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Diversity of electronic transitions and photoluminescence properties in nanocrystalline Mn/Fe-doped tin dioxide semiconductor films: An effect from oxygen pressure

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Transition metal (TM: Mn or Fe) doped tin dioxide (SnO2) films with the compositions of 5% (Sn0.95TM0.05O2) have been deposited on sapphire substrates by pulsed laser deposition under oxygen pressure (Po) varied from 10^-4 to 1 Pa. The x-ray diffraction, scanning electron microscopy, and infrared spectroscopy analysis indicate that different TM dopants can affect the variations of crystallization and lattice distortion. Moreover, x-ray photoelectron spectroscopy reveals that the effective Po during the growth does not change the valence state of Sn4+ in the Sn0.95TM0.05O2 films. The spectral behaviors of the films have been investigated in the photon energy range of 0.47-6.5 eV (2650-190 nm). From transmittance spectra, the shoulder structures become more prominent for the Sn0.95Fe0.05O2 film than those for the Sn0.95Mn0.05O2 film due to the Fe repelling effect of a stronger p-d hybridization. The refractive index values for the Sn0.95Mn0.05O2 film are found to be larger than those for the Sn0.95Fe0.05O2 film at the photon energy of 0.47 eV. The main peaks at about 1.9 and 2.2 eV in photoluminescence (PL) emission spectra for both Sn0.95Mn0.05O2 and Sn0.95Fe0.05O2 films can be observed, and it could be explained by the fact that the electrons in the conduction band of SnO2 relax to defect states and then radiatively recombine with the holes. From direct comparison of PL and transmittance results for the films, the electronic transition energies, the emission peaks’ intensities and positions are shown to present the Po dependent behavior. The distinct trends indicate that the incorporation of Mn and Fe elements can provide a significant difference in the crystalline and electronic band structure. It can be concluded that the oxygen pressure and dopant contributions are responsible for the adjustment of electronic band structures and result in different optical response behaviors for the Sn0.95TM0.05O2 films. © 2011 American Institute of Physics. [doi:10.1063/1.3669374]

I. INTRODUCTION

Tin dioxide (SnO2) is one of the most used key functional materials, which has two structural characteristics: cations with mixed valence states and anions with deficiencies. By varying either or both of these characteristics, the electrical, optical, and magnetic properties can be modified, giving the possibility of fabricating optoelectronic devices, transparent conducting electrodes, gas sensors for detecting leakages, and catalyst supports.1,2 In particular, SnO2 doped with transition metal (TM) ion, such as Fe, Mn, Ni, Co, etc., has been extensively studied because of its excellent optical transparency, high refractive index, tunable carrier concentration, and dilute magnetic semiconductor.3,4 Theoretical calculations predict that ferromagnetism is the ground state and the Curie temperature is expected to have a higher value for Fe doped SnO2. However, paramagnetism is more stable than ferromagnetism in Mn doped SnO2. Moreover, TM-oxygen vacancy-TM groups can be formed in Fe doped SnO2, but the phenomenon does not appear in the cases of Mn doping.5 Considering the different effects from the doping TM elements, it is interesting to investigate the electronic band structures of Mn and Fe doped SnO2 by a comparison with their optical properties.

Spectral and photoluminescence (PL) measurements are highly helpful to investigate optoelectronic properties of the nanostructured films, which are affected by the structure defects and impurity levels of the material.6 For the oxide materials, many physical properties are driven by defects, which are mostly due to the varied oxygen content. It has been calculated that removal of the bridging O atoms leads to the formation of a dispersed band within the forbidden band gap, which is the cause of oxygen vacancies. The removal of the in-plane oxygen atoms, however, can induce the formation of a single defect level above the valence band.7,8 Furthermore, oxygen vacancies are extremely important for determining the electrical conductivity of SnO2,7 and they are also responsible for an efficient luminescence activity in SnO2 nanocrystalline. Intense and orange light emission from SnO2 nanostructures has recently been found, suggesting that SnO2 may be a promising candidate for luminescent materials.5,9 Although there are the remarkable attentions on SnO2-based semiconductors, the experimental results reported by different research groups have been...
frequently controversial on the origin of PL emission properties.

It is known that a given material preparation method has strong effect on the microstructure and physical properties. As compared with other deposition methods, pulsed laser deposition (PLD) technique has the ability to exceed the solubility of magnetic impurity and to permit high quality film grown at low substrate temperature. Additionally, PLD is done in high vacuum and allows precise control of background reactive gas pressure. Oxygen is one of the common background sources and affects the sample growth in the PLD process because it is a major constituent of oxides. Moreover, the first principle calculation also shows that the oxygen vacancy and tin interstitial can be easily induced due to surprisingly low formation energies and strong mutual interactions. Thus understanding the role of surrounding oxygen is essential to the microstructure and properties of the oxides. Up to date, it has been reported that the crystallinity and PL property for ZnO strongly depend on the oxygen pressure (P_o). Some groups also discussed the effect of oxygen concentration on structure and ferromagnetism for SnO2 nanoparticles, and the PL emission was found to be sensitive to the oxygen concentration. Nevertheless, systematical experimental works to reveal the P_o dependence of optical response behaviors in TM (Mn or Fe) doped SnO2, especially a contrast to the two kinds of films, are very limited. Therefore, it is desirable to carry out a delicate study regarding the mutual correlation between the magnetic elements and oxygen levels in the TM doped SnO2 materials.

In this paper, comprehensive characterizations are performed to explore the morphology, crystallinity, and the chemical states of the TM (Mn or Fe) doped SnO2 films with the compositions of 5% (SnO0.95TM0.05O2) prepared under varied P_o values. We demonstrate the crucial role of surrounding oxygen on electronic band structures and optical properties by means of infrared (IR) reflectance, ultraviolet-near-infrared (UV-NIR) transmittance, and PL spectra. The comparative study on the Sn0.95Mn0.05O2 and Sn0.95Fe0.05O2 films will be presented and oxygen vacancy contribution associated with the 3d dopants will be discussed in detail.

