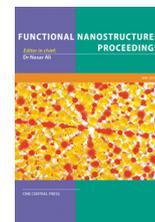


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Nanostructure and Magnetism of Self-Assembled Co_xC_{60} Hybrid Films

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ABSTRACT

In this report we present promising organometallic films produced through self-assembling of Co and C_{60} during their simultaneous deposition on Si(100). The self-assembling leads to the dominant formation of magnetic Co_2C_{60} fulleride in the dilute Co_xC_{60} mixture films ($x < 2$). At the higher Co concentrations ($x > 2$) the abundant Co clustering results in superparamagnetic behavior of the films. It is shown that the increase of the film saturation magnetization with x increasing originates from enhancement of both spatial density and average size of the Co clusters. The obtained results imply a remarkable way to tune the Co_xC_{60} mixture self-assembling through adjustment of the x parameter in order to optimize nanostructure and magnetism of the Co_xC_{60} nanomaterials for their spintronic applications. Additional application potential of the Co_xC_{60} films with $x > 2$ concerns to their structural and magnetic responses on air exposure yielding formation of the Co/CoO core shell clusters in the composite $\text{Co}_x(\text{O}_y)\text{C}_{60}$ films.

I. INTRODUCTION

Combination of C_{60} fullerene with metals is an intriguing way promising variety of nanomaterials with interesting functions. The bright example here is the detection of conductivity and superconductivity in alkali-metal fullerenes [1]. Creation of the magnetic metal (Me)- C_{60} nanomaterials would elucidate other attractive Me_xC_{60} nanostructures with valuable properties. Thus, detection of large magnetoresistance in the Co_xC_{60} films predicts an attractive application potential of the organometallic materials in spin-transfer electronics [2-4]. A suspected promising future of the material requires comprehensive knowledge on the material nanostructure and its magnetic properties in order to control the spin-transfer effects. Here, we present the detailed analysis of the nanostructure and magnetic properties of the Co_xC_{60} films ($0 < x < 50$) that allows us to discuss the structure self-assembling and the detected magnetic effects. In order to examine applicability of the materials we have studied also the effect of air exposure on the hybrid films.

II. MATERIALS AND METHODS

The Co_xC_{60} films were fabricated by simultaneous sublimation of C_{60} and Co on Si(100) substrates at room temperature (RT) in high vacuum 10^{-6} mbar. Nanostructure of the films was establishing due to self-assembling of the depositing mixtures. After the deposition completing, the films were exposed to the ambient air for 0.5 h. The chemical composition of the films was verified by Rutherford backscattering spectroscopy (RBS). Nanostructure and phase composition of the films were studied by atomic force microscopy (AFM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Magnetic properties of the films have been studied by means of SQUID magnetometer.

III. RESULTS AND DISCUSSION

Nanostructure. RBS characterization of the air-exposed Co_xC_{60} films revealed existence of oxygen in the film composition. The RBS spectra argues almost uniform distribution of O along the film depth suggesting easy penetration of the O_2 molecules into the C_{60} -based phases of the film. Typical RBS spectra of the $\text{Co}_x(\text{O}_y)\text{C}_{60}$ films

are shown in Figure 1a. We found a non-monotonic variation of O content y with increase of Co content x in the $\text{Co}_x\text{O}_y\text{C}_{60}$ mixtures. As shown in Figure 1b, the $y(x)$ dependence has a dome-like shape with broad maximum at $x=10\div 15$. Well-observed growth of y in the concentration interval of $x>2$ designates critical change in the film nanostructure at the value of $x=2$. This conclusion is consistent with AFM results, which show great change in surface morphology in vicinity of $x=2$. The mentioned results together with XRD analysis implies domination of Co intercalation into the prior assembled fcc- C_{60} lattice in the Co_xC_{60} mixture depositing at $x<2$.

