# THERMALLY INDUCED TRANSFORMATION OF NICKEL-FULLERENE HYBRID ASSEMBLY

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## Abstract

Metal-fullerene composites represent a specific class of materials exhibiting interesting properties. However, the thin hybrid assemblies are thermodynamically unstable, thus the destructive processes such as thermal annealing can change their structure and properties.

In this work, the thermal stability of nickel-fullerene composites was investigated over a broad temperature range. The evolution of the samples was monitored using Neutron Depth Profiling, Rutherford backscattering, micro-Raman spectroscopy and Scanning Electron Microscopy. The results showed that the hybrid films exhibit phase transformation upon heating, which leads to a dramatic change in their structure and in formation of a new self-assembled material.

**Keywords:** Energy storage systems, ion beam modifications, nanofilms

## 1. INTRODUCTION

Metal-fullerene thin films have attracted permanent attention for both fundamental and practical reasons. Unusual properties, such as structural variability and proclivity for selforganization [1], high charge transfer and unique electronic and spin transport properties [2, 3] leading to their practical applications (e.g., in electronics [4], medicine [5], catalysis [6], thermoelectricity [7]) underline the long-term interest in their research. The materials bonding is driven by complex interactions, such as metal-$\pi$ bonding and $\pi$-stacking that enable to grow the hybrid systems in a complex organometallic architectures with various functional supramolecular structures.

The integrated hybrid systems are, however, thermodynamically unstable (due to vulnerability of fullerene molecules exposed to air or UV illumination [8], confined environment with (immiscible) metal elements [9], elevated temperatures [10], or ion and laser irradiation [11, 12]. Fullerenes are easily oxidized or fragmented and form with other elements new basic building units for the formation of various structures with self-organizing abilities.

Here we report on thermal response of the Ni+$C_{60}$/Ni and Ni/$C_{60}$/Ni thin multilayers annealed in a broad temperature range. The aim was to determine how the structures of a thin layer of hybrid immiscible composites (in the form of a multilayer or mixture) develop depending on temperature of annealing.

## 2. METHODOLOGY

The experiment was realized in the research infrastructure of the Center of Accelerators and Nuclear Analytical Methods (CANAM) established in NPI ASCR Řež [13]. The hybrid structures Ni/$C_{60}$/Ni and Ni+$C_{60}$/Ni were deposited in the UNIVEX / MBE system under the background pressure $10^{-6}/10^{-7}$ mbar using the electron gun (for evaporation of Ni) and effusion cell (for evaporation of $C_{60}$). As substrates for the hybrid films were used single crystals of Si(001) of the 10x10 mm (or 5x10 mm) size. For the Ni/$C_{60}$/Ni assembly, altering vapor procedure was used, for the Ni+$C_{60}$ mixed layer, co-evaporation of both components with similar deposition rates was applied. Vaporization of Ni and $C_{60}$ was accomplished by electron bombardment of Ni pellets (99.9%) or resistive filament heating (400-500 °C) of the fullerene powder (99.9%). To prepare a sandwich structure with the epitaxially grown buffer Ni and intermediate $C_{60}$ layers (the top layer was polycrystalline), a certain deposition kinetics was used: deposition rate of Ni and $C_{60}$ < 1 Å/s, temperature of the Si (001) substrate 500 °C for the buffer Ni, 120 °C for $C_{60}$, top Ni, and Ni+$C_{60}$ mixture, and thickness for each layer ~ 300 nm.

The prepared hybrid samples were then gradually annealed in vacuum, in steps of 100 °C for 1 hr each, up to 500 °C. After each annealing step, the samples were systematically analyzed using Neutron Depth Profiling (NDP) and Rutherford Backscattering (RBS) for depth profiling. To enable NDP analysis, the samples were doped with lithium (Li) ions by immersion in a 5 M LiCl aqueous solution for 24 hours at room temperature. During this doping process, Li ions diffused into the stressed hybrid structure and filled the available free volume (microvoids], within the layer.

