Fabrication and characterization of flexible composite material based on Aerographite/InP micro-nanostructures

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***Abstract* — The goal of this work is to extend the class of flexible hybrid nanomaterials based on aerographite scaffolds. For this purpose, we developed the technological conditions for the deposition of InP:Zn micro- and nanostructures on both as-grown samples and specimens preliminarily decorated by Au dots. InP·Zn deposition was realized by using Hydride Vapor Phase Epitaxy (HVPE), while the gold dots were deposited by sputtering with subsequent annealing of the samples. For the characterization of morphology and chemical composition of the specimens, we used transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX).**

***Index Terms* — flexible material, aerographite, indium phosphide, nanoparticle, nanorod.**

INTRODUCTION

Over the last years, increasing interest has been paid to the development of functional flexible carbon materials. Their applications are oriented towards pressure sensors, energy storage systems, biomedical scaffolds etc. Our group recently reported on fabrication and systematic characterization of three-dimensional architectures consisting of GaN and ZnO micro-nanocrystallites deposited on Aerographite scaffolds [1, 2] as well as on development of ultra-lightweight flexible pressure sensors based on carbon aerogels decorated by GaN or SnO_2 nanocrystalline thin films [3]. These investigations have demonstrated new possibilities to create suspended semiconductor nanoparticles on the Aerographite networks [1]. The hybrid structures maintain their mechanical properties, and can be subjected to multiple compression/decompression tests, with the restoration of the initial shape. Aerographite/semiconductor structures are prominent candidates for biomedical and sensor applications. Three dimensional interconnected networks under consideration exhibit all features inherent to nanoscale sizes and, in addition, one can easily handle them for various advanced applications.

I. MATERIALS AND METHODS

We report on HVPE growth of InP crystals on the Aerogrphite template produced by the one step chemical vapor deposition (CVD) [4]. The network of interconnected ZnO tetrapodes were used as sacrificial template. They are converted by a CVD process, which incorporates a heat treatment at 760°C in an Argon/Hydrogen atmosphere. Graphite layers on the ZnO network are nucleating and grow from the toluene vapors, at the same time it occurs the ZnO decomposition and elimination by the hydrogen flow. Afterwards, the Aerographite template is thermally treated at 900°C to clean it from ZnO residues [4].

The HVPE growth process was carried out in a chamber with three heat regions at a constant Hydrogen flow, under atmosphere pressure. The first heat region was maintained at 750°C to generate In vapors. In the second region, maintained at 720° C, the In vapors reacted with PCl_3. The constant flow of H_2 transported the gaseous phases to the third region where they crystalized on the substrate at the temperature of 650°C. The growing process of InP nanoparticles is schematically illustrated in Figure 1.

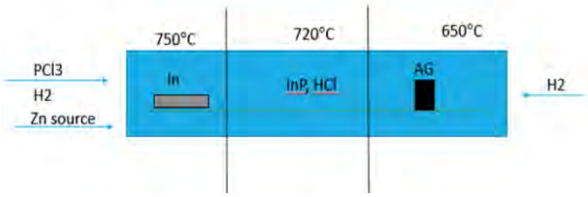


Figure 1. Schematic representation of three heat regions.

The morphology of obtained structures was investigated by scanning electron microscopy instruments Zeiss Ultra Plus and VEGA TESCAN TS 5130MM. The compositional analysis of Aerographite/InP networks was carried out using EDX, in combination with SEM. Transmission electron microscopy analysis was performed on a Tecnai F30 STwin electron microscope.

II. RESULTS AND DISCUSSIONS

Our experiments with HVPE deposition showed that crystallization of InP takes place on both inner and outer surfaces of Aerographite tubular structures. According to the results of SEM analysis (Fig. 2a), short-time deposition

leads to formation of nanoparticles, while with the increase of the deposition time InP micro-crystallites form (Figure 2b,c). It is to be noted that the micro-crystallites exhibit well-developed facets, see Figure 2d.