II. EXPERIMENTAL DETAILS

A. Preparation of the Sn0.95TM0.05O2 films

The Sn0.95TM0.05O2 (TM: Mn or Fe) targets in the diameter of 3 cm were prepared using a conventional solid-state reaction sintering. During the preparation, MnO or Fe2O3 powder was mixed with SnO2 powder (99.99%) in which Mn or Fe mole fraction was 5%, then corresponding target of Sn0.95Mn0.05O2 or Sn0.95Fe0.05O2 was obtained. In order to obtain better crystalline quality, double-sided polished c-sapphire wafers were used as the substrates. The substrates were rigorously cleaned in pure ethanol with an ultrasonic bath and were rinsed several times by de-ionized water before the deposition. Finally, the wafers were dried in a pure nitrogen stream before the deposition of the films. The PLD growth process was carried out using a Q-switched pulse yttrium aluminum garnet (Nd:YAG) laser with the wavelength of 532 nm and duration of 5 ns, which works at the repetition rate of 10 Hz and an energy of 40 mJ/pulse, was used for the target ablation. The films were grown immediately after the target was preablated. The distance between the target and substrate was kept at 3 cm and the deposition time was set to about 30 min. Then during the post-annealing process, the substrate temperature of the films was maintained at 900 °C in air atmosphere for 30 min.

B. Sample characterizations

The crystalline structures of the Sn0.95TM0.05O2 (TM: Mn or Fe) films on c-sapphire substrates were analyzed by x-ray diffraction (XRD) using Cu Kα radiation (D/MAX-2550 V, Rigaku Co.). In the XRD measurement, a vertical goniometer (Model RINT2000) and continuous scanning mode (θ-2θ) were selected with a scanning rate of 10°/min and interval of 0.02°. The surface and cross-sectional microstructures of the films were studied by scanning electron microscopy (SEM). The x-ray photoelectron spectroscopic (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV). Because the sapphire substrate is not transparent in the IR region, the near-normal incident (~10°) reflectance spectra were collected over the frequency range from 200 to 1200 cm⁻¹ using a Fourier transform infrared spectrometer (Bruker Vertex 80V). Gold and aluminum mirrors, whose absolute reflectances were measured, were taken as the references for the spectra in the high and low frequency regions, respectively. The spectral transmittance experiments were carried out with a double beam spectrophotometer (PerkinElmer Lambda 950) from 190 to 2650 nm (0.47-6.5 eV) with a spectral resolution of 2 nm. The PL spectra were recorded by a Jobin-Yvon LabRAM HR 800 ultraviolet spectrometer with a He-Cd laser as the excited light, which is operated at the wavelength of 325 nm (3.82 eV). Note that the experiments were carried out at room temperature and no smoothing was performed.

III. RESULTS AND DISCUSSIONS

A. Structural and morphology analysis

The XRD characterization of the Sn0.95TM0.05O2 films with different P_o reveals the tetragonal rutile structure of SnO2, as shown in Fig. 1. The peaks suggest that the films are polycrystalline. With increasing the P_o values, the intensity of (110) diffraction peak for the Sn0.95Mn0.05O2 film increases but that for the Sn0.95Fe0.05O2 film decreases until the pressure reaches 10⁻¹ Pa. Moreover, there are the (110) preferred orientation under the maximum P_o value of 1 Pa, while the intensity of (101) diffraction peak becomes compared to that of (110) diffraction peak under the low P_o in the present work. It is necessary to point out that the peak at Bragg angle of about 18.4° can be observed for the Sn0.95Mn0.05O2 films with the P_o of 10⁻² and 10⁻¹ Pa, identified as the (001) diffraction peak at about 450 °C and deposited in vacuum (~10⁻⁴ Pa) or in O₂ ambient at total pressures of 10⁻², 10⁻¹, and 1 Pa without any buffer gas, respectively. A Q-switched pulse yttrium aluminum garnet (Nd:YAG) laser with the wavelength of 532 nm and duration of 5 ns, which works at the repetition rate of 10 Hz and an energy of 40 mJ/pulse, was used for the target ablation. The films were grown immediately after the target was preablated. The distance between the target and substrate was kept at 3 cm and the deposition time was set to about 30 min. Then during the post-annealing process, the substrate temperature of the films was maintained at 900 °C in air atmosphere for 30 min.
peak for the tetragonal phase of SnO (remarked with *). However, the additional peak cannot be found for the Sn 0.95 Fe 0.05O 2 films. The \(a\)-axis lattice constant in the inset of Fig. 1, determined using the (110) diffraction peak, shows a different variation trend with the Po for the Mn and Fe doping films, respectively. The deviation indicates the different crystalline formation with the varied Po because of the dopant contributions. Moreover, the average values of the \(a\)-axis lattice constant are estimated to be about 4.68 Å and 4.67 Å for the Sn 0.95Mn 0.05O 2 and Sn 0.95Fe 0.05O 2 films, respectively. Both of them are much smaller than those reported SnO 2 with doped by 5% Mn (4.72 Å) or Fe (4.73 Å and 4.79 Å) using other preparation methods,14,15 which can be ascribed to different deposition technique, crystallinity, and lattice mismatch with the substrate. According to the Scherrer equation, the average crystallite sizes of the Sn 0.95Mn 0.05O 2 and Sn 0.95Fe 0.05O 2 films are about 14 and 12 nm, respectively. During the PLD process with the varied Po, the oxygen content in all samples can be considered to be changed and the remarkable discrepancy of above structure parameters for the Sn 0.95TM 0.05O 2 films could be related to the Po effect and its interaction with the dopants.

