P-type SnO thin films and SnO/ZnO heterostructures for all-oxide electronic and optoelectronic device applications

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Abstract

Tin monoxide (SnO) is considered as one of the most important p-type oxides available to date. Thin films of SnO have been reported to possess both an indirect bandgap (~0.7 eV) and a direct bandgap (~2.8 eV) with quite high hole mobility (~7 cm²/Vs) values. Moreover, the hole density in these films can be tuned from 10¹⁵-10¹⁹ cm⁻³ just by controlling the thin film deposition parameters. Because of the above attributes, SnO thin films offer great potential for fabricating modern electronic and optoelectronic devices. In this article, we are reviewing the most recent developments in this field and also presenting some of our own results on SnO thin films grown by pulsed laser deposition technique. We have also proposed a p-n hetero-structure comprising of p-type SnO and n-type ZnO which can pave way for realizing next-generation, all-oxide transparent electronic devices.

Keywords: p-type SnO, p-type TCO, SnO/ZnO heterostructures

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1. Introduction

Transparent semiconducting oxides (TSO) constitute an important class of materials which are widely used in numerous unconventional areas of applications[1,2]. Many variety of materials which belongs to this group have been reported since the first report of such an oxide (CdO) in 1907[3]. SnO_2 , In_2O_3 , ZnO and dozens of its doped versions are well known n-type TSOs that are widely tested for various electronic/optoelectronic devices as passive or active components. Majority of known TSOs show n-type conduction. P-type TSOs are very few in number and their performance is not as good as their n-type counterparts. Performance of p-type oxide materials is mainly limited by the low mobility of holes in the valence band compared to the mobility of electrons in the conduction band. In most of the p-type oxide semiconductors, valence band originates from highly directional oxygen p-orbitals which severely limit carrier transport in a slightly disordered structures[4–6]. However, in SnO , the contributions of Sn 5s states near the top of valence band facilitates appreciable hole mobility and hence is considered a suitable candidate for developing oxides based active electronic devices[7]. The interest in SnO thin film research got further ignited by the report of its use as a channel layer in a p-type thin film transistor (TFT) in the year 2008[8]. After this, many reports have appeared regarding the deposition and characterization of SnO thin films, a vast majority of which were concentrated specifically for TFT applications[9–15]. In view of the numerous advantages of SnO over other p-type oxides, in this paper we made an attempt to review the recent developments in SnO thin film research for device applications.

SnO is a metastable phase of Sn-O system which undergoes disproportionation reaction to Sn and SnO_2 above certain temperatures[16,17]. According to Moh, SnO phase is stable up to 270°C

[17]. The study conducted by Platteeuw et al. showed partial decomposition of SnO into Sn and SnO₂ at 300°C [18]. Gieffers et al. also reported that SnO undergoes decomposition at 300°C [19]. The rate of decomposition reaction depends strongly on the temperature. At 300°C, the reaction is very slow and it takes more than 50 hours to start the reaction, whereas at temperatures above 400°C the reaction becomes too fast and SnO gets fully decomposed within a few minutes. These studies were conducted on powder samples by annealing in vacuum conditions. However, in thin film research there are many reports indicating the stability of SnO films even at temperatures much higher than these values. Improved stability in such cases are speculated as an effect of reduced surface area of the film compared to the powder samples [20,21].

2. Crystallographic properties of SnO

At normal pressures, SnO forms a PbO type layered structure with tetragonal unit cells (α -SnO) that belongs to $P4/nmm$ space group [22,23]. As shown in the figure 1, each Sn atom in SnO has four O neighbors, all of them located at the same side of Sn atom forming a pyramid structure [24]. The positive charges on Sn²⁺ ions in SnO are screened by the electron charge clouds of Sn 5s states that do not participate in the bonding. These charge clouds are distributed between the Sn planes and reduce the columbic repulsion between them [25]. This non-bonding electron distribution is termed as lone pairs and is considered as an intermediate state between an inert spherical s^2 type orbital that is centered around the nucleus and a non-bonded hybridized orbital lobe that is localized away from the atomic nucleus [26]. However, Sn 5s² electrons are not chemically inert. These electrons strongly interact with oxygen p states giving rise to bonding and antibonding states. These antibonding states appear at the top of the upper valence band [27]. Walsh et al. suggests that, if cation s states and anion p states are closer in

energy, then strong interaction between them can lead to active lone pairs with distorted crystal structures for the stabilization of occupied electronic states[27].

