Carbon 103 (2016) 425–435

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Phase evolution in mixture of cobalt and fullerene deposited from vapor

V. Lavrentiev [a, *], A. Stupakov [b], M. Barchuk [c, d], I. Lavrentieva [a], J. Pokorný [b], J. Vacik [a], P. Čapková [c], A. Dejneka [b]

[a] *Nuclear Physics Institute AS CR, Rez-130, Husinec 250 68, Czech Republic*
[b] *Institute of Physics AS CR, Na Slovance 2, Prague 182 21, Czech Republic*
[c] *The University of J.E. Purkyně, Pasteurova 1, 400 96 Ústí nad Labem, Czech Republic*
[d] *Institute of Materials Science, Gustav-Zeuner-Str. 5, 09599 Freiberg, Germany*

ARTICLE INFO

Article history:
Received 13 November 2015
Received in revised form
11 March 2016
Accepted 19 March 2016
Available online 21 March 2016

ABSTRACT

Recently we reported the evidence of solubility of Co in solid C_{60} found from magnetization of the Co_xC_{60} mixture films (Phys. D: Appl. Phys. 48, 2015, 335002). In the present study we identified the Co solubility limit ($x_c = 2$) and specified phase evolution in the Co_xC_{60} mixtures in a wide interval of the Co concentrations ($0 < x < 50$) that was carried out through systematic characterization of the film surface morphology, chemical and phase composition. The effect of air exposure allowed us to recognize three intervals of x where phase evolution is controlled by rather different mechanisms. In the first interval ($0 < x < 2$, dilute mixtures) the phase evolution yields two separated phases, namely fcc-C_{60} and Co_2C_{60}. The dilute films do not include Co clusters and almost insensitive to the air exposure. Within the second and third intervals (supersaturated mixtures) designated as $x_c < x < x_m$ and $x_m < x$, respectively ($x_m = 10 \div 15$), the formation of the Co clusters dominates in the phase evolution, which are found to be sensitive to the air exposure. The Co clustering in the mixtures from the second interval is completed by formation of critical nuclei. Within the third interval of x the phase evolution is controlled by growth of the Co clusters due to coalescence process.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Intercalation of metal into fullerene network is a challenging subject promising new functional materials with attractive properties [1]. The most convincing results within this subject concern to the A-C_{60} systems (*A* is alkali metal), where the formation of the conductive and superconductive alkali fullerides A_nC_{60} ($n = 1,2,3,4,6$) was established [1–5]. As for the latter, the superconductive transition at the temperature $T_c = 18$ K was reported firstly for the K_3C_{60} fulleride [6]. This discovery yields whole set of the superconductive A_nC_{60} fullerides with even higher T_c [7,8] that revealed a remarkable application potential of the metal-fullerene compounds. A highest transition temperature ($T_c = 38$ K) was reported for the Cs_3C_{60} fulleride synthesized by a solvent-controlled method [9].

The attempts to create the fulleride phases in the Me–C_{60} systems (here *Me* is *d*- or *f*-metal) using sequential deposition (applied for creation of the *A*-C_{60} systems) [1,2] were found to be useless due to relatively high cohesive energy of the metals [1,10,11]. The concept of cohesive energy was used also to explain the formation of the composite nanostructure in the Me_xC_{60} mixture produced by simultaneous deposition [12–14]. Despite the difficulties in access of the homogeneous Me fullerides in such mixtures (due to easy Me precipitation), the Me_xC_{60} composite nanostructure is of enhanced attention owing to the formation of the Me clusters as a precursor of the intriguing properties of the materials [15–17]. The bright example here is the Co–C_{60} nanocomposites. Although the previous study of conductivity in such materials did not reveal a superconductive transition [18,19], the unique coexistence of the Co clusters and the C_{60}-based matrix yielded their remarkable magnetic and magnetotransport properties suggesting valuable applications [20–22]. Evidently, variation of the Co concentration in the Co_xC_{60} mixture will influence the phase composition [18,22] and, respectively, the material properties. In our recent report we demonstrated the dramatic difference

---

[*] Corresponding author.
E-mail address: lavrent@uj.cas.cz (V. Lavrentiev).

http://dx.doi.org/10.1016/j.carbon.2016.03.045
0008-6223/© 2016 Elsevier Ltd. All rights reserved.

in magnetic properties of the dilute and supersaturated Co–C_{60} mixture films [23]. We found that the dilute mixture ($x < 1$) includes the Co_2C_{60} fulleride and does not include Co clusters suggesting solubility of Co in fcc-C_{60}. We can expect a variety of the phase transitions in the Co_xC_{60} mixture films with different Co concentrations x. In order to specify these statements we performed the systematic characterization of the Co_xC_{60} mixture films within broad range of the Co concentrations ($0 < x < 50$). Taking into account the importance of the proper fabrication and the adequate identification of the dilute mixture films (which compositional interval can be roughly determined as $x < 5$ [18,24]) we have applied special deposition setup [23] as well as used ion-beam method for accurate control of the chemical composition. The experimental conditions in this study imply exposure of the samples to atmospheric air. To control the effect of the air exposure we provided the same history for all samples and fixed the duration of the air exposure.

2. Experimental

The method of the mixture film fabrication was described elsewhere [23]. Thin films (about 80 nm in thickness) of the Co_xC_{60} mixture ($0 < x < 50$) were fabricated by simultaneous deposition of pure C_{60} (99.99 mass. % C_{60}) and pure Co (99.995 mass. % Co) using respectively Knudsen cell and the electron gun for the material evaporation. The mixture films were deposited onto Si(100) in vacuum of 10^{-4} Pa at room temperature (RT). In order to obtain the required compositions in the depositing film, the Co/C_{60} ratio was turned precisely by adjusting the electron beam current at the fixed temperature of the Knudsen cell. A special design of the sample holder allowed us to prepare correctly sets of the Co_xC_{60} samples with different x including the very dilute mixture films [23].

