GRAPHENE: Graphene-Based Revolutions in ICT And Beyond

S. Bellucci (in charge of scientific and technical/technological aspects), R. Baldini (Tecn.), S.Bistarelli (Dott.), M. Bozzi (Ass.), A. Cataldo (Ass. Ric.), A. Maffucci (Ass.), D. Mencarelli (Ass.), F. Micciulla (Ass. Ric.), L. Pierantoni (Ass.)

We participate to the project Graphene-Based Revolutions in ICT And Beyond, GRAPHENE, Grant agreement number 604391CP-CSA, one of the most important initiatives in the European research. Among participants there are 23 Italian partners including research institutes, universities and enterprises, with 16 new partners including Istituto Nazionale di Fisica Nucleare represented by the NEXT group at LNF, led by Stefano Bellucci. Owing to the new partnerships the consortium binds together more than 140 organizations from 23 Countries, with the common aim of transfering graphene and related composite materials from academic laboratories to everyday applications.

The Graphene Flagship Project represents a European investment of 1 billion euro for the next decade and is part of the Flaghship Initiatives for future emerging technologies (TEF) announced by the European Commission in January 2013. Italy is already a leader in the development of important areas of the Graphene Flagship Project, including research in composite materials and energy applications, and it is involved in technology transfer and dissemination, as well. The participation of INFN is focused on the realization of multi-layered sandwich graphene devices, within the workpackage of high frequency applications. The NEXT group at LNF participates to the work package **WP13 Functional Foams and Coatings, and it is leader of the Task 13.3.6: Nanocomposite coatings for EMI shielding (INFN).**

Achievements

Our graphene applications [1,2], range from novel electronic circuitry, to antennas design, electromagnetic shielding, radar absorbing materials, space applications. In our nanotechnology group called NEXT, i.e. Nanoscience EXperiments for Technological applications, we produce graphene in the form of few-layered flakes obtained by microwaves (800 W) irradiation, starting expandable graphite generously provided by ASBURY [3-7] followed by a sonication in ultrasonic bath in water-alcohol solution for size reduction, and further enriched by centrifugation. Images (SEM and TEM) are seen in Fig. 1

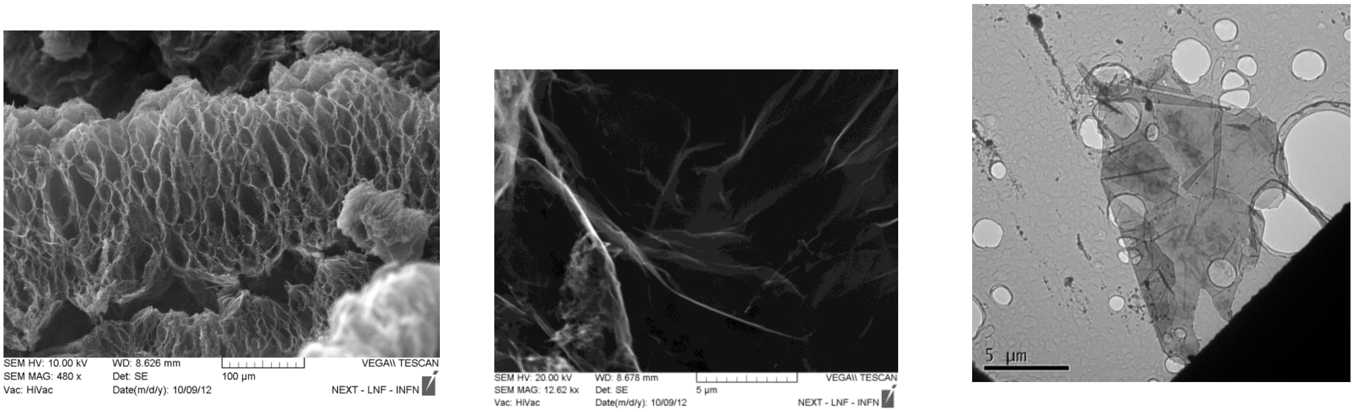


Fig. 1 SEM (first two panels) and TEM (last panel) of the produced flakes

Raman spectra document the low density of defects (absence of a D band), seen in Fig. 2 (left), and the 2D band evolution (Fig. 2 right)

