Synthesis and functional characterization of poly(p-xylylene)-MnSb nanocomposite films

L N Oveshnikov1,2, S A Zav’yalov1, D R Streltsov1,2, N K Chumakov1, I N Trunkin1, A A Nesmelov1 and S N Chvalun1,3

1 National Research Center "Kurchatov Institute", Moscow, Russia
2 P.N. Lebedev Physical Institute RAS, Moscow, Russia
3 N.S. Enikolopov Institute of Synthetic Polymeric Materials RAS, Moscow, Russia

E-mail: Oveshln@gmail.com

Abstract. In this study, structure and magnetic properties of poly(p-xylylene)-MnSb nanocomposite films with different inorganic filler content were investigated. The thickness of all studied films was about 200-300 nm as determined by scanning electron microscopy. It was found that the filler concentration strongly affects surface morphology of the composite films. AFM revealed that the film with the lowest MnSb content has globular surface morphology, presumably formed by polymeric grains with small MnSb nanoparticles on their surface. Ferromagnetic hysteresis loop was observed for all studied films at room temperature with the saturation magnetization values correlating with the MnSb content.

1. Introduction

Bulk MnSb and MnSb-based solid solutions have been studied for several decades, due to the high temperature ferromagnetism and its close relation to the caloric, optical and structural properties usually observed in these materials. The Curie temperature, \( T_c \), for MnSb is reported to be \( \sim 600 \) K [1, 2]. The earlier investigations of relation between ferromagnetic response and the microstructure of MnSb films [3] revealed an option to adjust magnetic properties of such systems, which is desirable for spintronic applications. It was found that pure MnSb is not suitable for implementation of some spintronic devices. Therefore, the most recent researches were focused on the MnSb-based composite systems. Earlier studies of MnSb composite films with III-V semiconductor matrix [4] revealed several advantages of such systems, compared to more widely used materials - diluted magnetic semiconductors, such as (Ga,Mn)As. Basically, the phase segregation allows to combine high temperature ferromagnetic state due to formation of MnSb inclusions and relatively good crystalline quality of semiconducting matrix (which results in higher mobility values) in a single material. For comparison, the carrier mobility of (Ga,Mn)As does not exceed 10 \( \text{cm}^2/(\text{V} \cdot \text{s}) \), while maximum \( T_c \) value for this material is about 200 K [5]. However, basic spintronic applications require high degrees of carrier spin polarization, and in this sense MnSb composites have an apparent drawback. The formation of metallic MnSb inclusions in the semiconductor matrix is accompanied by the appearance of Shottky barriers at their interfaces. The amplitude (and thus, the transparency) of such barriers depends on the matrix properties. As a result, composite films with the narrow-gap InSb matrix show no signs of carrier spin polarization at room temperature [6], while films based on GaSb matrix (with larger bandgap) revealed the presence of spin-polarized current at 300 K [7]. Thus, it seems to be...
promising to use more insulating matrix to achieve higher degrees of spin polarization. As a possible way to realize such system we decided to use polymer matrix, which also may add some new features to the system. It is worth mentioning that the MnSb inclusions in solid-phase composites usually are relatively large (25-100 nm [6, 7]) and yield ferromagnetic response, which is quantitatively similar to that of the bulk MnSb. However, for smaller MnSb nanoparticles (below 30 nm), the size decrease eventually leads to the transition into superparamagnetic state [8]. But only limited number of studies are devoted to size-dependent effects on the properties of MnSb nanoparticles, partially because only few methods were developed for fabrication of such systems (e.g. epitaxial [3] and solution-based [9, 10] ones).

