Decoupling free-carriers contributions from oxygen-vacancy and cation-substitution in extrinsic conducting oxides

Y. H. Lin,¹ Y. S. Liu,¹ Y. C. Lin,¹ Y. S. Wei,¹ K. S. Liao,² K. R. Lee,² J. Y. Lai,² H. M. Chen,³ Y. C. Jean,³ and C. Y. Liu^{1,a)}

¹Department of Chemical and Materials Engineering, National Central University, Zhongli 32001, Taiwan

²R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Zhongli 32023, Taiwan

³Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA

(Received 7 August 2012; accepted 2 January 2013; published online 18 January 2013)

The intrinsic oxygen-vacancies and the extrinsic dopants are two major fundamental free-carrier sources for the extrinsic conducting oxides, such as Sn-doped In_2O_3 . Yet, the individual contributions of the above two free-carrier sources to the total carrier concentrations have never been unraveled. A carrier-concentration separation model is derived in this work, which can define the individual contributions to the total carrier concentration from the intrinsic oxygen-vacancies and the extrinsic dopants, separately. The individual contributions obtained from the present carrier-concentration separation model are verified by the two-state trapping model, photoluminescence, and positron annihilation lifetime (PAL) spectroscopy. In addition, the oxygen-vacancy formation energy of the Sn: In_2O_3 thin film is determined to be 0.25 eV by PAL spectroscopy. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4776781>]

I. INTRODUCTION

The carrier concentrations of the extrinsic transparent conducting oxides (TCO), such as Sn-doped In_2O_3 (ITO), are known to attribute to the intrinsic oxygen vacancies and the extrinsic dopants (so-called cation-substitution reaction).^{1–12} In the past, the detail ionization mechanism of the dopants and oxygen vacancies in the extrinsic transparent conducting oxides has been well discussed in the subjects of the defect chemistry of oxides.^{13–18} However, the individual contributions to the entire carrier concentration from the cation-substitution reaction and oxygen vacancies have never been defined. Without this critical information, the detail ionization mechanism of the dopants and oxygen vacancies of the extrinsic transparent conducting oxides cannot be understood. In this study, a carrier-concentration separation model was developed to define the individual contributions of the Sn-doped In_2O_3 thin films from cation-substitution reaction and oxygen vacancies, separately. The individual contributions obtained from the present carrier-concentration separation model are verified by the two-state trapping model and positron annihilation lifetime (PAL) spectroscopy.^{19–22} By knowing the individual contributions from the intrinsic oxygen-vacancies and the extrinsic dopants, the basic physics of the ionization process of the dopants (both the intrinsic and extrinsic dopants) would become accessible.

II. EXPERIMENTAL PROCEDURE

The 200-nm pure In_2O_3 and Sn: In_2O_3 thin films were deposited on the quartz substrates by a magnetron sputtering system. The as-deposited pure In_2O_3 and Sn: In_2O_3 thin films were annealed at the elevated temperature ranging from 200 °C to 600 °C in the low vacuum ambient and the oxygen ambient.

The oxygen partial pressures in the low vacuum ambient and in the oxygen ambient were 1×10^{-2} Torr and 152 Torr, respectively. The carrier concentrations of the annealed pure In_2O_3 and Sn: In_2O_3 thin films were measured by ac-Hall measurement with a van der Pauw configuration. Photoluminescence (PL) spectra were performed on the studied films at room temperature with a 325 nm HeCd laser as the excitation source. PAL spectroscopy was used to determine the types of defects, and used to calculate the oxygen-vacancy formation energy.

III. RESULTS AND DISCUSSIONS

A. Derivation of carrier-concentrations separation model for extrinsic TCOs

The oxygen-vacancy formation and the cation-substitution reaction are the two main mechanisms that create the free carriers in extrinsic TCOs.

1. Oxygen-vacancy mechanism

In this study, we assume every oxygen vacancy in extrinsic TCOs contributes two free electrons, as shown in the following equation:

where $\text{O}_\text{o}^\times$ represents the oxygen sites occupied by oxygen atoms, $\text{V}_\text{o}^{\bullet\bullet}$ is the oxygen vacancy, and the dot in the superscript represents the positive electron charge.