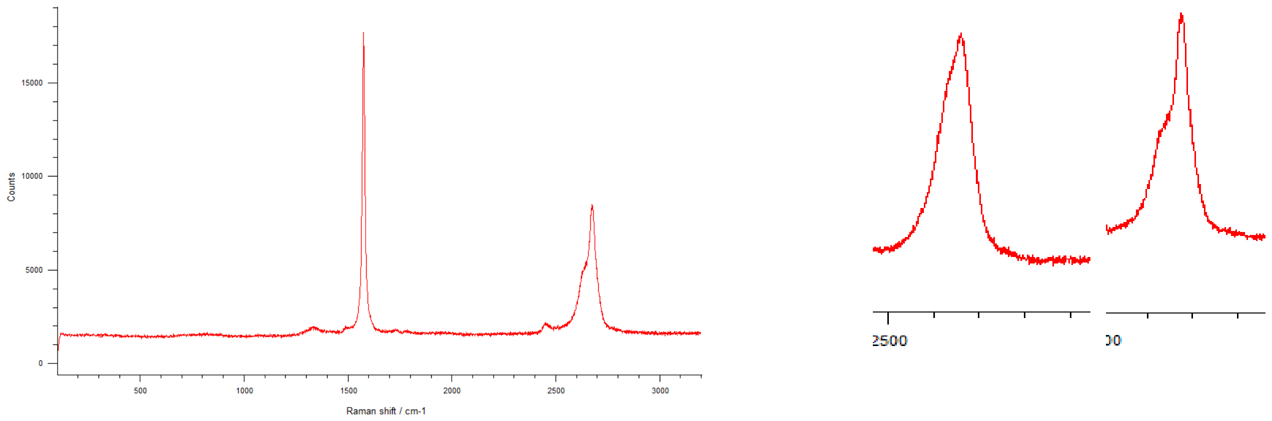
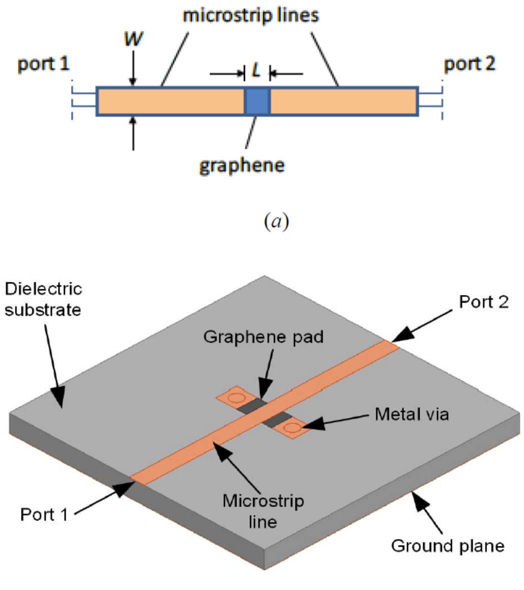


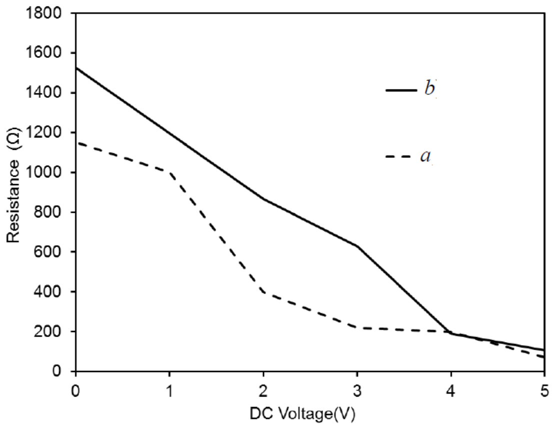
Fig. 2 Raman spectra with the 2D band evolution