Polymer composites with ferromagnetic filler have various potential applications. However, most of the related works are focused on elemental ferromagnetic metals or the oxides. In this case, there is a common problem of additional oxidation or reduction of the initial filler material during the synthesis process. Thus, the resultant chemical structure of the filler inclusions (nanoparticles) is often unpredictable and strongly depends on the synthesis conditions. By using binary ferromagnetic material, we expected to suppress this problem. In this work, we studied poly(p-xylylene)-MnSb (PPX-MnSb) nanocomposite films synthesized using a vapor deposition polymerization (VDP) method. Unlike solution-based deposition techniques (such as reported in [9, 10]), VDP synthesis route does not involve any solvent or catalyst, which prevents additional byproducts appearance. In addition, polymer matrix stabilizes inorganic nanoparticles, thus no additional coating to prevent their aggregation is needed. It is worth mentioning that PPX is widely used for various applications because of its high dielectric and barrier characteristics. In the VDP process, formation of inorganic nanoparticles starts with the molecular clusters of the filler, which, combined with cryogenic temperatures maintained during the condensation step (see below), may result in a substantial alterations of the nanoparticle crystal structure, as compared to the bulk material [12]. It should be mentioned that the components of polymer composite may substantially affect the properties of one another. For example, the nanoparticles of inorganic filler can affect the kinetics of polymer crystallization, while the polymer matrix often defines the spatial distribution of nanoparticles and, as a consequence, the resultant characteristics of the nanoparticles ensemble. While some basic relations between films properties evolution and synthesis parameters variation are applicable to PPX-based composites, the actual microstructure of the film (and as a consequence, its functional properties) have strong dependence on the filler material. Therefore, in this work we focused on the investigation of some basic correlation between the PPX-MnSb films morphology and their magnetic properties as a function of the filler content.

2. Methods

The poly(p-xylylene)-MnSb nanocomposite films were synthesized on Si substrates via lowtemperature vapor deposition polymerization (VDP) technique [13], which includes two basic steps performed in a high vacuum ($10^{-5} - 10^{-6}$ Torr) chamber. The first one is the cocondensation of monomer (p-xylylene) and filler (MnSb) vapors on a substrate, cooled by liquid nitrogen ($T = 77$ K). The MnSb powder was evaporated from a tantalum boat. The monomer precursor, [2.2]p-cyclophane, was sublimated at $T_{sub} \approx 330 - 370$ K. In the pyrolysis zone ($T_{pyr} \approx 920$ K), constrained p-cyclophane molecule decays with formation of two reactive p-xylylene monomer molecules. Then the monomer and MnSb vapors adsorb simultaneously on the substrate and form metastable co-condensate. The second step is the slow heating of the co-condensate up to room temperature, during which the polymerization of monomer into poly(p-xylylene) (PPX) and formation of MnSb inclusions occur. The resultant composite films consist of MnSb inclusions stabilized in the polymer matrix. To obtain composite films with different PPX/MnSb ratio we varied the intensity of monomer flow (governed by the value of $T_{sub}$), while keeping the filler flow constant. In this work, we studied three samples, one of which (Sample A) is a pure MnSb film deposited on a Si substrate held at room temperature, and two others are PPX-MnSb films with low (Sample B) and high (Sample C) polymer content.
Table 1. [2.2]p-cyclophane sublimation temperature $T_{sub}$; film thickness $d$; coercive force $H_c$ and saturation magnetization $M_{sat}$ at room temperature for studied samples.

| Sample   | $T_{sub}$ (K) | $d$ (nm) | $H_c$ (Oe) | $M_{sat}$ (emu / cm$^3$) |
|----------|---------------|---------|-----------|------------------|
| Sample A | -             | 320     | 305       | 400              |
| Sample B | 340           | 190     | 205       | 390              |
| Sample C | 370           | 250     | 245       | 180              |

The thickness of the films was estimated using dual beam scanning electron microscope/focused ion beam (SEM/FIB) Versa 3D (FEI, USA), equipped with a Schottky field emission gun. Surface morphology of the films was investigated by atomic force microscopy (AFM) in PeakForce Tapping mode using a Multimode 8 microscope with a Nanoscope V controller (Bruker, USA). All images were recorded in air at room temperature. Magnetic properties of the synthesized films at room temperature were investigated using a vibrating sample magnetometer 7400 (Lake Shore Cryotronics, USA), magnetic field was oriented in the sample plane.

3. Results and discussion

In general case, the growth rate (and as a consequence, thickness, $d$) of a composite film, obtained in the VDP process, depends, mostly, on the sticking coefficients of monomer and filler molecules to the substrate. However, the actual values of these coefficients may vary with the intensities of each flow. Thus, to eliminate this uncertainty from the following discussion, we estimated the thickness of each studied film. We used Ga+ FIB (Versa 3D) to etch a small region (of about 10 $\mu$m $\times$ 10 $\mu$m) of the sample surface to obtain clear edge of the film. To protect the film around the etching region we deposited on top of the sample a thin layer of W (by an electron beam), followed by a 2 $\mu$m-thick W layer deposited by an ion beam, before the FIB procedure. Figure 1 shows the SEM image of the obtained films edge for Sample C, tilted by $52^\circ$, relative to the sample holder plane. One can distinguish the PPX-MnSb film from the Si substrate and protective W layer and thus, estimate its thickness. Obtained $d$ values are given in table 1. We should mention that all studied films had relatively even contrast in the acquired SEM images. Thus, no clear indications of phase segregation was observed. However, it can be related to the low spatial resolution of obtained SEM images, meaning that characteristic sizes of the inclusions of each component are small, e.g. in comparison with the film thickness. We should also mention, that ion beam could affect the film edge region blurring its fine microstructure.

