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# PREPARATION AND CHARACTERIZATION OF $C_{60}/C_{70}$+Ni POLYCRYSTALLINE THIN FILM GROWN ON DIFFERENT SUBSTRATES

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$C_{60}/C_{70}$ + Ni films were obtained by thermal evaporation method in a wide range of Ni concentration (from 1.5 to 10 wt. %). The polycrystalline structure was detected in layers with Ni concentration of 1.5 wt. %. For this Ni concentration, growth of grains in columnar form was observed by SEM. TEM examination showed existence of crystalline grains of a size of a few micrometers and 10 – 200 nm thick. The electron and X-ray diffraction exhibited Bragg distances of approx. 0.87, 0.83, 0.50 and 0.32 nm, and in electron diffraction 1.0, 0.76 and 0.65 nm interplanar distances were found. In Raman spectra, typical fullerenes and two other bands placed at 580 and 1100 $cm^{-}1$ were observed. The intensity of the latter bands depends on Ni concentration. For Ni concentration higher then 1.5 wt. %, the degradation of fullerene structure was observed by HRTEM, electron and X-ray diffraction.

## 1. *Introduction*

Experimental studies of $C_{60}$ layers deposited on different substrates have been carried on by many groups with the aim to understand the mechanism of growth of ordered layers in various conditions. The fundamental problem was the qualification of the layer-substrate interaction responsible for the introduction of crystalline order into the grown layer. The problem of influence of the lattice mismatch and deposition temperature on the orientation and size of obtained crystallites was studied. For this purpose, different kinds of substrates were used, e.g. GaAs [110] [1] , Si[100] [2], Si[111] [3], CaF [4], MoS [5], mica [6] and many other metallic substrates such as Au, Ag and Cu [7,8]. $C_{60}$ mono- and multilayered structures have been obtained in the ultra-high vacuum system as molecular beam epitaxy, although layers were also grown at the higher pressure by traditional vacuum evaporation.

In this paper, we present results of investigation of $C_{60}/C_{70}$ + Ni layers obtained by the traditional thermal evaporation method. A destructive behaviour of nickel observed in earlier studies of $C_{60}$ : 3Ni solids [9 ] motivated us to work on the problem how nickel influences the fullerenes and their layer structure. The interesting problem was to obtain $C_{60}$ : Ni crystalline structure and to induce controlled nickel-fullerenes interactions.

## 2. *Experimental*

The fullerenes used in our experiment were obtained by the traditional arc method and were conditioned at the temperature of 473 K to remove traces of solvents used during purification process. The $C_{60}/C_{70}$ (of the 85:15 weight ratio) and Ni compounds were placed into separated Ta boats, they were heated (up to 473 K) and pumped to $10^{-4}$ Pa for 2 hours. The substrates (n-type GaAs[100], glass and metallic) were cleaned and etched before introducing them into the vacuum chamber. The evaporation process was carried out under the pressure $10^{-3}$ Pa at the temperature on the surface of the substrates of 453–473 K. The deposition rate was 4–10 nm/min.

The films were obtained in a wide range of Ni concentration (from 1.5 to $\approx$ 10 wt. %). The thickness of deposited films was in the range of 200 – 1200 nm, depending on the duration of the deposition.

The deposited layers were investigated with high resolution transmition electron microscopy (HRTEM) with a JEOL JEM2000EX microscope, scanning electron microscopy (SEM) with a JEOL JXA50 microscope and an X-ray microanaliser, X-ray diffraction with a SIEMENS D500 diffractometer and Raman spectroscopy with a Cary82 spectrophotometer and the 514.5 nm line of $Ar^+$ laser as the excitation source.

