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Spontaneous growth of the polyhedral fullerene crystals in the supersaturated Ni–C_{60} composite

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ABSTRACT

Transition metal (e.g., Ni, Co, Ti)–fullerene (C_{60}) hybrid composites represent interesting materials which exhibit unusual properties, e.g., charged transfer, spontaneous self-organization, biocompatibility, etc. It is of basic interest to inspect the properties of the hybrid systems, including their structural integrity and relaxation proclivity.

In this work, we report on a slow-paced transformation of the Ni + C_{60} thin film in ambient atmosphere at room temperature. The Ni + C_{60} system was synthesized on the Si(1 1 1) wafer as a supersaturated composite of two immiscible phases. Because of high internal stress, the Ni + C_{60} binary system was disposed to structural relaxation that resulted in a moderate alteration of its surface morphology. In the period of a year, several micrometer-large fullerene particles randomly evolved in a scattered array of about 200 objects per mm^2. The particles acquired various polyhedral forms with typical hexagonal, icosahedral and other shapes. The spontaneous formation of fullerene crystals, as a result of stress relaxation of the fullerene-based hybrid system, is a newly observed phenomenon that posses an unusual constructive aspect. This aspect might be interesting for the design of highly-organized functional materials.

In this paper the spontaneous transformation of the binary mixture and mechanism of fullerene polyhedra nucleation and growth is discussed.

1. Introduction

Structural transformations of the componential systems represent an interesting issue in materials science. Phenomena, such as phase segregation and self-organization, have become a leitmotif of many studies in the last few decades (see, e.g., Proceedings of the MRS meetings, [1]) that have brought a rich gallery of structural transformations of composite materials, particularly for the inorganic-organic or metal-organic hybrid systems.

In this work, we report on an unusual, slow-paced transformation of the Ni + C_{60} hybrid structure that evolved in ambient atmosphere at room temperature (RT). The Ni + C_{60} system, prepared by co-deposition of immiscible Ni and C_{60} components [2], was grown on the Si(1 1 1) substrate as a binary supersaturated composite with considerable internal stress. Because of the weak Van der Waals C_{60}-C_{60} bonding, complex Ni-C_{60} interaction [3] and structural vulnerability of the C_{60} molecules, the Ni + C_{60} binary system was disposed (even at RT) to a structural stress relaxation.

The relaxation proclivity of stressed materials is an interesting issue in materials science, but a serious problem in modern technology. Hybrid composites, synthesized from immiscible components, can exhibit a (lengthy) phase segregation, which could alter their properties and eventually limit their lifetime. Contrariwise, phase segregation may also lead to a spontaneous innovation of their original structure, acquiring a new design and, consequently, new functionality. It has been acknowledged, that constructive phenomena, such as self-organization and co-ordinate phase segregation, have a high potential to become technologically relevant.

The transitional metal - fullerene composites represent a novel material that (in thin film forms) exhibits a strong tendency to self-organization (in all nano-, meso- and micro-scales) [4,5]. This aspect can be attractive for practical applications. It is then of basic interest to inspect the properties of the hybrid systems, including their structural integrity and relaxation proclivity. The long-term stability of the supersaturated Ni + C_{60} composites has therefore become a focus of this study.

2. Experimental

The Ni + C_{60} composites were synthesized in the Molecular Beam Epitaxial chamber (with background pressure ~ 10^{-8} Torr) by simultaneous electron beam bombardment of the 99.9% pure Ni pellets and thermal heating of the 99.9% pure C_{60} powder. The depo-

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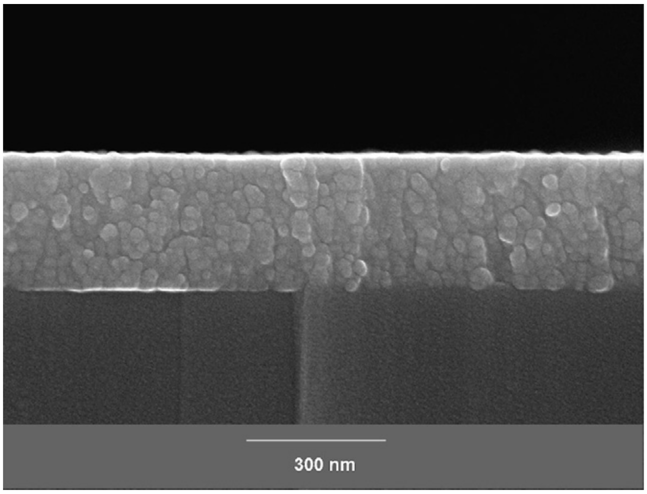

Fig. 1. a. Cross-section SEM micrograph of the as-deposited Ni + C_{60} morphology. b. The TEM micrograph of the 20 nm thin Ni + C_{60} film deposited at RT. In the TEM image separated particles with the size of ~ 10 nm can be seen. The particles consist of Ni core with a thin C_{60} rind. c. The EELS (0–80 eV) analysis of the thin Ni + C_{60} hybrid composite.

