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Co AND C_{60} INTERACTION UNDER CONDITIONS OF MIXTURE

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Mixture between Co and C_{60} were prepared by simultaneous deposition of the components on (0001) α-Al_2O_3 and (001) NaCl at room temperature in a vacuum of 10^{-5} Pa. Atomic force microscopy show granule structure with average granule size of about 30 nm. Transmission electron microscopy revealed mixed structure consisting of fcc-Co nanocrystals and C_{60}-based substance, which contains diamond, graphite and cobalt carbides. Analysis of electron energy loss and Raman spectra indicate some chemical interaction between Co atoms and C_{60} molecules in mixture.

Keywords: cobalt; fullerene; mixture; separation; diamond

During last years the composition of cobalt with carbon has received much interests after successful encapsulation of metal nano-particles by graphitic layers [1–3]. To produce Co-C encapsulated structure different techniques have been employed. Thus, arc-discharge between Co and graphite resulted in encapsulation of fcc-Co nano-crystals by thin graphitic layers [4,5]. Similar type of structure containing hcp-Co crystals and meta-stable Co_2C carbide were prepared by co-sputtering cobalt and graphite [1,2]. Recently an encapsulation was produced by mechanical mixing and subsequent annealing of cobalt and diamond nano-particles [6]. In this study we report the structural consequences of interaction between cobalt and C_{60} in a mixture prepared by co-deposition of the components.

Mixed Co+C_{60} films were grown up to 200 nm in thickness at room temperature on (0001) α-Al_2O_3 by simultaneous deposition (co-deposition) of the components under 10^{-5} Pa vacuum. Co-deposition was executed from different crucibles in the same vacuum chamber by electron beam evaporation of cobalt (99.9 mass.% Co) and thermal sublimation of C_{60} (99.9 mass.% C_{60}). Co-deposition has been also realized on (001) NaCl.

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The deposition rates of the components were chosen to achieve a Co:C atomic composition in mixture as 2:1. Pure Co and C_{60} films were additionally deposited under the same conditions.

The surface morphology of deposited films was studied by atomic force microscopy (AFM) using JEOL scanning probe microscope (JSPM-4200). The phase and structure analysis were made by transmission electron microscopy (TEM) on JEM-4000FX device operating at 200 to 400 kV. The TEM instrument was calibrated with a pure gold standard sample. The electron energy loss spectra (EELS) were recorded with spectrometer installed in the same TEM microscope. The Raman spectra were obtained from 200 to 2000 cm^{-1} using 514 nm Ar^+ laser and 3 mW incident power.

Figure 1 shows the AFM image of as-deposited Co+C_{60} film with a thickness of 200 nm. The granule structure of film with average granule size of about 30 nm can be recognized. White spots in AFM image with 150 to 200 nm in diameter correspond to hills mounting 20 to 25 nm above the film surface. This phenomenon implies accumulation of local internal stresses in the mixture during co-deposition.

Figure 2 shows high-resolution TEM image of 20 nm thick Co+C_{60} film deposited on (001) NaCl at room temperature. This image clearly demonstrates a separation of Co crystals (the crystal lattice is visible) by some carbon-based substance (whitish contrast) and formation of encapsulated structure. A ripple-type contrast from carbon-based substance with periodic distance of about 1 nm implies C_{60} molecules in space between metal crystals.

Selected area electron diffraction permits to recognize fcc structure of Co crystals and existence of diamond and cobalt carbides (Co_2C-orthorombic and Co_3C-orthorombic) in as-deposited Co+C_{60} film

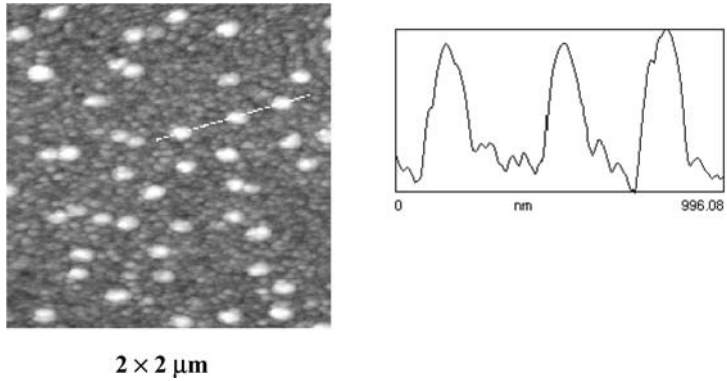

FIGURE 1 AFM image of as-deposited Co+C_{60} film (left) and surface profile along the white line (right).

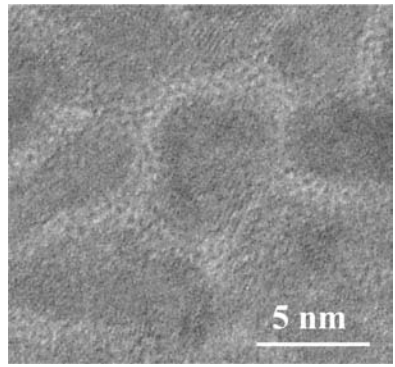

FIGURE 2 High-resolution TEM image of as-deposited Co+C_{60} film.

