

## Shallow donor state of hydrogen in $\text{In}_2\text{O}_3$ and $\text{SnO}_2$ : Implications for conductivity in transparent conducting oxides

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Muonium, and by analogy hydrogen, is shown to form a shallow-donor state in  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . The paramagnetic charge state is stable below  $\sim 50$  K in  $\text{In}_2\text{O}_3$  and  $\sim 30$  K in  $\text{SnO}_2$  which, coupled with its extremely small effective hyperfine splitting in both cases, allows its identification as the shallow-donor state. This has important implications for the controversial issue of the origins of conductivity in transparent conducting oxides.

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Optically transparent materials are generally also insulating. However, from as early as the 1950s, it was realized that certain post-transition metal oxides could support very high concentrations of electrons,<sup>1</sup> despite their large fundamental band gaps. There has been an enormous and sustained interest in such transparent conducting oxides (TCOs), spurred by both current and potential future applications in transparent electronics.<sup>2,3</sup> Nevertheless, the origins of conductivity in these materials are still under intensive debate.<sup>4–13</sup> Most commonly, high unintentional conductivities in TCOs are attributed to shallow-donor states resulting from oxygen vacancies.<sup>14</sup> However, a number of studies have questioned this interpretation. Kılıç and Zunger<sup>6</sup> argued that Sn interstitials could play an important role in the conductivity of  $\text{SnO}_2$ , although this was later disputed by Singh *et al.*<sup>12</sup> In ZnO, there are both theoretical<sup>8,11</sup> and experimental<sup>15</sup> evidence that the oxygen vacancy is deep and so does not contribute to conductivity in a conventional manner. Lany and Zunger<sup>11</sup> proposed that persistent photoconductivity may occur in ZnO and also  $\text{In}_2\text{O}_3$ , resulting from metastable excited oxygen vacancies. Van de Walle,<sup>5</sup> however, suggested an alternative explanation, namely that adventitious incorporation of hydrogen, forming a shallow donor in ZnO, gives rise to its unintentional conductivity. Furthermore, while an observed dependence of conductivity on oxygen partial pressure is usually taken as evidence for the importance of native defects, Janotti and Van de Walle<sup>10</sup> showed that substitutional hydrogen in a multicenter bond configuration can also account for the partial pressure dependence of electrical conductivity.

Hydrogen is certainly a ubiquitous impurity in semiconductors, present in many growth environments and normally being electrically active. Interstitial hydrogen is generally considered to be a “negative-U” defect, where the formation energy for the neutral charge state ( $\text{H}^0$ ) always lies above that of either the positive donor ( $\text{H}^+$ ) or negative acceptor ( $\text{H}^-$ ) center,<sup>16</sup> as illustrated in Fig. 1(a). Hydrogen, therefore, primarily forms donor (acceptor) states when the Fermi level

lies below (above) an energy  $\text{H}(+/-)$ , which lies midway between the acceptor [ $\text{H}(0/-)$ ] and donor [ $\text{H}(+/0)$ ] levels. In conventional semiconductors such as GaAs,<sup>17</sup> the  $\text{H}(+/-)$  level lies close to the middle of the fundamental band gap, as shown in Fig. 1(a). Consequently, hydrogen acts to compensate the prevailing conductivity, as a donor in *p*-type and an acceptor in *n*-type material. Van de Walle<sup>5</sup> showed that, for ZnO, the  $\text{H}(+/-)$  level should instead be resonant with the conduction band, causing hydrogen to act as a shallow donor even in *n*-type material, as represented in Fig. 1(b). These predictions, which have subsequently been confirmed by experiment,<sup>18,19</sup> reveal a novel electrical nature of hydrogen in ZnO, and raise the question of how it behaves in other TCO materials.

