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Investigation of charge compensation in indium-doped tin dioxide by hydrogen insertion via annealing under humid conditions

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The behavior of hydrogen (H) as an impurity in indium (In)-doped tin dioxide (SnO_2) was investigated by mass spectrometry analyses, with the aim of understanding the charge compensation mechanism in SnO_2. The H-concentration of the In-doped SnO_2 films increased to $(1-2) \times 10^{19} \, cm^{-3}$ by annealing in a humid atmosphere (WET annealing). The electron concentration in the films also increased after WET annealing but was two orders of magnitude less than their H-concentrations. A self-compensation mechanism, based on the assumption that H sits at substitutional sites, is proposed to explain the mismatch between the electron- and H-concentrations. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870425]

Tin dioxide (SnO_2) is an oxide semiconductor and is used as a transparent conductor[1] and an active material for chemical sensors.[2] As SnO_2 exhibits native n-type conductivity, its nonstoichiometry, particularly its oxygen deficiency, is believed to be the cause of its conductivity. For instance, Samson and Fonstad[3] indicated that oxygen vacancies are the origin of very shallow donor levels formed in undoped SnO_2.

However, density-functional-theory (DFT) simulations have started to provide evidence that the above-stated idea may not be true. One prediction based on DFT simulation results is that the nonstoichiometry of SnO_2 is probably not the reason for its electrical conductivity.[4] To explain the difference between the measured n-type conductivity of nominally undoped SnO_2 and that predicted by theoretical calculations, one has to assume the existence of unintentional impurities such as hydrogen (H).[4,5] On the other hand, the ability to inject holes into oxide semiconductors is of importance with regard to the development of oxide-based electronic devices. For instance, p-type ZnO has been investigated with the aim of developing ZnO-based light-emitting diodes.[6,7] As DFT simulations have predicted that SnO_2 doped with group III elements would be a good p-type oxide semiconductor,[4] experimental studies involving the doping of SnO_2 with indium and gallium have been performed.[8,9]

However, the existence of p-type conduction in doped SnO_2 has not been proven.

It is essential to bridge the divide between theoretical predictions and the results obtained from experimental observations. Hence, we attempted to elucidate the role of H as an impurity in doped SnO_2. The theoretical predictions made regarding H as a donor impurity in SnO_2[10] are similar to those made for zinc oxide (ZnO).[11] In fact, studies have shown that H in ZnO behaves as a shallow donor.[12] Thus, the difficulty in synthesizing p-type SnO_2 is attributable to the presence of unintentionally doped H, which compensates for the intentionally doped acceptors.[10] In this study, we attempted to answer the following question: Is there a correlation between the behavior of H in In-doped SnO_2 and the electrical properties of In-doped SnO_2?

To answer this question, the study was divided into two parts. In the first part, as-grown samples of SnO_2 were subjected to H-analyses, while in the second part, SnO_2 samples annealed in a humid atmosphere were subjected to H-analyses. As SnO_2 is a volatile material, we did not anneal SnO_2 in H_2 gas. Indeed, our preliminary study showed that SnO_2 decomposed into metallic Sn when heated in mixture of Ar/H_2 gases at $400\,°C$. Therefore, we performed the annealing, which was done to insert H-atoms into the SnO_2 lattice, in an atmosphere containing water molecules. We did not use normal water ($^{1}H_2O$) but used heavy water instead ($^{2}H_2O$) for annealing in humid gas, to distinguish between the inserted H-atoms and the existing H-atoms using mass spectrometry. We found that H-atoms could be inserted into In-doped SnO_2 films by annealing in humid gas, but their effect on the electronic properties of SnO_2 was limited in terms of solubility and electron injection.

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The SnO$_2$ samples were grown by molecular beam epitaxy. The growth procedure used has been described previously.[8,13] To elucidate the behavior of H in In-doped SnO$_2$, we also studied nominally undoped SnO$_2$ films grown by the same process. Samples with different In-concentrations (n[In]) were prepared and actual n[In] in the obtained films were determined by secondary ion mass spectrometry (SIMS). Hereafter, the films with In-doping levels of $1.9 \times 10^{18}\,\mathrm{cm^{-3}}$, $1.9 \times 10^{19}\,\mathrm{cm^{-3}}$, and $1.9 \times 10^{20}\,\mathrm{cm^{-3}}$ are referred to as IN-18, IN-19, and IN-20, respectively, while the nominally undoped SnO$_2$ film is called IN-0.