The equilibrium constant (K_I) of Eq. (1a) can be expressed as follows:

$$K_I = C_\text{v} \cdot n^2 \cdot P^{1/2}, \quad (1\text{b})$$

where n is the carrier concentration, C_v is the oxygen-vacancy concentration, and P is the oxygen partial pressure

^{a)}Electronic mail: chengyi@cc.ncu.edu.tw.

in the ambient. In addition, the equilibrium constant (K_I) of Eq. (1a) can be characterized by the Arrhenius equation, as follows:

$$K_I = K' \exp\left(\frac{-g_{f,V}}{kT}\right), \quad (1c)$$

where k is Boltzmann's constant, T is temperature, $g_{f,V}$ is the oxygen-vacancy formation energy, and K' is the pre-exponential constant for the oxygen-vacancy formation.²³ Thus, by combining Eqs. (1b) and (1c), we obtain

$$C_v \cdot n^2 \cdot P^{1/2} = K' \exp\left(\frac{-g_{f,V}}{kT}\right). \quad (1d)$$

2. Cation-substitution mechanism

As the host-cations in the extrinsic TCO are substituted by the doped-cations with a higher valence number, free carriers are created, which is defined as the cation-substitution reaction. For example, in Sn:In₂O₃, a free electron is created as one Sn⁴⁺ substitutes one In³⁺. The cation-substitution reaction in Sn:In₂O₃ is described as

where $\text{Sn}_{\text{In}}^{\bullet}$ represents the Sn⁴⁺ substituting for the host In³⁺. Using the same derivation of Eq. (1d), the equilibrium constant (K_{II}) of Eq. (2a) can be expressed as

$$K_{II} = \frac{[\text{Sn}_{\text{In}}^{\bullet}] \cdot n}{[\text{SnO}_2]} = K'' \exp\left(\frac{-g_{f,S}}{kT}\right), \quad (2b)$$

where $[\text{Sn}_{\text{In}}^{\bullet}]$ is the concentration of the Sn⁴⁺-In³⁺ substitution, the concentration of SnO₂ ($[\text{SnO}_2]$) is equivalent to the Sn-doping concentration in Sn:In₂O₃, $g_{f,S}$ is the reaction energy of the cation-substitution reaction, and K'' is the pre-exponential constant for the cation-substitution reaction. Assume that every Sn⁴⁺-In³⁺ substitution generates a free carrier. Therefore, the Sn⁴⁺-In³⁺ substitution concentration ($[\text{Sn}_{\text{In}}^{\bullet}]$) represents the carrier concentration contributed by the cation-substitution, which is denoted as n_s . Therefore, Eq. (2b) can be further modified as

$$K_{II} = \frac{n_s \cdot n}{[\text{SnO}_2]} = K'' \exp\left(\frac{-g_{f,S}}{kT}\right). \quad (2c)$$

Note that the term in the right-hand side of Eq. (1d) only depends on temperature. Thus, at a specific temperature, the left-hand terms of Eq. (1d) under two distinct oxygen partial pressures, P_1 and P_2 , should be equal, which yields

$$n_{v,1} \cdot n_1^2 \cdot P_1^{1/2} = n_{v,2} \cdot n_2^2 \cdot P_2^{1/2}. \quad (3a)$$

The subscripts (1 and 2) denote the two distinct oxygen partial pressures and n_v is denoted as the carrier concentration contributed by the oxygen vacancies, which is twice the value of the oxygen-vacancy concentration (C_v). Using the same approach above, at a specific temperature, the left-hand terms of Eq. (2c) under two distinct oxygen partial pressures, P_1 and P_2 , should be equal, which yields

$$\frac{n_{s,1} \cdot n_1}{[\text{SnO}_2]_1} = \frac{n_{s,2} \cdot n_2}{[\text{SnO}_2]_2}. \quad (3b)$$