In semiconductors, the  $\text{H}(+/-)$  level has been argued to be equivalent to the charge neutrality level (CNL) of the material.<sup>16,20</sup> While in GaAs, as in the majority of semiconductors, the CNL lies within the fundamental band gap, it can sometimes be located above the conduction band minimum (CBM) as in ZnO, consistent with the differing nature of hydrogen in these materials. Following the revision of its

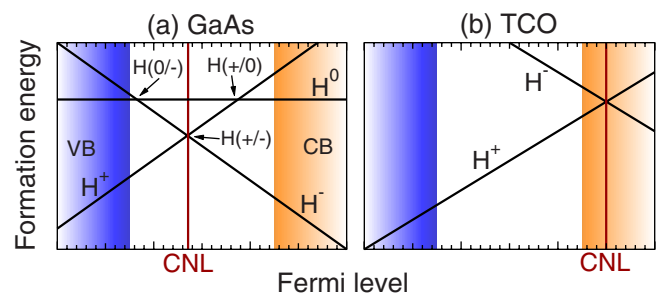


FIG. 1. (Color online) Schematic representation of the formation energies as a function of Fermi level position for donor ( $\text{H}^+$ ), acceptor ( $\text{H}^-$ ), and neutral ( $\text{H}^0$ ) hydrogen in (a) GaAs and (b) TCOs. The CNL, equivalent to the  $\text{H}(+/-)$  transition level, is shown in each case. The valence band (VB, blue [dark gray]) and conduction band (CB, yellow [light gray]) are represented by shading.

fundamental band gap,<sup>21</sup> recent experimental investigations have also shown the CNL to be located above the CBM in  $\text{In}_2\text{O}_3$ .<sup>22</sup> While no such experimental determination has yet been performed for  $\text{SnO}_2$ , theoretical calculations also suggest that the CNL lies within the conduction band in this material.<sup>23</sup> It is therefore of interest to investigate the nature of hydrogen in these materials, which are perhaps the archetypal TCOs.

When a positive muon is implanted into a semiconductor, it can bind with an electron to form muonium,  $\text{Mu} = [\mu^+, e^-]$ . This can be treated as a light isotope analog of hydrogen ( $m_{\text{Mu}}/m_{\text{H}} \approx 1/9$ ), and has the advantage that the muon has very well defined creation and decay properties. Consequently, spectroscopic study of muonium via muon spin rotation and relaxation ( $\mu\text{SR}$ ) spectroscopy is considered as a powerful tool to develop an understanding of the microscopic behavior of hydrogen in materials.<sup>18,24,25</sup> This technique is used here to search for a shallow-donor signal of muonium, and by analogy, hydrogen, in  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . Such a signal is indeed found, and the implications of this for conductivity of TCOs are discussed.

$\mu\text{SR}$  measurements were performed using the EMU spectrometer of the ISIS pulsed muon facility, Rutherford Appleton Laboratory, U.K. A 100% spin-polarized muon beam was injected into samples (99.999% purity powders from Alfa Aesar) of  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . The samples were mounted in a closed-cycle refrigerator, and placed in a transverse magnetic field of 10 mT. Measurements were performed over a 5–110 K temperature range. The muon spin precession was probed via the forward-backward asymmetry of the positrons emitted during the muon decay.

In each case, the dominant signal detected was due to the diamagnetic state,  $\text{Mu}^+$ , that is, an oscillatory signal resulting from precession of the muon at its Larmor frequency,  $\nu_L$ , damped due to depolarization resulting from nuclear dipolar coupling. The depolarization was modeled as a Gaussian relaxation for  $\text{In}_2\text{O}_3$ , whereas for  $\text{SnO}_2$ , with its much lower natural abundance of isotopes with nonzero nuclear spin, a slowly relaxing Lorentzian was employed. A shallow-donor state should also be observable at low temperatures when the muon binds to an electron, forming neutral muonium,  $\text{Mu}^0$ . This paramagnetic state is characterized by a hyperfine interaction, which leads to precession about the applied magnetic field at a frequency  $\nu_L \pm \frac{A}{2}$ , where  $A$  is the hyperfine splitting, in addition to the contribution from the diamagnetic state. The measured forward-backward asymmetry was fitted accounting for these three contributions,<sup>26</sup> and the resulting amplitudes for the diamagnetic and paramagnetic components in  $\text{In}_2\text{O}_3$  are shown in Fig. 2.