Fig. 2 presents the surface and cross-sectional SEM images from the Sn 0.95TM 0.05O 2 films deposited under the Po of 10 \(^{-1}\) Pa. Note that both the samples present the uniform granular structures on the sapphire substrates. Nevertheless, the Sn 0.95Fe 0.05O 2 film seems to contain a rough surface and dense topography. Also, the films with the Fe doping are of the distinct interface between the film and substrate, as compared to those from the Sn 0.95Mn 0.05O 2 films. The results suggest that different doping elements could directly affect the crystalline structure and surface morphology of the films. From the cross-sectional SEM image, the thickness of the selected films is evaluated to about several tens of nanometers, which is similar to the values obtained in fitting process. Therefore, it can be concluded that the presence of Fe or Mn could provide a strong relation to the oxygen level and a different perturbation in the structures for the Sn 0.95TM 0.05O 2 films, which is further supported by the following analysis.

B. XPS of the Sn 0.95TM 0.05O 2 films

Elemental composition and chemical states of the Sn 0.95TM 0.05O 2 films were studied by XPS measurements. The survey spectra for all films indicate that only C 1s, Sn 3d, O 1s, and TM 2p related core levels can be detectable. The C 1s peak at 284.6 eV is used as an internal standard, and the other spectra are calibrated with the C 1s peak to correct the binding energy position. For example, high resolution spectra of Sn 3d and TM 2p for the films grown under the Po of 10 \(^{-1}\) Pa are shown in Fig. 3, and the given atomic percentages of Mn and Fe are 5.66% and 4.95%, respectively. The peaks at binding energies of 486.6/486.4 eV (Sn 3d 5/2) and 495/494.8 eV (Sn 3d 3/2) for the Mn/Fe doped film with a spin-orbit splitting of 8.4 eV can be observed in Fig. 3(a), which is in good agreement with the findings for the Sn 4+ bound to oxygen in the matrix.9 In addition, all values of Sn 3d for the Sn 0.95TM 0.05O 2 films (see Table I) are close...
indexed with the rutile-type tetragonal structure of SnO₂.

The observed peaks in the XRD pattern have been mostly its only one symmetric lineshape without any shoulder, and under different oxygen pressure, the chemical state of Sn⁴⁺ also been found in the literatures.9,19 It is known that oxygen sorbed O-containing species.9,20,21 The relatively high intensity of the “Ochem” component is due to the very high surface sensitivity.20 Based on the experimental and fitted XPS peak areas and their sensitivity factors, we quantificationally obtained a relative atomic concentration ratio O₁:(Sn+Mn) of 1.93 for the Sn₀.₉₅Mn₀.₀₅O₂ with the Pₒ = 10⁻⁴ Pa. Moreover, there is one marginal shoulder at about 527 eV from the O 1s signals for the Sn₀.₉₅Fe₀.₀₅O₂ films. It is probably formed by the iron oxides, as previously described by Yamashita and Hayes.22 On the other hand, the Mn 2p₁/₂ and Mn 2p₃/₂ peaks centered around 642.₅ and 654 eV for the Sn₀.₉₅Mn₀.₀₅O₂ samples were the characteristics of Mn⁴⁺.16,18

In the case of the Fe doped films, the Fe 2p region is divided into the Fe 2p₁/₂ peak at 726 eV and Fe 2p₃/₂ peak at 711.₅ eV, corresponding to the Fe³⁺ feature. Furthermore, the Fe 2p₁/₂ peak has associated satellite peaks at 715.₈ eV, which is clearly distinguishable from Fig. 3(c). The presence of the satellite peak may be due to the existence of Fe²⁺.22 Then the Fe element seems to behave as mixed valences of Fe²⁺ and Fe³⁺ situated in the tetragonal Sn₀.₉₅Fe₀.₀₅O₂ films. However, Grosvenor et al. reported that a peak with a binding energy of about 715 eV has been found in the XPS spectra of Fe₂O₃.23 The exact assignment of the peak is still an unresolved issue for the Fe doped SnO₂ material. Interestingly, the core level peaks of Sn 3d and TM 2p in the Sn₀.₉₅Mn₀.₀₅O₂ and Sn₀.₉₅Fe₀.₀₅O₂ films show a slight shift with the varied oxygen pressure and the contrasted changes could be observed under the low oxygen pressure region, which is induced by the doping behaviors. It again indicates the difference in the atomic environment surrounding incorporated TM ions, as seen in the XRD patterns. Note that all binding energy positions of the elements for the Sn₀.₉₅TM₀.₀₅O₂ films are summarized in Table I.

The deconvolution of the O 1s XPS spectra for the Sn₀.₉₅TM₀.₀₅O₂ films are fitted by two components and the complicated results are provided in Table I and Fig. 4. One of the O 1s peaks (remarked O₁) located at 530 eV for all samples is ascribed to the lattice oxygen of the O-Sn⁴⁺ bonds.17 While the higher binding energy peak in O 1s for the Sn₀.₉₅Mn₀.₀₅O₂ films reveals the presence of the chemisorbed O-containing species.9,20,21 The relatively high intensity of the “Ochem” component is due to the very high surface sensitivity.20 Based on the experimental and fitted XPS peak areas and their sensitivity factors, we quantificationally obtained a relative atomic concentration ratio O₁:(Sn+Mn) of 1.93 for the Sn₀.₉₅Mn₀.₀₅O₂ with the Pₒ = 10⁻⁴ Pa. Moreover, there is one marginal shoulder at about 527 eV from the O 1s signals for the Sn₀.₉₅Fe₀.₀₅O₂ films. It is probably formed by the iron oxides, as previously described by Yamashita and Hayes.22 On the other hand, the Mn 2p₁/₂ and Mn 2p₃/₂ peaks centered around 642.₅ and 654 eV for the Sn₀.₉₅Mn₀.₀₅O₂ samples were the characteristics of Mn⁴⁺.16,18