The few-layered graphene was used in electronics as a thin film to realize a tunable attenuator device made of a patch deposited in two configurations; firstly in the gap of a microstrip line (see Fig.3 [8,9]) and secondly, as a novel enhanced design, in two graphene patches located between the main microstrip line and two metal vias (see Fig.4 [10]). The results show for the first configuration a wide band functionality from DC to 20 GHz, with a tunability of 7 dB and minimum insertion loss of 5 dB, and for the second an operation in a frequency band of DC to 5 GHz, with 14 dB tunability and minimum insertion loss of 0.3 dB.



(*a*)

(*b*)



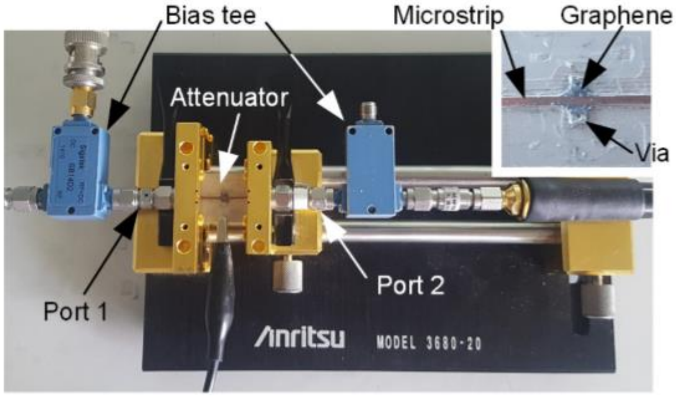


Fig. 3 Tunable attenuator based on graphene

The Enhanced Graphene Attenuator in Fig. 8 shows a reduction in the graphene resistance on an increase in the bias voltage, along with lower transmission on lower resistance and vice versa, as well as a higher dissipative attenuation, in comparison with the reflective contribution.

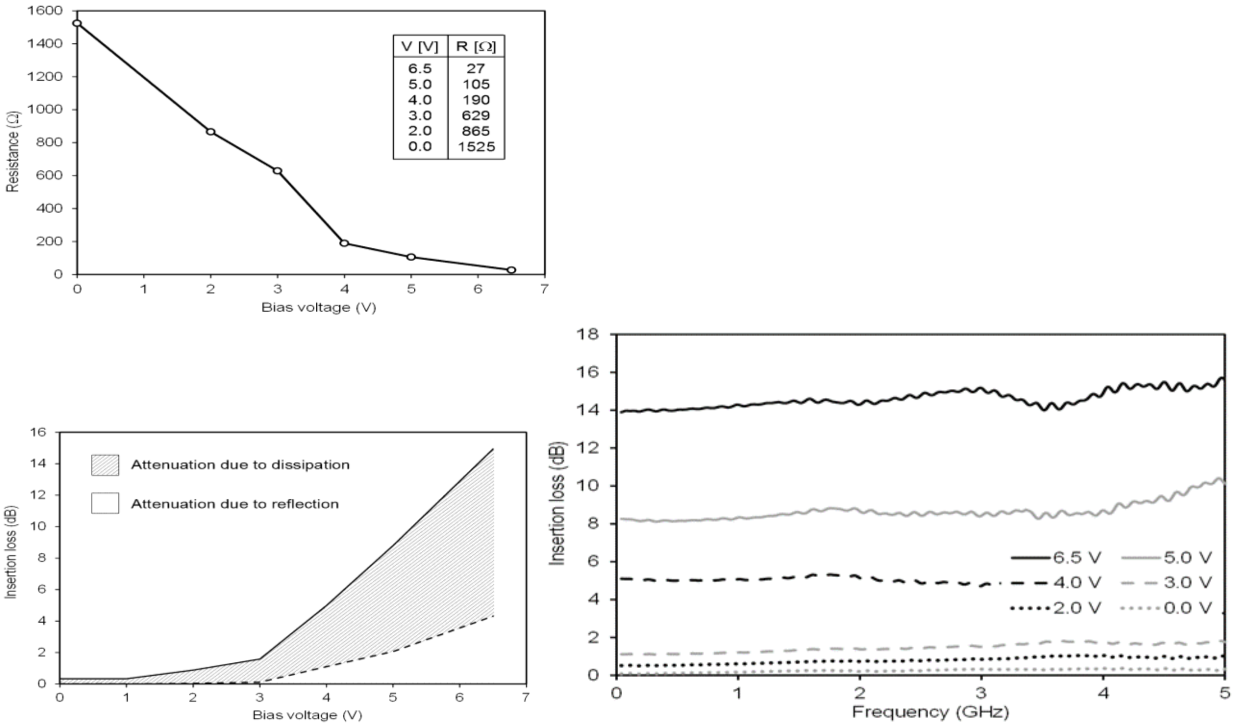
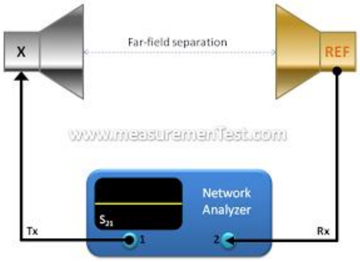
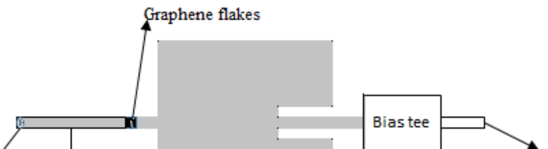