Composition of the deposited mixture films after the controlled exposure to air was verified by the Rutherford backscattering spectroscopy (RBS) equipped under the Tandetron accelerator. In the RBS experiments we have used a beam of the 2 MeV He^+ ions tilted by 10° in respect to the normal to the sample surface in order to avoid the channeling effects in the Si(100) substrate. The RBS experiments were performed in a vacuum of 10^{-5} Pa at RT. To convert the measured RBS spectra into the respective depth profiles of the elements we have used the RUMP and SIMNRA computer codes [23].

Surface morphology of the deposited films was studied by AFM under the noncontact mode in vacuum at RT using the NTEGRA Aura instrument. Raman spectra were recorded using the Renishaw InVia spectrometer with the laser wavelength of 514.5 nm. In order to avoid the destructive effects from the laser irradiation, the beam intensity was reduced to about 2 W/cm^2 and the acquisition time was properly minimized. The setup parameters during the Raman experiments were optimized prior to the sample analysis by testing of the standard C_{60} films deposited on Si(100). The X-ray diffraction (XRD) spectra have been taken with the CuK_α-radiation in the asymmetric scan at the fixed incident angle of 2.5° using Philips powder diffractometer.

The magnetic properties of the mixture samples were studied using the standard superconducting quantum interference device (SQUID) supplied by a 7 T superconducting magnet, which able to measure a magnetization with precision of 5×10^{-8} emu. The dc magnetization curves $M(H)$ were measured at well-stabilized temperatures in the range from 5 to 300 K with the in-plane direction of the applied magnetic field H.

In contrast to the previous works [18,21,22] we did not cover the deposited samples by any protective layer trying to exclude possible modification effects on pristine nanostructure by the layer formation as well as to have an opportunity for correct characterization of the surface nanostructure. Before the analytical experiments the deposited films were exposed to air for about 30 min.

3. Results and discussion

3.1. AFM results

Our former results suggest that effects of surface morphology can be useful in characterization of the hybrid films [25,26]. In particular, the mixture films with high Co content ($x >> 1$), which nanostructure includes Co nanoparticles (supersaturated mixture, SSM), reveal the hillocks on the film surface [26]. It is reasonable to expect that gradual decrease of the Co concentration in the mixture finally will impede Co clustering in the mixture. So, in case of very low Co concentrations (ultra-dilute mixture, UDM) the Co clustering could be completely suppressed and intercalation of the rare Co atoms in the fcc-C_{60} lattice will occur. In such a case, the internal stress yielding the hillocks does not generated that should influence surface morphology. The analysis of the UDM and SSM Co_xC_{60} films performed in our recent study [23] nicely support this idea. In order to confirm this idea, here we performed a systematic study of surface morphology in a huge number of the Co_xC_{60} films.

Fig. 1a–g shows the AFM images of the several Co_xC_{60} mixture films with different Co content, x. The respective surface profiles taken from the AFM images are presented in Fig. 2a, b. As seen, surface morphology of the mixture films with C_xC_{60} composition in vicinity of $x = 2$ is significantly changed. Surface of the mixture films with $x < 2$ is appeared to be very smooth and consists of the small granules with size of about 5–10 nm (see Fig. 1b–d and Fig. 2a). There is an evident smoothing the C_{60} film surface upon the introduction of any small amount of Co (see Fig. 1a, b). This surface effect is evidently a consequence of the Co and C_{60} bonding in the mixture.

Surface morphology of the mixture films is dramatically changed if the Co content in the Co_xC_{60} film increases to the interval of $x > 2$. The AFM images of such a film surface are presented in Fig. 1, e-g. In this case, the surface nanostructure includes the well-defined hillocks, which size and distribution depends on the metal content x in the mixture (see Fig. 1e–h and Fig. 2b). The hillock-like surface nanostructure was found for all mixture films, which Co content corresponds to the interval of $x > 2$. Taking into account our former results [26] we can state that the formation of the hillocks on the surface of mixture film is a sign of the SSM film, which nanostructure includes the Co clusters. On the contrary, surface of the mixture film with low x ($x < 2$, UDM films) is very smooth and does not include the regular hillocks that implies absence of the Co clusters in the film.

Thus, using AFM we can study phase transformations in the Co_xC_{60} mixture films occurred upon the increase of the Co concentration. In particular, we can specify the „critical" composition x_c, which access generates the transformation of UDM into SSM. The parameter x_c designates a solubility limit for Co in solid C_{60} as well as the minimal Co concentration when the Co clusters start to nucleate. In some reports the x_c value was estimated as $x_c \approx 5$ [21,24].

For precise evaluation of x_c we can describe surface morphology quantitatively by surface roughness simulated from the AFM images. Fig. 3 shows the detail dependence of the root mean square roughness (R_{rms}) of the Co_xC_{60} film surface on the Co content x. As seen, R_{rms} reveals sharp increase just at $x = 2$ by almost one order of magnitude during x increasing. Evidently, the roughness increase is related mainly with formation of the hillocks on the film surface. Gradual decrease of the surface roughness in the mixture films with x observed in the interval $x > 2$ implies changes in the hillock size

Download English Version:

https://daneshyari.com/en/article/1413222

Download Persian Version:

https://daneshyari.com/article/1413222

Daneshyari.com