The percentage of Sn-doping ($[\text{SnO}_2]$) in the commercial ITO is approximately 10 wt.%, which equals to an atomic concentration of $3 \times 10^{21} \text{ cm}^{-3}$.¹⁷ The value of $3 \times 10^{21} \text{ cm}^{-3}$ also represents the maximal carrier concentration possibly contributed by the cation-substitution mechanism. However, the typical carrier concentration of the Sn:In₂O₃ is in the order of 10^{20} cm^{-3} , which is approximately one order smaller than the Sn-doping concentration. It implies that only a small percentage of Sn dopants in Sn:In₂O₃ will substitute the In host cations and create the carriers. Therefore, the Sn-doping concentration ($[\text{SnO}_2]$) in Eq. (3b) can be considered as a constant value under different partial pressures (P_1 and P_2), i.e., $[\text{SnO}_2]_1 = [\text{SnO}_2]_2$. Subsequently, Eq. (3b) can be further simplified as

$$n_{s,1} \cdot n_1 = n_{s,2} \cdot n_2. \quad (3c)$$

The total carrier concentration (n) of an extrinsic TCO is the sum of the n_s and n_v . Therefore, the total carrier concentrations (n_1 , n_2) under two distinct oxygen partial pressures, P_1 and P_2 , can be expressed by the carrier concentrations ($n_{v,1}$, $n_{v,2}$) contributed by the oxygen vacancies and the cation-substitution reaction ($n_{s,1}$, $n_{s,2}$), as shown in the following equations:

$$n_1 = n_{s,1} + n_{v,1}, \quad (4a)$$

$$n_2 = n_{s,2} + n_{v,2}. \quad (4b)$$

Multiply Eqs. (4a) and (4b) by n_1 and n_2 , respectively. Subsequently, Eqs. (4a) and (4b) could be re-written as follows:

$$n_1^2 = n_1 \cdot n_{s,1} + n_1 \cdot n_{v,1}, \quad (5a)$$

$$n_2^2 = n_2 \cdot n_{s,2} + n_2 \cdot n_{v,2}. \quad (5b)$$

By combining Eqs. (3c), (5a), and (5b), we can further eliminate $n_{s,1}$ and $n_{s,2}$ and obtain the following equation:

$$n_1 \cdot n_{v,1} = (n_1^2 - n_2^2) + n_2 \cdot n_{v,2}. \quad (6)$$

Using Eq. (3a), $n_{v,2}$ in Eq. (6) can be replaced by $n_{v,1}$ and the total carrier concentrations (n_1 , n_2) at two distinct oxygen partial pressures (P_1 and P_2). Subsequently, as shown in Eq. (7a), $n_{v,1}$ can be expressed by the total carrier concentrations (n_1 , n_2) at two distinct oxygen partial pressures (P_1 and P_2)

$$n_{v,1} = (n_1^2 - n_2^2) \cdot \frac{n_2 \cdot (P_2)^{1/2}}{n_1 n_2 \cdot (P_2)^{1/2} - n_1^2 \cdot (P_1)^{1/2}}. \quad (7a)$$

Using the same approach, $n_{v,2}$ can also be expressed by the total carrier concentrations (n_1 , n_2) at two distinct oxygen partial pressures (P_1 and P_2), as shown in the following equation:

$$n_{v,2} = (n_1^2 - n_2^2) \cdot \frac{n_1 \cdot (P_1)^{1/2}}{n_2^2 \cdot (P_2)^{1/2} - n_1 n_2 \cdot (P_1)^{1/2}}. \quad (7b)$$

Equations (7a) and (7b) imply that, by knowing the total free carrier concentrations (n_1 , n_2) at two different oxygen partial pressures (P_1 and P_2), the carrier concentrations ($n_{v,1}$, $n_{v,2}$) contributed by the oxygen vacancies can be calculated out. In the other words, the carrier concentrations ($n_{v,1}$, $n_{v,2}$) contributed by the oxygen vacancies can be calculated out by knowing the total free carrier concentrations (n_1 , n_2) at two different oxygen partial pressures (P_1 and P_2). Furthermore, as $n_{v,1}$ and $n_{v,2}$ of the extrinsic TCO are known, the carrier concentrations contributed by the cation-substitution reaction ($n_{s,1}$, $n_{s,2}$) of the extrinsic TCO can be deduced by Eqs. (4a) and (4b). Ultimately, the carrier concentration (n_v) contributed by the oxygen vacancies and the carrier concentration (n_s) contributed by the cation-substitution reaction can be separated.