The fabricated films were annealed at $300\,^\circ$C for 1 h in a humid atmosphere using a homemade reactor.[14] The humid atmosphere consisted of pure Ar as the carrier. Water vapor was produced by evaporating water at $60\,^\circ$C; thus, the dew point of the humid Ar was $60\,^\circ$C. To examine the removal of H by the heat treatment, some of the SnO$_2$ films were also annealed in dry Ar. Further, as mentioned previously, annealing was performed using isotope-enriched ^{2}H$_2$O as the H source so that ^{2}H could be used as the mass tracer. Hereafter, we use the labels AS, DRY, and WET to refer to the unannealed, as-deposited samples, the annealed-in-dry-Ar samples, and the annealed-in-humid-Ar samples, respectively. The notation (DRY + WET) means that the sample was first annealed in dry Ar and subsequently in humid Ar. For example, IN-20-WET refers to the In-doped ($1.9 \times 10^{20}\,\mathrm{cm^{-3}}$) film annealed in the humid atmosphere.

The n[H] values were determined as functions of the depth from the surface using SIMS. The relative sensitivity factor for H of our SIMS spectrometer was set using a standard sample prepared by H-ion implantation. The desorption of H-containing molecules from the inside of the spectrometer or from the sample surface can result in n[H] being overestimated. Thus, to ensure the reliability of the measurements, the so-called "shaped-beam method"[15] was employed for the H-analyses. This method involves subtracting the background H counts from the observed total H counts; however, it is only useful when the amount of H sputtered from the sample is greater than that from the background. Thus, we could not analyze n[H] values lower than $10^{18}\,\mathrm{cm^{-3}}$ in the present study. The accuracy and reliability of the n[H] measurements are discussed below.

Figure 1(a) shows the depth profile of the total n[H] of the IN-0 films. Here, the total n[H] is the sum of the concentrations of ^{1}H (n[^{1}H]) and ^{2}H (n[^{2}H]). Here, it is important to estimate the error in n[H]. Figure 1(b) shows the depth profiles of n[^{1}H] and n[^{2}H] of IN-0-(DRY + WET). The observed n[^{2}H] was almost one order of magnitude less than n[^{1}H]. Similar results were obtained for IN-0-WET. This means the n[H] shown in Fig. 1(a) was nearly equal to the observed n[^{1}H] and suggests that the error in measuring n[H] in the IN-0 films could be determined from that in measuring n[^{1}H]. In Figure 1(a), n[H] for the deeper parts ($>0.4\,\mu$m) is represented by the filled symbols. In this depth range, the observed n[^{1}H] shown in Fig. 1(b) was nearly constant ($\approx 4 \times 10^{18}\,\mathrm{cm^{-3}}$) and close to the background n[^{1}H] level. In other words, it is possible that the observed n[H] values represented by the filled symbols in Fig. 1(a) were overestimated. On the other hand, the ^{2}H from the samples could be detected with precision, since the observed n[^{2}H] was two or
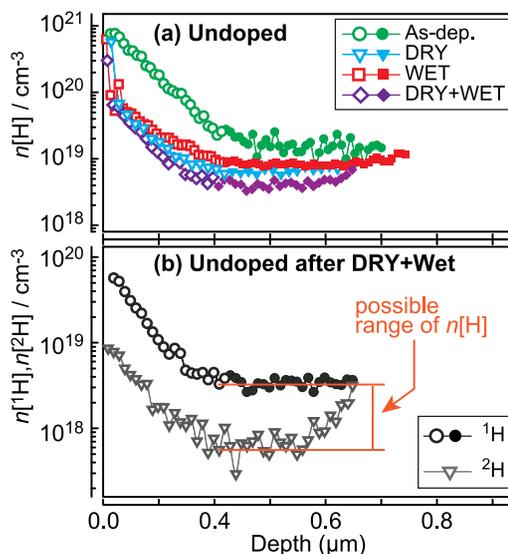

