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Full Length Article

# Magnetic and plasmonic properties in noncompensated Fe-Sn codoped $In_2O_3$ nanodot arrays

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ABSTRACT

The noncompensated Fe-Sn codoped $In_2O_3$ nanodot arrays with the Sn concentration of 0.02, 0.05, 0.1, 0.15 and 0.2 were deposited on $Al_2O_3$ (0 0 0 1) substrates using laser molecular beam epitaxy with the aid of anodic aluminium oxide templates. The structural and compositional results reveal that the nanodot arrays show the single phase cubic $In_2O_3$ structure and Sn and Fe dopant ions substitute $In^{3+}$ sites of the $In_2O_3$ lattice with a tetravalence ($Sn^{4+}$) and a mixed-valence ($Fe^{2+}/Fe^{3+}$), respectively. All the nanodot arrays exhibit the obvious room temperature ferromagnetic behavior and the localized surface plasmon resonance (LSPR) band. Moreover, the ferromagnetism and the LSPR absorption peak can be tuned by the Sn concentration or sizes of nanodot arrays.



## 1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted considerable interest due to their potential applications in spintronic devices [1–4]. Since Dietl et al. [5] predicted that room temperature ferromagnetism (RTFM) might be realized in Mn doped ZnO, many oxide-based DMSs, such as $TiO_2$, $SnO_2$, $In_2O_3$ doped with 3d transition metal ions, have been reported to exhibit ferromagnetic behavior with Curie temperature near or above 300 K [6–8]. Particularly, Fe-doped $In_2O_3$ DMS is regarded as a promising material for spintronic device application because a homogeneous material can be realized due to the high solubility of Fe ions into $In_2O_3$ lattice [9–11]. As many researchers reported that the substitution of Fe dopant ions exhibited the mixed valences of $Fe^{2+}$ and $Fe^{3+}$ in the Fe doped $In_2O_3$ [12,13], $Fe^{2+}$ is a kind of p-type dopant. It is well known, $Sn^{4+}$ is a kind of n-type dopant in $In_2O_3$, and Sn-doped $In_2O_3$ film is widely used in optoelectronic devices due to its high optical transparency in the visible light and high electric conductivity [14,15]. Moreover, Sn-doped $In_2O_3$ nanocrystals or nanoparticles can exhibit the localized surface plasmon resonance (LSPR) band in near to mid infrared region because of the free electrons provided by Sn doping [16,17], which have potential applications in surface-enhanced infrared absorption [18], sensing [19], and optoelectronic devices [20].

In the current study, we choose Fe-Sn codoped $In_2O_3$ (IFSO) as noncompensated p-n codoping to achieve homogeneous DMS [11,13]. The advantage of this method is that the electrostatic attraction between the p- and n-type dopants can enhance both the thermodynamic and kinetic solubility of doped $In_2O_3$; on the other hand, the noncompensated nature of the p-n pairs leads to the generation of net carriers, which can tune the magnetic, transport and optical properties [21,22]. This method was well demonstrated in our previous work of ZnO DMS films [23,24].

As research in nanoscale microelectronics and spintronics is flourishing, the ability to synthesize nanostructures with a high degree of uniformity and regularity is important in achieving control of their properties. The method of porous templates, such as porous anodic aluminium oxide (AAO) templates [25,26], is a promising technique to fabricate well-ordered nanodot arrays because of its low equipment cost, the rapid manufacture of large size arrays, and the possibility of preparing nanodot arrays made from a large class of materials.

In this work, the well-ordered Fe-Sn codoped $In_2O_3$ nanodot arrays were fabricated using the laser molecular beam epitaxy (LMBE) with the aid of AAO templates. It is observed that IFSO nanodot arrays exhibit the obvious RTFM and LSPR properties, which can be modified by change of Sn concentration or the size of nanodot arrays. This combination of magnetism and plasmonics is possible to develop the multifunctional magneto-optoelectronic devices for $In_2O_3$ systems.