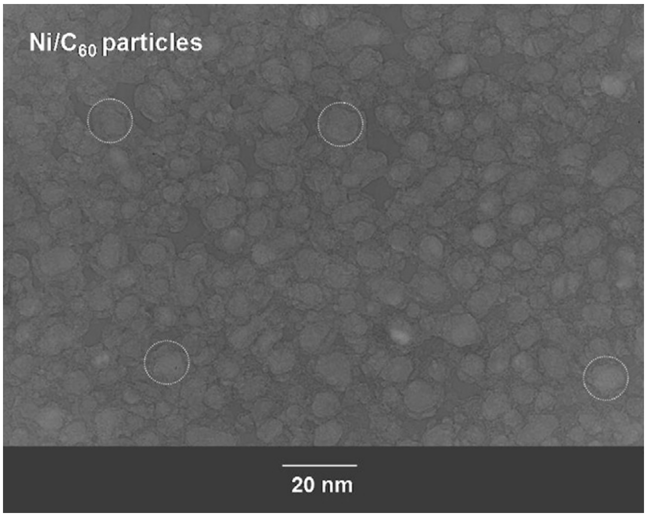

Fig. 2. a. Random array of the micro-cracks formed in the first period of the C_{60} crystal growth. b. The C_{60} polyhedral crystals grown inside and around the micro-cracks. c. The C_{60} polyhedral crystals grown in supersaturated Ni + C_{60} composite with density of ~ 200 mm^{-2} at the spots of micro-cracks.

sition rates of both phases were about 0.1 nm/s, the final thickness of the composites about 300 nm (for an additional TEM inspection the film was only about 20 nm thick). Both parameters were monitored by the quartz microbalance system placed close to the sample. During co-deposition the substrate, Si (1 1 1) single crystal wafer, was kept at RT in order to avoid possible temperature-induced outdiffusion or fragmentation of the C_{60} molecules [6]. After deposition, the sample was stored at RT in ambient atmosphere and examined (monthly) by the SEM and micro-Raman techniques. For the SEM analysis, a JOEL JSM-5600 and Tescan Vega-3 microscopes (both equipped with an energy dispersive spectroscopy system EDX) were used; for the μ-Raman measurement, a Renishaw Ramascope 1000 (using 514.5 nm Ar^+ laser system with a beam diameter < 5 μm and power < 1 mW) was applied. The TEM nanostructure of the very thin films was analyzed by the TEM (JOEL JEM-2100F: 200 keV) microscope.

3. Results and discussions

Fig. 1a shows the SEM micrographs of the cross-section morphology of the sample soon after preparation. One can see, that as deposited the Ni + C_{60} thin film was grown as a nano-structured composite system with typically ~ 50 nm large particles, densely packed into a compact block without any abrupt structural irregularities (e.g., large vacancies or microscopical particles). The detailed TEM and EELS (0–80 eV) analyses of the 20 nm thin Ni + C_{60} film (see Fig. 1b and Fig. 1c) showed that the particles (in this case with the size ~ 10 nm) consisted of a Ni core encompassed with a graphite or fullerene-like thin rind. This is in correspondence with other experimental results [7,8].

The SEM inspection of the sample pointed out a gradual change of its morphology. The stressed Ni + C_{60} composite began to relax soon after its synthesis. It was found that during the first several months a random array of micro-cracks formed in the film (see Fig. 2a). In the following period, a delicate structural transformation was under way (see Fig. 2b) – gradually, particles with a density of about 200 objects per mm^2 (see Fig. 2c) were grown at the spots of the micro-cracks. The particles grew up to about 10 μm during the first 12-month period and acquired various polyhedral forms, with hexagonal, icosahedral or other polyhedral shapes (typical for the multiple twinned C_{60} crystals). It was found that in a single crack several crystals, stacking (often) in a peculiar aggregation, appeared.

In Fig. 2c large ripples on the surface can be observed. The originally smooth surface of the composite layer (with a local roughness of about 20 nm) evolved (during a period of ~1 year) into a wavy structure indicating a dramatic relaxation process. The as-deposited stressed and compact hybrid system relaxed (by slow phase separation) and the transformation resulted in a structure with larger proportions.