In the case of the Fe doped films, the Fe 2p region is divided into the Fe 2p₁/₂ peak at 726 eV and Fe 2p₃/₂ peak at 711.₅ eV, corresponding to the Fe³⁺ feature. Furthermore, the Fe 2p₁/₂ peak has associated satellite peaks at 715.₈ eV, which is clearly distinguishable from Fig. 3(c). The presence of the satellite peak may be due to the existence of Fe²⁺.22 Then the Fe element seems to behave as mixed valences of Fe²⁺ and Fe³⁺ situated in the tetragonal Sn₀.₉₅Fe₀.₀₅O₂ films. However, Grosvenor et al. reported that a peak with a binding energy of about 715 eV has been found in the XPS spectra of Fe₂O₃.23 The exact assignment of the peak is still an unresolved issue for the Fe doped SnO₂ material. Interestingly, the core level peaks of Sn 3d and TM 2p in the Sn₀.₉₅Mn₀.₀₅O₂ and Sn₀.₉₅Fe₀.₀₅O₂ films show a slight shift with the varied oxygen pressure and the contrasted changes could be observed under the low oxygen pressure region, which is induced by the doping behaviors. It again indicates the difference in the atomic environment surrounding incorporated TM ions, as seen in the XRD patterns. Note that all binding energy positions of the elements for the Sn₀.₉₅TM₀.₀₅O₂ films are summarized in Table I.

C. IR reflectance from the Sn₀.₉₅TM₀.₀₅O₂ films

In order to further clarify the influence of Pₒ on structural properties, IR reflectance spectra for the Sn₀.₉₅TM₀.₀₅O₂ films were measured. Compared to the sapphire substrate, the spectrum of the Sn₀.₉₅Mn₀.₀₅O₂ film with Pₒ = 10⁻¹ Pa in Fig. 5(a) indicates that the three intense peaks at about 248, 289, and 601 cm⁻¹ can be assigned to the E₁u transverse optical (TO) phonon modes,10 which are correlated to the vertical displacements of Sn and O ions.24,25 The Δ₂g phonon mode appears in the small band region of 450–500 cm⁻¹. The lattice vibrations and optical functions of the Sn₀.₉₅TM₀.₀₅O₂...
the highest frequency $(TO)$ modes for the Sn$_{0.95}$TM$_{0.05}$O$_2$ systems, as exhibited in Fig.5. With increasing the Po, the films in the frequency range of 200–1200 cm$^{-1}$ can be expressed using the Lorentz multi-oscillator model,

$$
\tilde{e}(\omega) = e_{\infty,IR} + \sum_{k=1}^{4} \frac{S_k \omega_{TO,k}^2}{\omega_{TO,k}^2 - \omega^2 - i\omega \Gamma_k},
$$

Here, $e_{\infty,IR}$, $S_k$, $\omega_{TO,k}$, $\Gamma_k$, and $\omega$ represent, in order, the high frequency dielectric constant, constant TO phonon strength, TO phonon frequency, the damping parameter of the TO phonon, and the frequency of the incident infrared light, respectively. A detailed theoretical consideration of the films can be found in Ref. 26. The former four fitting parameters ($e_{\infty,IR}$, $S_k$, $\omega_{TO,k}$, $\Gamma_k$) could be obtained from the fitting calculation and those values with the Po can be listed in Table II. As can be seen, the low $E_u$ (TO) phonon frequencies are not strikingly changed corresponding to the Po. However, the distinct deviations can be observed in the highest $E_{\infty}$ (TO) vibration modes for the Sn$_{0.95}$TM$_{0.05}$O$_2$ systems, as exhibited in the panels (b), (c), and (f) of Fig. 5. With increasing the Po, the highest frequency $E_u$ (TO) phonon mode for the Sn$_{0.95}$TM$_{0.05}$O$_2$ films shifts toward different frequency sides due to the doping elements and oxygen level, which can together contribute to the phonon characteristics. It should be emphasized that the optical functions of the Sn$_{0.95}$TM$_{0.05}$O$_2$ films can be uniquely determined by fitting the function model to the experimental data in the IR frequency region. For comparison, Fig. 5(d) and 5(e) display the variations of the refractive index $n$ and extinction coefficient $\kappa$ for the Sn$_{0.95}$TM$_{0.05}$O$_2$ samples deposited under the P$_o$ of 10$^{-1}$ Pa, respectively. The strengths of the low $E_u$ (TO) frequencies in the Sn$_{0.95}$Fe$_{0.05}$O$_2$ film are stronger than those of the Sn$_{0.95}$Mn$_{0.05}$O$_2$ sample at the special pressure, suggesting that the Fe/Mn doping could differently affect the x-y plane movements and bond strength of Sn and O ions in SnO$_2$ system.\textsuperscript{25} The behavior is a result of the doping effects on the crystalline and local lattice distortions, which was confirmed by the XRD measurements.