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## 2. Experimental details

### 2.1. The synthesis of IFSO nanodot arrays

The Fe-Sn codoped $In_2O_3$ nanodot arrays were deposited on $Al_2O_3$ (0 0 0 1) substrates using the LMBE with the aid of AAO templates at a substrate temperature of 800 °C. Firstly, the nominal composition $(In_{0.95-x}Sn_xFe_{0.05})_2O_3$ (x = 0.02, 0.05, 0.1, 0.15, 0.2) ceramic targets were prepared from high-purity $In_2O_3$, $Fe_2O_3$ and $SnO_2$ powders. The powders were mixed, ground, pressed into a pellet, and then sintered at 1200 °C for 10 h in the air. In order to obtain nanodot arrays, we prepared well-ordered AAO templates by the two-step anodization process. The first anodization process was performed by applying the DC voltage of 40 V in 3.6 wt% $H_2C_2O_4$ at 0 °C for 2 h. Then, the oxidized alumina layer was removed in mixture solution of $H_3PO_4$ and $CrO_3$. The second anodization step was conducted for 3 min under the same conditions as the first anodization. After the second anodization, the top surface of the AAO layer was coated with PMMA and the remaining unoxidized aluminum substance was removed in saturated $CuCl_2$ solution. Next, the remaining alumina layer was immersed in 5 wt% $H_3PO_4$ for 45–65 min to remove the bottom barrier layer and widen the pore diameter. The AAO templates with different pore diameters were obtained by varying the dipping time in 5 wt% $H_3PO_4$. Next, the AAO template was transferred on the $Al_2O_3$ (0 0 0 1) substrate in water. Finally, the targets were ablated using a KrF excimer laser with energy of 360 mJ and frequency of 10 Hz at a base pressure (about $4.0 \times 10^{-4}$ Pa). After the deposition, the template was dissolved in 2 wt% NaOH for a few minutes and rinsed several times with distilled water.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patters of the Fe-Sn codoped $In_2O_3$ nanodot arrays were obtained by employing the Ultima IV X-ray diffractometer with 2 theta ranging from 20° to 80°. The surface morphology and cross-sectional views were characterized by using a JSM-7500F scanning electron microscope (SEM). The UV–Vis–NIR absorption spectra were recorded using both U-3310 UV–Vis spectrophotometer and SolidSpec-3700DUV UV–Vis–NIR spectrophotometer. The magnetic measurement was performed using a superconducting quantum interference device (Quantum Design MPMS-XL-5 Magnetometer). The valence state of IFSO nanodot arrays was confirmed by X-ray photoelectric spectroscopy (XPS), which was carried out on an Escalab-250 photoelectric spectrometer.

## 3. Results and discussion

### 3.1. Morphology, structure and composition

The morphology of ultrathin AAO templates with different pore diameters are shown in Fig. 1(a)-(c), and the morphology of 10% Sn and 5% Fe codoped $In_2O_3$ nanodot arrays with different diameters are shown in Fig. 1(d)-(f). The size distributions for the pores and corresponding nanodots were obtained using the software of Nano Measurer (Fig. S1 of the supplementary material). It is found that the AAO templates and nanodot arrays are all well-ordered, and the diameter of IFSO nanodots is similar to the pore diameter of AAO templates. So it is feasible to prepare size-controlled IFSO nanodot arrays by controlling the pore diameter of AAO templates. Fig. 1(g)-(i) show the cross-sectional views of nanodot arrays with different diameters. It can be seen that the shape of these nanodots varies from hemiellipsoid, hemisphere to nanodisk with the increment of diameter. The observed shape changes of these nanodots are ascribed to the closure effect in the deposition process and the shadowing effect of the AAO template [27].