![Figure 1. SEM image of the film edge, obtained by the ion beam etching, for Sample C. Sample was tilted by 52°, relative to the sample holder plane. Due to the differences in contrast, one can distinguish the PPX-MnSb film from the substrate and protective W layer.](image)
The surface morphology of studied films changes along with the increase of polymer content. As one can see from the AFM height image for Sample A (figure 2a), the surface of pure MnSb film has notable surface roughness. The areas with maximum height (of about 20 nm) have lateral sizes of 10-40 nm, while the distances between such areas are about 100-300 nm. Addition of a small portion of polymer leads to grain-like morphology, as it is shown for Sample B (figure 2b). Here, the highest regions also have maximum height of about 20 nm and lateral sizes of 10-30 nm, however, distances between such neighbour regions are much smaller - well below 100 nm. Further increase of polymer content results in the qualitative change of surface morphology. For the Sample C, AFM reveals globular-like surface morphology (figure 2c), formed by close-packed globules with maximum height of about 40 nm and lateral size of about 60-150 nm. One can see small particles on the surface of each globule, which can be illustrated by the provided adhesion map (figure 2d), where such particles correspond to darker areas and have characteristic lateral sizes of about 10-15 nm. Similar surface morphology was observed for PPX-Ag composites earlier [14] and it was suggested that such surface consist of PPX globules with Ag nanoparticles on its surface and inside them. Probably, the same interpretation can be applied for Sample C, implying that surface nanoparticles consist of manganese antimonide. Thus, the obtained data suggests that the increase of polymer content not only enlarge the 

Figure 2. AFM height image of 1 μm × 1 μm surface region for (a) Sample A, (b) Sample B and (c) Sample C. (d) Corresponding adhesion map for Sample C.
surface roughness of composite film, but may also decrease the characteristic sizes of MnSb inclusions.

While the qualitative picture of the PPX-MnSb films microstructure evolution upon the increase of polymer content is in line with our previous results for PPX-based composites, the most important feature in our case is the composition effect on the magnetic properties of the system. Magnetization curves, shown in figure 3, were obtained at room temperature. As one can see from the figure, all studied films exhibit pronounced ferromagnetic hysteresis. Above the saturation field we also observed small linear contribution to the $M(H)$ dependence, which was subtracted from the data shown in figure 3, as it is, most probably, related to the Si substrate. The presented data was used to determine coercive force, $H_c$, and saturation magnetization, $M_{sat}$, values, summarized in table 1. The $M_{sat}$ values for Sample A and Sample B seems to be very close, while the saturation magnetization for Sample C is much lower, which agrees well with lower MnSb content in this film. However, the minimum $H_c$ value is observed for Sample B (table 1).

![Figure 3](image)

**Figure 3.** Field dependence of room temperature magnetization for studied samples. Linear contributions, observed in higher fields, were subtracted. Numerical values of saturation magnetization and coercive force are given in table 1.

It is important to note that the $M_{sat} \approx 400 \text{ emu/cm}^3$ value for Sample A is in good agreement with the results for MnSb nanoparticles with the average size of 30 nm on Si substrate [8]. While, in our case, we observe smaller $H_c$ value (305 Oe instead of 450 Oe), which, however, is close to that of thin MnSb films on GaAs substrate with $M_{sat} \approx 300 \text{ emu/cm}^3$ [3]. It should be mentioned that the variations of $M_{sat}$ and $H_c$ values were ascribed to the differences in Mn distribution or to the appearance of surface manganese oxide [3]. Unfortunately, we do not have enough data yet to make a reliable explanation of the discrepancies between our results and reference data. However, we can use $M_{sat}$ value for Sample A as a "baseline" and estimate the polymer content in other samples. In this estimation we assume that overall saturation magnetization of PPX-MnSb film depends solely on the volume fraction of MnSb phase, neglecting any additional effects, such as surface oxidation. It is worth mentioning that the possible transition into superparamagnetic phase for smallest particles should not, however, substantially affect this estimation, because it have only a limited effect on the $M_{sat}$ value for such particles. For Sample B the polymer content appears to be very small - about 2.5
vol.%, while for Sample C it is about 55 vol.%. As one can see from Figure 2c, the concentration of surface particles is rather high, however, such high MnSb content (45 vol.%) suggests that a portion of MnSb nanoparticles is also present within the polymer globules. As it was said earlier, the characteristic size of surface MnSb nanoparticles is about 10-15 nm, while the substantial part of such particles have sizes \( \leq 10 \) nm, and, according to reference results [8], should not exhibit ferromagnetic response at room temperature, which does not agree with our estimations. Thus, there can be two possible reasons: either the boundaries between adjacent nanoparticles are very small, so that they can actively interact with each other (effectively forming a larger particles), either the most part of these nanoparticles volume is buried into the polymer globules.