## 3. *Results and discussion*

We investigated the structure of the films obtained as a function of Ni concentration and the most interesting structures we obtained were for Ni concentration of 1.5 wt. %. For this concentration, grains of a columnar shape were observed by SEM. More detailed HRTEM investigations of specimens taken from GaAs and glass substrates showed that the grains obtained on the GaAs substrate were of similar shapes (their size is approx. 1 $\mu$m and thickness about 50 nm) and more regular then the grains obtained on the glass substrate. Figures 1 and 2 show HRTEM images of grains from the layer grown on GaAs and glass substrate, respectively. These images exhibit more defects, twins and greater contribution of disordered grains into the layer morphology for the samples grown on the glass substrate than on GaAs. That was confirmed by electron diffraction in these films. In the electron diffraction pattern of these films, we observed the interplanar distances of $d$ = 1.0, 0.87, 0.835, 0.76, 0.512, 0.435 and 0.32 nm, what could be attributed to fcc fulleride structure with lattice parameter $a$ = 1.446 nm (in pure $C_{60}$ crystal the lattice parameter is 1.417 nm). Similar results were obtained from X-ray diffraction of the layers. The Bragg distances of layers deposited on different substrates were $d$ = 0.870 - 0.873, 0.826 - 0.831, 0.511 - 0.517, 0.429 - 0.433 and 0.407-0. 411 nm, depending on the kind of the substrate. Figure 3 shows the X-ray diffraction pattern for $C_{60}/C_{70}$ + Ni films deposited on different substrates. One can see that the best texture of layer in direction [111] was obtained for GaAs substrates despite of big lattice mismatch layer-to-substrate. To prove the texture was indeed observed, we powdered the sample for X-ray diffraction (Fig. 3c). The ratios of peak intensities were very close to the ratio of peak intensities for powdered crystalline $C_{60}$ [10]. Ni or NiC, peaks in the electron diffraction and in X-ray diffraction patterns were not registered, what seems to be due to a homogeneous distribution of Ni in the layer structure and to the absence of Ni/NiC microcrystallites.

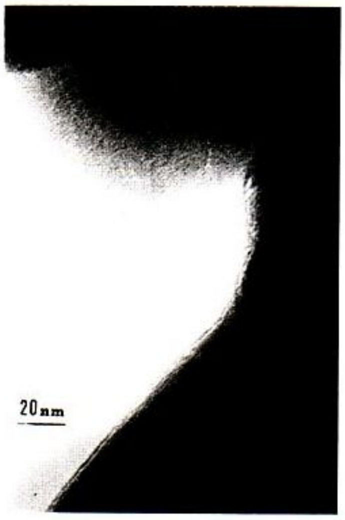



*Fig. 1. HRTEM image of film obtained on the* GaAs *substrate.*

*Fig. 2. HRTEM image of film obtained on the glass substrate (right).*

We noticed that the best adhesion film-to-substrate was obtained for films deposited on GaAs substrate, and the worst for films deposited on the glass substrate.

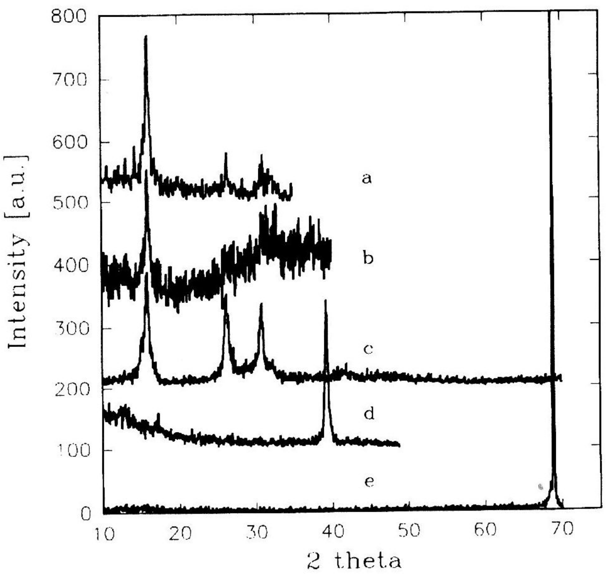


*Fig. 3. X-ray diffraction pattern obtained for layers with 1.5 wt. %* Ni *deposited on a)* GaAs *b) glass. X-ray diffraction pattern for powdered samples with c) 1.5 wt. %, d) 4 wt. % and e) 10 wt. %* Ni.