### D. Transmittance properties of the Sn$_{0.95}$TM$_{0.05}$O$_2$ films

Optical characterization of the Sn$_{0.95}$TM$_{0.05}$O$_2$ films was performed over the UV-NIR photon energy range by measuring the transmittance of the films. Both Sn$_{0.95}$Mn$_{0.05}$O$_2$ and Sn$_{0.95}$Fe$_{0.05}$O$_2$ films exhibit the excellent transparency with spectral transmittance of about 80% in a NIR-visible wavelength region, as shown in the inset of Fig. 6. There are few interference oscillation periods in the transparent region due to the finite film thickness. Extrapolation from the linear parts of the transmission spectra in the strong absorption region yields the fundamental absorption edge, which was determined to be near 4 eV for the films. Besides a minor change in the transmittance lineshape due to the effects of P$_o$ for the Sn$_{0.95}$Mn$_{0.05}$O$_2$ films, it can be also seen that the Sn$_{0.95}$Fe$_{0.05}$O$_2$ films have some sharp shoulders around the photon energy region of 2–4 eV since the 3d electrons form an impurity band in the forbidden band gap from the crystal field transition. It was reported that diffuse reflectance spectroscopy of Fe and Mn doped ZnO showed the existence of additional absorption bands, which were explained by the impurity d-band splitting model.\textsuperscript{25} Furthermore, based on the first principle calculations, there are not only Fe-d states but also the oxygen 2p states staying at the Fermi level, induced by the Fe doping. It suggests the strong p-d coupling and hopping in Fe doped SnO$_2$ films. However, the phenomena

### Table II. The Lorentz multi-oscillator parameter values for the Sn$_{0.95}$TM$_{0.05}$O$_2$ (TM: Mn or Fe) films with the varied oxygen pressure are extracted from the best fitting to infrared reflectance spectra in Fig. 5.

<table>
<thead>
<tr>
<th>Samples</th>
<th>P$_o$ (Pa)</th>
<th>$e_{\infty,IR}$</th>
<th>$S_1$</th>
<th>$\omega_{TO,1}$ (cm$^{-1}$)</th>
<th>$\Gamma_1$ (cm$^{-1}$)</th>
<th>$S_2$</th>
<th>$\omega_{TO,2}$ (cm$^{-1}$)</th>
<th>$\Gamma_2$ (cm$^{-1}$)</th>
<th>$S_3$</th>
<th>$\omega_{TO,3}$ (cm$^{-1}$)</th>
<th>$\Gamma_3$ (cm$^{-1}$)</th>
<th>$S_4$</th>
<th>$\omega_{TO,4}$ (cm$^{-1}$)</th>
<th>$\Gamma_4$ (cm$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>A$_{Mn}$</td>
<td>10$^{-4}$</td>
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<td>0.79</td>
<td>246</td>
<td>7.91</td>
<td>0.15</td>
<td>288</td>
<td>5.15</td>
<td>0.60</td>
<td>604</td>
<td>49.3</td>
<td>0.80</td>
<td>466</td>
<td>56.1</td>
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<tr>
<td>B$_{Mn}$</td>
<td>10$^{-2}$</td>
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<td>0.78</td>
<td>247</td>
<td>8.66</td>
<td>0.15</td>
<td>288</td>
<td>5.56</td>
<td>0.72</td>
<td>601</td>
<td>53.5</td>
<td>0.70</td>
<td>468</td>
<td>53.3</td>
</tr>
<tr>
<td>C$_{Mn}$</td>
<td>10$^{-1}$</td>
<td>4.33</td>
<td>0.79</td>
<td>248</td>
<td>11.6</td>
<td>0.18</td>
<td>289</td>
<td>7.54</td>
<td>0.57</td>
<td>591</td>
<td>49.1</td>
<td>0.95</td>
<td>471</td>
<td>53.8</td>
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<tr>
<td>D$_{Mn}$</td>
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<td>1.55</td>
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<td>0.64</td>
<td>290</td>
<td>16.5</td>
<td>0.63</td>
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<td>50.6</td>
<td>0.95</td>
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<tr>
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<td>0.55</td>
<td>246</td>
<td>6.99</td>
<td>0.11</td>
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<td>4.36</td>
<td>1.14</td>
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<tr>
<td>C$_{Fe}$</td>
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<td>1.36</td>
<td>248</td>
<td>13.7</td>
<td>0.40</td>
<td>288</td>
<td>11.3</td>
<td>0.29</td>
<td>602</td>
<td>27.3</td>
<td>0.98</td>
<td>473</td>
<td>51.7</td>
</tr>
</tbody>
</table>
are weak in the case of Mn doping and consequently the shoulder transition related to the hybridization is also insignificant.\textsuperscript{5} On the other hand, oxygen vacancies play an important role in determining optical properties of the materials. When Fe substitutes Sn in the Sn\textsubscript{0.95}Fe\textsubscript{0.05}O\textsubscript{2} films, the octahedral environment may be varied if the oxygen vacancies are introduced in the first coordination sphere of Fe\textsuperscript{3+}.\textsuperscript{28} It has been demonstrated that the Fe introduction largely facilitates the formation of oxygen vacancies.\textsuperscript{29} Other data indicate that oxygen vacancy has a strong tendency to be close to the Fe ions, but the Mn ions have a small influence on the distribution of oxygen vacancy.\textsuperscript{5} So we attribute the appearance of those shoulders to the correlation between oxygen vacancies and dopant in the films, particularly the effects from the Fe contribution because of the distinct phenomenon in the Sn\textsubscript{0.95}Fe\textsubscript{0.05}O\textsubscript{2} films under the identical condition. It is evident that the different TM ions, together with the varied P\textsubscript{o}, have a great influence on the oxygen vacancy distribution and then further result in different optical response behaviors.