A number of computational studies using density functional theory (DFT) have been conducted on SnO to understand its crystal structure [28–32]. Table 1 summarizes the lattice parameter values reported from experimental studies and computational analysis. The deviation of computed lattice parameters from experimental values are reported due to the non-consideration of van der Waals interaction between SnO layers while considering models for computational analysis. Including these interactions in computational analysis predicts more reasonable lattice parameters and bandgap values [29]. A hybrid-DFT approach predicts that though O defects do not affect the crystal structure too much, interstitial Sn causes significant distortions in SnO crystal structure by displacing Sn and O atoms away from interstitial Sn[33].

3. Band structure and electronic properties

The electronic structure of SnO has been studied in various theoretical models and experiments [32,34,35]. Assuming complete oxidation, Sn in SnO possesses $5s^2$ ground state. McLeod et al. suggests that, in these types of systems, valence band maximum (VBM) is dominated by O $2p$ states [35]. But, resonant photo emission studies on SnO indicates that Sn $5s$ levels hybridize with O $2p$ levels to form the highest occupied states while Sn $5p$ and O $2p$ states contribute to lowest unoccupied states [34].

The band structure and projected density of states (PDOS) analysis using first principle calculations shows that the maximum energy region of the valence band is mainly derived from

nearly equal contributions of O 2*p* and Sn 5*s* states while conduction band minimum (CBM) shows strong nature of Sn 5*p* orbitals (figure 2a)[28]. Many of the later computational analysis agree well with this kind of band formation in SnO in which Sn 5*s* states have greater impact than Sn 5*p* states on valence band [24,31,36].

The defect analysis in SnO shows O_i and V_{Sn} as most favorable defect states under O rich conditions. However, O_i does not contribute to the hole electrical conductivity as it is not likely to get ionized at normal temperatures. The formation energy for Sn_i is high and not very likely to affect the electronic properties of SnO (figure 2b). On the other hand, V_{Sn} introduces acceptor like defects near VBM and is not found to affect the lone pair electron distribution in the open space[28]. Almost similar predictions were made by hybrid-DFT analysis performed by Allen et al.[33]. The observed p-type conductivity in SnO can then be considered mainly as a consequence of Sn vacancy rather than O interstitial. According to Varley et al., native p-type conduction due to tin vacancy is promoted by hydrogen, forming V_{Sn} -H complexes which acts as shallow acceptors[37].

Experimentally, p-type conduction was reported in cation deficient SnO thin films [8,23]. Pan et al. suggested that in this situation some of the Sn atoms transform to Sn^{3+} state to maintain the charge neutrality[23]. This transformation is equivalent to Sn^{2+} and a weakly bonded hole. These holes are responsible for creating acceptor levels in the bandgap close to VBM [23]. Deposition conditions greatly affect the electronic properties of the resulting SnO thin films. Deposition at reduced oxygen pressure reduces the O chemical potential relative to Sn chemical potential which favors small defect formation energies for p-type defects such as O_i and V_{Sn} [33].

Valence band electronic structure, determined from x-ray photo electron spectroscopy (PES) of epitaxial SnO thin films is shown in the figure 3 (arrows in the figure indicate the observed positions of the Fermi Energy). Since the photo ionization cross section between Sn 5s and O 2p is much higher for hard x-rays (HX-PES with 7940 eV) than for soft x-rays (SX-PES with 1486 eV), the spectral enhancement in HX-PES supports the theoretical predictions of Togo et al. that VBM has major contribution from Sn 5s states [38].

