Evaporation-induced self-assembly synthesis of Ni-doped mesoporous SnO₂ thin films with tunable room temperature magnetic properties†

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Mesoporous Ni-doped SnO₂ thin films synthesized from variable [Ni(II)/Sn(IV)] molar ratios (0 : 100, 5 : 95, 10 : 90, 15 : 85 and 20 : 80), thicknesses in the range of 100–150 nm, and average pore sizes lower than 10 nm were obtained through a sol–gel based self-assembly process using Pluronic P-123 as a structure-directing agent. Grazing incidence X-ray diffraction experiments indicate that the films mostly possess a tetragonal SnO₂ structure with Ni²⁺ in substitutional positions, although energy-dispersive X-ray analyses also reveal the occurrence of small NiO clusters in the films produced from high [Ni(II)/Sn(IV)] molar ratios (corresponding to a Ni amount of 8.6 at%). X-ray photoelectron spectroscopy experiments indicate the lack of metallic Ni and the occurrence of oxygen vacancies in the mesoporous films. Interestingly, the magnetic properties of these mesoporous films significantly vary as a function of the doping percentage. The undoped SnO₂ films exhibit a diamagnetic behavior, whereas a clear paramagnetic signal dominates the magnetic response of the Ni-doped mesoporous films, probably due to the presence of NiO as a secondary phase. A small ferromagnetic-like contribution superimposed to the paramagnetic background is observed for samples with high Ni contents, possibly stemming from the combined effect from Ni incorporation and the occurrence of oxygen vacancies.

1. Introduction

Oxide semiconductors are among the most widely investigated materials in contemporary condensed matter physics and inorganic chemistry due to their wide range of technological applications in areas like energy conversion and storage, environmental remediation, light emission, magnetic and resistive memory devices or optoelectronic devices.1–7 In recent years, the introduction of transition metals (TMs) as doping atoms into the crystallographic structure of oxide semiconductors has emerged as a primary method to modify their electronic band configuration and, consequently, tailor some of their physical properties (e.g., electric conductivity, resistive switching behavior or magnetism), eventually leading to enhanced or even new functionalities.5–7

Many of the applications of semiconducting oxides (e.g., photocatalysts, gas sensors or electrochemical energy storage devices) take advantage from the use of materials with a large surface area-to-volume ratio. Hence, much progress is being made to develop new synthetic pathways to grow these materials in the form of nanoscale objects (e.g., nanowires or nanoparticles)8,9 or as highly nanoporous frameworks (powders or films) with precise control of the degree of porosity, pore size and crystallinity of the pore walls.10–12 Diverse strategies can be utilized to generate nanoporosity, by either removing materials from the fully-dense counterpart by, e.g., chemical etching or ion irradiation (the top-down approach), or assembling small building blocks in three-dimensions while leaving voids or empty spaces in-between (the bottom-up approach).

For the synthesis of mesoporous (with pore size ranging between 2 to 50 nm) oxide powders, both soft and hard templating methods can be utilized.13 Soft templating is mostly used for, but not restricted to, the preparation of mesoporous silicates, mixed oxides, metallophosphates, organic–inorganic hybrids or mesoporous carbon powders.14,15 It employs organic (soft) templates (surfactants and their supramolecular assemblies) as structure-directing agents during the chemical reaction to produce nanoporous scaffolds. In turn, hard templating or nano-casting uses porous rigid templates (typically mesoporous silica or carbon) as molds to form nanoporous oxide semiconductors of interest, which constitute the negative replica of the parent template.