Fig. 1 shows the carrier concentrations (n) of In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ thin films annealed under the low vacuum ambient (P_1) and the oxygen ambient (P_2) at various annealing temperatures. The carrier concentrations of the $\text{Sn}:\text{In}_2\text{O}_3$ thin films can be greatly enhanced by the Sn doping, i.e., the cation-substitution reaction. Using the present separation model, i.e., Eqs. (7a), (7b), and (4b), and the measured total carrier concentrations (n_1 , n_2) of the $\text{Sn}:\text{In}_2\text{O}_3$ thin films under two different oxygen partial pressures (P_1 and P_2), the carrier concentrations contributed by the oxygen vacancies ($n_{v,1}$, $n_{v,2}$) and by the substitution reaction ($n_{s,1}$, $n_{s,2}$) of the $\text{Sn}:\text{In}_2\text{O}_3$ thin films can be calculated out. Fig. 2 plots the calculated carrier concentrations ($n_{v,1}$, $n_{v,2}$) contributed by the oxygen vacancies and the carrier concentrations contributed by the cation-substitution reaction ($n_{s,1}$, $n_{s,2}$) of the $\text{Sn}:\text{In}_2\text{O}_3$ thin films annealed under two distinct oxygen partial pressures (P_1 and P_2).

B. Verification by positron annihilation lifetime spectroscopy

One method to verify the calculated carrier concentrations (n_v) contributed by the oxygen vacancies is to actually

FIG. 1. Carrier concentrations of the In_2O_3 and the $\text{Sn}:\text{In}_2\text{O}_3$ thin films annealed in vacuum ambient (open) and oxygen ambient (solid) at various temperatures.

FIG. 2. Calculated carrier concentrations ($n_{v,1}$, $n_{v,2}$) contributed by the oxygen vacancies and the carrier concentrations contributed by the cation-substitution reaction ($n_{s,1}$, $n_{s,2}$) of the annealed $\text{Sn}:\text{In}_2\text{O}_3$ thin films (open) and oxygen ambient (closed) at various temperatures.

measure the oxygen-vacancy concentrations (C_v) in the $\text{Sn}:\text{In}_2\text{O}_3$ thin films. PAL spectroscopy is a powerful technique to probe the vacancy-type defects in semiconductors and oxides (for example, the oxygen vacancy in this work).^{19–22} As implanting positrons into bulk or thin-film materials, the implanted positrons would be annihilated with the electrons and emit γ photons (~ 511 keV). The energy dispersion of γ photons, called Doppler spectra, can be used to interpret the types of the defects in the studied materials. The energy distribution of γ photons is characterized by two parameters of S (shape parameter) and W (wing parameter). The S parameter is defined as the ratio between the integral intensity under the curve in the central spectrum (N_P) and the integral intensity under the entire curve in the spectrum (N_{total}). The central spectrum (N_P) is defined as the γ photons with an energy range in 511 ± 0.8 keV. The W parameter is regarded as the ratio between the integral intensity under the curve besides the central spectrum (N_w) and the integral intensity under the entire curve in the spectrum (N_{total}).

Three ITO thin films annealed at three distinct temperatures (200 °C, 400 °C, and 600 °C) in vacuum ambient were analyzed by PAL spectroscopy. The parameters of S (shape parameter) and W (wing parameter) of the $\text{Sn}:\text{In}_2\text{O}_3$ thin films were determined from the PAL spectra. We discovered that all curves in the S - W plots of the annealed $\text{Sn}:\text{In}_2\text{O}_3$ thin films are linear. Fig. 3 shows the S - W plot of the $\text{Sn}:\text{In}_2\text{O}_3$ sample annealed at 400 °C. The linear curve in the S - W plot suggests that only one type of point defect in the $\text{Sn}:\text{In}_2\text{O}_3$ thin films.²⁴ The possible point defects in the $\text{Sn}:\text{In}_2\text{O}_3$ thin films are vacancy and impurity. However, we know that positrons would only be trapped by the defect with open space. Therefore, we believe that the point defect in the $\text{Sn}:\text{In}_2\text{O}_3$ thin film should be the oxygen vacancy.