4. Conclusions
We have synthesized PPX-MnSb nanocomposite films with thickness of about 200-300 nm on Si substrates using VDP method. Using ion beam etching procedure we obtained SEM images of the film edge for studied samples, that were used for the film thickness estimation. Using AFM we investigated the surface morphology of studied films. The increase of polymer content leads to the increase of surface roughness and eventually imparts globular-like morphology. All studied films are ferromagnetic at room temperature, which make them perspective for spintronic applications.

Acknowledgments
This work was partially supported by the Russian Foundation for Basic Research (grant No.18-33-20240). The study was carried out using the equipment of the Resource Centers of Kurchatov’s Complex of NBICS-Technologies.

References
[1] Teramoto I and Van Run A M J G 1968 J. Phys. Chem. Solids 29, 347–355
[2] Novotortsev V M, Kochura A V, Marenkin S F, Fedorchenko I V, Drogunov S V, Lashkul A and Lahderanta E 2011 Russ. J. Inorg. Chem. 56, 1951–1956
[3] Low B L, Ong C K, Lin J, Huan A C H, Gong H and Liew T Y F 1999 J. Appl. Phys. 85, 7340–7344
[4] Rylkov V V, Aronzon B A, Danilov Yu A, Drozdov Yu N, Lesnikov V P, Maslakov K I and Podol’skii V V 2005 JETP 100, 742–751
[5] Wang M, Marshall R A, Edmonds K W, Rushforth A W, Campion R P and Gallagher B L 2014 Appl. Phys. Lett. 104, 132406
[6] Yakovleva E I, Oveshnikov L N, Kochura A V, Lisunov K G, Lahderanta E and Aronzon B A 2015 JETP Lett. 101, 130–135
[7] Oveshnikov L N, Nekhaeva E I, Kochura A V, Davydov A B, Shakho M A, Marenkin S F, Novodvorskii O A, Kuzmenko A P, Vasiliev A L, Aronzon B A and Lahderanta E 2018 Beilstein Journal of Nanotechnology 9, 2457–2465
[8] Zhang H, Kushvaha S S, Chen S, Gao X, Qi D, Wee A T S and Wang X -S 2007 Appl. Phys. Lett. 90, 202503
[9] Hettiarachchi M A, Abdelhamid E, Nadgorny B and Brock S L 2016 J. Mater. Chem. C. 4, 6790–6797
[10] Hettiarachchi M A, Abdelhamid E, Nadgorny B and Brock S L 2019 Nanoscale 11, 6886–6896
[11] Ozerin S A, Vdovichenko A Yu, Streltsov D R, Davydov A B, Orekhov A S, Vasiliev A L, Zubavichus Y V, Grigoriev E I, Zavyalov S A, Oveshnikov L N, Aronzon B A and Chvalun S N 2017 J. Phys. Chem. Solids 11, 245–253
[12] Nesmelov A A, Oveshnikov L N, Ozerin S A, Zavyalov S A, Zubavichus Ya V, Orekhov A S, Streltsov D R, Kiryukhin Yu I and Chvalun S N 2019 J. Phys. Chem. C 123, 10517–10528
[13] Grigoriev E I, Zavyalov S A and Chvalun S N 2006 Nanotechnologies in Russia 1, 58–70
[14] Streltsov D R, Mailyan K A, Gusev A V, Ryzhikov I A, Erina N A, Su C, Pebalk A V, Ozerin S A and Chvalun S N 2013 Applied Physics A: Material Science and Processing 110, 413–422