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This technique has emerged as perhaps the most cost-effective method to produce ordered nanoporous oxide powders with a precise control of the pore size in diverse geometrical architectures.66

However, many applications require nanoporous films instead of powders. Tunable porosity can be achieved in metal oxide films by block-copolymer templating17,18 or colloidal crystal templating followed by solution dipping. In the first case, well-defined microdomains of block copolymers with different etching sensitivities allow them to be used as nanolithographic resists. The latter consists of first assembling a monolayer (or a multilayer) of polymeric spheres onto a substrate, then soaking the substrate into the precursor solution and finally performing calcinations to burn off the polymer and convert the precursor into the desired oxide.19 Compared to the block-copolymer templating approach, though, the resulting pores are macroporous – typically beyond 200 nm, which correspond to the diameter of commercially available spheres. Alternatively, the so-called evaporation-induced self-assembly (EISA) method can be used to prepare oxide semiconductors and insulators in the form of nanoporous films (e.g., In2O3, ZnO, TiO2, SiO2, etc.).20–22 EISA is based on the solution phase co-assembly of an inorganic precursor and the surfactant molecules to form hybrid intermediate entities. Films are first deposited by, for example, dip-coating onto polar substrates and then withdrawn from the precursor solution at a constant rate under controlled humidity and temperature. nanoporous films are obtained after cross-linking the inorganic framework and simultaneous removal of the organic template by calcination. Pore sizes well below 50 nm are achieved.

Compared to mesoporous metal oxide powders, the literature dealing with the synthesis of thin film analogues is less abundant. This is particularly true for SnO2, a paradigmatic transition metal oxide whose powder synthesis has been intensively pursued for chemoresistive gas sensing applications.23,24 Mesoporous SnO2 films have been prepared by EISA and related sol–gel chemistry procedures accompanied by post-synthetic hydrothermal transformations.25,26 The focus has been mainly on investigating the influence of the synthesis variables on the final characteristics of the thin films,27,28 or exploring their optical and electrochemical properties.29 A common feature of these works is the use of the Pluronic F-127 polymer as a structure-directing agent. Reports dealing with the synthesis of multimetallic or “doped” nanoporous SnO2 films are more scarce,30–32 in spite of the aforementioned interest of these types of materials. While the magnetic properties of fully-dense oxide semiconductors are a topic of extensive research (i.e., the so-called oxide diluted magnetic semiconductors), the magnetic behavior of mesoporous TM-doped oxide films is generally not studied, as these materials are mainly synthesized for chemical or physico-chemical purposes/applications. It is surprising that although many of the cutting-edge technological applications in magnetism and spintronics also rely on surface or interface magnetic phenomena, the use of nanoporous magnetic frameworks in these technologically-relevant fields has just emerged during the last few years.33–38

During the last few years, we have reported the synthesis and magnetic characterization of the TM-doped oxide semiconducting mesoporous powders prepared by nanocasting.35–37 Doping with TMs confers a magnetic character to these types of materials, which can then be categorized as mesoporous oxide-diluted magnetic semiconductors (MODMSs). These mesoporous frameworks may be appealing for spintronic applications, where the spin of the electrons (and not only the electric charge) can be used for the processing of information. Additionally, MODMSs could exhibit additional unique properties, as compared to their bulk counterparts, such as quantum-confinement effects, surface spin-glass or uncompensated spins, and combined optical and magnetic surface effects. Aside from their fundamental interest, in order to use these types of materials in real electronic devices, full assessment of the magnetic performance of MODMS films instead of powders is required.

In this work, we report on the growth of mesoporous Ni-doped SnO2 films using the EISA method, employing Pluronic P-123 as a structure-directing agent. Detailed structural characterization of the obtained materials, with an emphasis on the role of Ni as a doping TM, its distribution and speciation, is performed. We also examined the magnetic properties of the thin films and found out that the incorporation of Ni induces large variations in the magnetic susceptibility together with a small ferromagnetic-like contribution.

2. Experimental section

2.1 General remarks

Anhydrous tin(iv) chloride (SnCl4, 99.995%), nickel(ii) chloride (NiCl2, 98%), absolute ethanol (CH3CH2OH, 99.8%) and the Pluronic P-123 block copolymer [HO(CH2CH2O)20(CH2CH2(CH3)O)70(CH2CH2O)30H] were purchased from Sigma Aldrich and used as-received without further purification. Milli-Q water (≥18.2 MΩ cm) was obtained through an EMD Millipore Simplicity™ Water Purification System (Millipore S.A.S., 67120 Molsheim, France). Silicon chips (1 × 3 cm2) with {111} orientation were used as substrates for dip-coating.