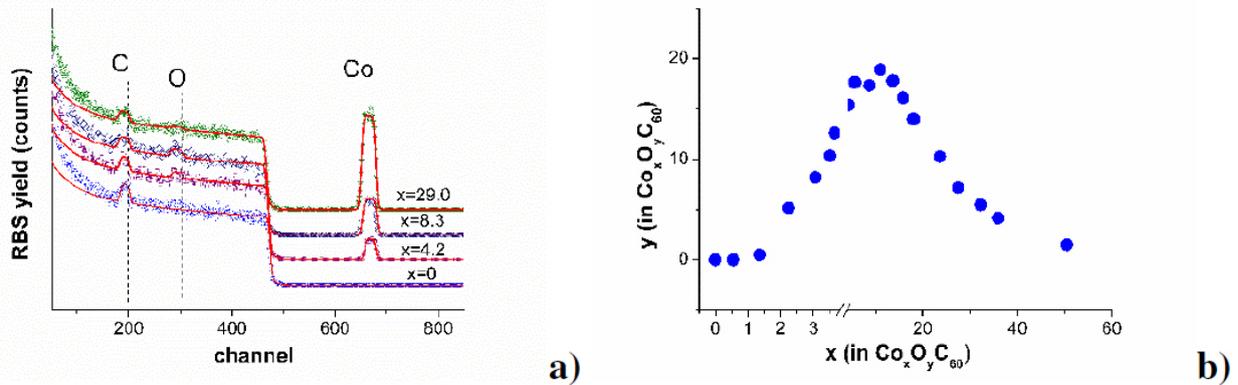


Figure 1 (a) RBS spectra of some Co_xC_{60} films exposed to air. Simulated spectra are shown by the red curves; (b) variation of O content y in the air-exposed Co_xC_{60} films with increasing Co concentration x .

Great increase of the oxygen content in the mixture films with $x>2$ we relate with pronounced Co precipitation in such mixtures and with oxidation of the appeared Co clusters during the air exposure of the films. Figure 2 demonstrates the bright field TEM micrographs obtained from the $\text{Co}_x\text{O}_y\text{C}_{60}$ films with rather different Co concentration in the interval of $x>2$. The presented TEM results evidence a formation of the Co clusters (dark spots) in the films. The whitish background corresponds to C_{60} -based matrix separated the Co clusters.

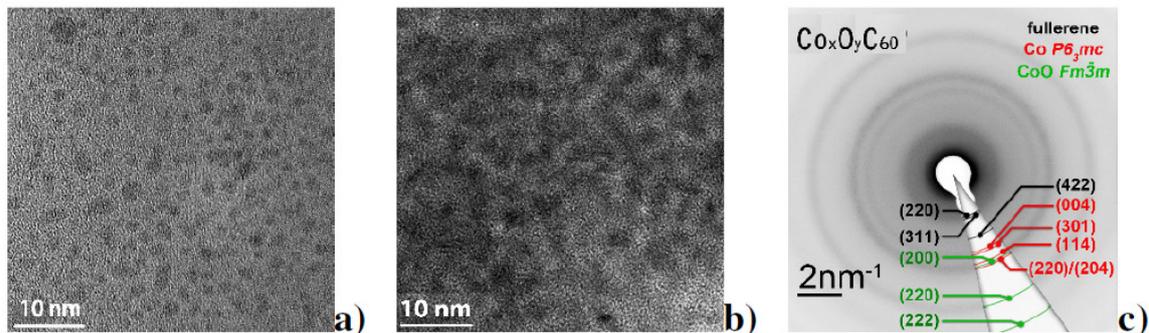


Figure 2 (a, b) bright field TEM micrographs taken from the air-exposed Co_xC_{60} films with: (a) $x=6$, (b) $x=45$; (c) selected area electron diffraction obtained from the air-exposed Co_xC_{60} film with $x=12$.

