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Impact of stoichiometry on the linear and nonlinear optical response of SnO_x thin films

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Abstract SnO is a promising p-type oxide semiconductor materials for applications such as transparent electronics and solar cells. However, further improvement of its performance is hindered by its diverse stoichiometry. We investigated the nonlinear and saturable absorption characteristics of pristine SnO and O-rich SnO_x films by femtosecond degenerate pump-probe measurements at 515 nm. UV-Vis absorption data indicate bandgap blueshift with increasing oxygen concentration. Pristine SnO film exhibit saturable absorption while nonlinear absorption is observed in O-rich SnO_x films. Our results shed light on the utilization of SnO in future device applications.

1. Introduction

Recently, transparent metal oxides (MOs) have garnered tremendous research attention due to their potential applications in transparent electronics, sustainable energy, nano-photonics, etc [1]. Among various oxide semiconductors, tin monoxide (SnO) has attracted numerous interests owing to its unique p-type conductivity, high carrier mobility and wide optical band gap [2-7]. However, a fundamental issue with SnO is that the stability of SnO is rather low, which can be easily either over-oxidized into SnO_2 or reduced into metallic Sn. As a result, considerable efforts have been focused on the preparation and characterization of tin monoxide with distinct stoichiometry. Previous studies revealed that stoichiometry play a critical role in the electronic properties of SnO_x materials [4,5,7]. However, few experimental studies have been conducted on the effect of stoichiometry on the linear or nonlinear optical response of SnO materials. Therefore, it is essential to study the optical response of SnO_x materials for further improving the performance of optoelectronic and solar energy devices based on SnO. In this paper, the static and dynamic optical response of pristine SnO and O-rich SnO_x ($1<x<1.5$) thin films were investigated using UV-Vis and femtosecond degenerate pump-probe measurements, respectively. Our results demonstrate that stoichiometry plays a significantly role in the optical response of tin monoxide materials.

2. Experiment

The films used in this study were prepared on quartz glasses using reactive rf magnetron sputtering under different oxygen partial pressure (P_O), with a thickness of ~200 nm. The crystallinity of the obtained films was characterized by x-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer) with Cu Kα radiation. Transmittance spectra were recorded via a UV-vis-IR spectrophotometer (Perkin-Elmer, Lambda 950). Details about the film fabrication and property characterizations can be found elsewhere [5]. The femtosecond degenerate pump-probe measurements were performed using a standard femtosecond pump-probe spectroscopy [8]. The light source was a Yb:KGW femtosecond laser (1.20 eV, 190 fs, 6 kHz). The 515 nm laser pulse used in the present work were generated by second harmonic generation with KDP crystal. The temple resolution of the measurement system was ~280 fs. To suppress many-body effects, the pump fluence was kept below 30 μJ/cm^2. All measurements were performed at room temperature.

3. Results

Figure 1(a) shows the XRD patterns of the pristine SnO and O-rich SnO_x films. Clear XRD peaks were observed in the pristine SnO film, which can be unambiguously

assigned to those of the α-SnO crystal structure (P4/nmm, JCPDS card No.06-0395). However, the XRD pattern became broad and featureless for the SnO_x film prepared with P_O above 10.7%, indicating the amorphous nature of the films. Figure 1(b) presents the linear transmittance spectra of the SnO films. It is found that the transmittance spectra of the two films are similar. However, the optical bandgap of the O-rich SnO_x film slightly blueshift, which is a good agreement with the previous report [5]. Furthermore, the optical transmittance spectra clearly demonstrate that there is absorption below the band edge, which is related to the vacancies induced defect state within the band gap.