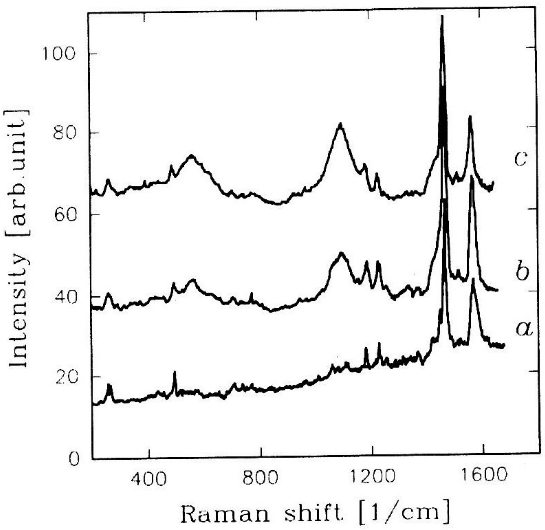


*Fig. 4. Raman spectra of* $C_{60}/C_{70}$ + Ni *layers with increasing Ni concentration in ascending order from a) to c)* (Mo *substrate). Curve a) was obtained for Ni concentration of 1.5 wt. %.*

All films with 1.5 wt. % Ni concentration retained fullerenes structure. It was shown by Raman spectroscopy. The Raman spectra exhibited typical $C_{60}$ fulllerene bands placed at 1467, 1425, 495 $cm^{-1}$ (Ag modes) and 273 $cm^{-1}$ (Hg mode) and $C_{70}$ fullerene bands at 1569, 1517, 1448, 1231, 1186, 1062 and 261 $cm^{-1}$ as well as some weaker bands belonging to $C_{60}$ and $C_{70}$ molecular vibrations. We did not observed any strong shift of band, what could be interpreted as a lack of significant deformations of fullerenes molecules. With a slight increase of concentration of Ni, we observed two additional bands (at 580 and 1100 $cm^{-1}$). The intensity of the bands increased with increasing Ni concentration (Fig. 4). This effect would be correlated with HRTEM images (Fig. 5), where for Ni concentration slightly higher than 1.5 wt. %, we observed the dark shapes surrounded by very fine structure with interplanar distance approximately equal to 0.35 – 0.4 nm. The image could be interpreted as Ni clusters enclosed in graphite-like structure or multishell macrofullerene.

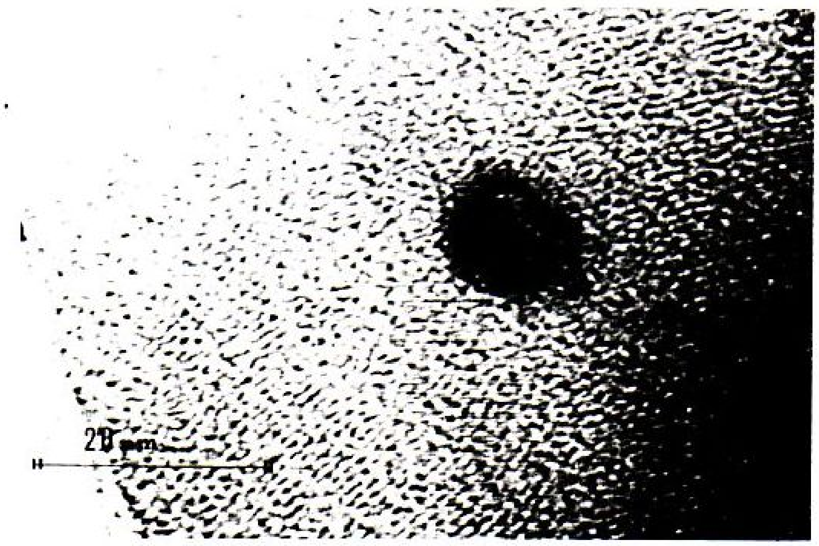


*Fig. 5. HRTEM image of* $C_{60}/C_{70}$ + Ni *layer with Ni microcrystallites (*GaAs *substrate).*