Fig. 4 Performance of the Enhanced Graphene Attenuator

The graphene flakes thin film was used for a tunable patch antenna [11], obtaining a change in the radiating frequency of the antenna, as well as almost 500 MHz of shift in its resonant frequency at 5GHz, see Fig. 5.





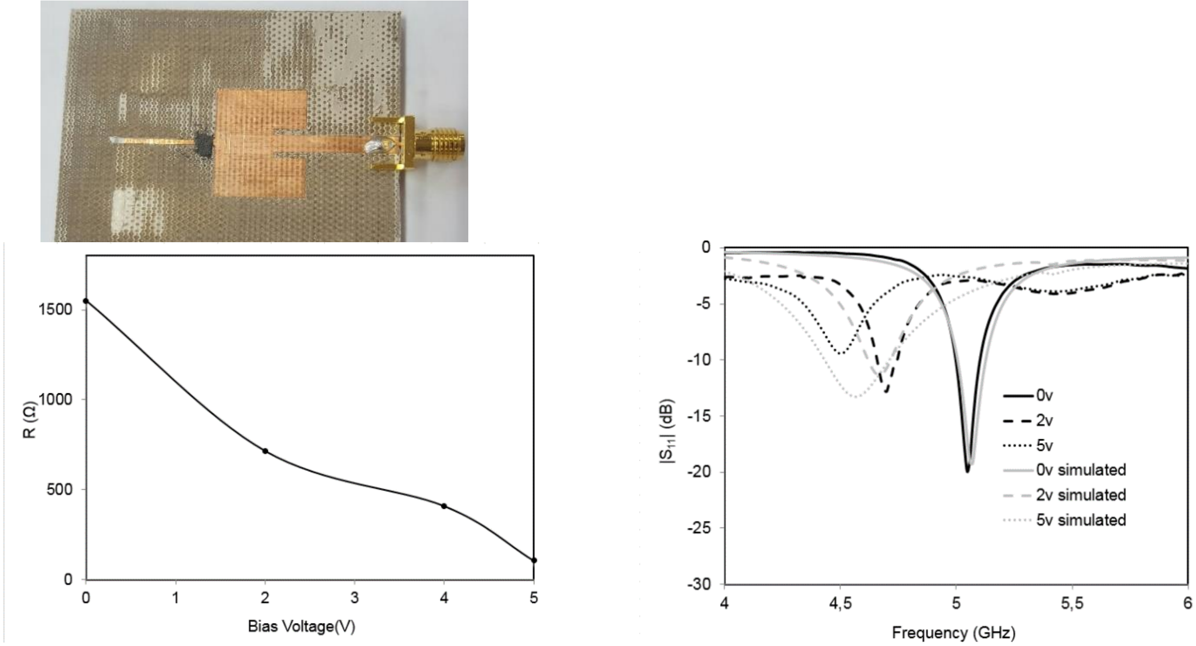


Fig. 5 The design and realization of a tunable patch antenna

One of the important directions of DNA - chips improvement is the increasing selectivity and sensitivity in expense of enhancement of electric signal and target probe hybridization stability. Efficiency of such devices as DNA-sensors and DNA-chips depends on precise prediction of experimental parameters responsible for thermal stability of nucleic acids duplexes and specific times of formation of DNA duplexes. Some following factors influence on the thermodynamics of hybridization, in particular: the density of single-strand DNA assays (the length 25-49 nucleotides) immobilized on the surface; the presence of competing hybridization; and some other factors. Development of DNA-sensors imposes specific requirements on the effectiveness of hybridization on the interface solid-solution.

One of the main requirements to the DNA-sensors is the high sensitivity and selectivity, which in its turn, demands a maximal effectiveness of hybridization and minimal non-specific adsorption on the interface of solid and liquid phases. The nucleic acids hybridization depends substantially on the temperature, salt concentration, viscosity, GC-content and other physical-chemical features. The increase of selectivity and sensitivity of DNA-sensors can be reached by using electro-chemically active compounds with higher affinity to the dsDNA than to the ssDNA. This kind of compounds can substantially increase the dsDNA stability and at the same time, the amplitude of generated signal, which increases the DNA-sensor sensitivity.