The XRD patterns of $(In_{0.95-x}Sn_xFe_{0.05})_2O_3$ (x = 0.02, 0.05, 0.1, 0.15, 0.2) nanodot arrays were shown in Fig. 2. The diameter and height of nanodot arrays are 70 and 40 nm, respectively. The spectra are plotted on a log scale to better inspect any low-level secondary-phase peaks. Clearly, all doped nanodot arrays are observed to be polycrystalline and the XRD patterns matches well with the cubic bixbyite of $In_2O_3$ structure. No traces of metallic Fe and Sn and their oxides are observed within the XRD detection limit. It is also found that the orientation of IFSO nanodot arrays shows a dependence on the Sn doping concentration. The intensity of (2 2 2) peak decreases and (4 0 0) peak increases with an increase of Sn concentration. Generally, $In_2O_3$ films have a preferred orientation along the (1 1 1) plane due to its lowest surface energy [28]. Golovanov et al. calculated that the $In_2O_3$ (4 0 0) surface with full oxygen coverage was stable [29]. In the Sn doped $In_2O_3$, in order to compensate the additional positive charge which is introduced in the surface region by replacing $In^{3+}$ atoms with $Sn^{4+}$ dopants, the surface oxygen content increases for higher Sn doping, resulting in the stabilization of the (4 0 0) surface [30]. Therefore, the IFSO nanodot arrays preferentially oriented to (4 0 0) direction were observed for higher Sn doping. The XRD patterns of 10% Sn and 5% Fe codoped $In_2O_3$ nanodot arrays with different diameters also show the single phase cubic $In_2O_3$ structure with a preferred orientation along (4 0 0) plane (Fig. S2 of the supplementary material).

To determine the composition and valence states, a detailed XPS analysis for 10% Sn and 5% Fe codoped $In_2O_3$ nanodot arrays with diameter of 70 nm was performed. The survey scans show that no additional peaks corresponding to secondary phases are detected (Fig. S3 of the supplementary material), which is in accordance with the XRD measurements. Fig. 3(a) shows the In 3d XPS spectrum, where the binding energies for In $3d^{5/2}$ and $3d^{3/2}$ are located at 444.6 eV and 452.2 eV, respectively, corresponding to the binding energy of $In^{3+}$ in $In_2O_3$. The Sn 3d XPS spectrum is displayed in Fig. 3(b). The observed energies for Sn $3d^{5/2}$ and $3d^{3/2}$ are located at 486.5 eV and 494.9 eV, respectively, which confirms that Sn atoms are +4 valence state [31]. As shown in Fig. 3(c), the O 1s spectrum is asymmetric, indicating the presence of oxygen vacancies [32,33]. Fig. 3(d) displays that the peak of Fe $2p^{3/2}$ locates at 709.8 eV, which excludes the formation of Fe metal clusters since the binding energy of Fe $2p^{3/2}$ for Fe metal is 706.7 eV [34]. Furthermore, the peak of Fe $2p^{3/2}$ is between 709 eV ($Fe^{2+}$ $2p^{3/2}$) and 711 eV ($Fe^{3+}$ $2p^{3/2}$), indicating the Fe element with the mixed valences of +2 and +3 [12,13]. It is also noted that the Fe $2p^{3/2}$ peak has the satellite structure, which illustrates that the mixed valence state of Fe ions in IFSO nanodot arrays does not originate from $Fe_3O_4$ [12]. The existence of $Fe^{2+}$ in the IFSO nanodot arrays is attributed to the reduction of some $Fe^{3+}$ in the presence of high carrier density introduced by Sn dopant and amounts of oxygen vacancies.

### 3.2. Magnetic properties

Hysteresis loops of Fe-Sn codoped $In_2O_3$ nanodot arrays were measured by SQUID at 300 K. The magnetic field was applied in the plane of the substrate and the diamagnetic signals have been subtracted. The magnetization (M) vs magnetic field (H) plots for IFSO nanodot arrays with different Sn doping were shown in Fig. 4(a), and the magnified M vs H plots of these samples were shown in the inset. It is observed that all the samples display obvious room temperature ferromagnetism with saturation magnetization and the coercive force around 4.0 $\mu_B$/Fe and 100 Oe, respectively. The M-H curves of the 10% Sn and 5% Fe codoped $In_2O_3$ nanodot arrays with different diameters also exhibit a clear