2.2 Preparation of precursor solutions

P-123 (0.12 g) was dissolved in absolute ethanol (6 mL) by vigorous stirring (300 rpm) at room temperature. Next, SnCl4 (0.55 g) and deionized water (0.4 mL) were added to the previous solution. The resulting mixture led to a pure SnO2 film (Section 2.3), which was taken as a reference. For the Ni-doped SnO2 films, precursor solutions containing [Ni(n)/Sn(n)] molar ratios of 5 : 95, 10 : 90, 15 : 85 and 20 : 80 were targeted. To this end, different amounts of NiCl2 (0.0144 g, 0.0304 g, 0.0483 g, 0.0684 g, respectively) were added to the Sn(n) solution. Notice that the SnCl4 concentration was kept constant in each synthesis. The resulting solutions were sealed and aged for 12 h at room temperature before deposition.

2.3 Fabrication of thin films via an EISA process

Prior to use, each Si substrate was cleaned with acetone and Milli-Q water in an ultrasonic bath for 5 min each, and then rinsed with absolute ethanol. The mesoporous films were prepared in an automatic dip coater (Coater 5 AC, ID LAB) at a withdrawal speed of 5 mm s⁻¹ under a relative humidity of around 20%. After deposition,
the resulting coatings were dried under an ambient atmosphere for 30 min and then put into the furnace to be calcined under air at 100 °C for 12 h (heating ramp 1 °C min⁻¹). Subsequently, the temperature was increased to 200 °C for 2 h (heating ramp 3 °C min⁻¹) to consolidate the microstructure. Finally, the furnace was heated to 600 °C for 1 h (heating ramp 3 °C min⁻¹) to eliminate all the remaining organic residues.

2.4 Characterization

The morphology and microstructure of the films were characterized using high resolution scanning and scanning transmission electron microscopes (HR-SEM and HR-STEM, respectively). HR-SEM observations were carried out on a Zeiss Merlin microscope operated at 0.8 keV. Grazing incidence X-ray diffraction (XRD) patterns were recorded on a PANalytical X’pert PRO MRD (Materials Research Diffractometer) using Cu Kα radiation (λ = 0.154 nm) at an incidence angle of 1.18°. The patterns were acquired in the 2θ angular range varying from 20° to 80° with a step time of 0.8 s and a step size of 0.03°. The values of crystallite sizes, microstrains and lattice parameters as a function of Ni doping were extracted from Rietveld refinement of the XRD full-patterns by utilizing the “Materials Analysis using Diffraction” (MAUD) software.39 HR-STEM analyses were performed on a Tecnai F20 microscope equipped with energy dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED). For STEM-EDX analyses, ultra-thin cross-sections were prepared and placed onto holey carbon Cu TEM grids. The cross-section specimens were obtained by mechanically slicing the mesoporous films, followed by mechanical polishing/thinning and subsequent ion milling. X-ray photoelectron spectroscopy (XPS) analyses (PHI 5500 Multitechnique System) were carried out using a monochromatic X-ray source (Kα Al line of 1486.6 eV energy and 350 W power) under ultra-high vacuum (UHV), placed perpendicular to the analyzer axis and calibrated using the 3d₅/₂ line of Ag with a full width at half maximum (FWHM) of 0.8 eV. During the measurements, the chamber pressure was kept between 5 × 10⁻⁹ and 2 × 10⁻⁸ Torr. Ar⁺ ion etching (1 min) with an energy of 3 keV and ion current density of a few microamperes was applied at a raster circle of 0.8 mm diameter. Peaks were charged and corrected to adventitious C 1s set to 284.50 eV. Experimental core-level spectra were fitted using Gaussian curves. A Shirley background subtraction was included in the fitting procedure. Magnetic hysteresis loops were acquired using a vibrating sample magnetometer (VSM) from Micro-Sense (LOT-Quantum Design) at room temperature. To minimize the spurious magnetic response from the substrate, all presented loops correspond to the measurements after subtracting the signal of the bare substrate.