The crystallization of polymers is a way of modification of parameters for the polymeric systems and composite materials. We plan to use it in the frameworks of the current project to control the features of composite electrodes. As a result of the crystallization only a part of macromolecules are involved in crystallite formation, while remained parts, such as folds, macromolecules pass through crystallites and the ends of chains constitute an amorphous phase of inter crystalline sheet. The formed amorphous-crystalline structure is in a metastable state, whose properties, in general, are controlled b kinetic effects. It is important to mention that the crystallization temperature of polymers in general is lower than melting temperature. Supercooling of polymer in laboratory conditions may be carried even at 100K.

It is known that the process of crystallization begins in the so-called crystallization centers, which are located near different types of heterogeneities and structural defects. One may assume that in some cases the mixture of the nanoparticles and flexible chain polymers may manifest as this kind of defects. Our project is focused mainly on the carbon nanotubes, as nanofillers for the polymer composites. Carbon nanotubes (CNTs) can be produced in a number of different ways. One usually distinguishes two kinds of carbon nanotubes, referred to as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). This means, that the transfer of the SWCNT from the flexible chain's melt to the crystallite is thermodynamically favored and indicated the possibility of the nanohybrid shish–kebab (NHSK) structures formation around SWCNTs as centers of crystallization for polymers. The predicted NHSK structure is a unique polymer single crystal/CNT hybrid material, which was experimentally observed in Fig. A1.1, reported in [12]-

Electrochemical sensing using composite coatings based on carbon nanostructures, were obtained by a modification of screen printed electrodes (SPE) with nanocomposite materials made of epoxy resin as a matrix and 10% of different fillers, from carbon nanotubes (CNT) to graphene nanoplatelet (GNP) flakes (see Figs. 6-8).