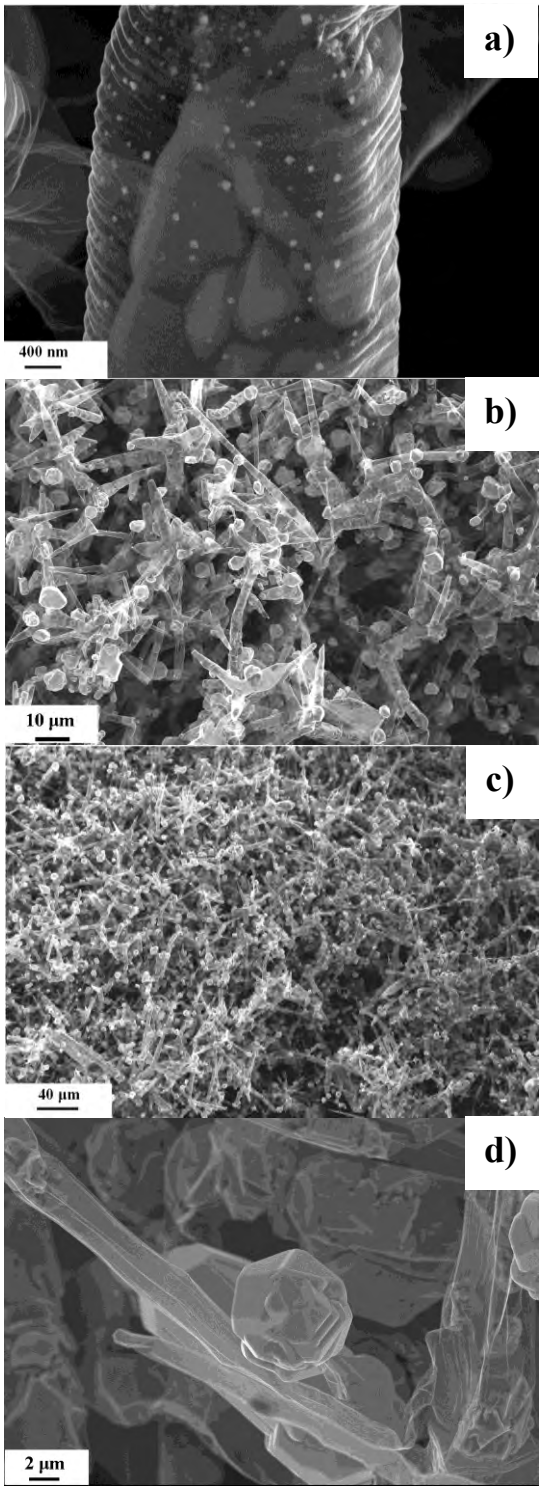


Figure 2. SEM images of Aerographite/InP composite material.

Initiation of the process of InP crystallization on the Aerographite template is caused by the presence of broken chemical bonds on the surface of graphite microtubes. Note that in the HVPE process, vapors penetrate inside the hollow graphite tetrapods through openings and wall defects, leading to InP crystallization also on the inner surface of graphite microtubes.

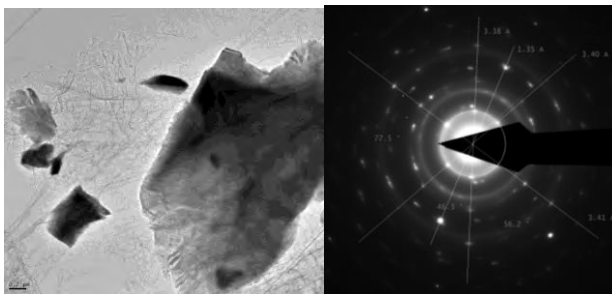


Figure 3. TEM image (left) and SAED pattern (right) of InP particle deposited on inner surface of the graphitic wall (see text for details).

In contrast to the mirror surfaces characteristic to microcrystallites deposited on the outer surface of aerographite microtubes, the InP particles deposited on the inner surfaces exhibit a granular structure, see Fig. 3a. TEM diffraction patterns disclosing Bragg reflections from individual nanocrystals consist of blurred spots, which make up rings (Fig. 3b), thus demonstrating that inner InP particles represent agglomerations of accreted nanocrystals of InP $F\bar{4}3m$.