The NDP measurement was carried out on thermal neutrons in the nuclear research reactor LVR-15 (operated by the Czech International Centre of Research Reactors in Řež, [14]). For 10 MW reactor power, the flux of the neutron beam, filtered by the neutronguide (based on the Ni/Ti supermirrors of SwissNeutronics with m = 3 reflectivity factor [15]) was ~ $7\text{x}10^{7}$ $\text{cm}^{-2}\text{s}^{-1}$, the thermalization of the beam, express as a Cd ratio, was $R_{Cd}$ ~ $10^{4}$. For measurements, Canberra fully depleted detectors with 50 $\text{mm}^{2}$ sensitive area with high energy resolution (12 keV) were used. The energy spectra were evaluated (simulated) using LiBor [16] and SIMNRA [17] codes.

The RBS measurement was performed in the Tandetron accelerator 4130 MC using 2 MeV alpha particles. The samples were analyzed after each annealing step under the same experimental conditions (ion current ~ 10 nA, ion fluence ~ 5 mC). For analysis were used the same samples as for NDP that is counted as nondestructive technique. For evaluation of the experimental data was also utilized SIMNRA code.

## 3. RESULTS

Given the immiscibility of the constituent elements Ni and $C_{60}$ in the hybrid composites Ni+$C_{60}$/Ni and Ni/$C_{60}$/Ni, it could be expected that the mixed layer and the interface between Ni and $C_{60}$ would be highly stressed, and would tend to seek a mutually favorable energetic configuration. The internal stress in such a stressed structure can be significant enough to induce spontaneous migration of the components and a self-organized restructuring of the layer [1, 18-20].

**Figure 1** shows the RBS measurements of both prepared hybrid structures, as-deposited and after 1-hour annealing at temperatures of 100 °C, 200 °C, 300 °C, 400 °C and 500 °C. The presented spectra clearly reflect the structure of the prepared samples and indicate the significant changes that occur in them during annealing.

For the as-deposited Ni+$C_{60}$/Ni/Si(001) composite (**Figure 1, left**), the spectrum clearly shows the division of the combined layer into the upper part of the mix (440 ch – 560 ch) with approximately equal proportions of both components, Ni and C ($C_{60}$), and the buffer Ni layer (380 ch – 440 ch). The increased intensity of the spectrum between the Si edge (250 ch) and the buffer Ni (380 ch) indicates a high level of porosity in the upper hybrid layer of Ni+$C_{60}$, where part of the lower sections (including the Si substrate) is not fully covered by the hybrid layer, allowing the backscattering signal from these parts to appear in higher energies. The development of the energy spectra after annealing shows a significant restructuring of the sample. As can be deduced, fullerenes (either in the form of $C_{60}$ or as fragments) diffuse throughout the entire volume of the sample, and part of Ni from the upper hybrid layer moves toward the substrate, where an interface Ni layer forms (see the growing peak around ~320 ch). It can be assumed that an epitaxial ani film is being formed becoming more pronounced as the annealing temperature increases.