Band structure of SnO shows an anisotropy in hole effective mass at VBM. Electron lone pairs, centered around the Sn atom, spread into the open space between the layers which promotes the hole conduction much easily in the $\Gamma \rightarrow Z$ direction. Allen et al. computed an effective mass of $2.6 m_0$ (m_0 is the electron rest mass) for holes at VBM and $0.27 m_0$ for electrons at CBM [33]. This large difference in hole and electron effective masses suggests that electron mobility in SnO will be much higher than the hole mobility. However, Liu et al. reported very low effective mass for holes in SnO (0.172 - $0.538 m_0$ for holes and 0.107 - $0.58 m_0$ for electrons) [30]. They showed that the effective mass of holes ($0.172 m_0$) is smaller than the effective mass of electrons ($0.58 m_0$) in $\Gamma \rightarrow Z$ direction.

Metastability of SnO causes the coexistence of metallic Sn or SnO₂ phases along with SnO phase in the thin films. This often makes the quantitative analysis of the chemical composition of the deposited thin films very essential. Most of the authors report the chemical compositions of the SnO thin films by Sn 3d core level x-ray photoelectron spectroscopic (XPS) analysis. The valence states of Sn are almost indistinguishable from Sn 3d_{5/2} or 3d_{3/2} core level photo emission spectra

as the chemical shifts of Sn^{2+} and Sn^{4+} from Sn^0 state is very small and binding energy difference of Sn^{2+} and Sn^{4+} from O 1s is also very small (see figure 4a and table 2). However, the measurement of energy separation between Sn $4d_{5/2}$ peak and leading edge of valence band can clearly distinguish between SnO and SnO_2 [39]. Figure 4b shows the XPS spectra of valence band and Sn $4d$ core level of SnO and SnO_2 , which shows increased separation between valence band and Sn $4d$ core level in SnO [39]. The additional states at VBM of SnO is attributed to lone pair Sn $5s$ states which are also supported by the density of states calculations by computational analysis [28,33]. The binding energy difference between Sn $4d$ level and the leading peak of valence band is 21.5 eV for SnO_2 and 23.1 eV for SnO which shows a separation of 1.6 eV between the peaks of SnO and SnO_2 . The increased separation of SnO peak is a consequence of the smaller bandgap of SnO compared to SnO_2 [39].

Vibrational frequencies of optical phonons in SnO

Raman spectroscopy is a powerful tool used for characterizing SnO as it can clearly distinguish various oxidation states of Sn. Raman scattering in SnO can even be used as a fingerprint to predict the crystallographic orientation in SnO thin films[40]. Geurts et al. predicted following vibrational modes for SnO [41]:

$$\Gamma = A_{1g} + B_{1g} + 2E_g + A_{2u} + E_u + 3 \text{ acoustic modes}$$

Among these, four modes ($A_{1g}, B_{1g}, E_g, E_g''$) are Raman active and two modes (A_{2u}, E_u) are IR active. In A_{1g} mode, Sn atoms vibrate towards or away from O atoms. B_{1g} mode involves out of plane vibrations of O atoms and E_g mode involves the in-plane vibrations of Sn and O atoms within their sub-lattice and with respect to each other sub-lattice. In IR modes Sn sub-lattice is displaced with respect to O sub-lattice which results a dipole moment in the molecule along c-

axis (A_{2u}) or perpendicular to c-axis (E_u). Figure 5 shows schematic representation of various modes of vibration in SnO.

Table 3 lists the possible vibrational frequencies in SnO. There is some controversy regarding the frequency of B_{1g} vibrational mode. Geurts et al. has reported experimental observation of B_{1g} vibrational mode at 113 cm^{-1} [41]. However, theoretical calculations predict almost three times higher vibrational frequency for B_{1g} mode. Latest understanding about different vibrational modes in SnO suggests that the assignment of Raman shift at 113 cm^{-1} to B_{1g} mode is not precise and this fits more to low frequency E_g vibrational mode [32,40,42].