To further verify the oxygen-vacancy defect in the studied $\text{Sn}:\text{In}_2\text{O}_3$ thin films, PL analysis was performed on the $\text{Sn}:\text{In}_2\text{O}_3$ thin films annealed in the low vacuum ambient and the oxygen ambient at 400 °C. Fig. 4 shows the PL spectra of the $\text{Sn}:\text{In}_2\text{O}_3$ thin films annealed in the low vacuum ambient and the oxygen ambient at 400 °C. The peak locates at 388 nm (3.2 eV) matches to the near band edge emission.^{25,26} It has been reported that the oxygen vacancy defect level is a

FIG. 3. S-W plot of the Sn:In₂O₃ thin film annealed at 400 °C.

shallow level right below the bottom of conduction band.²⁷ The peaks located at 438 nm, 441 nm, and 446 nm should attribute to the defects in the Sn:In₂O₃ thin films.^{25,26} Wu *et al.* reported that the peak at 441 nm in PL spectra corresponds to the defect level of the oxygen vacancy.²⁶ Thus, we can further confirm that the point defects in the Sn:In₂O₃ thin films should be the oxygen vacancies. In addition, the peak intensity (at 441 nm) of the Sn:In₂O₃ thin film annealed in the oxygen ambient is lower than that of the Sn:In₂O₃ thin film annealed in the vacuum ambient. We know that the oxygen vacancies in the Sn:In₂O₃ thin films typically would be reduced with being annealed in the oxygen ambient. Therefore, it also supports our finding that oxygen vacancy is the dominant defect in the studied Sn:In₂O₃ thin films.

The two-state trapping model has been used to estimate the oxygen-vacancy concentration of the semiconductors and oxides.^{28–30} The two-state trapping model assumes that the positrons exist in two states in a material; either in a free state or in a trapped state. The trapping rate (κ_d), which is the rate of the positron trapped by the defect in the studied material, can be expressed by the positron annihilation lifetimes in the perfect crystal (τ_1) and in the defect (τ_2), as shown in the following equation:

FIG. 4. PL spectra of Sn:In₂O₃ thin films annealed in the low vacuum ambient and the oxygen ambient at 400 °C.

$$\kappa_d = I_2 \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right), \quad (8)$$

where I_2 is the corresponding intensity of τ_2 .

The trapping rate is proportional to the defect concentration, as shown in the following equation:³¹

$$\kappa_d = \mu_d C_d, \quad (9)$$

where μ_d is the trapping coefficient of the particular defect, and C_d is the concentration of the particular defect.

In the previous section, the S-W plot revealed that the major defect detected by PAL spectroscopy in the studied Sn:In₂O₃ thin film was the oxygen vacancy. The defect concentration (C_d) in Eq. (9) can be substituted by the expression of the oxygen-vacancy concentration (C_v , shown in Eq. (1d)). Subsequently, Eq. (9) can be modified as

$$\kappa_d = \mu_d K' \exp\left(\frac{-g_{f,v}}{kT}\right) n^{-2} P^{-1/2}. \quad (10)$$

Use log in both sides of Eq. (10), then, Eq. (10) can be rearranged as

$$\ln(\kappa_d n^2 P_{O_2}^{1/2} K'^{-1}) = \ln \mu_d + \frac{-g_{f,v}}{k} \cdot \frac{1}{T}. \quad (11)$$

The positron annihilation lifetimes (τ_1) and (τ_2) of the annealed Sn:In₂O₃ thin films can be determined using the PAL spectra. Hence, with the positron annihilation lifetimes, the trapping rates (κ_d) of the Sn:In₂O₃ thin films annealed at 200 °C, 400 °C, and 600 °C can be defined via Eq. (8). The positron annihilation lifetimes (τ_1) and (τ_2), the trapping rates (κ_d), and the carrier concentrations (n) of the annealed Sn:In₂O₃ thin films are shown in Table I. With the information in Table I, the $\ln(\kappa_d n^2 P_{O_2}^{1/2} K'^{-1})$ versus $1/T$ plot of the Sn:In₂O₃ thin film annealed at 400 °C can be drawn, as shown in Fig. 5. Then, the μ_d value ($1.46 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) of the Sn:In₂O₃ thin film annealed at 400 °C can be calculated by the intercept of the linear curve at the y-axis in the plot of $\ln(\kappa_d n^2 P_{O_2}^{1/2} K'^{-1})$ versus $1/T$. Also, the slope of the linear curve ($\frac{-g_{f,v}}{k}$) in Fig. 5 provides the vacancy formation energy (0.25 eV). Using the above approach, the μ_d values of the Sn:In₂O₃ thin films annealed at 200 °C and 600 °C were obtained and is tabulated in Table I. Once the trapping rate (κ_d) and the trapping coefficient (μ_d) are obtained, the oxygen-vacancy concentrations (C_v) of the three annealed

TABLE I. The values of the positron annihilation lifetimes in the perfect crystal τ_1 and in the defect τ_2 , the trapping rate κ_d and the oxygen vacancy concentration C_v obtained by the PAL for the Sn:In₂O₃ thin films annealed in vacuum ambient at 200 °C, 400 °C, and 600 °C.