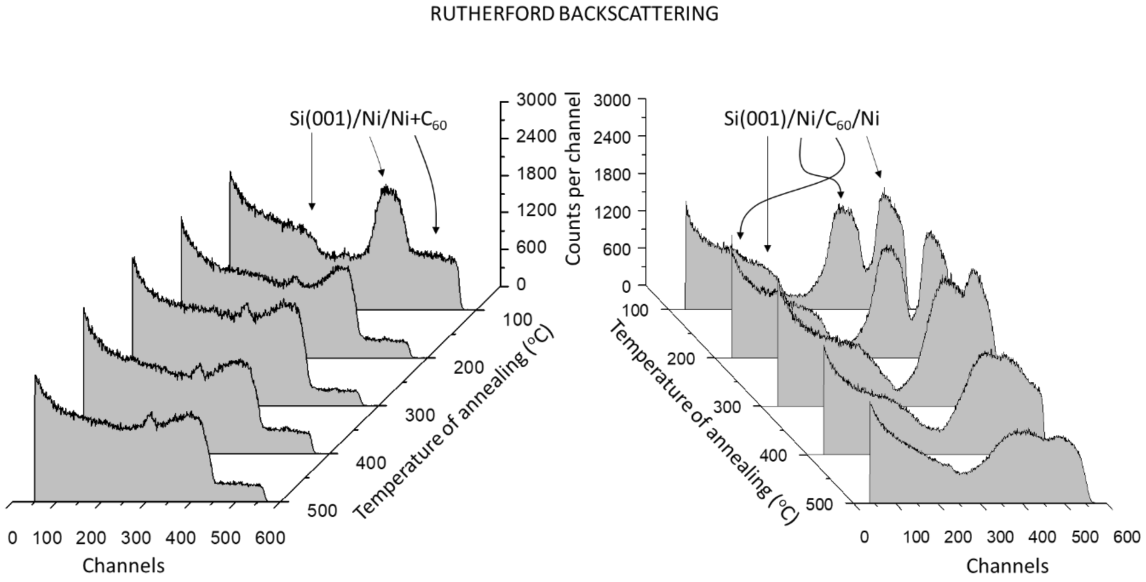

**Figure 1** RBS spectra of the as-deposited and gradually annealed Ni+$C_{60}$/Ni/Si(001) and Ni/$C_{60}$/Ni/Si(001) thin hybrid films.

A similarly significant restructuring of the structure due to thermal annealing can be observed in the sample where layers of Ni and $C_{60}$ alternate (see **Figure 1, right**). In the spectrum, the sandwich structure Ni/$C_{60}$/Ni is represented by two strong peaks (corresponding to the upper and lower Ni layers), which are separated by a wide dip due to the thick fullerene layer between them. The change in the multi-layer structure during annealing is clearly visible – as the temperature increases, the gap gradually decreases, and the Ni layers begin to merge. At around 400 °C, the gap between the Ni peaks disappears. Given the flattening of the spectrum edge (480 ch – 560 ch), it can be assumed that a significant portion of the fullerenes has moved toward the surface. The noticeable significant broadening and simultaneous reduction of the entire Ni signal (300 ch – 560 ch) indicates that the carbon component has spread throughout all parts of the sample – to the surface, the substrate, and into both Ni layers. The noticeable broadening and lowering of the entire Ni signal (300 ch – 560 ch) suggests that the carbon component has spread throughout all parts of the sample – to the surface, the substrate, and into both Ni layers. This development exhibits similar features to the previous sample with a hybrid region; however, in the sandwich layer, no buffer layer forms at the interface with the Si, likely due to the greater amoun.t of carbon component that diffused from the thick $C_{60}$ layer in all directions, including toward the substrate

An interesting perspective on both structures is in terms of the creation of voids due to the stress caused by immiscible components (Ni vs. C) and their mutual intensified intermigration due to thermal annealing. The development of voids in the stressed layers of the samples was monitored using a diffusion marker, Li, and a nondestructive method, NDP, which allows for mapping the existence and development of free space in thin samples.

**Figure 2** on the left shows where the Li marker settles in the Ni+$C_{60}$/Ni composite during various stages of annealing. In the as-deposited sample, the main concentration of Li is in the lower part of the hybrid region at the interface with (and in) the buffer Ni layer. Obviously, some Li also penetrates (due to its high mobility) into the Ni layer and toward the interface with Si. As a result of annealing, Li accumulates more significantly on the surface and in the expanding subsurface region of the hybrid layer. At 400 °C, Li is evenly distributed throughout the hybrid layer, but at 500 °C, Li again settles more prominently at the interface with the buffer Ni layer. The formation and development of voids due to annealing reflects the evolution of the stressed structure of the hybrid region of the sample, confirming and complementing the data obtained from the RBS measurements.