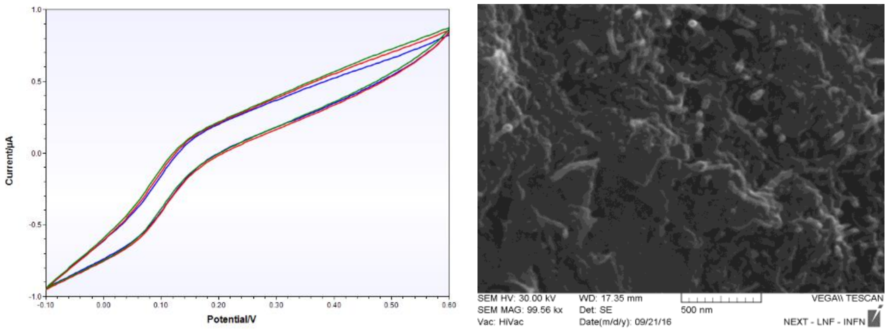


Fig. 6 Cyclic Voltammetry and SEM images of nanocomposite Epoxy-CNT 10%

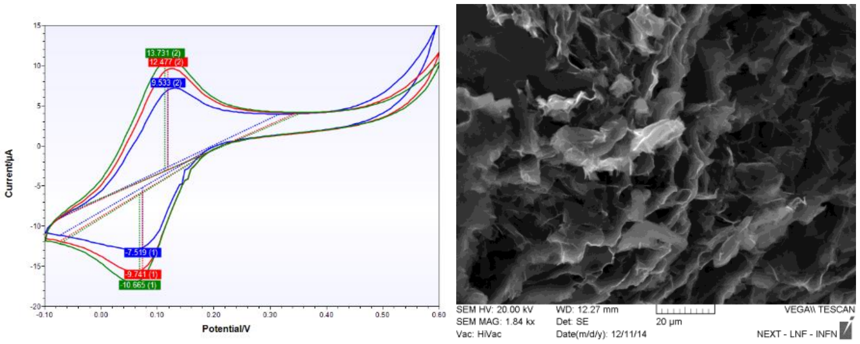


Fig. 7 Cyclic Voltammetry and SEM images of nanocomposite Epoxy-GNP

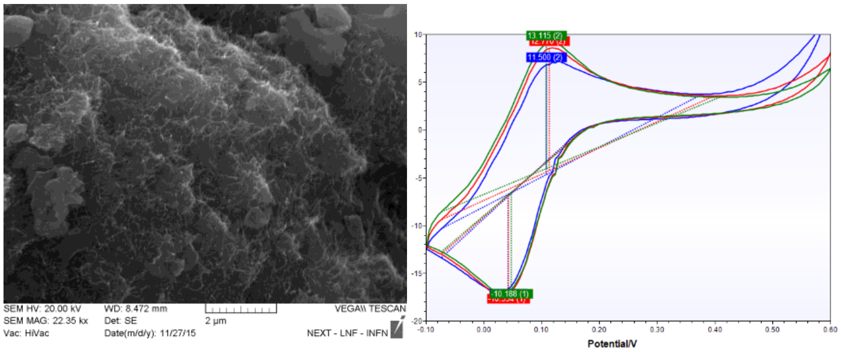


Fig. 8 Cyclic Voltammetry and SEM images of nanocomposite Epoxy-10% CNT-NH₂ functionalized (<5% amine groups)

It is seen that the SPE modified with Epoxy-CNT-NH₂ 10% and Epoxy-CNT-NH₂ 10% are far more sensitive than SPE unmodified, see Fig. 9