FIG. 1. Hydrogen concentration in the undoped SnO$_2$ films annealed under various conditions.

three orders of magnitude higher than its background level. If we assume that all the ^{1}H that existed in IN-0-AS was completely replaced by ^{2}H during annealing using ^{2}H$_2$O, the actual n[H] should be the same as the observed n[^{2}H], and all ^{1}H should be from the background. That is, the observed n[^{2}H] would be the lowest possible value of the actual n[H]. Considering those possibilities, we can safely say that the n[H] value of the IN-0 films was 5×10^{17} to $5 \times 10^{18}\,\mathrm{cm^{-3}}$ in the bulk region.

Interestingly, the H-atoms that existed at the subsurface level of IN-0-AS were removed by WET annealing at $300\,^\circ$C, indicating that they were thermally unstable even at $300\,^\circ$C; this was probably owing to a reaction between moisture and SnO$_2$ during storage in air. It should be noted that, even at the subsurfaces of the annealed samples, the observed n[^{1}H] was always higher than n[^{2}H]. This indicates that the ^{1}H $\longleftrightarrow$ ^{2}H exchange rate was not high enough to make n[^{2}H] greater than n[^{1}H]. Considering that n[H] near the sample surface decreased after annealing, regardless of the conditions, it is presumable that the rate of H out-diffusion was much higher than that of H in-diffusion under the investigated annealing conditions.

The behavior of n[H] in the IN-20 film was quite different from that in the IN-0 film. As shown in Fig. 2(a), the depth profile of n[H] was almost constant with respect to the depth. Further, n[^{2}H] was higher than n[^{1}H] in IN-20-WET and IN-20-(DRY + WET), as shown in Fig. 2(b). As ^{2}H (not ^{1}H) was the dominant H-isotope in the WET-annealed films, the error in measuring n[H] was assumed to be very low in the IN-20 WET-annealed films. While we have to consider the fact that n[H] for IN-20-AS was overestimated, the n[H] values of IN-20-WET and IN-20-(DRY + WET) were accurate.

We found that n[H] in the IN-20 film increased after both WET and (DRY + WET) annealing. In fact, the actual n[H] of IN-20-AS was equal to or less than $5 \times 10^{18}\,\mathrm{cm^{-3}}$, and the n[H] of the films WET annealed was greater than $1 \times 10^{19}\,\mathrm{cm^{-3}}$. This means that the annealing process was dominated by the in-diffusion of H in the IN-20 films, while out-diffusion was dominant in the IN-0 films. It should also
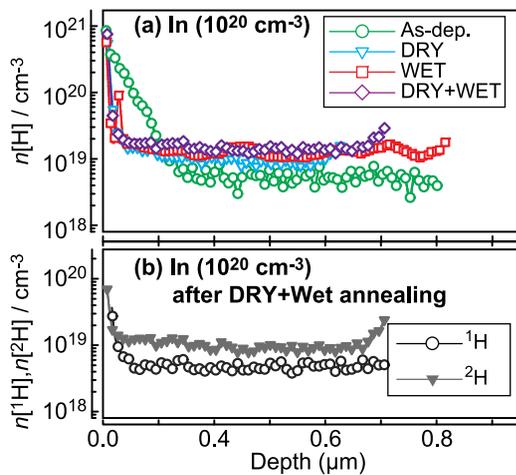
FIG. 2. Hydrogen concentration in the heavily In-doped ($1.9 \times 10^{20}\,\mathrm{cm}^{-3}$) SnO$_2$ films annealed under various conditions.

TABLE I. Hydrogen concentrations at subsurface, $n[\mathrm{H}]_{\mathrm{Srf}}$, and in bulk, $n[\mathrm{H}]_{\mathrm{Blk}}$, of the In-doped SnO$_2$ films before and after annealing in humid (WET) atmosphere.