Generally, the reliability of the fitting method mainly depends on the validity of the dielectric function model. It is a challenge to choose the most suitable model for material and the spectral range studied. There are some well-known dispersion functions, which are derived from the band parameters and can be used to express the optical response behavior.\textsuperscript{30} Among them, the Tauc-Lorentz (TL) model is an available approach to describe the dielectric response of wide band gap materials in the NIR to UV range including the exciton effects. Moreover, the positions of electronic transitions can be accurately determined by the TL model, which are helpful to understand the absorption processes. The TL model can be derived from the Tauc joint density of states (DOS) and the standard quantum mechanical or Lorentz calculation for \( \varepsilon_2 \) (imaginary part of dielectric function) of a collection of non-interacting atoms.\textsuperscript{31} If the multiplied transitions are considered, \( \varepsilon_2 \) is written as
\[
\varepsilon_2(E) = \begin{cases} 
0, & E < E_g \\
\frac{A E_0 C (E - E_g)^2}{(E^2 - E_0^2)^2 + C E^2 E}, & E > E_g 
\end{cases}
\] 

The real part of the dielectric function \( \varepsilon_1 \) is given by Kramers-Krönig integration,
\[
\varepsilon_1(E) = \varepsilon_{\infty,\text{UV}} + \frac{2}{\pi} \int_{E_g}^{\infty} \frac{\varepsilon_2(\xi)}{\xi^2 - E^2} d\xi. 
\]

Equation (2) depends on the following five parameters: the parameters \( A, E_0, C \) correspond to the amplitude, the peak transition energy, and the broadening for the electronic transitions, respectively. The parameter \( E_g \) is the band gap energy and \( \varepsilon_{\infty,\text{UV}} \) is the high-frequency dielectric constant. The above TL dielectric function model has been successfully applied in many semiconductor and dielectric materials from the transparent to strong absorption region.\textsuperscript{32–35} It should be pointed out that the effect of the surface rough layer, whose value is much less than the film thickness, can be neglected in the evolution of the optical properties for the Sn\textsubscript{0.95}TM\textsubscript{0.05}O\textsubscript{2} films. Because relatively big light spot (about 4 mm in diameter) and vertical incident accessory are used in the present experiments, the transmittance spectra cannot be sensitive to the porous surface layer. Therefore, a three-phase layered structure (air/film/substrate) and the TL dielectric model were used to calculate the UV-NIR transmittance spectra of the Sn\textsubscript{0.95}TM\textsubscript{0.05}O\textsubscript{2} films.

The experimental transmittance curves and fitting data with the TL model for the Sn\textsubscript{0.95}TM\textsubscript{0.05}O\textsubscript{2} films grown under the \( P_o \) of 10\textsuperscript{-1} Pa are presented in the Fig. 6. Note that two TL dispersion functions are used for the Sn\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{2} and four TL dispersion functions are necessary for the Sn\textsubscript{0.95}Fe\textsubscript{0.05}O\textsubscript{2} films due to the distinguished shoulder structures. It reveals that more than one single type of electronic transitions dominate the optical absorption for the films,\textsuperscript{35} and the Fe introduction can cause the shoulder patterns to become much stronger. The TL parameters obtained from the fitting are summarized in Table III. It can be seen that the \( \varepsilon_{\infty,\text{UV}} \) is smaller than the \( \varepsilon_{\infty,\text{IR}} \) because the physical parameter accounts for the so-called high-frequency limit. Nevertheless, the values of both \( \varepsilon_{\infty,\text{UV}} \) and \( \varepsilon_{\infty,\text{IR}} \) are well located in a reasonable magnitude region, as compared with some typical wide band gap semiconductors and insulators. Correspondingly, it indicates that the contributions from the high energy electronic transition for the films in the IR region are remarkable compared with that in the UV-NIR region. As an example, the optical functions for the Sn\textsubscript{0.95}TM\textsubscript{0.05}O\textsubscript{2} films deposited under the \( P_o \) of 10\textsuperscript{-1} Pa are plotted in the left panel of Fig. 7, showing a normal dispersion in both Fe and Mn doped films. It is found that, at any pressure of the present work, the \( n \) for the Sn\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{2} films is larger than that of the Sn\textsubscript{0.95}Fe\textsubscript{0.05}O\textsubscript{2} films in mostly all studied photon energy region of 0.47-6.5 eV (not shown). Moreover, at the limited energy of 0.47 eV, the \( n \) values approximately vary from 2.07 to 2.10 and from 1.88 to 2 corresponding to different \( P_o \) for the Sn\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{2} and Sn\textsubscript{0.95}Fe\textsubscript{0.05}O\textsubscript{2} films, respectively. The deviation implies that the optical functions of the Sn\textsubscript{0.95}TM\textsubscript{0.05}O\textsubscript{2} films are very sensitive to the experimental oxygen level and doping effects, which could induce the corresponding crystalline and band structure change. From the right panel of Fig. 7, the \( E_0 \) transition in the Sn\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{2} films decreases with increasing \( P_o \) and approaches the
minimum at the $P_0$ of $10^{-1}$ Pa, then increases with further increasing $P_0$. But a distinct trend occurs in both $E_{01}$ and $E_{02}$ for the Sn0.95Fe0.05O2 films due to the different dopants. As previously discussed, the varied $P_0$ results in the change of electronic band structures and strongly affects the interband transition properties of the films. Thus, the optical transmission of the Fe and Mn doped systems depend on different TM dopants and varied $P_0$ parameters.

### E. Oxygen pressure effects on photoluminescence emissions

To further explore the influence of $P_0$ on structures, defects, and impurities in nanostructures, PL experiments of the Sn0.95TM0.05O2 films were done at room temperature. As illustrated in Fig. 8, there are some broadening emission bands between 1 and 3.5 eV with the maximum at about 2.2 eV, which is close to the reported ones\(^9,26\) and the experimental data for the undoped SnO2 films (not shown). It can be seen that there are three obvious peaks in the spectra of the films, including the emissions from SnO2 and TM contributions, respectively. In order to determine the peak positions of emissions, a three peak fit of the PL spectra was carried out by Gaussian curve and the positions with varied $P_0$ were listed in Table I. As a comparison between the pure SnO2 and Sn0.95TM0.05O2 systems, besides the main peaks ($P_{TM-1}$ and $P_{TM-2}$) characterized by a broadening feature around 2.2 eV with a small emission shoulder at 1.9 eV, there is a sharp peak ($P_{TM-3}$) centered at near 1.5 eV owing to the Mn introduction in the Sn0.95Mn0.05O2 films.\(^{26}\) Moreover, for the pure SnO2 and Sn0.95Mn0.05O2 films, the behavior that intensity reduction with increasing the oxygen pressure of the main peaks could be due to the similar $P_0$ effect on the PL mechanism. Although the Mn composition is kept as a constant, the position and intensity of the $P_{TM-3}$ are quite sensitive to the $P_0$. It indicates that the variations are a result of different $P_0$ values, which affects the d electronic configuration induced by the Mn doping. It is widely believed that PL emission band centered in the range of 580–630 nm (2.14–1.97 eV) for SnO2 nanostructures are derived from oxygen vacancy centers or surface states (e.g., tin vacancies/interstitials).\(^{11,36}\) But the exact mechanism of these bands is still controversial.