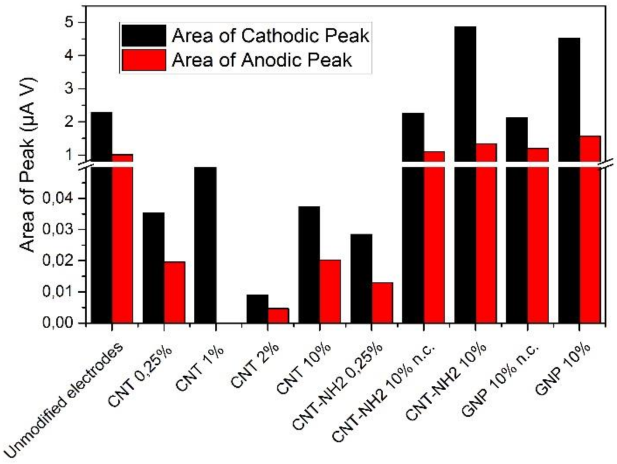


Fig. 9 Comparison of sensitivity of different sensor made of nanocomposites obtained varying both filler kind and concentration (percentage weight)

The high-resolution ultrasonic technique (impulse acoustic microscopy) was applied for observing the bulk microstructure of nanocomposites with various types of carbon nanoparticles as filler (see Fig. 10 [12-15]). It was shown that ultrasonic methods are excellent tools for studying nanoparticle distribution over the material bulk and for revealing probable nonuniformity. The acoustic microscopy technique allows for looking through the bulk microstructure of objects by means of layer-by-layer visualization and object cross-sectional imaging. In composites based on dispersed micrometer-sized particles of exfoliated graphite, the particle distribution over the composite material bulk was observed. In nanocomposites with various kinds of low-dimensional carbon nanofillers, i.e., nanoflakes, nanoplatelets, and nanotubes, the technique allowed the cluster architecture of the nanoparticle distribution to be revealed. Contact conjugation of low-dimensionality nanoparticles led to fractal clusters despite significant technological efforts for providing homogeneity to the nanocomposite materials and uniformity to their properties. A pronounced tendency to form micrometer-sized fractal agglomerates was found for 2D carbon nano-particles: nanoflakes and nanoplatelets. The impulse acoustic microscopy technique provides visualization of the agglomerate distribution over the nanocomposite material bulk. Another kind of nanoparticle distribution was observed with carbon nanotubes (CNTs). The latter formed CNT packings having different densities. Such regions were seen in acoustical images as small-sized areas of various brightness.

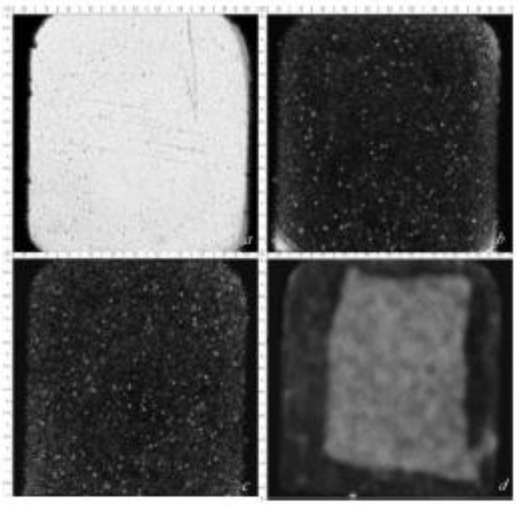


Fig. 10. Internal microstructure of carbon–epoxy nanocomposite with addition of graphite nanoplatelets (epoxy+1.0 wt.% GNP). Acoustic images (60-mm thick layers) are given at different depths inside the 1.56 mm thick specimen: (a) upper surface; (b) at 260mm deep; (c) at 380 mm deep; (d) bottom image. The dark area corresponds to the specimen fixing zone. Operation frequency is 100 MHz; scanning field is 10x11 mm2. Bright spots are agglomerates of carbon particles.

In conclusion and as a summary, we were able to carry out the following tasks and achieve the corresponding goals:

- Measurement of the stability parameter of double – stranded DNAs complexes with ligands
- The effect of intercalating ligands on the sensitivity and selectivity of the DNA - sensor
- Implementation of spin coating for preparing polymer substrate suitable for functionalization
- Raman observation of small percentage of functionalizing molecules put on the substrate
- The impulse acoustic microscopy characterization of the nanocarbon cluster architecture in the composite to modify screen printed electrodes is made
- The Raman characterization of nanocomposite modified screen printed electrodes was made
- Development of the electric scheme for the DNA – biosensor prototype

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Interactions with other WPs, other projects

Collaboration with WP7 Electronic Devices (Polina Kuzhir)
Interaction with the EU-7th FP project “NAmiceMC—Nano-thin and micro-sized carbons: Toward electromagnetic compatibility application”, 2014-2017.

