Spontaneous partitioning of the Ni + C\textsubscript{60} thin film grown at RT

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\textbf{A B S T R A C T}

We report on the pattern formation in the thin film of the Ni + C\textsubscript{60} mixture deposited on the MgO(001) substrate at room temperature (RT). Using magnetic force microscopy a periodic array of the magnetic domains has been revealed. The domains reflect hidden partitioning of the Ni + C\textsubscript{60} film (i.e., separated Ni- and C\textsubscript{60}-rich zones) that has not been observed by other applied methods. The effect indicates that even at RT, spontaneous separation of the Ni and C\textsubscript{60} phases may set in during the growth of the hybrid film. Thermal annealing (for 1 h at 500 °C) leads to dramatic rearrangement of the Ni + C\textsubscript{60} structure which (consequently) also results in the loss of the magnetic domain system. This phenomenon points out the thermodynamic instability of the as-prepared hybrid film that can (at elevated temperatures) trigger the process of the Ni and C\textsubscript{60} phase separation.

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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 [1–5] and the possibility of their applications (e.g., in electronics [1,6]).

One of the interesting aspects that draws attention to this composite material is its amazing proclivity towards pattern formation. Several reports have been published on this theme. In [7], e.g., an intricate system of periodic domains was formed when C\textsubscript{60} and Ni were co-deposited on MgO(001) at the elevated temperature 500 °C. The domains (with the thickness of about 1 μm and with the aspect ratio ∼10\textsuperscript{5}) consisted of the 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 (arisen in the binary system of the immiscible phases) has been proposed. In [8] the thermal response of another hybrid system, also based on the Ni and C\textsubscript{60} components, has been inspected. Thermal processing of the NiC\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 [9,10]. The laser impact led to the 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 structures). The mechanism of the LIPSS formation was similar as in [7], 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 undergo spontaneous self-organization points out the complex physiochemical processes that are incited in the system during deposition, after energetic irradiation, or post-deposition thermal processing. Generally, the structural partitioning of the system (as has already been suggested in the previous reports [7–10]) is obviously due to the energy relaxation of the stressed film. The process of relaxation is however complicated and its detailed elucidation is still missing.

In this paper, our attention was again paid to the binary system of Ni + C\textsubscript{60} deposited on MgO(001) with low deposition rates and at room temperature (RT). It has been supposed that the film, grown under such steady deposition kinetics, would exhibit a homogeneous nanostructure that might be, however, thermodynamically very unstable (due to immiscibility of the Ni and C\textsubscript{60} components). It is an issue whether such a structurally stressed system would exhibit any partitioning, and what would be its thermal response.

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2. Experimental

The hybrid Ni + C_{60} thin films were deposited on the MgO(001) single crystals (commercially available as 10 mm × 10 mm × 1 mm plates). The composites were prepared by co-deposition of Ni and C_{60} in the MBE deposition system under the background pressure of 10^{-7} Torr. Vaporization of the Ni atoms and C_{60} molecules was carried out through the electron bombardment of the Ni pellets (99.99%) in the e-cell, and heating (at 450 °C) of the C_{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 of deposition the thickness of the composite layers was around 750 nm. For the purpose of the experiment the substrates were kept at RT during the deposition. The prepared specimens were analyzed by several analytical techniques: surface morphology by the scanning electron microscope (JEOL JSM-5600), the molecular composition by Raman spectroscopy (using the Renishaw 2000 micro-Raman spectrometer with a probing beam diameter of about 1 μm, 488 nm laser wavelength and 0.5 mW laser beam power), surface morphology (topography) and magnetic response by atomic and magnetic force microscopy (using the Veeco CP-II microscope), and the depth profiling of the hybrid system (i.e., C and Ni elements) by Rutherford backscattering (using 2 MeV 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 of 10^{-7} Torr) for 1 h at 500 °C and analyzed again by the techniques mentioned above.

3. Results and discussion

Fig. 1 represents the typical SEM micrographs (cross-sections and surface tilt) of the hybrid Ni + C_{60} composite, synthesized at RT. The cross-section images show a dense aggregation of the rod-type fine particles with a variable size (<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 [7] the particles consist of a metallic core (Ni nanocrystal) that is encompassed with a thin rind of C_{60} (and also other carbon allotropes—due to the strong catalytic properties of Ni the C_{60} molecules partly decay and their fragments are transformed to various carbon forms, mainly to a-C).