3. Results and discussion

3.1 Morphological and structural characterization

The surface morphology of the Ni-doped SnO₂ films was investigated by SEM. Fig. 1 indicates that the films are not
fully-dense but, instead, they exhibit a nanoporous morphology. Tiny pores are homogeneously distributed on the whole surface of the samples, irrespective of the [Ni(II)]/[Sn(IV)] molar ratio used in the synthesis. When compared with undoped SnO$_2$ films (Fig. S1, ESI†), the incorporation of Ni does not seemingly cause any relevant morphological change. Namely, both undoped and Ni-doped films exhibit nanosized worm-like channels throughout the surface and, importantly, they are very flat and crack-free. Low-magnification cross-section SEM images (Fig. S2, ESI†) show that pores span the whole film thickness (which is in the range of 100–150 nm, as indicated in the figure). Table 1 lists the Ni content in the films as determined by XPS analyses. As expected, the amount of Ni increases with the [Ni(II)]/[Sn(IV)] ratio, from 0.0 to 8.6 at%.

Grazing incidence X-ray diffraction (XRD) patterns reveal that the pore walls are nanocrystalline (Fig. 2). The main peak to 8.6 at%.

<table>
<thead>
<tr>
<th>[Ni(II)]/[Sn(IV)]</th>
<th>Actual Ni content (from XPS) (at%)</th>
<th>Crystallite size of SnO$_2$ phase (nm) (±0.8)</th>
<th>Microstrains of SnO$_2$ phase (±3 × 10$^{-4}$)</th>
<th>a (Å) of SnO$_2$ phase (±2 × 10$^{-3}$)</th>
<th>c (Å) of SnO$_2$ phase (±2 × 10$^{-3}$)</th>
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<tr>
<td>0:100</td>
<td>0.0</td>
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<td>1.1 × 10$^{-4}$</td>
<td>4.726</td>
<td>3.182</td>
</tr>
<tr>
<td>5:95</td>
<td>1.9</td>
<td>6.2</td>
<td>2.6 × 10$^{-3}$</td>
<td>4.729</td>
<td>3.187</td>
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<tr>
<td>10:90</td>
<td>4.8</td>
<td>6.4</td>
<td>5.1 × 10$^{-3}$</td>
<td>4.731</td>
<td>3.184</td>
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<tr>
<td>15:85</td>
<td>5.1</td>
<td>7.4</td>
<td>5.3 × 10$^{-3}$</td>
<td>4.721</td>
<td>3.178</td>
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<td>4.736</td>
<td>3.183</td>
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</table>

Fig. 2 Grazing incidence XRD patterns of the mesoporous undoped and Ni-doped SnO$_2$ films synthesized from varying [Ni(II)]/[Sn(IV)] molar ratios. Additional diffraction peaks indicated by arrows in Fig. 2 match the positions of SnO (JCPDS card No. 72-1012) and Sn$_3$O$_4$ (JCPDS card No. 16-0737). It has been reported that the formation of SnO, SnO$_2$ and Sn$_3$O$_4$ is both oxygen- and temperature-dependent during heat treatment. In our work, however, the temperature was held constant during heat-treatment of all films (600 °C) and therefore, the occurrence of SnO and Sn$_3$O$_4$ cannot be attributed to differences in temperature. The same holds for the atmosphere (i.e., all films were heat-treated in air). Close inspection of the diffractograms reveals that the SnO phase is present in all Ni-doped samples (see the shoulder/peak ca. 51°), although the relative proportion is different, except for the film produced from a Ni(II):Sn(IV) 15:85 molar ratio. For this film, the Sn$_3$O$_4$ phase is clearly detected. Note that the amount of Ni$^{2+}$ dissolved in the tin oxide lattice is the maximum for this film. Hence, it seems that the occurrence of SnO and Sn$_3$O$_4$ phases is linked to the introduction of Ni$^{2+}$ in the material, although the relationship is somewhat complex.