List of Conference Talks by LNF Authors in the Year 2017

Maffucci A Applied Computational Electromagnet...26-03-2017
Carbon nanotube interconnects with negative temperature coefficient of the resistance
Firenze Italia

Micciulla F Semiconductor Conference (CAS), 2017 11-10-2017
Ageing effects on composite nano carbon based materials, Sinaia Romania

Bellucci S Semiconductor Conference (CAS), 2017, 11-10-2017
Graphene-based tunable microstrip attenuators and patch antenna, Sinaia Romania.

Publications by LNF Authors in the Year 2017

	Titolo	Autori	Sigla	Rivista	Autori NEMESYS	Autori Totali
1	A Planar Antenna With Voltage-Controlled Frequency Tuning Based on Few-Layer Graphene	**Yasir, Muhammad** et al.	GRAPHENE	IEEE ANTENN WIREL PR , **-16**	3	7
4	Calibration of the fine-structure constant of graphene by time-dependent density-functional theory	**Sindona, A.** et al.	GRAPHENE	PHYS REV B , **20-96**	1	6
6	Cluster microstructure and local elasticity of carbon-epoxy nanocomposites studied by impulse acoustic microscopy	**Levin, Vadim** et al.	GRAPHENE	POLYM ENG SCI , **7-57**	4	7
7	Enhanced Tunable Microstrip Attenuator Based on Few Layer Graphene Flakes	**Yasir, Muhammad** et al.	GRAPHENE	IEEE MICROW WIREL CO , **4-27**	1	6
10	Graphene nanoplatelets: Thermal diffusivity and thermal conductivity by the flash method	**Potenza, M.** et al.	GRAPHENE	AIP ADV , **7-7**	2	6
11	Graphene-based Tunable Microstrip Attenuators and Patch Antenna	**Bellucci, Stefano**	GRAPHENE	INT SEMICONDUCT CON , **-**	1	1
12	Highly tunable and Large Bandwidth Attenuator Based on Few-Layer Graphene	**Yasir, Muhammad** et al.	GRAPHENE	, **-**	1	6
13	Integral equation technique for scatterers with mesoscopic insertions: Application to a carbon nanotube	**Shuba, M. V.** et al.	GRAPHENE	PHYS REV B , **20-96**	1	9
14	Modeling, Fabrication, and Characterization of Large Carbon Nanotube Interconnects With Negative	**Maffucci, Antonio** et al.	GRAPHENE	IEEE T COMP PACK MAN , **4-7**	1	5

	Temperature Coefficient of the Resistance					
15	Plasmon properties of doped or gated graphene nanoribbon arrays with armchair shaped edges	**Sindona, A.** et al.	GRAPHENE	, **-**	1	7
16	Real time polymer nanocomposites-based physical nanosensors: theory and modeling	**Bellucci, Stefano** et al.	GRAPHENE	NANOTECHNOLOGY , **35-28**	1	6
17	Resistivity and low-frequency noise characteristics of epoxy-carbon composites	**Pralgauskaite, Sandra** et al.	GRAPHENE	J APPL PHYS , **11-121**	1	11
18	RHEOLOGICAL BEHAVIOR OF GRAPHENE/EPOXY NANODISPERSIONS	**Ivanov, E.** et al.	GRAPHENE	APPL RHEOL , **2-27**	1	7
19	Tunable and Input-Matched Attenuator Based on Few-Layer Graphene	**Yasir, Muhammad** et al.	GRAPHENE	EUR MICROW CONF , **-**	1	6