Fig. 3 shows the detail of the typical surface morphology of the C_{60} crystals. The surface exhibits pronounced periodic and scattered corrugation, predominantly on the edges of the [1 1 1] facets. The corrugation has a certain wave-length of typically 100 nm. The detail survey of a number of crystals showed that the crumpling exists (i) only on the well-developed crystals with a size > 1 μm and (ii) predominantly on the [1 1 1] facets. The mechanism of periodic corrugation is not clear, it might, however, be due to the variations of zones with crystalline order and disorder, as it is reported in [9]. The crystals contain a large amount of defects due to the presence of Ni and O (the analysis by EDX showed that Ni and O were present in a fraction < 1% and ~ 4%, respectively) and their growth mechanism favours the formation of stacking faults.

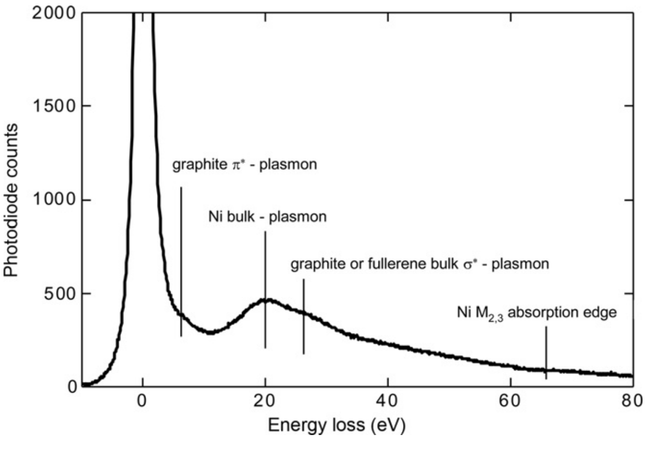

Fig. 3. The typical surface morphology of the C_{60} crystals with the pronounced surface corrugation.

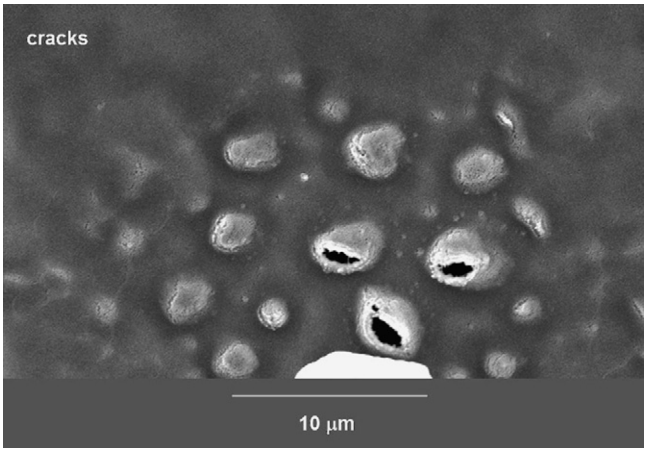

Fig. 4. μ-Raman analysis (514 nm Ar^+ laser, beam diameter < 5 μm, power < 1 mW) of the crystal and the neighbor Ni + C_{60} matrix. For comparison, Raman spectrum from the C_{60} standard is also shown.

The micro-Raman analysis of the particles (see Fig. 4) showed a typical pattern of the C_{60} standard (characterized by a series of the H_g and A_g vibration modes), i.e., identifying the C_{60} based crystal particles. The positions of the H_g and A_g modes of the C_{60} crystals were slightly down- or up-shifted (the shifts did not exceed 4 cm^{-1}) and also the $A_g(2)/H_g(8)$ or $A_g(2)/H_g(7)$ peak intensity ratio showed declination from the typical value of the C_{60} standard. Moreover, several new vibration modes (around the position 523, 954, 1310 and 1625 cm^{-1}) were also activated. These modes were mainly due to fullerene polymerized phases [10], induced by high internal stress in the composite films, and by the metal (Ni) doping effect [11]. Another reason might also result from the oxidation of the C_{60} molecules [12] or photoinduced polymeric transformation [13]. It should be mentioned that the peak on the position ~1615 cm^{-1} indicates partial amorphization of the crystal particles. Because of only small contamination by Ni and O, the structure of the fullerene crystals is predominantly C_{60}-C_{60} polymerized.

The μ-Raman analysis of the C_{60} crystals neighborhood (see Fig. 4) pointed to the existence of the D and G bands encompassing the $H_g(7)$, $A_g(2)$ and $H_g(8)$ modes. One can see, that during the lengthy storage in the ambient atmosphere most of the C_{60} molecules, residing in the deposited film, disintegrated and formed graphite-like flakes. A small part, however, survived in the form of the C_{60} molecules, either polymerized or metal-doped. One can see (Fig. 4) that yet another part of the fullerenes exists, and could migrate on the surface of the stressed composite. This part can serve as a source of the C_{60} building blocks for the fullerene crystals growth, once the micro-cracks have formed across the composite films and a Si(1 1 1) template is exposed to the migrating fullerene molecules.