4. SnO thin film research

4.1 Thin film deposition

Most of the SnO thin film deposition work reported in literature has been performed using physical vapor deposition (PVD) techniques like sputtering [43–47], pulsed laser deposition (PLD) [8,48–50], and evaporation techniques [20,51,52]. As SnO is not a thermodynamically stable material, most of the PVD growth methods have a very narrow process window to get phase pure SnO thin films, particularly if the target material is metallic Sn. Phase purity of the deposited films strongly depends on the deposition conditions like oxygen partial pressure, deposition rate, growth temperature and energy involved in the process. Slight deviation from the optimized conditions may result in mixed phases of SnO with metallic Sn and/or SnO_2 impurities. Phase separation between these phases can lead to irregular electrical conduction in the films [53].

The first and the most important step in any PVD process is the selection of a suitable target material. Preparation of a ceramic target from SnO powder by conventional pellet pressing and sintering process is very difficult and always leads to impurity phases of SnO₂ and metallic Sn. Hosono et al. employed spark plasma sintering process at 320 °C to get phase pure SnO ceramic target for pulsed laser deposition [49]. However, precipitation of metallic Sn was observed at slightly higher sintering temperature (340 °C). Because of the difficulties associated with target preparation, majority of research groups have used either metallic Sn [9,14,43,46] or SnO₂ [20,51–55] as target material for depositing SnO thin films. However, low melting point of metallic Sn severely limits the maximum power that can be used in the deposition process. Hsu et al. recently demonstrated that this issue can be overcome by the use of mixed phase target [11]. They prepared mixed phase Sn/SnO₂ sputtering target by hot pressing of SnO powder at high temperature and pressure.

Pan et al. reported the epitaxial growth of SnO thin films on α -Al₂O₃ substrate ($\bar{1}012$) by electron beam evaporation technique [23]. Epitaxial growth was achieved by heating the substrate up to 600 °C during the deposition process. Ogo et al. reported epitaxial SnO thin film growth at 575 °C by PLD technique on yttria stabilized zirconia (001) substrates [8]. Deposition on other substrates often gives amorphous or poly-crystalline thin films [52]. The optimum growth/annealing temperature strongly depends on the ambient oxygen partial pressure during the thin film growth/annealing process. Many groups have reported poly-crystalline SnO phase formation at around 300 °C for several different PVD growth techniques (table 4).

We have demonstrated the growth of single phase SnO films on sapphire (0001) substrates over a temperature range of 250-550°C. We used KrF laser with an energy density 1.8 J/cm^2 at 5 Hz repetition rate to ablate a sintered SnO target. Figure 6 shows the Raman spectra of our PLD grown SnO thin films on sapphire substrate. Pure SnO phase was obtained in all films deposited at substrate temperatures ranging from 250 to 550 °C as indicated by the A_{1g} peak of SnO at 211 cm^{-1} . No other impurity peaks were observed in the Raman spectra.

SnO thin films can get oxidized due to the surface reaction with atmospheric O and/or due to the internal dis-proportionation reaction [47,56]. Exposure of SnO films to air over an extended period of time can lead to the formation of an ultra-thin layer of SnO₂ due to the air oxidation, even at room temperature [20,39]. According to Pan et al., SnO reacts with chemisorbed O in the film surface at temperatures >200°C and form a very thin layer of SnO₂ on the surface [55]. In the temperature range of 300-500°C, oxidation process mainly occurs through internal oxidation through local O dis-proportionation reaction. This internal O dis-proportionation can result in excess O (which can exist between the layers of SnO) and the segregation of metallic Sn in the film [41,55,57]. This reaction can be represented by $(1+x)\text{SnO} \rightarrow x\text{Sn} + \text{SnO}_{1+x}$ which results the formation of higher, less stable, oxidation states of tin oxides and precipitation of metallic Sn [41]. At still higher temperatures, O diffusion in the crystal lattice is fast which promotes further oxidation process in the film to form SnO₂ phase.

