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Investigation of the interactions of PVDF shell films with Ni core submicron wires and AAO matrix

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ABSTRACT

Arrays of Ni submicron wires surrounded by poly (vinylidene fluoride) (PVDF) submicron tubes were prepared via solution-processed polymer and Ni electrodeposition into anodic aluminum oxide template. The PVDF solution was filtered in vacuum through the template and the resulting dried structure was used for the electrodeposition of Ni wires. The obtained core-shell submicron wire structure consists of a metallic magnetic nanowire core of about 50 μm in length and about 300 nm diameter surrounded by a polymer tube shell with thickness less than 10 nm. The specific ferroelectric β-phase of the polymer was obtained whereas the magnetic behavior of the Ni-cores was proven to be specific to an array of ferromagnetic Ni cylindrical wires (about 0.62 μ_B/Ni atom) with magnetization reversal mechanisms dominated by dipolar interactions and domain wall displacements. No significant differences of the magnetization reversal mechanism were observed in case of Ni submicron wires surrounded by PVDF tubes and similar Ni wires without PVDF shell, suggesting that magneto-coupling effects in such systems might be observed only by measuring the perturbation of the electric state of the polymer shell under a magnetic excitation of the Ni cores.

1. Introduction

The coverage of metal surfaces with thin polymer films allowed metals to be used in new applications. Thus, thin polymer layers deposited on metals can be used for modulation of adhesion, lubrication, wettability, friction, and biocompatibility of the underlying substrate. Development of heterogeneous nanostructures based on ultrathin polymers layers deposited on nanostructured metal surfaces can permit construction of devices in which the properties of the metallic nanostructures (magnetism, electrical conductivity, etc.) can be influenced by those of the polymer and vice-versa.

Multiferroic materials are those in which ferromagnetic and ferroelectric orders coexist, the two phases being coupled through a so called magnetoelectric (ME) interaction [1–3]. In the case of multiferroic heterostructures, the ME coupling is interfacial and can come from charge, elastic strain and exchange bias interactions [4]. The low dimensional composite materials can provide tighter coupling between ferroelectric and ferromagnetic phases and offer additional degrees of freedom in controlling size, interface and epitaxial strain to enhance the ME coupling [5]. Although the experience in preparing nano-composite systems consisting of magnetic nanoparticles in different polymeric matrices is quite extended [6–8] the advantage of using a nanowire like configuration for the magnetic component, in interaction with a polymeric shell with ferroelectric properties resides in the much better activation of magnetostrictive effect in one dimensional magnetic systems, leading to an expected better ME effect.

The mechanical strength, dimensional stability and good heat and chemical resistance of anodic aluminum oxide (AAO) make it one of the most used nanomaterials for the fabrication of nanoscale devices in electronic and optoelectronic applications [9,10]. Nanowire arrays of different materials have been fabricated using AAO template [11–18]. Magnetic transition metal (Ni, Co, Fe) nanowires [11,14,15] prepared by electrochemical deposition into AAO template show convenient and easy to tailor magnetic response whereas their low fabrication costs have also attracted much technological interest.

PVDF is one of the most important polymeric materials for advanced applications due to its piezoelectric and ferroelectric properties. In addition, PVDF is easily processable and has good chemical resistance and high thermal stability [19,20]. Flexible PVDF films have been used in tactile sensors [21–24] and energy harvesters [25,26]. It can exist in four main crystalline phases (α, β, γ and δ). The β phase is however the one that exhibits the best piezoelectric and ferroelectric properties and

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a variety of methods like mechanical stretching [27], application of an electrical field [28] or incorporation of some additives [29,30] have been used to obtain this crystalline phase. A PVDF homopolymer nanotube array with ferroelectric β-phase was also fabricated in an anodic alumina membrane template [31].

In this work, arrays of nickel submicron wires surrounded by PVDF submicron tubes were grown into anodic aluminium oxide matrix by combined electrochemical and chemical routes. We have identified the interactions which transform PVDF film in a ferroelectric material and also the interactions between this polymeric film and Ni wires. The magnetic behavior of such heterogenous multiferroic structure was also investigated. In this context, we suggested that the ME coupling constant in this multiferroic system has to be measured only by observing the perturbation of the electric state of the polymer shell under a magnetic excitation of the submicron wire cores.

2. Experimental details

2.1. Material and methods

Commercial available alumina template (Whatman Anodisc filters) used for fabrication of magnetic core/shell wires is 60 µm in thick and contains cylindrical pores having 200 nm in diameter. Before using it as template, AAO membrane was immersed in 3M NaOH solution for 1 min, washed by filtration and dried at 80 °C. Polymeric tubules were obtained in the enlarged pores (e.g. outer diameters of about 300 nm are expected) by vacuum filtration of a PVDF (Sigma Aldrich, Mw ~ 534 000) solution prepared at a concentration of 10 wt % with the solvent of dimethylformamide (DMF)/acetone (1:1 in volume). The residual PVDF layer on top of the membrane was chemically etched with DMF and then the membrane was dried at 80 °C for 10 min. This membrane with PVDF tubules was covered by sputtering on one side with a thin gold film, which was thickened by electrochemical deposition of a copper layer. Electrodeposition of Ni submicron wires was conducted potentiostatically in a conventional three-electrode cell configuration at room temperature using a Watts-type bath [32]. The Ni wires were grown both in the membrane with PVDF tubules (sample code: Ni/PVDF-wires) as well as in membranes without PVDF tubules (sample code: Ni-wires), according to a same procedure. The composition of the bath was 0.76 M $NiSO_4 \cdot 6H_2O$, 0.17 M $NiCl_2 \cdot 6H_2O$, and 0.65 M H_3BO_3, and the potential used in the electrodeposition was a −1.0 V vs Ag/AgCl reference electrode. The electrochemical processes were performed using an Autolab PGSTAT 30 potentiostat digitally controlled by a PC computer (see Fig. 1).