No peaks related to either metallic Ni or NiO are present. This suggests that Ni has entered the SnO$_2$ lattice. However, the SnO$_2$ peaks in the diffractograms of the Ni-containing films are not shifted compared to the undoped sample. This can be explained considering the nearly equal ionic radius of Ni$^{2+}$ (0.69 Å) and Sn$^{4+}$ (0.69 Å). The crystallite size of the SnO$_2$ phase, together with the microstrains and cell parameters, was calculated using the Rietveld method (Table 1). When compared to the undoped sample, the crystallite size decreases in the doped films, although not in a monotonous manner. In turn, the microstrains increase by one order of magnitude, indicating that the incorporation of Ni in the SnO$_2$ framework induces some strain. Although the lattice parameters “a” and “c” do not show pronounced variations upon Ni doping, “a” increases while “c” decreases with the introduction of Ni (except for the sample synthesized from 15:85 [Ni(II)]/[Sn(IV)]).

In order to further investigate the overall crystallographic structure and the eventual occurrence of NiO in the films with the highest Ni content, TEM characterization was carried out. The cross-section images and corresponding SAED patterns of the films containing 5.1 and 8.6 at% Ni are shown in Fig. 3(a) and (b), respectively. Fig. 3 further confirms that the whole films are entirely porous. However, compared with Fig. 3(a), the TEM image of Fig. 3(b) shows some darker areas. The SAED patterns from the marked regions (white circles) are shown in the right panels of Fig. 3(a) and (b). The two SAED patterns are similar, although a few spots corresponding to the NiO phase are indeed detected for the sample synthesized from
[Ni(II)/Sn(IV)] = 20:80 (with 8.6 at% Ni). It is worth mentioning that whilst pure mesoporous SnO\textsubscript{2} thin films were already synthesized by EISA in the past, to the best of our knowledge there is only one work reporting on the synthesis of mesoporous NiO thin films using this approach\textsuperscript{42}. In that work, poly(ethylene-co-butylene)-block-poly(ethylene oxide) (KLE) was employed as a structure-directing agent. Here, both materials (SnO\textsubscript{2} and NiO) coexist in the same mesostructured skeleton.

Detailed HR-TEM images of the mesoporous films with 5.1 at% Ni and 8.6 at% Ni are shown in Fig. 4. The pore walls consist of tiny crystallites, whose interplanar distances match the SnO\textsubscript{2} tetragonal structure, in agreement with the XRD and SAED results. Sub-10 nm pores are also clearly visible (as indicated in the figure) and the width of the pore walls is in the 5–10 nm range. The size of the crystallites is actually in agreement with the results obtained from the Rietveld refinement of the XRD patterns (Table 1). The occurrence of a few NiO clusters embedded in the Ni-doped SnO\textsubscript{2} nanoporous film is confirmed for the sample with 8.6 at% Ni (see Fig. 4(b) and (c)).

To precisely locate the NiO phase within the SnO\textsubscript{2} network, the films with 5.1 and 8.6 at% Ni (NiO as a secondary phase was clearly detected by SAED in the latter) were selected for EDX mapping characterization. Fig. 5 shows the STEM and corresponding EDX mapping of a selected region for these samples. Remarkably, for the mesoporous films with the highest Ni amount, several bright areas (notice that the contrast is the opposite in TEM images) were visible in the film cross-section. EDX mappings of a zoomed detail of the cross-sections were conducted to determine the distribution of Sn, Ni and O elements (top panel of Fig. 4(a) and (b)). In both cases, O and Sn elements are distributed rather homogeneously across the whole area. Ni is also evenly distributed in the film with 5.1 at% Ni but not in the film with 8.6 at% Ni. For this sample, Ni preferably accumulates in the brighter area. This result is in agreement with previous TEM and SAED analyses and suggests that, although no peaks from NiO can be detected by XRD (because their amounts are below the detection limit of the XRD technique), a few aggregates enriched in Ni of around 20 nm are indeed formed for sufficiently large Ni contents. Note that these aggregates do not apparently show a mesoporous structure (see Fig. 3b and 5b). The aggregates are denser, which is very clear from the cross-section STEM images. Hence, the formation of these aggregates partially disrupts the mesostructure of SnO\textsubscript{2}. This is the reason why their size is larger than the pore wall thickness of SnO\textsubscript{2}.