Annealing temperature T (°C)	Positron annihilation lifetimes (ns)		Trapping rate κ_d (ns ⁻¹)	Oxygen vacancy concentration C_v (cm ⁻³)
	τ_1	τ_2		
200	7.38×10^{-2}	2.69×10^{-1}	4.41	3.02×10^{20}
400	1.69×10^{-1}	3.28×10^{-1}	8.84	6.05×10^{19}
600	1.22×10^{-1}	2.76×10^{-1}	2.27	1.56×10^{20}

FIG. 5. Plot of $\ln(k_d n^2 P_{O_2}^{-1/2} K^{-1})$ versus $1/T$.

FIG. 6. The carrier concentrations contributed by the oxygen vacancies by the separation model and PAL analysis.

Sn:In₂O₃ thin films can be calculated through Eq. (9), which are listed in Table I. Then, the carrier concentrations contributed by the oxygen vacancies ($n_{v,PAL}$) can be obtained as twice the value of the measured oxygen-vacancy concentrations, as shown in the square markers in Fig. 6. The carrier concentrations contributed from the oxygen vacancies by the separation model ($n_{v,sepa}$) are also plotted in Fig. 6, as indicated by the triangle markers. The magnitudes of the $n_{v,PAL}$ are reasonably close to that of $n_{v,sepa}$. Particularly, for the Sn:In₂O₃ thin films annealed at 400 °C and 600 °C, the difference between the carrier concentrations obtained by PAL and by the separation model is within a factor of two. Therefore, the developed carrier-concentration separation model can be used to evaluate and separate the carrier concentrations contributed by the oxygen vacancies and the cation-substitution reaction for extrinsic conducting oxides.

IV. CONCLUSION

In summary, a carrier-concentration separation model was developed to decouple the individual carrier concentrations contributed from the oxygen-vacancy and the cation-substitution reaction in extrinsic transparent conductive

oxides. The oxygen vacancy in the dominated defect in the Sn:In₂O₃ thin films was verified by the PL spectra and PAL spectroscopy. Using the annealed Sn:In₂O₃ thin films as examples, the carrier concentrations ($n_{v,sepa}$) contributed from the oxygen-vacancies of the annealed Sn:In₂O₃ thin films can be deduced by the carrier-concentration separation model. The calculated $n_{v,sepa}$ values were verified by the carrier concentrations ($n_{v,PAL}$) measured directly by PAL spectroscopy and two-state trapping model. We discovered that the $n_{v,PAL}$ magnitudes are reasonably close to the values of $n_{v,sepa}$. Therefore, the developed carrier-concentration separation model can be used to evaluate and separate the carrier concentrations contributed by the oxygen vacancies and the cation-substitution reaction for extrinsic conducting oxides.

ACKNOWLEDGMENTS

This work was supported in part by the National Central University's Plan to Develop First-class Universities, a Top-level Research Centers Grant (100G903-2), and grants from the National Science Council (NSC 101-2221-E-008-036-MY3 and NSC 101-3113-E-008-001).

