnetic domains has been revealed. The domains reflect the certain partitioning of the Ni+C\textsubscript{60} film that however was not observed by other methods. The effect indicates that even at RT a separation of the phases in the Ni+C\textsubscript{60} system sets in.

Keywords: Fullerene; Composite materials; Vapour deposition; AFM; MFM

1. Introduction

The binary composite thin films based on fullerenes (C\textsubscript{60}) and (transitional) metals have been studied for about a decade. The research on these hybrid materials has been fueled by their attractive properties [1] and an apparent possibility of their applications (e.g., in electronics [2]).

One of the interesting aspects that draw attention onto this composite material is its amazing proclivity towards the pattern formation. Several reports have been published on this theme. In [3], e.g., an intricate system of periodic domains has been formed when C\textsubscript{60} and Ni were co-deposited on MgO(001) at the elevated temperature 500\textdegree C. The domains (with the thickness of about 1 micrometer and with the aspect ratio \( \sim 10^4 \)) consisted of Ni fine particles (Ni crystalline droplets) that were encompassed with a C\textsubscript{60} rind of a polymeric structure. As a principal mechanism of this pattern formation, a sequential drift and coordinate release of the thermodynamic instability (grown in the binary system of the immiscible phases) has been proposed. In [4] thermal response of another hybrid system based also on the Ni and C\textsubscript{60} components has been inspected. Thermal processing of the Ni/C\textsubscript{60}/Ni multilayer led to the formation of an array of micrometer-sized octagonal pits and rod-type particles with axes parallel to the crystallographic axis of the MgO(001) substrate. Surprising structural variability of the hybrid films has also been observed after irradiation by energetic laser beam [5,6]. The laser impact led to formation of various mesoscopic periodic surface patterns called LIPSS – Laser Induced Periodic Surface Structure. The LIPSS objects comprised a massive central nucleus (made of a-C, amorphous carbon) that was surrounded with an array of periodic domains (made of C\textsubscript{60}(a-C)--Ni complex mix). The mechanism of the LIPSS formation was similar as in [3], i.e., coordinated relaxation of the stressed structure during the rapid dissipation of the laser beam energy.

. The unusual ability of the metal-fullerene (Ni-C\textsubscript{60}) composites to readily undergo self-organization points out the complex physiochemical processes that are incited in the system during deposition (at elevated temperatures) or after energetic irradiation or

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thermal processing. Generally, the structural partitioning of the system (as has already been suggested in the previous reports [3-6]) is due to the energy relaxation of the stressed film. The process of relaxation is however complicated and its detailed description is still missing.

In this paper, our attention was paid to the binary system of Ni+C\textsubscript{60} deposited on MgO(001) with low deposition rates and at room temperature (RT). It was supposed that the film, grown under such deposition kinetics, would exhibit a homogeneous nanostructure (consisting of well mixed Ni and C\textsubscript{60} components) that would however be thermodynamically very unstable. It is an issue whether such stressed system would also show any organized or disorganized (random) spontaneous partitioning.

2. Experimental

The hybrid Ni+C\textsubscript{60} thin films were deposited on the MgO(001) single crystals (commercially available as 10x10x1 mm\textsuperscript{3} plates). The Ni+C\textsubscript{60} composites were prepared by co-deposition of Ni and C\textsubscript{60} in the MBE deposition system under the background pressure 10\textsuperscript{-7} Torr. Vaporization of the Ni atoms and C\textsubscript{60} molecules was carried through electron bombardment of the Ni pellets (99.99%) in the e-cell, and heating (at 450\degree C) of the C\textsubscript{60} powder (99.99%) in the Knudsen cell. The deposition rates were: \~3 Å/s for fullerenes and \~1 Å/s for Ni. After about 30 min deposition the thickness of the composite layers was around 750 nm. For purpose of this experiment the substrates were kept at RT during the deposition. The prepared specimens were analyzed by several analytical techniques: surface morphology by scanning electron microscope (JEOL JSM-5600), the molecular composition by Raman spectroscopy (using the Renishaw micro-Raman spectrometer with a probing beam diameter of about 1 micrometer), surface morphology (topography) and magnetic response by atomic and magnetic force microscopy (using Veeco CP-II microscope) and the depth profiling of the hybrid system by Rutherford backscattering (using 2 MeV \textsuperscript{4}He ion beam probe with a 10 nA current intensity and 5 C charge fluence). For comparison, the same samples were also annealed (in vacuum) for 1 hr at 500\degree C and analyzed again by the techniques mentioned above.

3. Results and discussion

Fig. 1 represents typical SEM micrographs (cross sections and surface tilt) of the hybrid composite Ni+C\textsubscript{60}, synthesized at RT. The cross section images show a dense aggregation of the rod-type fine particles with a variable size (but < 100 nm). The particles are spread homogeneously across the film with no apparent compaction or preferable orientation (except the top layer where the particles are packed parallel along their elongated parts). According to [3] the particles consist of a metallic core (Ni nanocrystal) that is encompassed with a thin rind of C\textsubscript{60} (and some other carbon allotropes – due to the strong catalytic properties of Ni, C\textsubscript{60} cage partly decays and its fragments are transformed to various carbon forms, mainly to amorphous carbon, a-C).