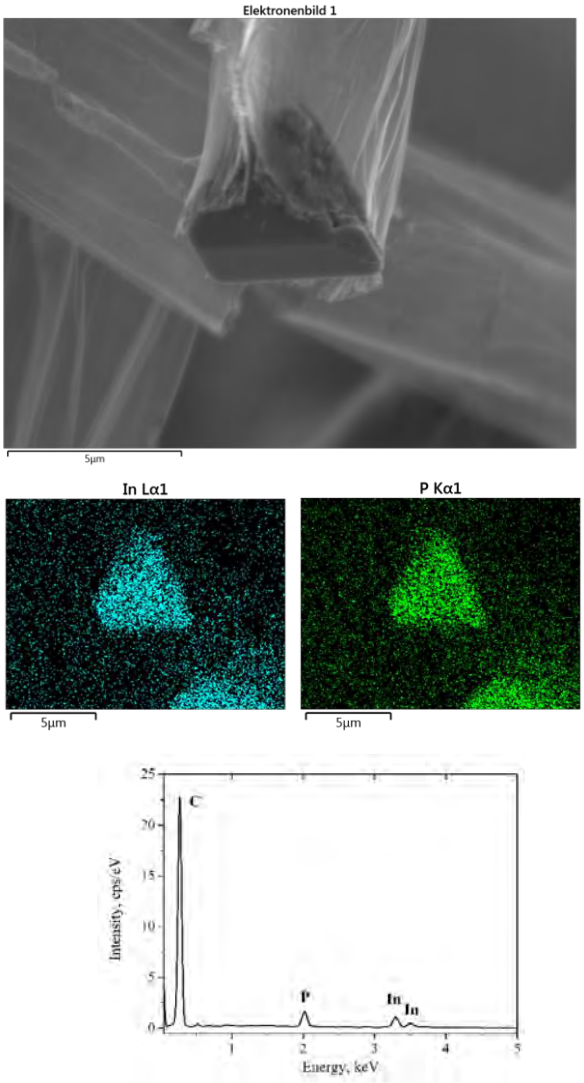


Figure 4. EDX map and element concentration for InP microcrystals.

TABLE I. ELEMENT CONCENTRATION FOR INP MICROPARTICLES

Element	Line Type	Wt %	Atomic %	Standard Label
In	L series	79.91	51.75	InAs
P	K series	20.09	48.25	GaP
		100%	100%	

The multiple EDX mapping and line scanning of deposited InP structures show a stoichiometric composition (Figure 4, Table 1). The deposited InP was doped by Zn impurity during the growth process, its concentration varying between 0.02 at% and 4.21 at%.

In continuation of the experiments, we attempted to modify the architecture of Aerographite/InP structures. Thus, on Aerographite scaffolds in the sputtering process Au was deposited and thermally treated at 400°C to convert it into nanoparticles. As a result, InP particles grow in form of rods. We found that InP starts to nucleate on Au dots and grow into rods, exhibiting an Au dot on the top.

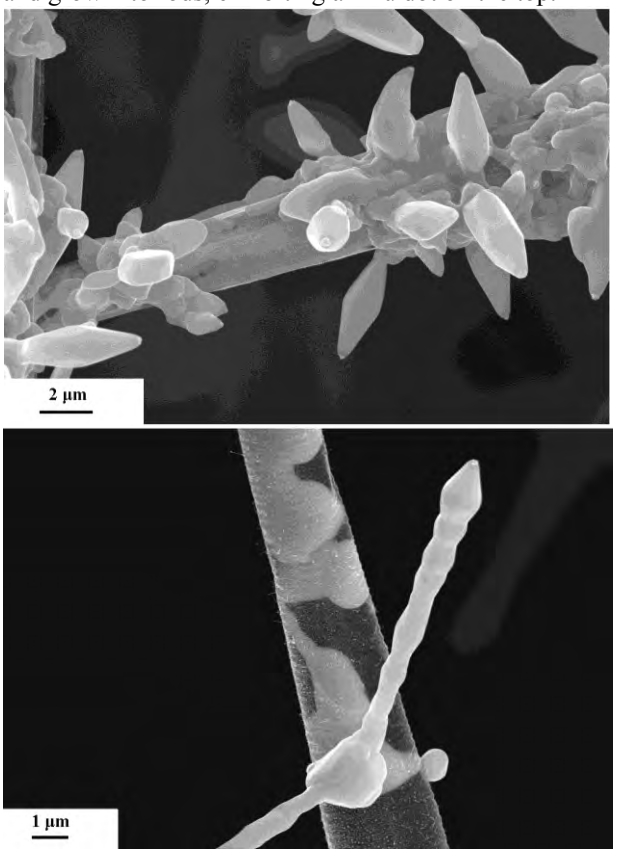


Figure 5. SEM images of InP/Au rods grown on the Aerographite template.

TEM analysis confirms that InP rods, similarly to microparticles, have F$\bar{4}$3m crystal structure. However, both the bright field image as well as the diffraction show a twinned structure (twinning plane is (112)) with individual domains between 25 and 35 nm thick.

