Atomic layer deposition for the fabrication of magnonic metamaterials

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Abstract

Atomic layer deposition (ALD) allows to conformally coat three-dimensionally prepatterned templates relevant for the creation of artificial materials. We explore ALD to prepare thin films of nickel as required for magnetic metamaterials. Using tailored pulse sequences of nickelocene $NiCp_2$ and gaseous precursors in the ALD growth chamber ferromagnetic material is obtained after, both, oxidization and reduction steps performed *in situ*. For the first tim we observe ferromagnetic resonance on ALD-grown Ni. The findings offer novel perspectives for magnonic devices with a three-dimensional surface topology operating in the GHz frequency regime.

1. Introduction

Conformal coating with ferromagnetic thin films is expected to offer novel perspectives for three-dimensional (3D) devices in magnetoelectronics [1] and magnonics [2]. Starting from a periodically patterned nanotemplate it allows the combination of photonics and magnetism if, e.g. a photonic crystal is covered by a magnetic film. Grigoriev *et al.* [3] prepared a 3D opal-like structure of Ni by electrochemical deposition in a colloidal crystal film. Here the structural and magnetic properties already reflected the periodically arranged 3D nanotemplate. Based on chemically assisted deposition, in particular, atomic layer deposition (ALD) allows further improvements and the conformal coating in a layer-by-layer growth mode using tailored precursor chemicals. By ALD [4] Rill *et al.* coated a 3D prepatterned polymer template first with a thin layer of SiO_2 at low temperature. This provided mechanical stability as well as a chemical protection for the following chemical vapor deposition of a metal film such as Ag. The resulting 3D device exhibited a full photonic bandgap and metamaterial properties. In this paper we explore ALD of ferromagnets [5, 6, 7] to allow the preparation of periodically patterned magnetic metamaterials. Ferromagnets offer devices where a tailored ferromagnetic resonance (FMR) and spin waves modify the susceptibility χ in the microwave frequency regime. This goes beyond photonic devices where split-ring resonators are used to control the magnetic response at high frequencies [4]. To grow ferromagnetic layers successfully by ALD, specific requirements need to be fulfilled. E.g., the surface chemistry needs to be optimized by a seed layer. At the same time elevated temperatures are required to form a metallic ferromagnet [6, 7]. We report here the observation of magnetic hysteresis and, in particular, FMR of ALD-grown Ni on Al_2O_3 as the seed and protection layer. To our knowledge, FMR has not yet been reported for ALD-grown films.

2. Atomic layer deposition on prepatterned substrates for magnonic devices

We have obtained Ni films on different substrates, i.e., planar ones and prepatterned templates, by ALD. Therefore we used two complementary templates. On the one hand we addressed microcolums etched

ISBN 978-952-67611-0-7

from a Si substrate using photolithography and reactive ion etching. Using anisotropic etching the microcolumns exhibited a large aspect ratio w/h of about 30 where $w = 3$ μm ($h = 100$ μm) is the width (height). Microcolumns were separated from each other by several micrometers to allow detailed inspection by scanning electron microscopy (SEM) from different sides. On the other hand we used a template consisting of an array of holes etched into the Si membrane of a silicon-on-insulator (SOI) substrate. Here the etching mask of the holes was prepared by electron beam lithography. After reactive ion etching of the Si layer of the SOI membrane the underlying Si oxide was removed by a buffered HF etching solution. Note that a freestanding Si membrane with a periodic array of nanoholes forms a photonic crystal. Intentionally we used such a nanotemplate to demonstrate the combination of photonic with magnetic devices. In our device, the holes had a diameter of about 150 nm arranged on a square lattice with a periodicity of 1600 nm. SEM was possible from the top side.
To initiate the ALD growth of magnetic materials we first deposit a seed layer of Al_2O_3. We follow an

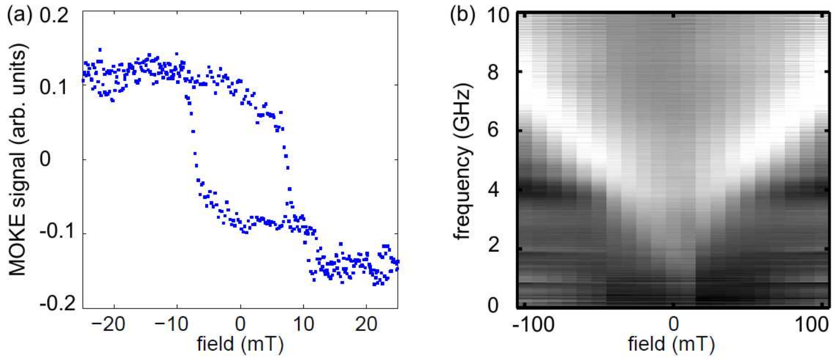

Fig. 1: (a) Magnetic hysteresis of a 20 nm thick Ni thin film prepared via the *ex situ* reduction process on a Si substrate. The field is applied in the film plane. Data are taken using the magneto-optical Kerr effect (MOKE). (b) FMR (bright color) of *in situ* processed 20 nm thick Ni as a function of increasing in-plane field. Straight vertical and horizontal lines in the gray-scale plot reflect data acquisition at discrete field positions and measurement artifacts, respectively.