Preparation	$n[\mathrm{In}]/\mathrm{cm}^{-3}$	$n[\mathrm{H}]_{\mathrm{Srf}}/\mathrm{cm}^{-3}$	$n[\mathrm{H}]_{\mathrm{Blk}}/\mathrm{cm}^{-3}$
As-deposited	≈ 0	10^{20}–10^{21}	$<(1\text{–}2) \times 10^{19}$
	1.9×10^{18}	10^{19}–10^{20}	10^{18}–10^{19}
	1.9×10^{20}	10^{18}–10^{20}	$<5 \times 10^{18}$
WET-annealed	≈ 0	10^{19}–10^{20}	$(0.5\text{–}5) \times 10^{18}$
	1.9×10^{18}	10^{19}–10^{20}	$(1\text{–}2) \times 10^{19}$
	1.9×10^{20}	10^{19}	$(1\text{–}2) \times 10^{19}$

be noted that $n[^2\mathrm{H}]$ in the films WET annealed was constant with respect to the depth. This suggests that H-migration in the IN-20 films was rapid. Assuming that the $n[\mathrm{H}]$ value of $1 \times 10^{19}\,\mathrm{cm}^{-3}$ was the steady-state solubility of H under the investigated annealing conditions, the in-diffusion of H can be regarded as chemical diffusion owing to a chemical potential gradient, instead of self-diffusion. This is the most likely reason for the extremely high migration rate of H in the IN-20 films.

Figure 3 shows the results of the H-analyses of the IN-18 films. The results for these films lay between those of the IN-0 and IN-20 films. The $n[\mathrm{H}]$ values of the films, determined via SIMS, are listed in Table I. It can be seen from Fig. 3(a) that the IN-18 films had relatively high $n[\mathrm{H}]$ values in the subsurface range, as was the case for the IN-0 films (see Fig. 1(a)). The effect of annealing on the subsurface $n[\mathrm{H}]$ value of the IN-18 films was similar to that in the case of the IN-0 films. In fact, $n[\mathrm{H}]$ at the subsurface of IN-18 decreased even after WET annealing. However, the inhomogeneity in the H-distribution of IN-18-AS was not as extensive as that observed in IN-0-AS. The $n[^2\mathrm{H}]$ value of IN-18-(DRY + WET), shown in Fig. 3(b), also lay
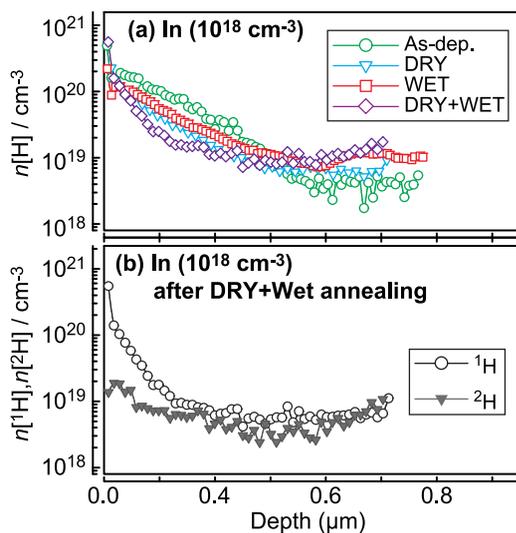
between those of IN-18-(DRY + WET) (see Fig. 1(b)) and IN-0-(DRY + WET) (Fig. 2(b)). In fact, $n[^2\mathrm{H}]$ of IN-18-(DRY + WET) was on the order of $10^{18}\,\mathrm{cm}^{-3}$, while those of IN-0-(DRY + WET) and IN-20-(DRY + WET) were on the order of $10^{17}\,\mathrm{cm}^{-3}$ and $10^{19}\,\mathrm{cm}^{-3}$, respectively. Hence, we can conclude that the effects of the WET and DRY + WET annealing processes on the films changed systematically with $n[\mathrm{In}]$.