4.2 Electrical properties

SnO thin films exhibit thermally activated conduction process. Ogo et al. reported an activation energy of 45 meV in epitaxial SnO thin films, which suggests an acceptor energy level 90 meV

above the VBM [8]. Poly-crystalline thin films show slightly higher activation energy (60 meV) compared to epitaxial SnO thin films [58]. Polycrystalline thin films also show increased barrier potentials at the grain boundaries which cause mobility deterioration in the films [58]. It has been shown that the SnO thin film texture also influences the mobility of charge carriers. SnO exhibits better hole mobility in the c-axis oriented thin films because of the enhanced hole transport in the a-b plane [48]. Granato et al. recently reported that Sn rich chemical composition in SnO thin films helps to contribute more metallic nature to VBM which results in higher hole mobility in mixed phase (Sn+SnO) thin films than pure SnO thin films [59]. Maximum mobility achieved in phase pure SnO thin film is $\sim 7 \text{ cm}^2/\text{Vs}$, whereas it is $18.7 \text{ cm}^2/\text{Vs}$ in the film having metallic Sn content along with SnO phase (table 5).

Optical bandgap

It has been reported that SnO possess both direct as well as indirect bandgaps. Computational studies suggest an indirect bandgap of 0.3-0.6 eV, which is slightly less than experimentally reported values [24,30,31,35,60]. These smaller values are often the result of underestimation of excited states energy in DFT calculation. In the case of direct bandgap, theoretical studies deviate to a great extent from experimentally reported values [28,30]. In order to resolve this discrepancy, Allen et al. incorporated van der Waals corrections in their first principle calculations [29]. However they found that though the incorporation of the above correction term predicts the lattice parameters very close to experimental values, it still under-estimates the fundamental indirect and direct bandgap values. Hybrid DFT analysis, with empirical dispersion corrections, showed an improvement in the band structure, predicting the indirect bandgap value

0.61-0.67 eV and direct bandgap value 2.6-2.76 eV, which are in good agreement with the experimental values [8,9,33,36].

4.3 Bipolar conduction and doping

Recently, there were reports about bipolar conduction in doped SnO thin films. The origin of bipolar conductivity in SnO is attributed as a consequence of very small fundamental bandgap, small ionization potential and large electron affinity [36,37,49]. Specifically, the VBM in SnO is located 5.8 eV below the vacuum level, similar to p-type oxides like Cu₂O and NiO while the CBM lies 5.1 eV below the vacuum level similar to n-type oxides like ZnO and In₂O₃[50]. This makes it possible to align both the band edges of SnO within electron and hole doping regimes (figure 7).

According to Hosono et al., a material with small indirect transition gap and large direct transition gap can be considered as an ideal candidate to exhibit transparent bipolar conduction [49]. They were able to change the carrier type from holes to electrons by doping with Sb (>5% Sb atoms in the SnO target). They showed that Sb substitutes Sn, and form $\text{Sb}_{\text{Sn}}^{3+}$ donor like defects in SnO. In contrast to above, Guo et al. reported an entirely different trend. Specifically they observed an improvement in p-type conductivity of SnO thin films by doping with Sb[52]. According to them the coulomb binding between $\text{Sb}_{\text{Sn}}^{3+}$ and the native defects results in the formation of charged defect complexes; $\text{Sb}_{\text{Sn}}^{3+} + 2\text{V}_{\text{Sn}}^{2-} \rightarrow (\text{Sb}_{\text{Sn}} - 2\text{V}_{\text{Sn}})^{-}$, and these defect complexes act as acceptors. However, recent DFT analysis shows that Sb substitution at O sites and Sb interstitials have much large formation energies than Sb substituting Sn sites [37]. Sb_{Sn} acts as shallow donor states and can lead to n-type conduction by suppressing $\text{V}_{\text{Sn}}\text{-H}$ complexes which compensates n-type doping. N-type conduction has also been reported on changing the

oxygen content in the film [43,46]. In this case, the p-type conduction in SnO is gradually compensated by the formation of SnO₂ phase and after full oxidation, the films show n-type conduction.