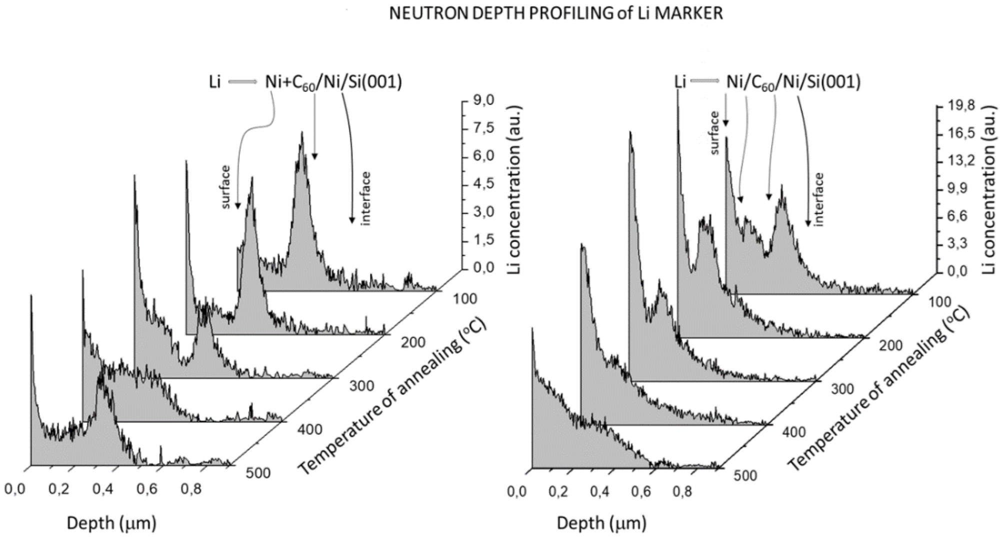

**Figure 2** NDP spectra of the as-deposited and gradually annealed Ni+$C_{60}$/Ni/Si(001) and Ni/$C_{60}$/Ni/Si(001) thin hybrid films after doping with Li diffusion marker.

**Figure 2** on the right demonstrates the distribution of Li diffused into accessible voids in the sandwich structure Ni/$C_{60}$/Ni. In the as-deposited sample, indiffused Li settled in the region of the buffer Ni layer, within the $C_{60}$ zone, and also in the surface Ni layer. During annealing, Li remains in a thin surface/subsurface layer, concentrating more in the surviving fullerene layer and diffusing through the buffer Ni layer toward the interface with the Si substrate. At 400 °C and 500 °C, voids are densely spread in the structure, so that Li diffuses through the sample without significant jumps in concentration, indicating that the structure is becoming unified with a uniform distribution of voids, reflecting a deep reorganization of the stressed microstructure of the sample.

As the experiment demonstrated, hybrid layers made from immiscible components of fullerenes and transition metals are highly sensitive to elevated temperatures, which must be considered in their potential applications. On the other hand, this also offers the opportunity to use this method for reshaping the structure (without compromising its integrity or performance), particularly when irradiation with energetic ions is applied, leading to fragmentation of fullerenes and subsequent stabilization of the structure [10].

## 4. CONCLUSION

Co-deposition or alternating deposition of Ni and $C_{60}$, as immiscible components, leads to the formation of hybrid composites with a nanostructure that is highly stressed and contains structural defects, such as microvoids and free radicals. RBS studies revealed that elevated temperatures in both Ni+$C_{60}$/Ni and Ni/$C_{60}$/Ni hybrid systems induce interdiffusion of the Ni and $C_{60}$ components, resulting in a complex, intermixed structure. Profiling of the Li diffusion marker by NDP highlighted the distribution and evolution of the free volume network, decorated with Li atoms. The study showed that free volume (microvoids) is formed either in distinct zones at the interfaces between composite sublayers (in the case of multilayers) or more uniformly within the hybrid sublayer (in the case of the mixture system). The formation of the free volume network is driven by high stress due to the immiscibility of Ni and $C_{60}$ building components.

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