#### Table III. The Tauc-Lorentz’s parameter values for the Sn0.95TM0.05O2 (TM: Mn or Fe) films are determined from the simulation to ultraviolet-near-infrared transmittance spectra in Fig. 6.

<table>
<thead>
<tr>
<th>Samples $P_0$ (Pa)</th>
<th>Thickness (nm) $e_{\infty,UV}$</th>
<th>TL1</th>
<th>TL2</th>
<th>TL3</th>
<th>TL4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_1$ (eV)</td>
<td>$E_{01}$ (eV)</td>
<td>$C_1$ (eV)</td>
<td>$E_{g1}$ (eV)</td>
<td>$A_2$ (eV)</td>
</tr>
<tr>
<td>AMn 10$^{-4}$</td>
<td>75</td>
<td>2.75</td>
<td>50.6</td>
<td>3.18</td>
<td>2.249</td>
</tr>
<tr>
<td>BMn 10$^{-2}$</td>
<td>76</td>
<td>2.59</td>
<td>56.0</td>
<td>2.314</td>
<td>2.52</td>
</tr>
<tr>
<td>CMn 10$^{-1}$</td>
<td>78</td>
<td>2.54</td>
<td>51.9</td>
<td>3.11</td>
<td>2.50</td>
</tr>
<tr>
<td>DMn 1</td>
<td>1</td>
<td>90</td>
<td>2.75</td>
<td>27.6</td>
<td>3.20</td>
</tr>
<tr>
<td>AMn 10$^{-4}$</td>
<td>93</td>
<td>2.03</td>
<td>37.7</td>
<td>1.83</td>
<td>0.45</td>
</tr>
<tr>
<td>BMn 10$^{-2}$</td>
<td>75</td>
<td>1.88</td>
<td>34.6</td>
<td>1.950</td>
<td>0.65</td>
</tr>
<tr>
<td>CMn 10$^{-4}$</td>
<td>91</td>
<td>2.22</td>
<td>53.0</td>
<td>2.107</td>
<td>0.27</td>
</tr>
<tr>
<td>DMn 1</td>
<td>1</td>
<td>119</td>
<td>2.32</td>
<td>27.3</td>
<td>1.90</td>
</tr>
</tbody>
</table>
In the present case, a possible explanation for the $P_{\text{TM}-1}$ and $P_{\text{TM}-2}$ of both pure SnO$_2$ and Sn$_{0.95}$TM$_{0.05}$O$_2$ films is that the electrons in the conduction band first relax nonradiatively to the defect states and then radiatively recombine with the holes in the valence band of SnO$_2$ as argued in the SnO$_2$/p-Si heterojunctions. The conclusion has been confirmed by PL spectra using different excitations (325 and 488 nm) for SnO$_2$ nanowires. The mechanism of above emissions should be associated with the defects, which act as trapped states within the band gap of SnO$_2$. There are various types of the defects, such as oxygen vacancies, tin vacancies, or tin interstitials, which give rise to different trapped states and contribute to the emission bands discussed above. Most commonly the oxygen vacancies exist with three different states ($V_o^0$, $V_o^+$, $V_o^{++}$). The $V_o^0$ center as very shallow donor, is very close to the conduction band edge and can capture electrons then form ionized vacancies. The presence of $V_o^+$ has been reported and confirmed by electron paramagnetic resonance study on SnO$_2$. It is expected that the $P_{\text{TM}-1}$ or $P_{\text{TM}-2}$ emission occurs due to the $V_o^+$ acceptor state. The $P_{\text{TM}-2}$ may be due to the presence of isolated $V_o^+$ centers, which lies in a higher energy in the band gap than the complex $V_o^{++}$ centers producing the $P_{\text{TM}-1}$ emission. Additionally, the $P_{\text{Fe}-3}$ around 2.9 eV for the Sn$_{0.95}$Fe$_{0.05}$O$_2$ films can be assumed to the conduction band-acceptor or donor-acceptor transitions owing to the formation of $V_o^{++}$ luminescent center. On the other hand, the oxygen vacancies interact with interfacial tin vacancies and lead to a considerable amount of trapped states within the band gap, then result in the PL emission signal. Zhang et al. reported that the strong emission at 554 nm (2.2 eV) was related to the oxygen vacancy and the shoulder at 625 nm (1.98 eV) may be related to tin interstitials. One also suggested that the observed peak at 2.1 eV is from the unoccupied electron states in the dangling bonds at the surface of SnO$_2$ crystals. These mentioned defect states are complex and can be influenced by the growth conditions.