To correlate the observed behavior of H in the films with their electronic properties, Hall effect measurements were made. The sign of the Hall coefficient was negative for all the samples, indicating that electrons were the major carriers in all the films. This suggested that the In acceptor atoms were not as activated in the films. As can be seen from Fig. 4, the electron concentration ($n[\mathrm{e}]$) of the AS films tended to decrease with the increase in $n[\mathrm{In}]$, indicating that the very highly resistance of In-doped SnO$_2$[8,9] was obtained by decreasing the residual electron concentration with the presence of In acceptor atoms. Hence, In can be regarded as a deep acceptor with respect to the films.

In the case of the IN-0 films, the $n[\mathrm{e}]$ values of IN-0-AS and IN-0-WET were similar. This means that WET annealing had no effect on $n[\mathrm{e}]$. The $n[\mathrm{H}]$ value at the subsurface of IN-0-AS was very high ($10^{21}\,\mathrm{cm}^{-3}$), as shown in Fig. 1(a). In addition, the $n[^2\mathrm{H}]$ value of IN-0-(WET + DRY), when averaged over the entire depth range, was on the order of $10^{18}\,\mathrm{cm}^{-3}$. As mentioned previously, the actual $n[\mathrm{H}]$ of IN-0-(WET + DRY) and IN-0-WET should be greater than $n[^2\mathrm{H}]$. Thus, $n[\mathrm{H}]$ in all the IN-0 films was on the order of $10^{18}\,\mathrm{cm}^{-3}$ or higher. On comparing the $n[\mathrm{H}]$ and $n[\mathrm{e}]$ values, it is clear that there was no correlation between the two and that, for all the IN-0 films, $n[\mathrm{e}]$ was much lower than $n[\mathrm{H}]$.

FIG. 3. Hydrogen concentration in lightly In-doped ($1.9 \times 10^{18}\,\mathrm{cm}^{-3}$) SnO$_2$ films annealed under various conditions.
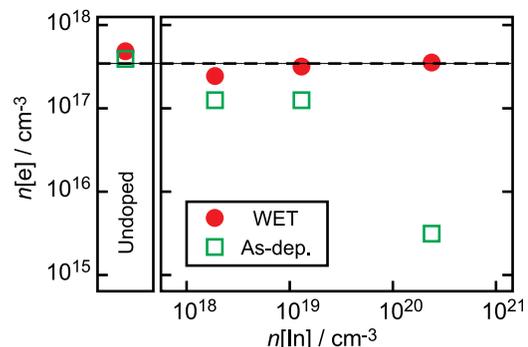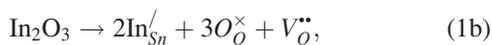

FIG. 4. Results of Hall measurements performed before and after annealing in humid (WET) condition.

In contrast, in the In-doped films, n[e] increased after WET annealing, indicating that n[H] had an effect on n[e]. However, the quantitative correlation between n[H] and n[e] could not be determined. As mentioned above, after annealing, n[H] was constant and approximately $(1–2) \times 10^{19}$ cm^{-3} in the In-doped films that were WET annealed. This n[H] value was 10 times higher than that of n[In] in IN-18 and approximately 10% of that of n[In] in IN-20. Note that n[H] (not shown) and n[e] in IN-19-WET were similar to that of IN-20-WET, although their n[In] was 10 times different. That is to say, n[H] had no direct correlation with n[In]. Moreover, n[e] in the annealed In-doped films was nearly constant ($\approx 10^{17}$ cm^{-3}) and nearly the same as that in the IN-0 films.

Here, we discuss the correlation between n[H] and n[e]. The enhanced n-type conductivity of In-doped SnO$_2$ by hydrogen insertion can be expressed by the following equations:

$$H_2 \rightarrow 2[H^+]_X^{\bullet} + 2e^{/} \approx 2H_i^{\bullet} + 2e^{/}, \tag{1a}$$

$$In_2O_3 \rightarrow 2In_{Sn}^{/} + 3O_O^{\times} + V_O^{\bullet\bullet}, \tag{1b}$$