5. SnO-ZnO System

ZnO is an n-type wide bandgap (~3.3 eV) semiconductor that has been the topic of intense research for many decades. A wide variety of structures and devices have been developed using pure and doped forms of ZnO [61–66]. One of the interesting feature of ZnO is its large excitonic binding energy (60 meV) which helps to achieve room temperature lasing action. Wang et al. recently reported ZnO-SnO nano composites as a better candidate for enhanced random lasing action (figure 8)[67]. According to them the carriers generated in SnO nanoparticles by optical absorption can easily move to ZnO nanorods. In addition, the defect emission of SnO nanoparticles is close to the band emission of ZnO nanorods which promotes resonant energy transfer between SnO and ZnO and thereby enhances the random lasing action of ZnO.

P-n junction is the basic building block of a wide variety of semiconductor devices. Therefore, fabrication of SnO p-n junction with compatible n-type oxides will have great impact on optoelectronic device development. Yang et al. has reported the fabrication of p-n junction using p-SnO and n-SnO₂:Sb on SiO₂ substrate with Ni as contact electrode to SnO and Ag to SnO₂. This diode exhibited a threshold voltage of 2.88 V, with ideality factor 6.4 [68]. Um et al. reported the fabrication of SnO/SnO₂ p-n junction using reactive RF magnetron sputtering technique [69]. However, the forward current through the junction was of the order of micro

amperes and the threshold voltage was very high. Hosono et al. fabricated a homo junction diode with threshold voltage 0.7 V, using p-type SnO and n-type SnO:Sb on YSZ/ITO substrate [49].

Tsai et al. reported nano heterojunction by depositing p-type SnO on hydrothermally grown n-type ZnO nanorods [70]. These junctions were sensitive to UV light illumination with fast response time showing its potential for use in photo detection and optical sensing applications (figure 9). Sanal et al. reported the fabrication of transparent p-n heterojunction using sputtered p-type SnO and n-type ZnO thin films. The junction showed rectifying behavior with forward to reverse current ratio of 12 at 4.5 V with an ideality factor of 11.2 [71]. High ideality factor was attributed to high density of defects at SnO/ZnO interface.

Even though SnO/ZnO heterojunction is an interesting candidate for various optoelectronic applications, these are not well studied systems. Further studies about the electrical conditions at SnO/ZnO interface is required to understand the current conduction through this junction. Energy band diagram is a good starting point to analyze the electrical performance of any p-n junction. Figure 10 shows the energy band diagrams of SnO and ZnO before and after forming the junction. For SnO thin films, Ogo et al. have reported an ionization potential of 5.8 eV and Fermi level 0.15 eV above the VBM [8,38]. So, based on electron affinity rule, SnO/ZnO junction would show a conduction band offset of 0.9 eV and a valence band offset of 1.7 eV. Assuming an acceptor density of $3.5 \times 10^{18} \text{ cm}^{-3}$ in SnO and donor density of $3 \times 10^{18} \text{ cm}^{-3}$ in ZnO, the built-in barrier potential across the junction would be 1.05 eV. As the relative permittivity of SnO is very large (18.8) [72] compared to that of ZnO (8.5), equilibrium electrostatic analysis shows an upward bending of the band edge in ZnO by 0.75 eV and downward bending of band

edge in SnO by 0.3 eV from the bulk of the respective semiconductor. Current in such a junction will mainly be limited by the band offset values. Since the barrier for holes to conduct from SnO to ZnO is large, the current in SnO/ZnO junction would be dominated by electron injection from ZnO, during forward bias.

6. Conclusion

We have outlined the potential of SnO thin films towards realizing all oxide transparent p-n junctions. Bipolar conduction process in SnO makes it an ideal material for developing transparent homo-junction devices even on flexible substrates. However, achieving high conductivity and mobility in SnO is still a challenge that needs to be addressed in future studies. The mechanism of doping in SnO is not yet clear as there are controversial reports of creating donor-like and acceptor-like defects with same type of dopants. So, more dopants have to be tried and significant efforts need to be made to improve the hole density in the films. Getting higher hole mobility in SnO films is also desired to realize better performing optoelectronic devices. Finally, we have shown that the integration of SnO films with n-type ZnO has the potential to facilitate next-generation all-oxide electronic and optoelectronic devices.