Fig. 2 shows a Raman spectrum measured on the Ni+C\textsubscript{60} composite. The spectrum points out a strong impact of the Ni component on the bonding integrity of fullerenes. Typically, the \textit{A}\textsubscript{g}(2) vibration mode, a sensitive indicator of the intramolecular bonding alterations, evidences a dramatic decrease in its intensity and a significant red-shift from the value 1468 cm\textsuperscript{-1} (standard) by 10 cm\textsuperscript{-1}. This spectral pattern is considered as
an evidence of (i) the Ni-C$_{60}$ bonding (i.e., metal doping effect, see [7]), and/or (ii) polymerization of fullerenes under presence of Ni atoms (similar effect was also observed in other metal-fullerene systems deposited on various substrates under various deposition kinetics, see, e.g., [1,8]).

In Fig. 3, a magnetic force microscopy scan of the Ni+C$_{60}$ film (prepared at RT) is shown. The observed MFM image is surprising. The corresponding surface topography measured by AFM mode (not shown here) does not reflect the observe MFM magnetic pattern. Similarly (see above), the SEM micrographs do not evidence any periodic compaction of particles that could resemble the observed magnetic domains. The result of the MFM scan represents new information - a pattern formation of the magnetic domains that the hybrid composites, prepared at RT, exhibit. This is a new phenomenon that deserves further inspection.

To clarify the depth distribution of Ni and C$_{60}$ (C) across the hybrid film, the RBS technique has been involved. The Fig. 4 shows the raw RBS spectra measured on the hybrid film as deposited (and also after annealing for 1 hr at 500ºC - see the text below). The graphs in Fig. 5 then represent the simulations (using the SINMRA 5.0 code) of the corresponding RBS spectra. From the RBS analysis follows a surprising result: as deposited, the hybrid film does not exhibit a homogeneous distribution of the components, as has been expected from the process of fabrication, and as has also been suggested by the SEM data. Contrary, the concentrations of Ni and C$_{60}$ (C) vary across the film: the zone with the higher Ni concentration is formed close to the interface with the MgO substrate, the C$_{60}$ (C) - very rich zone is located close to the surface. The (relative) concentration of Ni varies from the nominal 40% in the ‘Ni - rich’ zone to about 20% near the surface (if the narrow area with a very low Ni content close to the MgO is not taken into account). The concentration of C$_{60}$ (C) prevails in all parts of the film, the lowest concentration is around 60% and it rises up to about 80% at the surface.

The reason of the inhomogeneous distribution of the Ni and C$_{60}$ (C) components in the hybrid film is not clear. It might be related to a possible variation in the deposition rates of one or both components (though it is not probable because the evaporation rates were under control during the deposition), or it might also be due to the diffusion of the C$_{60}$ molecules towards the surface during the growth of the stressed composite film [4].

The RBS data clearly show that the Ni particles are surrounded with dominant carbon-allotrope matter. As mentioned above, the Ni nanocrystals are encapsulated in the C$_{60}$ (C) envelope and in addition the C$_{60}$ (C) clusters of a variable size fill the rest of the film. Both data from SEM (see above) and AFM (not shown here) suggest that there is no apparent large-scale periodic phase separation that would resemble the system of magnetic domains. On the other hand, the RBS data evidence certain partitioning of the film in the depth scale. The question is whether this partitioning is somehow related to the observed magnetic domain system. This question was unfortunately not possible to solve properly in this work. Nevertheless an attempt has been made. The hybrid films were annealed for 1 hr at 500ºC in order to change effectively the local concentrations of the components. The corresponding RBS data are given in Fig. 4 and Fig. 5. One can see that after the thermal processing the hybrid system has been completely rebuild: the positions of the Ni - and C - rich zones have been exchanged; the content of C has dropped down (due to the out-diffusion of C$_{60}$). The MFM analysis (not shown here) showed no pattern image - the periodic system of magnetic domains has been lost. Though the annealed hybrid film has been changed
also in its composition ($C_{60}$ molecules mostly decayed or out-diffused) one could suggested that an existence of the magnetic domains should be related with existence of certain (even ‘hiden’) Ni – rich domains in the hybrid film.

4. Conclusions

In conclusion, the Ni+$C_{60}$ hybrid composites grown at RT exhibit a new phenomenon – a pattern formation represented by a periodic system of magnetic domains. Interestingly, the system of domains has not been accompanied with a corresponding self-arranged system of the hybrid matter (as the SEM and AFM images suggested). From the RBS analysis however follows that a certain partitioning of the film has occurred - formation of the Ni and $C_{60}(C)$ rich zones evidenced a massive phase separation of the hybrid matter. The simple test with annealed Ni+$C_{60}$ film suggested that the ‘magnetic’ pattern formation might be accompanied also with corresponding partitioning of the hybrid film.

The existence of the periodic system of magnetic domains in the Ni+$C_{60}$ composite synthesized at RT is surprising. It indicates that even at RT (when only a very small additional energy may enter the system) a certain coordinated rearrangement (relaxation) of the stressed microstructure may appear.

The new result (as usually) has opened also new issues. It should be better clarified, e.g., the true conditions under which the periodic system of the magnetic domains can be formed, and whether the system of the domains does or does not correspond to visible partitioning of the hybrid matter with the same or similar length scale.

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References


Figure caption:

Fig. 1. SEM cross section and surface tilt micrographs of the Ni+C$_{60}$ composite film deposited on MgO(001) at RT.

Fig. 2. Micro-Raman analysis of the Ni+C$_{60}$ hybrid composite prepared at RT.

Fig. 3. MFM image of the Ni+C$_{60}$ composite as synthesized at RT.

Fig. 4. RBS spectra of the Ni+C$_{60}$/MgO(001) system as prepared, and after annealing for 1 hr at 500°C.

Fig. 5. Simulation of the RBS measurements by SIMNRA code.
Fig. 3

Fig. 4
Fig. 5