$$V_O^{\bullet\bullet} + 2e^{/} \rightarrow V_O^{\times}. \tag{1c}$$

Here, $[H^+]_X^{\bullet}$ represents a positively ionized H-ion (H$^+$-ion) sitting at position X in the films; the most likely appearance of $[H^+]_X^{\bullet}$ should be as an interstitial H-ion ($H_i^{\bullet}$). When we assume that only doubly ionized and neutral oxygen vacancies, namely $V_O^{\bullet\bullet}$ and $V_O^{\times}$, are the major defects in In-doped films, the difference between n[H] and n[In] should allow us to determine n[e]. For the IN-20-WET films, the observed n[H] and n[e] values were on the order of 10^{19} cm^{-3} and 10^{17} cm^{-3}, respectively, with both being an order of magnitude lower than n[In]. In this case, we may assume that most of the In-acceptors in the IN-20 films were ionized by the formation of $V_O^{\bullet\bullet}$ and that the increase in n[H] by the WET treatment resulted in enhanced n-type conductivity. On the other hand, for the IN-18-WET films, n[H], which was approximately 10^{19} cm^{-3}, was approximately 10 times higher than n[In], but n[e], which was 1×10^{17} cm^{-3}, was much smaller than n[H]. This means that n[e] in the IN-18-WET films could not be determined from the difference between n[H] and n[In].

A possible explanation for the inconsistency between n[H] and n[e] is that there are two kinds of H impurities present. Here, we assume that the H-ion sitting at the site represented by "Z" acts as an acceptor, as expressed by

$$H_Z^{/}: H_2 + 2e^{/} \rightarrow 2H_Z^{/} = 2[H^-]_Z^{/}. \tag{2}$$
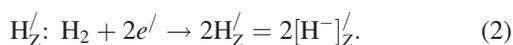
A possible site for $H_Z^{/}$ is the site at which an H-ion sits at an oxygen vacancy, $H_O^{/}$. Then, the possible charge compensation mechanism can be expressed by

$$V_O^{\bullet\bullet} + H_2 \rightarrow H_i^{\bullet} + H_O^{\bullet} = H_i^{\bullet} + [H^-]_O^{\bullet}. \tag{3}$$
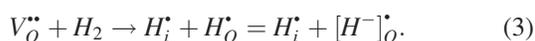
In our previous study,[16] highly immobilized H-atoms were found in SnO$_2$; these were attributed not to interstitial-H but to substitutional-H. Thus, this assumption is not far from the truth.

As the n[^{2}H] value in IN-20-(DRY + WET) was constant, we concluded that the H-migration in the IN-20 film during WET annealing was rapid even at relatively low temperatures (i.e., 300 °C). This is probably because the inserted H-atoms migrate through interstitial positions. However, there is no direct evidence to show the inserted ^{2}H-atoms finally sit at interstitial positions, because the diffusion behavior shown in Fig. 2 corresponded to chemical diffusion, which increased the n[H] value of the film. Thus, it is plausible that H-transport was through an interstitial mechanism; however, it is also possible that the ^{2}H-atoms inserted by WET annealing eventually occupy the substitutional positions. In Fig. 2(c), the n[^{1}H] value of IN-20 after the DRY + WET treatment was more than 40% of that of n[^{2}H]. This means that the in-diffusion of H in this film was rapid; however, not all the ^{1}H-atoms that existed in IN-20-AS were replaced by ^{2}H-atoms by WET annealing. Thus, there is a possibility that some of the H-atoms in IN-20-AS were already immobilized. Currently, we are unable to comment on the positions of ^{2}H-atoms post-WET treatment; however, one has to assume the existence of H-defect complexes, such as $H_O^{\bullet}$, to be able to determine the quantitative relationship between n[In], n[H], and n[e].

In summary, we examined the hydrogenation of SnO$_2$ by annealing in a humid atmosphere. H-insertion was evident in the In-doped SnO$_2$ film. We found that the hydrogenation resulted in electron injection. However, a simple quantitative relationship between n[e], n[H], and n[In] could not be established. We propose that a self-compensation mechanism of some kind is necessary to explain the observed behavior. The presence of immobilized H-atoms was confirmed; this was in keeping with the assumed mechanism. In addition, it is obvious that the characterization of the coordination structure of H is critical for understanding the charge compensation behavior in SnO$_2$ containing H.

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