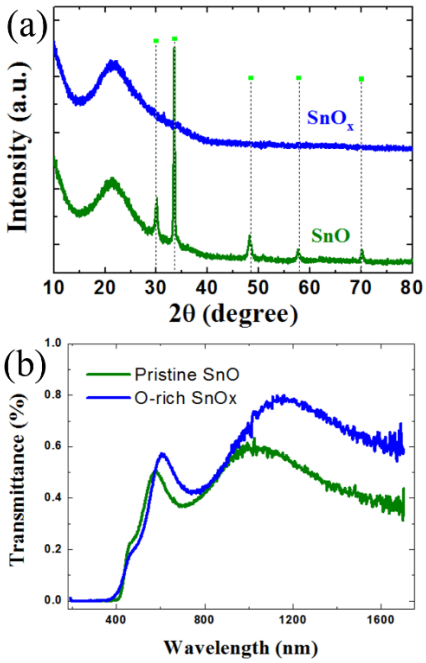

Fig. 1. (a) XRD patterns of the pristine SnO and O-rich SnO_x films. (b) The transmittance spectra of the SnO_x films.

Figure 2 illustrates the pump-probe curves of pristine SnO and O-rich SnO_x films at various time delays under 515 nm pulses excitation. Both films demonstrate a Gaussian-like dip/peak at zero time delay, which can be attributed to the coherent overlap of pump and probe pulses. Note that the transmission spectra of the two films reveal that bandtail states indeed exist in the SnO and SnO_x films, which could be excited by the pump photon (515 nm, 2.4 eV). However, the Gaussian-like function at zero time delay is an instantaneous process, which could be attributed to the convolution of the cross-correlation between the pump and probe pulses. In Fig. 2, the fitting curve of the convolution was shown in red line. The transient curve of the pristine SnO increase after pump excitation, which is related to the band-filling effects. The transient curve recover to negative value after 5 ps, qualitatively indicating the lifetime of carrier relaxation to the bandtail states. In contrast to the pristine SnO, the transient curve of the O-rich SnO_x film show a negative value follow by a decay feature, which are related to the free carrier-induced absorption mechanism (FCA). We utilized two exponential decay functions to fit the trace. And the corresponding characteristic time constants of the pristine SnO are 1.5 picosecond for the fast exponential decay function and ~13 ps for the other exponential function, respectively. These values agrees well with the pervious report [8]. However, the time constants of the O-rich SnO_x film are fitted to be around 10 ps and >50 ps, respectively. These results could be attributed to the defect state within bandgap induced by mixed valence state tin ions, which trap the photo-generated carriers. Our results clearly demonstrate that the dynamic optical response of tin monoxide rely heavily on the oxygen stoichiometry of the film.

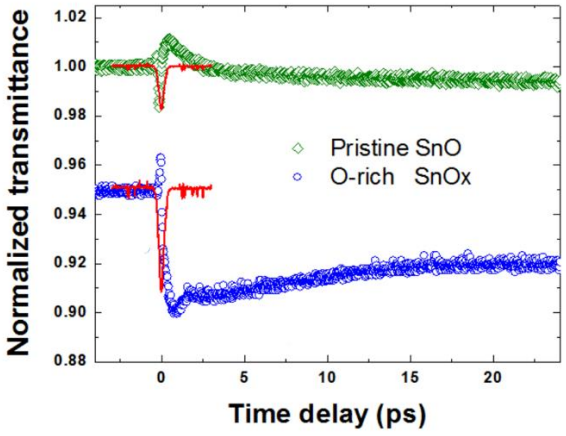

Fig. 2. Normalized pump-probe decay traces for pristine SnO and O-rich SnO_x films. The red lines represent the cross-correlation between the pump and probe pulses.

4. Conclusion

In summary, we studied the static and dynamic optical response of two SnO films with different oxygen stoichiometry. The thin film stoichiometry was found to play a critical role in determining the optical properties and dynamics of photo-generated carriers. The pristine SnO and O-rich SnO_x films show photo-bleaching and free carrier absorption after 515 nm excitation, respectively. And the carrier decay in the O-rich SnO_x film is slower than that of the pristine SnO film. Our reports may lead to some hints for improvement of the devices based on SnO materials.

Acknowledgment

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Reference

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