(not shown). Figure 3 shows nanodiffraction pattern from the mixture. According to this diffraction pattern fcc-Co and diamond crystals are adjacent. The lattice of Co crystal is distorted (the angle between (200) and (020) planes is about 83 degrees). On the contrary, diamond has almost perfect lattice. Detection of diamond and graphite infers a decomposition of C_{60} molecules during co-deposition process. Because thermal effect is negligible owing to the low deposition temperature the decomposition of C_{60} can be caused only by interaction of the Co atoms with buckyballs.

Figure 4 shows the EELS spectrum obtained near the cobalt $L_{2,3}$-edge for Co+C_{60} and pure Co films deposited at room temperature. Detection of the L_2 and L_3 peaks in the mixture shows an existence of the Co atoms in

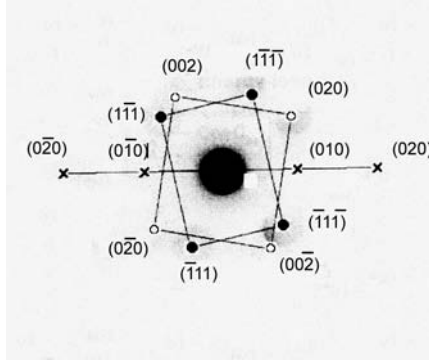

FIGURE 3 Electron nanodiffraction pattern from as-deposited Co+C_{60} film after evaluation: (100) fcc-Co (open circles); (110) cubic-C (filled circles); (100) hexagonal-C (crosses).

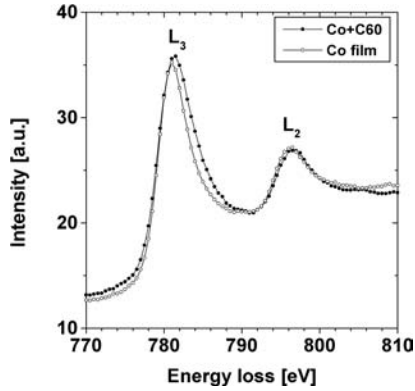

FIGURE 4 EELS spectrum near the cobalt $L_{2,3}$-edge from as-deposited Co+C_{60} film (filled circles) and pure Co film (open circles).

carbon-based substance. It is seen that L_3 peak in the mixture is much broader than the same peak in Co film. This broadening suggests increasing density of empty states owing to the chemical interaction of Co atoms with C_{60} molecules [7].

Analysis of Raman spectra (Fig. 5) confirms an existence of C_{60} molecules in mixture. Broadening and blue-shift of $A_g(2)$ and $H_g(8)$ modes indicate distortion of buckyballs and formation of polymeric chains [8]. Blue-shift ($25\,cm^{-1}$) of $A_g(2)$ mode corresponds to the transfer of four electrons from Co atoms to each C_{60} molecule in Co-C_{60} polymeric chains [9]. Small peak at $1329\,cm^{-1}$ as well as peak at $1358\,cm^{-1}$ and shoulder at $1583\,cm^{-1}$ testify to the existence of diamond and graphite, respectively.

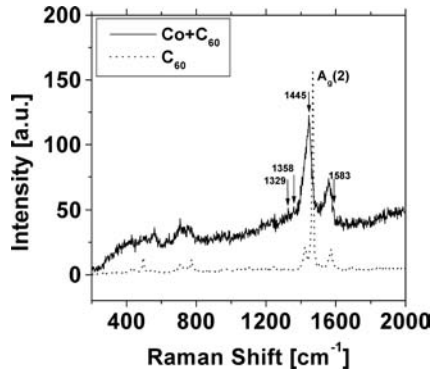

FIGURE 5 Raman spectra from as-deposited Co+C_{60} film (straight line) and pure C_{60} film (dotted line).

The present study demonstrates the remarkable features of Co+C_{60} mixture deposited at room temperature. In this mixture the allotropic conversion of C_{60} and the precipitation of Co will be caused simultaneously and competitively, which results in the organized structure such as the Co fine particles embedded in C_{60}-based layers (Fig. 2). The above inhomogeneous structure accumulates the inhomogeneous strain accompanied by hydrostatic component, also (see Fig. 1). On the other hand, the analysis with EELS and Raman spectroscopy reveals the chemical interaction between Co atoms and C_{60} molecules in the mixture, which could explain the formation of Co-C_{60} polymeric chains (see Fig. 4 and Fig. 5). Why do some Co atoms interact with C_{60} molecules or do the others keep the chemical inertness? It can be reasonably speculated that C_{60} has a tendency to be negatively charged influenced by the adjacent Co atoms (in the present case four) with the additional charge transfer during the collisional excitation. This procedure might be lead to the destruction of C_{60} molecules. Given interpretation provides higher probability for C_{60} to be destroyed near Co crystals where concentration of Co atoms in mixture should be increased. It is seen that formation of diamond under such conditions is not unexpected. Indeed, the effect of fcc-Co lattice as substrate and internal stresses can result in nucleation of diamond from incorporated C_{60} fragments (see Fig. 3). To summarize, interaction between C_{60} and Co atoms induces main driving forces for transformation of Co+C_{60} mixture into promising nano-composition.

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