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List of Tables

Table 1. Lattice parameters of SnO.

a=b (Å)	c (Å)	Type	Ref.
3.8029	4.8382	exp.	[19]
3.7986	4.8408	exp.	[25]
3.801	4.835	exp.	[26]
3.797	4.6513	comp.	[27]
3.885	4.983	comp.	[28]
3.810	4.915	comp.	[29]
3.8989	4.9812	comp.	[30]
3.801	4.843	comp.	[31]

Table 2. Comparison of reported binding energies of Sn $3d_{5/2}$, Sn $3d_{3/2}$ and its shift from O 1s line in SnO and SnO₂. The binding energy difference between Sn²⁺ and Sn⁴⁺ is only 0.3 eV in Sn $3d_{5/2}$ and Sn $3d_{3/2}$ core level spectra.

Oxidation states	Binding Energy E _{BE} (eV)			ΔE _{BE} with O 1s		Ref.
	Sn $3d_{5/2}$	Sn $3d_{3/2}$	O 1s	Sn $3d_{5/2}$	Sn $3d_{3/2}$	
Sn ⁰	485.1					[35]
Sn ⁰	484.9					[38]
Sn ⁰	484.65					[39]
Sn ²⁺	486.2					[35]
Sn ²⁺	485.6	494.0	529.7	44.1	35.7	[17]
Sn ²⁺	486.5					[40]
Sn ²⁺	486.4					[38]
Sn ⁴⁺	487.1					[35]
Sn ⁴⁺	486.6	495.0	530.4	43.8	35.4	[17]
Sn ⁴⁺	487.1					[38]
Sn ⁴⁺	486.4					[39]

Table 3. Phonon frequencies of SnO in units of cm^{-1} .

Vibrational	Ref [42]	Ref [41]	Ref [27]	Ref [43]
mode	Expt.	Expt.	Theory	Theory
A_{1g}	211	210	211	211-212
B_{1g}	113		370	350-357
E_g		110	143	113-122
E_g''			494	450-460
A_{2u}			396	240
E_u	260		296	267-271

Table 4: Optimum growth/annealing temperature for poly-crystalline SnO thin film preparation using different PVD techniques.

Deposition	Target	Substrate/Annealing	Ref.
technique	material	temperature ($^{\circ}\text{C}$)	
E-beam evaporation	SnO_2	350	[20]
RF magnetron sputtering	SnO	300	[57]
RF magnetron sputtering	SnO_2	300	[55]
PLD (532 nm)	SnO_2	300	[58]
PLD (KrF)	SnO	275-500	[49]
PLD (KrF)	SnO	250-550	our report

Table 5. Optical and electrical properties of SnO thin films.

Deposition technique	Target material	Resistivity (Ω -cm)	Hole density (cm^{-3})	Hole mobility (cm^2/Vs)	Direct bandgap (eV)	Ref.
E-beam evaporation	SnO ₂	58 - 156	2.8×10^{16} - 5.6×10^{16}	1.4 - 1.9	2.77	[17]
PLD	SnO	0.4 - 1.7	3.1×10^{16} - 4.9×10^{19}	0.26 - 2.1	2.7	[49]
PLD	Sn	50 - 140	10^{15} - 10^{17}	1 - 2.8	2.93	[63]
PLD	SnO	-	1×10^{17}	7	2.6	[35]
PLD	SnO	-	2.5×10^{17}	2.4	2.7	[8]
RF sputtering	SnO ₂	1.1 - 31.5	7.2×10^{16} - 5.8×10^{18}	1.02 - 3.0	2.71-2.76	[55]
RF sputtering	SnO	0.81	2.3×10^{18}	3.34		[64]
RF sputtering	SnO	3.76	1.1×10^{18}	1.58	2.78	[57]
RF sputtering	Sn	-	1×10^{18}	1.67		[44]
DC sputtering	Sn	1.5 - 25.3	2.2×10^{17} - 4.8×10^{16}	5.08 - 18.7	2.65-2.92	[9]*
ALD	-	4.9 - 14.5	3.5×10^{17} - 1.6×10^{18}	0.4 - 2.9	2.6 - 2.7	[65]
PLD	SnO	1.1	7.8×10^{17}	7.35	2.85	our report

*for various Sn+SnO compositions in the films. Mixed phase of Sn and SnO showed maximum mobility than pure SnO phase.