![Fig. 3 TEM images (left) and SAED patterns (right) of the cross-sections of the mesoporous Ni-doped SnO\textsubscript{2} thin films with (a) 5.1 at% Ni, and (b) 8.6 at% Ni. The indicated planes in (a) correspond to the SnO\textsubscript{2} phase whereas only those corresponding to the NiO phase have been indicated in (b) for the sake of clarity.](image-url)
3.2 XPS characterization

To shed light on the valence state of Ni and the occurrence of oxygen vacancies in the Ni-doped mesoporous films, XPS characterization was carried out. Fig. 6(a) shows the survey spectra of all samples including undoped SnO$_2$, taken as a reference sample. The corresponding core-level Sn 3d is displayed in Fig. 6(b). The peaks belonging to Sn 3d$_{5/2}$ and 3d$_{3/2}$ located at $\sim$ 486.1 eV and $\sim$ 495.5 eV are assigned to SnO$_2$. A slight shift toward higher binding energies is noted for the films with the highest Ni contents (5.1 and 8.6 at%).

As shown in Fig. 6(c) and (d), the O 1s spectrum of the samples containing 5.1 and 8.6 at% Ni can be deconvoluted into three main bands centered at 529.58 eV, 530.25 eV and 531.66 eV. The peaks located at 529.58 eV and 530.25 eV are attributed to O$^{2-}$ anions in the SnO$_2$ (and NiO) lattice, whereas the peak at 531.66 eV is associated with O ions in oxygen deficient regions or oxygen vacancies in the lattice. This peak might also be attributed to hydroxyl groups. Actually, some authors state that the peak at 531.66 eV could be well assigned to adsorbed oxygen (OH$^-$ groups) on the surface and oxygen vacancies. However, when compared with undoped SnO$_2$ films, there is a clear shift of the O 1s peak toward higher binding energy, suggesting that Ni incorporation into the SnO$_2$ structure gradually generates oxygen vacancies up to 5.1 at% Ni (see Fig. S3(a) in the ESI†).

The corresponding Ni 2p core-level XPS spectra of the samples containing 5.1 and 8.6 at% Ni are shown in Fig. 6(e) and (f), respectively (see the spectra of all samples in Fig. S3(b) of the ESI†). In this case, the profiles show some remarkable differences. In particular, the peak contribution with a binding energy of around 855.5 eV (Ni 2p$_{3/2}$) assigned to Ni$^{2+}$ in NiO notoriously increases in Fig. 6(f) compared to Fig. 6(e) (see also Table 2). This is in agreement with both the observed increase in the total amount of Ni incorporated into the film and the formation of relatively large NiO particles. Besides, the Ni 2p$_{3/2}$ peak located at $\sim$ 853.0 eV could be attributed to monovalent Ni species. Therefore, Ni possesses a mixed valence state of $1+/2+$.  

3.3 Magnetic properties of the Ni-doped SnO$_2$ films

The magnetic properties of the samples with varying Ni concentration were first studied by acquiring hysteresis loops at room temperature and subtracting the signal from the bare substrates. As shown in Fig. 7, the undoped SnO$_2$ films exhibit a diamagnetic behavior (negative magnetization vs. field slope), in agreement with previous studies on these types of oxide semiconductors. Conversely, a clear (positive) paramagnetic slope dominates the magnetic behavior of the samples with the highest Ni amounts (5.1 and 8.6 at% Ni). This positive slope can be attributed to the presence of NiO clusters, as evidenced by EDX and SAED analyses. Note that although bulk NiO is antiferromagnetic with a Néel temperature, $T_N$, of around 520 K, typically $T_N$ is considerably reduced in nanoparticles compared to the bulk. Superimposed to this positive linear background, a small ferromagnetic signal is observed. The origin of ferromagnetism in oxide diluted semiconductors is, in fact, a topic of extensive research by many research groups. Contradictory results are easily found in the literature, depending on the material under investigation (bulk, thin films, and nanoparticles) and the synthetic procedures, even when the same composition is maintained. In our case, the small ferromagnetic response cannot be attributed to the presence of metallic Ni clusters, since no evidence of their existence was obtained using TEM, XRD or XPS. Conversely, the small ferromagnetic response could be ascribed to the combined effect from the doping TM and the presence of oxygen...
Fig. 5  Cross-section STEM images (bottom) and elemental EDX mappings (top) of the samples with 5.1 and 8.6 at% Ni. The distribution of Sn, Ni and O elements corresponds to the encircled area shown in the STEM image detail of the upper right panel.
vacancies, in agreement with previous works on undoped SnO$_2$ films, TM-doped dense oxide semiconductor films and TM-doped InO$_2$ and SnO$_2$ mesoporous powders. Actually, a mechanism based on ferromagnetic exchange interactions mediated by shallow donor electrons trapped in oxygen vacancies was proposed to account for room-temperature ferromagnetism in dilute ferromagnetic oxides and nitrides. Ab initio energy-band calculations showed later that the donor impurities mainly consisted of hybridized 3d–4s TM-cation electronic states. This model was later confirmed by a number of works, both theoretical and experimental ones. Nonetheless, because of the size and surface effects, a full understanding of the magnetic properties of the investigated material is not easy. Uncompensated spins from antiferromagnetic NiO aggregates could contribute to some extent to the observed hysteresis behavior although, as aforementioned, NiO is probably paramagnetic at room temperature. The films with intermediate Ni contents show a

