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# Temperature dependence of electronic band transition in Mn-doped $SnO_2$ nanocrystalline films determined by ultraviolet-near-infrared transmittance spectra

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ABSTRACT

Mn-doped $SnO_2$ (SMO) nanocrystalline films with the composition from 2.5 to 12.5% have been prepared on quartz substrates by pulsed laser deposition. The temperature dependence of electronic structures and optical constants in the SMO films have been investigated by transmittance spectra from 5.3 to 300 K. Optical response functions have been extracted by fitting the transmittance spectra in the photon energy range of 0.5–6.5 eV with the Adachi's model. It was found that the absorption edge presents a red-shift trend with increasing Mn composition, and the optical band gap (OBG) is varied between 4.22 and 3.44 eV. Moreover, as the Mn composition increases, the temperature dependence of OBG becomes weaker. The band gap narrowing value [(5.3 K)–(300 K)] has been reduced from 98 to 3 meV and linearly decreases with the Mn composition. The phenomena could be attributed to the transition from low doping level $SnO_2$ band-like states to Mn-related localized states. Moreover, the Urbach energy shows the degree of the structural disorder, which could be explained by an empirical formulas in different temperature regimes.



## 1. Introduction

During the last few years, diluted magnetic semiconductors (DMSs) have attracted considerable attention for its potential technological applications in the fields of spintronics, optoelectronics, and magnetoelectronics [1,2]. Wide band gap DMSs combine their ferromagnetism with electrical conductivity and optical transparency, thereby opening up the possibility of other devices with unprecedented capabilities. Since the room temperature (RT) ferromagnetism was discovered in cobalt-doped titanium dioxide ($TiO_2$) films [1], much effort has been made on the studies of transition metal (TM) doped wide band gap oxide materials, such as zinc oxide (ZnO) [3,4], tin dioxide ($SnO_2$) [5–8], and $TiO_2$ [9], for the purpose of obtaining the diluted magnetic compounds with Curie temperature above RT. Among these oxides, $SnO_2$ presents attracting properties, such as large optical band gap, exciton binding energies, remarkable chemical and thermal stabilities, which is suitable for applications in gas sensors, transparent conducting electrodes, dye-based solar cells, catalysts, etc. [10,11]. Recently, Manganese (Mn)-doped $SnO_2$ (SMO) has received much attention. This is because the doping of Mn could result in the electronic band structure variation of $SnO_2$ and shows large magnetoresistance [11,12]. Gopinadhan et al. [5] has investigated SMO films prepared by spray pyrolyzing and predicted a Curie temperature above 550 K. Kimura et al. [12] indicated that SMO films can be prepared by pulsed laser deposition (PLD) and found that the magnetic moments per Mn site decreases with increasing Mn content. Liu et al. [13] reported that the saturated magnetization of Mn and Zn codoped $SnO_2$ films grown by PLD strongly depends on the carrier concentration.

So far, most of the studies have been focused on the magnetism properties of SMO. Besides the magnetic characteristics, another crucial step towards the realization of SMO devices is to clearly understand its optical properties, especially for Mn related phenomena. A detailed knowledge of the optical properties for SMO material is both of scientific interest and of important for devices applications. There have been some studies about the optical properties of pure $SnO_2$ [14,15], and the optical studies on SMO also have been concerned. Very recently, we have investigated the electronic and optical properties of SMO films [10]. However, the optical properties of SMO are still limited and deficient. In particular, the temperature effect on optical properties

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of SMO with different Mn composition was not discussed in detail. Therefore, a detailed spectral study is still necessary to exploit its optoelectronic applications of SMO materials.

It should be noted that the absorption spectrum of semiconductors can be generally divided into two regions: one is the intrinsic absorption region, which results from the optical transitions of electrons from the valence band to the conduction band, and the other is the Urbach absorption region, which results from interactions other than band-to-band transitions, such as electron holes, electron phonons, and electron impurities [16]. The structural properties, which are influenced by growth and processing procedures, could have a significant effect on the performance of SMO based devices. Therefore, a profound understanding of the band-tail characteristics in SMO is important not only for the elucidation of the structure and material quality, but also for the improvement of the relevant semiconductor devices.

In this article, we present a systematical and detailed investigation of temperature dependent optical transmittance in the SMO films with the aid of the comparison of experimental data with available theoretical models. These results not only provide reliable data for the optical properties of SMO films, but also address the dependence of these optical properties on the temperature and Mn composition. Furthermore, the temperature dependence of the optical band gap (OBG), Urbach band tail, and optical constant were also discussed in detail.

## 2. Experimental details and structural characterization

The SMO nanocrystalline films were prepared by PLD in an ambient of high vaccum ($1 \times 10^{-4}$ Pa). The SMO targets were prepared using a conventional solid-state reaction sintering. During the preparation, MnO powder was mixed with $SnO_2$ powder (99.99%) in which Mn mole fraction was varied as 2.5, 5, 7.5, 10, and 12.5%, respectively. Double-side polished quartz, which was selected for the ultraviolet transmittance measurements, was used as the substrates. A Q-switched pulse Nd:YAG (yttrium aluminum garnet) laser (532 nm wavelength, 5 ns duration), which works at a repetition rate of 10 Hz and a energy of 40 mJ/pulse, was used for target ablation. The films were annealed at 900 °C in an oxygen ambience by a rapid thermal annealing process after the deposition. A detailed preparation and characterization can be found in Ref. [10].