For SEM and EDX measurements, the membrane, covered on one side with gold and copper layer was dissolved in 4M NaOH solution to free the PVDF tubules and Ni wires that had been deposited within the pores. For comparative XRD and FTIR studies of PVDF crystal structure, PVDF foils have also been fabricated by casting PVDF solution on the surface of a glass substrate. The obtained layer was dried at 80 °C and then detached from the substrate.

2.2. Sample characterization

The morphologies of the prepared structures were imaged using a field emission scanning electron microscope Quanta InspectF (operating voltage 30 kV) equipped for chemical composition measurements with an EDX device (resolution 129 eV at MnKα) from EDAX. XRD analyses were carried out with $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å) at 45 kV and 40 mA on a Bruker D8 Advance type X-ray diffractometer, with Bragg-Brentano diffraction geometry, equipped with a copper target X-ray tube and a LynxEye one-dimensional detector. A Bruker FTIR spectrophotometer model Vertex 80 was used to characterize PVDF foil and submicron tubes and electrodeposited Ni foil. Hysteresis loops have been obtained at different temperatures on a SQUID magnetometer (7T MPMS, from Quantum Design) working in the sensitive reciprocal space option (RSO). Disk-like shaped samples (with a total area of about 7 mm^2 in case of sample Ni/PVDF wires and of about 21 mm^2 in case of sample Ni wires) were considered with the disk axis (cylindrical wire axis) oriented both parallel and perpendicular to the applied field.

3. Results and discussion

PVDF submicron tubes prepared into the pores of alumina template were examined by scanning electron microscopy, after templates dissolution in 4M NaOH solution. Fig. 2a shows bundles of PVDF tubes with length greater than 20 µm and Fig. 2b and c shows PVDF separated tubes having about 300 nm in diameter and wall thickness less than 10 nm. The EDX spectrum from Fig. 2d was measured on a selected area of PVDF submicron tubes bundle (Fig. 2a). The signals of fluorine and carbon are seen on this spectrum, confirming the presence of PVDF material. On the other hand, no aluminium peak was observed on this spectrum. The peaks of gold and copper from EDX spectrum come from Cu-Au layer on which PVDF tubules have been collected.

Fig. 3a shows Ni/PVDF wires of about 50 µm length prepared into the pores of AAO. The XRD pattern of Ni wires embedded in AAO membrane is presented in Fig. 3b. There are three sharp diffraction peaks which can be indexed by the (111), (200) and (220) reflection planes of face-centered cubic Ni phase (JCPDS, No 04–0850). Core Ni submicron wires surrounded by shell-like thin PVDF tubes are better evidenced by a top view of the SEM image (Fig. 4a). The wire diameters are roughly around 300 nm (Fig. 4b).

The XRD patterns of PVDF tubes prepared for growing the core-shell Ni/PVDF structures and of the reference PVDF foil, respectively, are shown in Fig. 5. The most intense broad peak at 20.7° from XRD pattern of PVDF tubules prepared for the Ni/PVDF structures (Fig. 4a) is

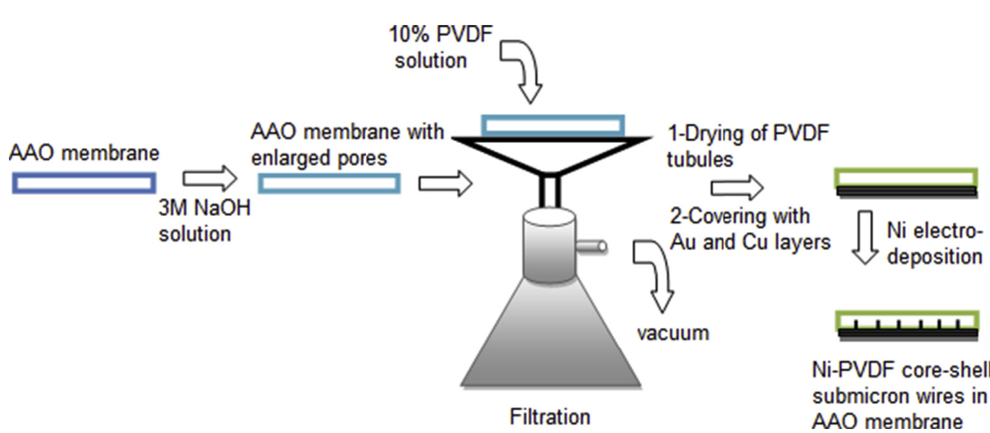

Fig. 1. Schematic illustration of core-shell Ni/PVDF wires preparation into AAO template.