Magnetic films of metal-graphene-polymer nanocomposites

H. Takacs1,2, B. Viala1, C. Gourgon2, F. Duclairoir3, J.-H. Tortai2

1CEA, LETI, MINATEC Campus, Grenoble, France
2LTM-CNRS-UJF, CEA, LETI, MINATEC Campus, Grenoble, France
3CEA, INAC, Grenoble, France
17 rue des Martyrs, 38054 Grenoble cedex 9, France
helene.takacs@cea.fr

Abstract

Over the years components miniaturization has been a crucial objective in microelectronics resulting in the integration of most of the passive components. To go further, ultra-miniaturization of RF inductors and antennas is yet to be done because it runs up against the paradigm of a highly permeable material with zero macroscopic conductivity. Neither ferrites (too low permeability), nor ferromagnetic alloys (too conductive) meet this requirement. Therefore, a breakthrough is essential regarding the way of developing such material. Here, we are interested in metallic-nanoparticle-loaded polymers with enhanced soft magnetic properties from the bulk. Only metals such as Ni, Co, Fe and alloys (i.e. FeCo) can address high permeability in microwave region due to high natural saturation magnetization (1.6 – 2.2 T).

So far mainly ferrites-based nanocomposites (i.e. magnetic oxides) have been elaborated because most of chemistries are highly oxidizing. But magnetic oxides have too low magnetic properties at high frequency, mainly due to the diluted saturation magnetization (0.2 – 0.5 T) [1], [2], [3]. The objective of this work is to synthesize core-shell metallic commercial nanoparticles-based nanocomposites. Original dual core-shell schemes are investigated. First a graphene shell prevents oxidation of the metallic particle core (M/C). Then a (co)polymer (P1) shell insulates the graphene-coated metallic particles (M/C//P1) and controls the inter-particle spacing at a nanometric scale. A second polymer (P2) can be used as an encapsulating matrix of the super beads (i.e. P2 can be P1 as well). Finally films of compacted metal-graphene-polymer (M/C//P1/P2) super particles are deposited on substrates by spin coating.

In this work, commercial <30nm> M/C nanoparticles of Co (from Sigma-Aldrich) are used. P1 consists in Pyrene-terminated Polystyrene with three different molecular weights (5.6, 26 and 355kg.mol\(^{-1}\)), while P2 is pure Polystyrene (molecular weight 35kg.mol\(^{-1}\)).

First ultra-sonication is used to break large aggregates of as-received commercial Co/C nanoparticles into small ones (~100nm). Then P1 is directly grafted on the graphene shell (Co/C//P1). The super particles of Co/C//P1 are further encapsulated with P2 which makes the whole nanocomposite cohesive (Co/C//P1/P2). Finally films of compacted Co/C//P1/P2 material are deposited on silicon substrates by spin coating.

The choice of using Pyrene-terminated Polystyrene as P1 is motivated by the presence of four aromatics cycles in Pyrene groups. Delocalized electrons can strongly interact with graphene sheet(s) surrounding NPs through π–π stacking [4]. Pyrene groups are also known to fluoresce and are used as fluorescent labeling agent for biological applications [5]. Here the Pyrene fluorescence peak around 500 nm is used as a marker of grafting onto the NPs.

Sedimentation dynamics of the solutions has been studied first. P1-grafting and further addition of P2 stabilize NPs and small aggregates, as can be seen on Figure 1 where relative area of integrated absorbance curves is plotted against sedimentation time, in the case of Co particles.

As can be seen on Figure 2, P1-grafting (where \(M_w(P_1)=5.6kg.mol^{-1}\)) can clearly be identified around typical 100 - 200nm aggregates which confirms the strength of π–π-interactions. Note that observation on single NP is difficult.

Figure 3 shows a cross-section of the film of Co/C//P1/P2 nanocomposite. For intermediate thickness (< 1μm), the films consist in a mixture of small aggregates and isolated NPs well dispersed inside the film volume. Such films of Co/C//P1/P2 nanocomposite exhibit a dominant soft ferromagnetic behavior at room temperature as shown on Figure 4 with moderate hysteresis (Hc of 23 Oe). The room temperature saturation magnetization is of 0.35T indicating a volume fraction of Co of about 20% from the bulk. The
relatively high anisotropy (i.e. suitable for high frequency use) may originate in chain-like arrangement of the Co NPs which is under investigation.

Finally, when considering thicker film (up to ~ 10µm), soft magnetic properties somehow deteriorate because of the presence of residual large aggregates of big particles (~ 100nm) which remain trapped during spin-coating.

Conclusion

Magnetic films of metal-graphene-polymer nanocomposites are synthesized by dispersing Co/C NPs in a PS matrix (P_2). The graphene shell is successfully functionalized by grafting Pyrene-terminated PS (P_1) via non-covalent interaction (π stacking). These first films of Co/C//P_1/P_2 consist in a mixture of small aggregates and isolated NPs well dispersed inside the film volume. Soft ferromagnetic-like behavior is observed at room temperature with a saturation magnetization of 0.35T indicating a volume fraction of Co of about 20%. Next steps will consist in increasing this number (~40%) by varying the ratio of Co/C//P_1 super particles vs. PS (P_2) in the solution.

References


Figures

Fig. 1: Relative area of integrated absorbance curves vs. sedimentation time

Fig. 2: SEM picture of an isolated P_1-coated Co/C aggregate

Fig. 3: SEM picture (cross-section) of Co/C//P_1/P_2 nanocomposite film

Fig. 4: Magnetic response of Co/C//P_1/P_2 nanocomposite film