Fig. 2 shows a typical Raman spectrum measured on the Ni + C_{60} composite. The spectrum points out a strong impact of the Ni component on the bonding character of fullerences. Typically, the A_{1g}(2) vibration mode, a sensitive indicator of the intramolecular bond-

![Fig. 1. SEM cross-section and surface tilt micrographs of the Ni + C_{60} composite film deposited on MgO(001) at RT.](image)

![Fig. 2. Micro-Raman analysis of the Ni + C_{60} hybrid composite prepared at RT.](image)
Fig. 3. MFM image of the Ni + C₆₀ composite as synthesized at RT.

Fig. 4. RBS spectra of the Ni + C₆₀/MgO(0 0 1) system as prepared, and after annealing for 1 h at 500 °C.

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

Fig. 4 shows the RBS spectra measured on the hybrid film as deposited and also after annealing for 1 h at 500 °C (see the text below). The graphs in Fig. 5 represent the simulations (using the SIMNRA 5.0 code) of the corresponding RBS spectra. From the RBS analysis follows a surprising result: as deposited, the hybrid film already exhibits inhomogeneous depth distribution of both Ni and C₆₀ (C) components. Their concentrations vary gradually across the film—the zone with the higher Ni concentration is formed close to the interface with MgO(0 0 1), the C₆₀ (C)-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(0 0 1) monocrystal is not taken into account). The concentration of C₆₀ (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 for the inhomogeneous distribution of Ni and C₆₀ (C) 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 rates were under control during the deposition), or it might be due to the diffusion of the C₆₀ molecules towards the surface during the growth of the (stressed) composite film [8]. The phenomenon of inhomogeneous depth distribution of the components in the C₆₀-based hybrid film is an interesting issue that has been inspected in various experiments (see, e.g., [13,14], and references therein).

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 C₆₀ envelope and, in addition, the C₆₀ (and also a-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 has not been developed apparent large-scale periodic phase separation that would resemble the system of the observed magnetic domains. On the other hand, the RBS data evidence certain partitioning (Ni- and C₆₀-rich zones) of the film along the depth scale. The question is whether this partitioning is related to the magnetic domain system. This question was not possible to solve properly in this work. Nevertheless, an attempt has been made. The hybrid films were annealed for 1 h at 500 °C in order to induce effective alteration in the local concentrations of the Ni and C₆₀ (C) phases. Subsequently, the impact of the structural disordering on the magnetic domain system was analyzed. The corresponding RBS data are given in Figs. 4 and 5. One can see that after the thermal processing the hybrid system has been completely rebuilt: the positions of the Ni-rich and C₆₀ (C)-rich zones have been exchanged, and the content of C₆₀ (C) has dropped down (probably due to the out-diffusion of the C₆₀ molecules). As expected, the MFM inspection (not shown here) has not re-confirmed the existence of the magnetic pattern—i.e., the periodic system of the magnetic domains has been lost. These results suggest that the magnetic domains exist due to the inhomogeneous distribution of the Ni and C₆₀ (C) phases, i.e., due to existence of the hidden Ni-rich zones with pronounced magnetic properties that can be, however, easily disrupted (together with the hybrid structure) at elevated temperatures.

4. Conclusions

In conclusion, the Ni + C₆₀ hybrid composites, grown at RT, exhibit a pattern formation represented by a periodic system of magnetic domains. Interestingly, the system of domains is not accompanied (according to the SEM and AFM data) with a corresponding surface morphology patterns. From the RBS analysis, however, follows that a certain partitioning of the film (i.e., Ni- and C₆₀-rich zones) may occur during the film deposition. The simple test with the annealed Ni + C₆₀ film suggests that the formation of the magnetic patterns might reflect the corresponding partitioning of the hybrid film (that is, however, hidden in the composite structure). The decay of the hidden partitioning (e.g., due to the thermal...
annealing) also results in the disruption of the magnetic domain system.

The existence of the magnetic domains in the Ni + C₆₀ mixture, synthesized at RT, is a surprising phenomenon. It indicates that even at low temperatures (when only a small additional thermal energy may enter the system) a coordinated rearrangement (relaxation) of the stressed hybrid microstructure may appear.

An interesting feature, the Ni + C₆₀ composite also exhibits, is a (Ni and C₆₀) phase zone distribution exchange that is triggered by temperatures ∼500 °C. This phenomenon points out the high thermodynamic instability of the composite that can trigger a dramatic phase separation with thorough structural rearrangement.

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