The dependence of the corresponding intensity and emission peak positions on the parameter $P_o$ is presented in Fig. 9 for the Sn$_{0.95}$Mn$_{0.05}$O$_2$ and Sn$_{0.95}$Fe$_{0.05}$O$_2$ films, respectively. The intensity at the $P_{\text{TM}-2}$ emission decreases as increasing $P_o$, then the minimum is obtained for the $P_o$ of 10$^{-1}$ Pa in the Sn$_{0.95}$Mn$_{0.05}$O$_2$ films, showing a remarkable response to oxygen level. In contrast, there is an opposite trend below and above the $P_o$ of 10$^{-1}$ Pa for the Sn$_{0.95}$Fe$_{0.05}$O$_2$ films. As we know, the oxygen vacancies can be present for the oxide materials during the PLD process. Supposed that the lower $P_o$ means less oxygen content, then a large amount of oxygen vacancies are supplied by the surrounding oxygen. Therefore, the intensity of the peak, which is related to oxygen vacancies acted as the defect states, decreases with increasing $P_o$. The similar situation can be seen in Fig. 9 for the Sn$_{0.95}$Mn$_{0.05}$O$_2$ films until the pressure reaches 10$^{-1}$ Pa. Further evidence on the relation between oxygen vacancies and intensity of the peak emission for SnO$_2$ nanostructures deposited at different oxygen flow rate has been found. It could be concluded that the less oxygen vacancies in the crystal can result in a weaker peak intensity, which again confirms the above emission mechanism. However, a different sign of the intensity in the Sn$_{0.95}$Fe$_{0.05}$O$_2$ films may be explained by the fact that increasing oxygen vacancies, whose formation would be facilitated by the Fe presence, cause the enhancement of relative intensity for $P_{\text{Fe}-2}$. Furthermore, the doping elements result in different structure evolution, which is indicated by XRD and IR reflectance measurements, and also could greatly affect the luminescence properties. From those views, the incorporation of Fe ion can be assumed as the dominant factor in the different PL phenomenon. So the effects, resulting from the Fe dopant and increased oxygen vacancies, together lead to the different optical activity for the Sn$_{0.95}$Fe$_{0.05}$O$_2$ films.

Note that the positions of $P_{\text{TM}-1}$ and $P_{\text{TM}-2}$ for the Sn$_{0.95}$TM$_{0.05}$O$_2$ films shift with increasing $P_o$ and the corresponding trends coincide with those of PL intensities and $E_{\text{01}}$ electronic transitions presented previously. Moreover, an interesting comparison can be made that these positions closely match the values of $E_{\text{01}}$ and $E_{\text{02}}$ transition energies determined from the TL model calculation, where the variations with the $P_o$ values have the same inflection point. It indicates that the varied $P_o$ not only modify the oxygen vacancy but also affect energy level of the TM ions, which are located in the band gap of SnO$_2$. Therefore, one may suggest that the variation trends of electronic and optical properties with the $P_o$ for the Sn$_{0.95}$Mn$_{0.05}$O$_2$ and Sn$_{0.95}$Fe$_{0.05}$O$_2$ systems could be different. It was reported that the absorption edge of SnO$_2$ has been assigned to interband transitions from the valence band edge with O 2p orbitals to the conduction band edge with Sn 5s orbitals. In TM (Fe or Mn) doped rutile SnO$_2$, O ions around TM ions form an octahedral crystal field, splitting 3d orbitals into lower $e_g$ states and upper $t_{2g}$ states. From previously discussed, strong p-d hybridization in the Sn$_{0.95}$Fe$_{0.05}$O$_2$ films has been found, showing not only d states but also the oxygen 2p states staying at the Fermi level. However, they are weak in the Mn doped case. In addition, the interband electronic transitions are related to the ability of electrons located in bands below the Fermi level to be excited to unoccupied levels above it, and their intensity is proportional to the density of states. Based on the first principle calculations, the DOS at the Fermi level is mainly derived from the O 2p states and only less than half
of the total states were contributed by Fe 3d states for Fe0.125Sn0.875O2. It indicates that the strong p-d hybridization exist when the 3d electrons form an impurity induced by Fe, which is essential to mediate the exchange interaction between the doped TM ions. Furthermore, Fe-O-Fe groups are common in the Sn0.95Fe0.05O2 system, but are not easily formed in the Sn0.95Mn0.05O2 film. Such special Fe-O-Fe bond and its distortion are expected to originate from the strong p-d hybridization and the smaller substitutional Fe ion radius (0.65 Å) compared with the Sn4+ (0.72 Å). In addition, it should be also noted that the ionic radius of Mn4+ (0.53 Å) is even smaller than that of Sn4+. Thus, the different doping elements could intensely affect the electronic band structure of the SnO2 matrix. Also, the Pe variation can affect oxygen content in the oxide films, then affect the O 2p and Fe/Mn 3d orbital distributions, which will induce the t2g and eg states located at different level in the energy space. It further results in different spectral response behavior with the doping in the varied Pe region due to the mutual interaction between TM ion and O levels. Hence, it could be understood that the electronic band and optical properties for the Sn0.95TM0.05O2 films strongly correlate with the energy levels of dopants in the SnO2 lattice, the electronic configuration, and the distribution of oxygen vacancy derived from the Pe.

IV. CONCLUSION

To summarize, the oxygen pressure effects on the electronic band structures and optical properties of the SnO0.95TM0.05O2 (TM: Mn or Fe) films have been determined by comprehensive characterizations. XRD analysis shows that the films are of the rutile structure and the variant Po behavior with the doping in the varied Po region due to the electronic band and its distortion are expected to originate from the strong p-d hybridization and the smaller substitutional Fe ion radius (0.72 Å) compared with the Sn4+ (0.65 Å). Thus, the different doping elements could intensely affect the electronic band structure of the SnO2 matrix. Also, the Pe variation can affect oxygen content in the oxide films, then affect the O 2p and Fe/Mn 3d orbital distributions, which will induce the t2g and eg states located at different level in the energy space. It further results in different spectral response behavior with the doping in the varied Pe region due to the mutual interaction between TM ion and O levels. Hence, it could be understood that the electronic band and optical properties for the Sn0.95TM0.05O2 films strongly correlate with the energy levels of dopants in the SnO2 lattice, the electronic configuration, and the distribution of oxygen vacancy derived from the Pe.

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