An EDX scan of the cap region suggests that there is a distinct gold layer and a strongly oxidized region at the apex, probably of indium oxide.

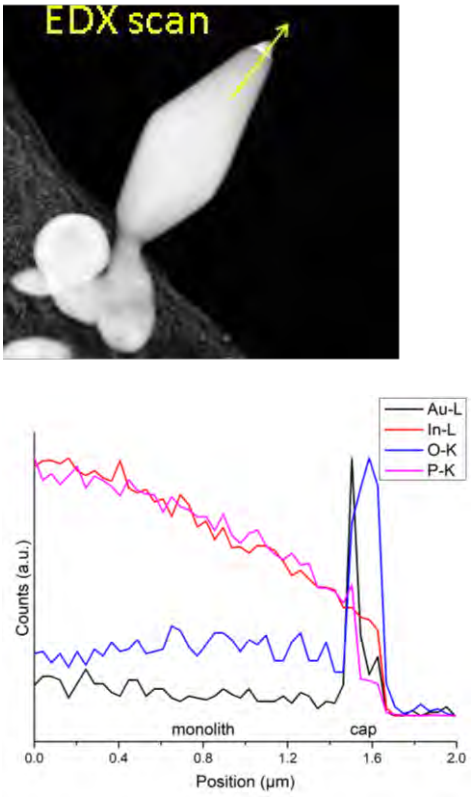
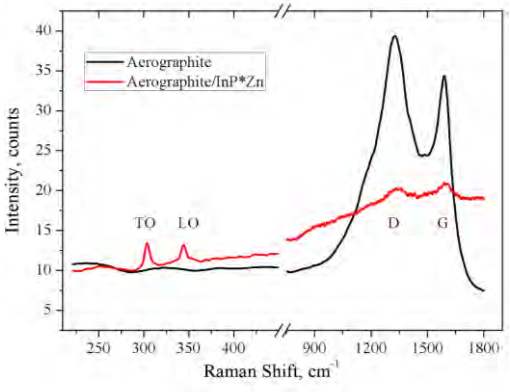


Figure 6. EDX line scan of the InP rod.

The Raman scattering spectra measured under 633 nm laser (low power 0.6 mW) excitation for InP microcrystals are very similar with the spectra inherent to bulk InP [5, 6], they being dominated by the TO (303 cm^{-1}) and LO (344 cm^{-1}) modes.

The different relative intensities of LO and TO vibrational modes from point to point are related to the different scattering geometries (different orientations of crystals in respect to laser direction and polarization, breakdown of the selections rules).

The region of C-C vibrations (D 1327 cm^{-1} and G 1590 cm^{-1} band) is also presented. As expected, the spectrum measured in the point with laser focused on the InP structures shows strongly suppressed D and G bands comparing to pure Aerographite region (Figure 5).



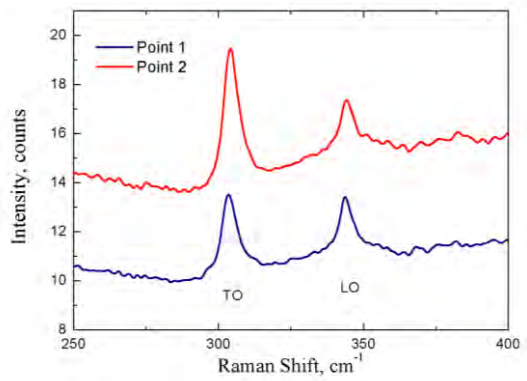


Figure 7. Raman scattering plot of pure Aerographite and Aerographite/InP microcrystals (top); Raman scattering in different points of Aerographite/InP structure (bottom).

III. CONCLUSION

We demonstrated the possibility to fabricate three-dimensional mechanically flexible hybrid Aerographite/InP architectures by using HVPE techniques. Depending on the duration of deposition, InP nanoparticles or microcrystallites with mirror facets form on the outer surface of Aerographite micritubes. At the same time InP nanocrystal agglomerates were found to be deposited on the inner surface of the walls of graphitic microtubes. The variation of Raman scattering intensities from point to point and ring formation on electron diffraction pattern indicate on different scattering geometries related to various spatial orientations of the nanoscale InP crystallites. Au dots deposited on the Aerographite surface induce the formation of InP rods with Au cap on the top.

ACKNOWLEDGMENTS

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