<table>
<thead>
<tr>
<th>Actual Ni content (from XPS) [at%]</th>
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<th>Binding energy (eV) 2p$_{3/2}$</th>
<th>Binding energy (eV) 2p$_{1/2}$</th>
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<td>5.1</td>
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<td>872.4</td>
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<td>8.6</td>
<td>Ni$^{2+}$</td>
<td>855.5</td>
<td>872.9</td>
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Fig. 6  (a) General XPS survey spectra of undoped and Ni-doped SnO$_2$ mesoporous films, (b) high resolution XPS spectra of Sn 3d. The corresponding deconvolution of O 1s [(c) and (d)] and Ni 2p [(e) and (f)] is shown for the films with 5.1 and 8.6 at% Ni, respectively. "Sat." denotes satellite peaks.
virtually zero and small positive magnetization versus applied field slope, respectively. This is due to the interplay between the diamagnetic response from SnO$_2$ and the paramagnetic background stemming from the secondary NiO phase. Finally, hysteresis loops corresponding to Ni-doped SnO$_2$ mesoporous films (with 5.1 and 8.6 at% Ni) were also measured at 100 K, 200 K and 296 K. The results are shown in Fig. 8. There is a clear increase in the high-field slope in both samples as temperature is decreased. It is well known that in paramagnetic materials, the susceptibility decreases with temperature, following the Curie–Weiss law. That can explain the change in the slope of the hysteresis loops. It could also be that the NiO clusters become truly antiferromagnetic at low temperatures and that could also give rise to an increase of the high-field magnetization, compared to the high-temperature paramagnetic state. Remarkably, the coercivity of the ferromagnetic-like contribution does not show a pronounced temperature dependence. It remains around 40–60 Oe at the three measured temperatures. Hence, the magnetic response contains a soft-ferromagnetic contribution at all temperatures.

4. Conclusions

Undoped and Ni-doped SnO$_2$ mesoporous films, containing different amounts of Ni, were successfully synthesized by evaporation induced self-assembly using P-123 as a structure directing agent. Truly 3D nanoporous structures, with a pore size in the range 5–10 nm, were observed in all mesoporous films. Deep structural characterization reveals that the mesoporous films mainly consist of the rutile-type tetragonal structure of SnO$_2$, although NiO clusters are formed in samples with large Ni contents (e.g., 8.6 at% Ni). The mesoporous films also contain large amounts of oxygen vacancies, as revealed by XPS analyses. From a magnetic viewpoint, the incorporation of Ni drastically changes the magnetic response, from a purely diamagnetic one (undoped mesoporous SnO$_2$) to a mainly paramagnetic one with a small ferromagnetic contribution (in the samples containing Ni). This work opens up new prospects for the use of mesoporous oxide semiconductor thin films with magnetic characteristics in new types of memory and spintronics devices, which could eventually be controlled by various means (e.g., electrolyte gating).

Acknowledgements

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