The basic mechanism of the fullerene particles formation is obviously related to the stress relaxation process of the Ni + C_{60} matrix. It is acknowledged that co-deposition of the Ni and C_{60} components, immiscible at lower temperatures [2], leads to a highly unstable stressed structure. Due to weakly bonded C_{60} molecules (to both C_{60} or Ni neighbours), the stress becomes a driving force for random-walk diffusion of the molecules on the surface (this does not relate to the Ni phase that forms static massive particles). In such conditions, the composites may undergo (even at RT!) the following 3-step structural transformation:

As mentioned above, soon after composite synthesis, a random array of the micro-cracks is formed in the Ni + C_{60} matrix at localities, where high internal stress is accumulated (apparently, due to the migration of the C_{60} molecules the stress in the composite can evolve, and at certain areas may reach a limit value, exceeding the integrity of the as-deposited film).

Once formed, the micro-cracks may serve as unsaturable traps (final destination sites) for the all-over migrating fullerene molecules. Based on the typical size of the C_{60} crystals (see item 3 below), the average arriving rate of the C_{60} molecules into the micro-cracks can be estimated for the first period of growth as about 10^4 C_{60} s^{-1}.

On the template of the Si(1 1 1) substrate (at the bottom of the micro-cracks) spontaneous nucleation and growth of the C_{60} crystals sets in. Obviously, the C_{60} crystals nucleate immediately after the arrival of the first C_{60} molecules. Because of the indispensable size of the micro-cracks, several C_{60} crystals may nucleate there within a short period. The crystals then grow in the crack independently in close vicinity and once joined, they adapt a common coalescent shape. As the SEM inspection revealed, the crystals grow in one spot, often in a peculiar stacking agglomeration.

It is expected that the crystals may grow for a relatively long period, depending on stress accumulated in the composite, but the growth rate should gradually decrease due to its continuous decline. Finally, after a lengthy growth period, the hybrid system should consist of a number of micron-sized polyhedral fullerene crystals on a stable Ni + C_{60} matrix with a reduced C_{60}/Ni ratio.

The process of the fullerene crystal formation can be, obviously, accelerated by thermal annealing (at higher temperatures the diffusion coefficients of C_{60} and Ni dramatically increase). The thermal processing may, however, result in a fragmentation of fullerenes (above 400 °C fullerenes decay due to the catalytic effect of the neighbour Ni), which affects the structural parameters of the hybrid system [14,15].

The growth of the fullerene molecules was observed at RT in ambient atmosphere due to the extreme internal stress evolved in the as-deposited supersaturated Ni + C_{60} film. One should expect that other environments (i.e., vacuum, inert gases, etc.) will affect the growth process only a little. The main driving force is stress, caused by immiscibility of the Ni and C_{60} phases. The stress might be influenced by polymerization or fragmentation of the C_{60} molecules (i.e., by phase separation). These processes cannot be, however, induced by non-disruptive atmosphere.

In principle, the locations of the micro-cracks and the rate of the crystal growth might be engineered intentionally (e.g., the regular array of the micro-discontinuities in the film could be prepared using a mask during deposition, and the mobility of the C_{60} molecules could be enhanced by elevated temperatures). This would allow for the fabrication of new kinds of materials with a well-designed network of the micron-size C_{60} crystals embedded in the hybridized Ni + C_{60} nano-composite matrix. Such material might find an application, e.g., in logic information devices.

4. Conclusions

In conclusion, the Ni + C_{60} hybrid composite, prepared as a (300 nm) thin film (with deposition rates of Ni and C_{60} ~0.1 nm/s) on a Si(1 1 1) substrate, exhibited (in ambient atmosphere and RT) a slow-paced structural transformation. The as-deposited composite, grown as a stressed supersaturated mixture of two immiscible phases, showed a strong proclivity to phase separation. The relaxation process was traced monthly for about a year. It was found that in the first period of several months an array of micro-cracks began to develop. Due to random diffusion of the fullerene molecules on the composite surface, the molecules could accidentally fall into the cracks and reside there. The cracks then served as efficient unsaturable traps of the C_{60} molecules. Once trapped the fullerenes could create (on the Si(1 1 1) substrate) nuclei for gradually growing fullerene crystals. It was estimated that the growth rate of the crystals was about 10^4 C_{60} s^{-1}, so after about 1 year the crystals could acquire a size of several micrometers and various polyhedral forms.

The lengthy process of the $Ni + C_{60}$ composite stress relaxation (proceeding in ambient atmosphere at RT) resulted in an effective phase separation (fullerene crystals formation). It is a newly observed effect in the study of the transition metal - fullerene hybrid systems. This effect has an interesting constructive aspect that might be attractive for the fabrication of functional materials and their applications.

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