The TEM shows that size of the Co clusters (d_c) is order of few nm and it slowly increases with x . Thus, in the film with $x=6$ the cluster size is $d_c=1.8$ nm (Fig. 2a). At the high Co concentration ($x=45$) the cluster size was increased only to $d_c=3-4$ nm. However, in the latter film spatial density of the clusters is much higher and inter-cluster spacing is much lower (Fig. 2b). Electron diffraction (Fig. 2c) argues a Co/CoO core shell structure of the clusters in the films with the moderate Co concentration, i.e. in the interval of $x<30$. TEM also proves that the O content in the film with $x>15$ is reducing. Thus, if $x>40$, the CoO phase is not identified. The crystal structure of the Co clusters is ϵ -Co in the films with lower x ($x<15$) and fcc-Co or hcp-Co in the films with higher x ($x>30$).

Magnetism. We found that the dilute mixture films (i.e., the films with $x<2$) are ferromagnetic with Curie temperature (T_c) to be much higher than RT. The evaluated film nanostructure claims to ascribe this effect to ferromagnetic origin of the Co_2C_{60} fulleride.

The $\text{Co}_x\text{O}_y\text{C}_{60}$ films with $x>2$ show superparamagnetic behavior reflecting existence of small Co/CoO clusters in the films (see Fig. 3a,b). Existence of the CoO phase evidences by long saturation tails in the magnetization curves well observed for the films with the moderate x ($2<x<30$, see Fig. 3b). Another strong confirmation of the Co/CoO core shell clusters we obtained from the $M(H)$ loops measured in zero field cooled (ZFC) and field cooled (FC) regimes. We observed upwards shift of the FC loops reflecting exchange bias-like effect caused by interaction of Co spins at the Co/CoO interface [5] (see Fig. 3b). The observed shift of the loops disappears if temperature T becomes higher than blocking temperature T_b ($T>T_b$, see Fig. 3b). In the films with rather high x ($x>35$), the loop shift disappears due to the low content of the remaining oxygen in such films (Fig. 3a).

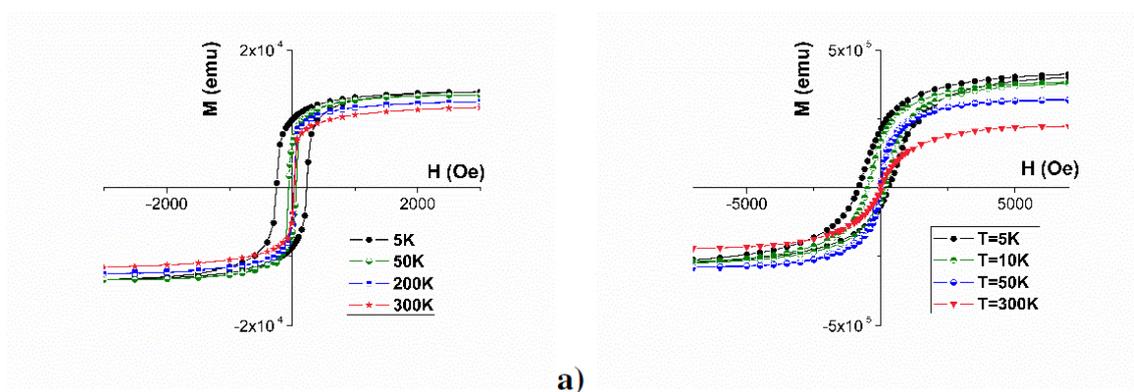


Figure 3 Field cooled (5 T) $M(H)$ magnetization curves of the $\text{Co}_x\text{O}_y\text{C}_{60}$ films at different temperatures: (a) $x=37, y=3$; (b) $x=12, y=14$.

IV. SUMMARY

This study presents the self-organize Co_xC_{60} hybrid films as the promising nanomaterials for spin-transfer electronics which functional properties could be tuned by the metal concentration. The discovered interface magnetism in the air-exposed films would greatly extend their application potential suggesting to consider these nanomaterials also for sensors, catalysis and gas storage.

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