established process consisting of trimethylaluminium (TMA) and H_2O which are pulsed into a nitrogen-purged reaction chamber in a sequential manner. The substrate temperature is 177 °C. Each precursor reacts with the surface of the sample, i.e., it chemisorbs. The second precursor chemisorbs and reacts with the already adsorbed precursor. The saturation of the surface in each pulse self-terminates the chemisorption process. Being a chemical deposition technique from the gas phase ALD allows one to deposit material with a homogeneous thickness also in porous substrates. This enables one to coat prepatterned templates conformally on the nanoscale. Using TMA a layer-by-layer growth is reached. For magnetic films we pulse a chemical precursor containing magnetic ions. We tested metalorganic precursor materials $NiCp_2$ and $FeCp_2$ for Ni and Fe, respectively. Here we will report on Ni. The process is complex in that, first, each deposited layer of $NiCp_2$ is oxidized by a pulse of O_3. At a substrate temperature of $T = 300$°C the growth rate of $NiCp_2/O_3$ amounts to 0.068 nm/cycle, i.e., less than a monolayer is formed per cycle. Using this recipe we deposit about 20 nm of nickel oxide on planar substrates such as Si, MgO and glass. Stimulated by Refs. [6, 7] we then perform *ex situ* reduction at 350 °C with H_2. Figure 1(a) shows the magnetic hysteresis of such a reduced Ni film on a Si substrate. It is found to be soft-magnetic with a small coercive field of $|\mu_0 H_c| \approx 8$ mT. SEM analysis (not depicted) shows nanopitches in the films. We attribute them to the volume reduction by about $1/3$ when reducing nickel oxide to nickel.
Improved magnetic properties are obtained by a special process which we have developed and outline in the following. The process is also based on the oxidation of $NiCp_2$ by ozone to form the nickel oxide. However, we perform a reduction step by H_2 after a small number of cycles, e.g., 3 cycles *in situ*. We

float the reaction chamber with H_2 staying at $T = 300°C$. After this process the film is found to be conductive. To enhance the conductivity, the completed film is annealed *in situ* even further at $T = 350°C$ in H_2. In Fig. 1(b) microwave absorption data are shown which are measured on a 20 nm thick Ni film. The bright curve reflects the ferromagnetic resonance (FMR) which is found to be field-dependent and hysteretic [8]. To our knowledge FMR has not yet been reported for ALD-grown ferromagnetic thin films. The observation substantiates low spin-wave damping of the *in situ* processed Ni film. Such films open the perspective of ALD-grown magnonic devices. In the following we show that our film deposition process allows to conformally cover the prepatterned substrates discussed above. SEM images are depicted in Fig. 2. In (a) Ni is prepared on the Si membrane incorporating the array of holes. An overgrown pillar is shown in Fig. 2(b). Both templates withstand the ALD and reduction processing steps making it possible to prepare 3D magnetic devices and magnonic metamaterials. The magnetic properties of such nanopatterned devices will be reported elsewhere [9].

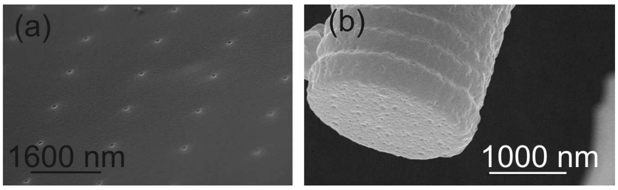

Fig. 2: Conformal coating of 20 nm thick Ni on (a) a Si membrane incorporating a photonic crystal and (b) a deep-etched Si micropillar.

3. Conclusions and Acknowledgement

Magnonic metamaterials are an emerging field of research. Using prepatterned templates and ALD ferromagnetic 3D artificial crystals can be fabricated which are expected to show metamaterial behavior by themselves and can be combined with photonic crystals. For further devices, alloys of in particular Fe and Ni are interesting as, e.g., $Ni_{80}Fe_{20}$, is known to exhibit very low magnetic damping leading to sharp spin-wave resonances. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under Grant No. 228673 (MAGNONICS). We thank J. Bachmann and K. Nielsch for continuous support and sharing their ALD expertise. We thank A. Fontcuberta i Morral and A. Dalmau from EPF Lausanne (EPFL) for Si micro- and nanopillars. D.G. thanks H. Brune and EPFL for the kind hospitality.

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