For Ni concentration still higher than 1.5 wt. %, we observed fullerenes destruction into the graphite-like structures by electron and X-ray diffraction. When Ni concentration was approx. 4 wt. %, in X-ray diffraction appeared only a peak at 0.34 nm, typical for a turbostratic graphite Bragg distance (002) (Fig. 3d). For even higher Ni concentration (10 wt. %), we registered in X-ray diffraction pattern a new peak attributed to Ni grains, with no trace of graphite peak (Fig. 3e). Samples with the highest concentration of Ni (10 wt. %) consisted of Ni microcrystals and graphite grains randomly distributed over the whole observed area, as proved by electron diffraction. The graphite and Ni microcrystals had different size and shape on different substrates, although the graphite microcrystals were to small to be seen by X-ray diffraction. HRTEM image of the film obtained on GaAs is shownn in Fig. 6. We could not register Raman spectra of these layers, what was comprehensible taking into account the fact of destruction of fullerenes and the small size of the graphite microcrystals.

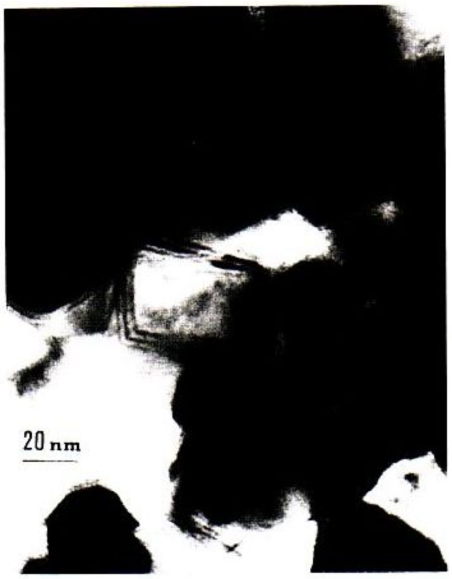


*Fig. 6. HRTEM image of layer deposited on* GaAs *substrate with* Ni *concentration 10 wt. %.*

## 4. *Conclusions*

We showed that there is very narrow Ni concentration and thermodynamic region where we were able to obtain polycrystalline $C_{60}/C_{70}$ layers. The influence of the substrate is visible for films deposited on different substrates. That is manifested by obtaining textured layers and their good adhesion on GaAs substrate. The effects observed could suggest that the morphology of the layer depends on the substrate structure and the kind of substrate-layer interaction.

The catalytic interaction of Ni atoms with fullerenes was seen when the concentration of nickel was higher than 1.5 wt. %. We obserwed the destruction of fullerenes into graphite-like structures as a result of this interaction. For lower nickel concentration (1.5 wt. %) we were not able to define the character of Ni-fullerenes interaction, but one could see that nickel atoms were homogeneously distributed in the fullerenes network and they could be treated as a dopant. It is not possible to determine exactly positions of Ni atoms in the unit cell of fcc crystalline structure, but we could associate the observed electron diffraction and the enlargement of lattice parameter with a fixed position of these atoms.

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## PRIPREMA I KARAKTERIZACIJA $C_{60}/C_{70}$ + Ni POLIKRISTALNIH TANKIH SLOJEVA NARASLIH NA RAZNIM PODLOGAMA

Tanki slojevi $C_{60}/C_{70}$ + Ni dobiveni su toplinskim isparavanjem s koncentracijom Ni od 1.5 do 10 tež. %. Polikristalna struktura je opažena u slojevima s 1.5 tež. % Ni. Pomoću SEM je u takvim slojevima opažen stupčast rast zrna. Pomoću TEM ustanovljena su zrna duljine nekoliko $\mu$m i debljine 10-200 nm. Ispitivanja su načinjena također elektronskom i rendgenskom difrakcijom. U Ramanovim spektrima opažene su tipične vrpce fulerena pri 580 i 1100 cm$^{-1}$. Za koncentracije Ni iznad 1.5 tež. % opažena je degradacija strukture fulerena.