List of Figures

Fig 1. (a) Crystal structure of SnO (Gray and red spheres represents tin and oxygen atoms respectively. (b) top view of SnO.

Fig 2. (a) Band structure (left) and PDOS (right) of the unit cell of the SnO perfect crystal. The energy of the highest occupied band at the Γ point is set to 0 eV. The highest occupied state is located between the Γ and M points. The lowest unoccupied state is given at the M point. The background of the band structure and PDOS figures denotes three characteristic energy regions in the valence band. (b) Formation energies as a function of the Fermi level at the O-rich limit after the band-gap correction. The shaded area denotes a variable range of the Fermi level at temperatures between 300 K and 1000 K determined from charge neutrality. Reprinted figure with permission from A. Togo, F. Oba, I. Tanaka, K. Tatsumi, Physical Review B, 74, 195128, 2006. Copyright 2006 by the American Physical Society.

Fig 3. VB PES spectra of SnO and SnO₂ films. Excitation sources are (a) soft X-ray Al K α ($h\nu = 1486$ eV, SX-PES) and (b) hard X-ray SR ($h\nu = 7940$ eV, HX-PES). Reprinted figure with permission from Y. Ogo, H. Hiramatsu, K. Nomura, H. Yanagi, T. Kamiya, M. Kimura, M. Hirano, H. Hosono, Physica Status Solidi A, 206, 2187, 2009. Copyright 2009 by John Wiley and Sons.

Fig 4. Schematic diagram of the relative positions of various oxidation states of Sn and O 1s level. Right side figure: XPS spectra of valence-band and near-core region of air-oxidized SnO (middle curve labeled SnO₂), sputtered SnO (top curve), and SnO₂ single crystals [SnO₂

(110),bottom curve]. The solid line represents smoothed data, and the binding-energy scale refers to the Fermi level. The VB region has been magnified with respect to the Sn 4d region on which the data have been normalized. Reprinted figure with permission from J.M. Themlin, M. Chtaïb, L. Henrard, P. Lambin, J. Darville, J.M. Gilles, Physical Review B, 46,2460, 1992. Copyright 1992 by the American Physical Society.

Fig 5. Schematic representation of different types of atomic vibrations in SnO. Gray spheres represent Sn atoms and red spheres represent O atoms.

Fig 6. Raman spectra of SnO thin films deposited on sapphire substrate using PLD technique. Substrate temperature during deposition is shown on corresponding spectra.

Fig 7. Band edge alignment of n-type and p-type oxide semiconductors. SnO has both its band edges between electron and hole doping limit. Various data are taken from [8,67–74].

Fig 8. (a) Emission spectra of random lasers compared between ZnO NRs and ZnO/SnO composite under the same pumping energy of 90 μJ . (b) Comparison of PL measurements between ZnO NRs and ZnO/SnO composite.Reprinted figure with permission fromC.S. Wang, H.Y. Lin, T.H. Lin, Y.F. Chen, AIP Adv. 2, 012133, 2012.

Fig 9. Transient response of photocurrent density of the p-SnO/n-ZnO under UV light (254 nm, $6\text{mW}/\text{cm}^2$) illumination.Reprinted figure with permission from F. Tsai, S. Wang, Y.Tu, Y. Hsu,

C. Kuo, Z. Lin, and R.Ko, Applied Physics Express, 4, 025002, 2011. Copyright 2011 by TheJapan Society of Applied Physics.

Fig 10. (a) Band diagram of SnO and ZnO (b) Band alignment after junction formation.

Figure 1

Figure2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10