The crystalline structure of the SMO films was analyzed by X-ray diffraction (XRD) using Cu $K\alpha$ radiation (D/MAX-2550 V, Rigaku Co.). There are the diffraction peaks (1 1 0), (1 0 1), (2 0 0), (2 1 1) and (2 2 0) from the X-ray diffraction (XRD) analysis [11], which confirm that the films are polycrystalline and exhibit the tetragonal rutile phase (not shown). Note that there are no $MnO_2$ or other impurity phases in the SMO films when the Mn composition is up to 12.5% in the experimental error range. It indicates that the Sn lattice position is partly occupied by the Mn dopant and the replacement is indeed realized in the $SnO_2$ matrix. The temperature dependent transmittance spectral measurement of SMO was performed on a double beam ultraviolet-infrared spectrophotometer (PerkinElmer Lambda 950) at the photon energy from 0.5 to 6.5 eV (190–2650 nm) with a spectral resolution of 2 nm. The film samples were under a variable temperature (5.3 K ≤ T ≤ 300 K) closed-cycle refrigerator system (Janis SHI-4-1). Note that the temperature dependent transmittance experiment of the quartz substrate was carried out under the same condition. To eliminate the effects from the windows of cryostat, the transmittance spectra of the quartz windows were also recorded at the corresponding temperature. It should be emphasized that no mathematical smoothing has been performed on the experimental data.

## 3. Results and discussion

### 3.1. Theoretical consideration

A three-phase layered structure (air/film/substrate) was used to calculate the transmittance spectra of the SMO nanocrystalline films [17]. At the normal incident configuration, the transmittance coefficient for light passing through the samples can be calculated using: $t = t_{01}t_{12}e^{-i\delta}/(1 + t_{01}t_{12}e^{-2i\delta})$. Where, the partial transmittance coefficient $t_{01}$ (air–film) and $t_{12}$ (film–substrate) are written as $t_{i,i+1} = 2\sqrt{\tilde{\varepsilon}_i}/\sqrt{\tilde{\varepsilon}_i} + \sqrt{\tilde{\varepsilon}_{i+1}}$ and the phase factor for the film with thickness $d$ is described by $\delta = 2\pi d\sqrt{\tilde{\varepsilon}_1}/\lambda$. Here, $\lambda$ is the incident wavelength, and the dielectric functions of vacuum, the film, and the substrate are $\tilde{\varepsilon}_0$ (=1), $\tilde{\varepsilon}_1$, and $\tilde{\varepsilon}_2$, respectively. Therefore, the spectral transmittance can be readily obtained from $T_{ran} = Real(\sqrt{\tilde{\varepsilon}_2})tt^*$. It should be noted that the absorption from the substrate must be taken into account to calculate the transmittance of the film–substrate system. And the refractive index $n$ and extinction coefficient $k$ of the substrate could be obtained from fitting the temperature dependent transmittance spectra of quartz. For wide band gap semiconductor materials, the dielectric response, which can be described by the contribution from the lowest three-dimensional $M_0$ type critical point (CP), is written as the following Adachi's model [18]:

$$\tilde{\varepsilon}(E) = \varepsilon_r(E) + i\varepsilon_i(E) = \varepsilon_\infty + \frac{\{A_0[2 - (1+\chi_0)^{1/2} - (1-\chi_0)^{1/2}]\}}{(E_g^{3/2}\chi_0^2)} \quad (1)$$

where, $\chi_0 = (E + i\Gamma)/E_g$, $\varepsilon_\infty$ is the high-frequency dielectric constant, $E_g$ the fundamental optical transition energy, $E$ the incident photon energy, $A_0$ and $\Gamma$ the strength and broadening parameters of the $E_g$ transition, respectively. The dielectric functions of the SMO films can be uniquely determined by fitting the function model to the experimental data. Furthermore, the above Adachi's model, which abides by the Kramers–Krönig transformation in the entirely measured photon energy region, is successfully applied in many semiconductor and dielectric materials [16,19]. According to the dielectric function, the refractive index and extinction coefficient can be obtained as: $n(E) = \sqrt{[\varepsilon_r(E)^2 + \varepsilon_i(E)^2]^{1/2} + \varepsilon_r(E)}/2$ and $k(E) = \sqrt{[\varepsilon_r(E)^2 + \varepsilon_i(E)^2]^{1/2} - \varepsilon_r(E)}/2$.

The fact that thermal broadening of the band tails can modify the optical-absorption edge according to Urbach–Martienssen rule, which is a very general phenomenon for semiconductors [20]. The absorption coefficient $\alpha(E)$ follows the relation: $\alpha(E) = \alpha_0 \exp[\sigma(E - E_0)/\kappa_B T]$. Where $\sigma$ is known as the steepness parameter, $\alpha_0$ is a material parameter, and $E_0$ is the energy of band gap at zero temperature. Note that $\sigma$, $\alpha_0$, $E_0$ are independent of the incident energy. The steepness parameter $\sigma$ of the Urbach rule, which describes the optical absorption coefficient just below the band gap, is given by the empirical relation [20]: $\sigma = 2\sigma_0\kappa_B T/h\nu_p \cdot \tanh(h\nu_p/2\kappa_B T)$. Here $\sigma_0$ is proposed to be the exciton–phonon interaction strength, and is a temperature-independent constant. The energy parameter $h\nu_p$ was considered to be an average phonon energy that accounts for the real spectral distribution of the vibrational density of states in electron–phonon coupling.

### 3.2. Optical band gap

In order to understand the effect of Mn composition on the electronic structure of SMO, optical transmission spectra have been investigated. As an example, the experimental transmittance spectra of the SMO films with different Mn composition recorded