CARBON ENCAPSULATION OF MAGNETIC METAL NANOPARTICLES: CORRELATION BETWEEN NANOSCALE STRUCTURE OF CARBON MATRIX AND ELECTROMAGNETIC PROPERTIES

1S. V. Kozyrev, 2V. I. Ivanov-Omskii, 2S. G. Yastrebov, 2T. K. Zvonareva, 2M. S. Chekulaev, 2A. V. Siklitskaya

1 Center for Advanced Studies, St. Petersburg, Russia
2 A.F. Ioffe Physicotechnical Institute RAS, St. Petersburg, Russia
SVKozyrev@spbcas.ru, Yastrebov@mail.ioffe.ru

PACS 81.05.ue

The dependence between the variation of microwave losses by \( a - C : H(Co) \) films measured at 10 GHz and alteration of Co content in the film was investigated. It was shown that microwave losses attain maximal value at approximately 33 at.% of cobalt. This dependence may be explained in terms of the formation of Co-containing clusters having various shapes. Because of property of conductive flakes to absorb microwaves, fragments of graphene modified with Co are considered as candidates for the microwave absorption. Estimations of the flake size using Raman and transmission electron microscopy data allow reproduce initial conditions for mathematical simulation of physical properties of the flakes.

Keywords: graphene, cobalt, intercalation, carbon, nanoclusters, encapsulation.

1. Introduction

Metal nanoclusters are promising materials for creation on their basis magnetic media for ultra-high density recording [1] and EM absorbers [2]. Methods for introducing metal clusters in a carbon matrix, also termed as “encapsulation”, are of two types (see, e.g., [3] and [4, 5]). In the first method, metallic clusters are encapsulated into carbon cages. In the second method, first developed in [4], nanoclusters are embedded into a matrix of amorphous carbon [4, 5]. This technique is less expensive, simpler and more effective than the first one [3] and compatible with thin film technologies for microelectronics. The ensembles of encapsulated clusters may show emerging quantum physical effects [6]. However, modification of hydrogenated amorphous carbon with Co is a more complex problem than encapsulation itself. That may be associated with modification of \( sp^2 \) part of amorphous carbon by metal [7]. In paper [7] modification of hydrogenated amorphous carbon with Co was performed by Raman spectroscopy that allows one to estimate mean size of graphene fragments. This observation is in a good agreement with sizes derived by transmission electron microscopy images [8], performed for the stacked graphene fragments that were termed in [8] as “graphite clusters”.

Actually, as one might expect for a relatively low concentration, Co atoms are stochastically scattering in the film and may interact with \( sp^2 \) constituent of the matrix not forming massive Co clusters. This \( sp^2 \) constituent consists of a set of graphene plane fragments either embedded in an amorphous matrix and isolated from each other by spaces of amorphous material (\( sp^3 \) -bonded) or even forming a network percolating through the sample.
The valuable property of graphene fragments is the possibility to adsorb atoms that may
occupy places above and below the planes. These atoms may form two-dimensional frag-
ments of metallic surfaces that may absorb electromagnetic radiation. Actually, if a flake
of graphene with adsorbed Co atoms may be formed, Co atoms may organize themselves
in a fragment of two-dimensional Co layer attaching to a graphene fragment surface. At
the same time classical electrodynamics predicts that two dimensional flakes (e.g. flat ellipt-
dical disks) may demonstrate a strong absorption of electromagnetic radiation through the
mechanism of surface plasmon excitation. The absorption emerges at microwave frequency
wavelengths for in-plane depolarization factor $L = 0$ that is typical for the flakes [9]. Thus,
flat metallic particles may absorb microwaves of different polarizations, if the particles are
randomly oriented in the volume of the sample. In this paper we revise the dependence of
the microwave radiation losses on overall Co concentration for Co-modified films of a-C:H
aiming explanation of this dependence.

2. Experimental

Films of $a - C : H(Co)$ were produced in our laboratory by simultaneous sputtering
of graphite and cobalt targets by Argon (80%) -Hydrogen (20%) plasma in DC magnetron.
The films were deposited on aramide tissue for microwave absorption experiments. Cobalt
content was varied by a change of surface of sputtering Co target. Its concentration in
the produced films was controlled by Rutherford backscattering method as previously de-
dcribed [7]. Microwave absorption experiments were performed using techniques published
elsewhere [6].

3. Discussion and conclusions

We exploited previously published data for microwave absorption [6] for analysis as
well as some unpublished data. The dependence of microwave losses measured at 10 GHz
on Co content is presented in Fig.1. It is seen that the dependence attains a maximal value
for a certain Co content, for approximately 33 at.%. One may speculate that in the area of concentration of Co less than 33 at%, fragments
of Co-modified graphene of limited size may exist and may work as absorber of microwaves
through excitation of the surface plasmons. But it may mean that for bigger than 33 at.
Co concentration, the formation mechanism for massive three dimensional clusters may
dominate over mechanism of Co adsorption by graphene flakes. Quite naturally, for this
case, the losses decrease with increased Co concentration, because the obvious change of
the depolarization factor $L$ varying from $L = 0$ for in-plane absorption by metal flakes
(that corresponds to the absorption of microwaves) to $L = 1/3$ for spherical clusters (that
corresponds to shift of maximum absorption of electromagnetic radiation from microwave to
visual and ultraviolet regions [9]).

Thus, fragments of Co-intercalated graphene might be responsible for the absorption
of microwaves. The hypothesis for the presence of the Co-modified graphene fragments in
Co-doped amorphous carbon is consistent with the experimental data presented in [7]. The
preliminary results published in [7] might be used for numerical investigation of physical
properties of the fragments via $ab$ initio methods. Moreover, TEM image analysis of amor-
phous carbon, together with analysis of Raman spectra of amorphous carbon modified with
Co, provide us with some information about the mean diameter of a mean graphene fragment
and mean number of hexagons constituting the fragment [7, 8].

For further estimation, one may use a relation between mean number of atoms forming
the fragment $N$ and mean number of hexagons: $N = 2(2M + 1)$. If $M$ fluctuates around 20,
Fig. 1. Black squares stand for the dependence of losses of microwaves measured at 10 GHz on Co content for a-C:H(Co) samples. The curve shows the trend therefore $N$ oscillates near 82. For reconstruction of Co-intercalated fragment one may use number of Co atoms equal to number of hexagons.

Thus, the study performed predicts approximate initial conditions for mathematical simulation of fragments of graphene embedded in a matrix of hydrogenated amorphous carbon.

The dependence of microwave losses observed in Fig.1 may be explained exploiting concepts for the existence of conductive 2-dimensional graphene flakes and massive three dimensional Co clusters, contributing to the absorption for different Co concentrations.

References