- ¹T. Minami and T. Miyata, *Thin Solid Films* **517**, 1474–1477 (2008).
- ²T. H. Chen, T. J. Wu, J. Y. Chen, and Y. Liou, *J. Appl. Phys.* **99**, 114515 (2006).
- ³J. D. Hwang, C. C. Lin, and W. L. Chen, *J. Appl. Phys.* **100**, 044908 (2006).
- ⁴N. Kikuchi, E. Kusano, E. Kishio, and A. Kinbara, *Vacuum* **66**, 365–371 (2002).
- ⁵Y. C. Lin, S. J. Chang, Y. K. Su, T. Y. Tsai, C. S. Chang, S. C. Shei, S. J. Hsu, C. H. Liu, U. H. Liaw, S. C. Chen, and B. R. Huang, *IEEE Photon. Technol. Lett.* **14**(12), 1668–1670 (2002).
- ⁶J. O. Song, D. S. Leem, J. S. Kwak, O. H. Nam, Y. Park, and T. Y. Seong, *IEEE Photon. Technol. Lett.* **16**(6), 1450–1452 (2004).
- ⁷S. J. Kim, *IEEE Photon. Technol. Lett.* **17**(8), 1617–1619 (2005).
- ⁸R. H. Horng, D. S. Wu, Y. C. Lien, and W. H. Lan, *Appl. Phys. Lett.* **79**(18), 2925–2927 (2001).
- ⁹R. H. Horng, C. C. Yang, J. Y. Wu, S. H. Huang, C. E. Lee, and D. S. Wu, *Appl. Phys. Lett.* **86**, 221101 (2005).
- ¹⁰J. K. Kim, T. Gessmann, E. F. Schubert, J. Q. Xi, H. Luo, J. Cho, C. Sone, and Y. Park, *Appl. Phys. Lett.* **88**, 013501 (2006).
- ¹¹S. J. Chang, C. F. Shen, W. S. Chen, C. T. Kuo, T. K. Ko, S. C. Shei, and J. K. Sheu, *Appl. Phys. Lett.* **91**, 013504 (2007).
- ¹²K. Y. Lee, C. Becker, M. Muske, F. Ruske, S. Gall, and B. Rech, *Appl. Phys. Lett.* **91**, 241911 (2007).
- ¹³J.-H. Hwang, D. D. Edwards, D. R. Kammler, and T. O. Mason, *Solid State Ionics* **129**, 135 (2000).
- ¹⁴G. Frank and H. Köstlin, *Appl. Phys. A* **27**, 197 (1982).
- ¹⁵G. B. González, J. B. Cohen, J.-H. Hwang, T. O. Mason, J. P. Hodges, and J. D. Jorgensen, *J. Appl. Phys.* **89**, 2550 (2001).
- ¹⁶G. B. González, T. O. Mason, J. P. Quintana, O. Warschkow, D. E. Ellis, J.-H. Hwang, J. P. Hodges, and J. D. Jorgensen, *J. Appl. Phys.* **96**, 3912 (2004).
- ¹⁷S. P. Harvey, T. O. Mason, Y. Gassenbauer, R. Schafranek, and A. Klein, *J. Phys. D: Appl. Phys.* **39**, 3959 (2006).
- ¹⁸A. Janotti and C. G. Van de Walle, *Rep. Prog. Phys.* **72**, 126501 (2009).
- ¹⁹R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors: Defect Studies* (Springer, 1998).
- ²⁰A. Janotti, J. B. Varley, P. Rinke, N. Umezawa, G. Kresse, and C. G. Van de Walle, *Phys. Rev. B* **81**, 085212 (2010).
- ²¹H. E. Schaefer, *Phys. Status Solidi A* **102**, 47 (1987).
- ²²A. Uedono et al., *J. Appl. Phys.* **92**(5), 2697–2702 (2002).
- ²³Y. M. Chiang, D. P. Birnie, and W. D. Kingery, *Physical Ceramics: Principles for Ceramic Science and Engineering* (Wiley, 1997).
- ²⁴R. B. H. Tahar, T. Ban, Y. Ohya, and Y. Takahashi, *J. Appl. Phys.* **83**(5), 2631–2645 (1998).

- ²⁵D. Beena, K. J. Lethy, R. Vinodkumar, A. P. Detty, V. P. Mahadevan Pillai, and V. Ganesan, *J. Alloys Comp.* **489**, 215–223 (2010).
- ²⁶P. Wu, Q. Li, X. Zou, W. Cheng, D. Zhang, C. Zhao, L. Chi, and T. Xiao, *J. Phys.: Conf. Ser.* **188**, 012054 (2009).
- ²⁷J. C. C. Fan and J. B. Goodenough, *J. Appl. Phys.* **48**, 3524 (1977).
- ²⁸M. J. Puska, C. Corbel, and R. M. Nieminen, *Phys. Rev. B* **41**, 9980–9993 (1990).
- ²⁹R. W. Siegel, *Annu. Rev. Mater. Sci.* **10**, 393–425 (1980).
- ³⁰S. Mantl and W. Triftshäuser, *Phys. Rev. B* **17**, 1645–1652 (1978).
- ³¹W. Brandt and R. Paulin, *Phys. Rev. B* **5**, 2430–2435 (1972).