A small, but non-negligible, paramagnetic component is present at temperatures below  $\sim 50$  K. The hyperfine splitting of the paramagnetic component resulting from the fits is  $0.17 \pm 0.02$  MHz. The temperature dependence of the amplitudes of the paramagnetic and diamagnetic components were fitted with an ionization model,<sup>25</sup> giving an activation energy of  $E_a = 47 \pm 6$  meV. From thermal equilibrium arguments, this corresponds to a donor depth of  $E_d = 2E_a = 94 \pm 12$  meV. However, it is unlikely that the electron occupations for  $\text{Mu}^0$  and the conduction band reach a local equilibrium within a muon lifetime, and so the effective do-

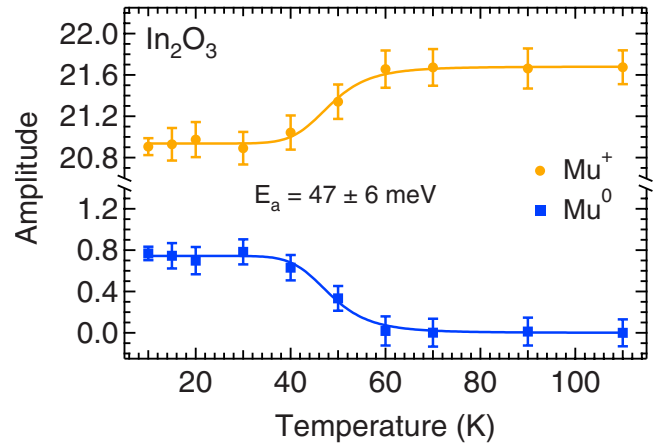


FIG. 2. (Color online) Amplitude of the paramagnetic fraction,  $\text{Mu}^0$  (squares), and diamagnetic fraction,  $\text{Mu}^+$  (circles), of muonium in  $\text{In}_2\text{O}_3$  as a function of temperature. The fits to an ionization model give an activation energy of  $47 \pm 6$  meV.

nor depth should be between these two values,  $47 \leq E_d \leq 94$  meV. The shallow-donor depth, and very small effective hyperfine constant (only  $\sim 4 \times 10^{-5}$  of the value for free muonium) both support an assignment of the paramagnetic signal as a shallow donor. These values can be compared with simple estimates for a shallow donor within the hydrogenic model. The effective shallow-donor binding energy can be estimated from

$$R^* = \frac{(m^*/m_0)R}{[\varepsilon(0)]^2}, \quad (1)$$

where  $m^*$  is the electron effective mass,  $\varepsilon(0)$  is the static dielectric constant, and  $R = 13.6$  eV is the Rydberg constant for hydrogen, giving a value of 60 meV for  $\text{In}_2\text{O}_3$ . Similarly, the effective shallow-donor radius can be estimated from

$$a^* = \frac{\varepsilon(0)}{(m^*/m_0)} a_0, \quad (2)$$

where  $a_0 = 0.53 \text{ \AA}$  is the Bohr radius, to be 1.35 nm. The expected hyperfine constant is therefore scaled from the value for free Muonium of  $A_0 = 4463$  MHz by

$$A^* = \left(\frac{a_0}{a^*}\right)^3 A_0, \quad (3)$$

giving an effective hyperfine splitting of 0.27 MHz. These simple estimates for the hyperfine splitting and donor binding energy are both within a factor of two of those obtained from the experiment, strongly supporting the assignment of the  $\text{Mu}^0$  signal as due to a shallow donor with a very extended wave function in  $\text{In}_2\text{O}_3$ .

Amplitudes for an equivalent investigation performed on  $\text{SnO}_2$  are shown in Fig. 3. Again, a paramagnetic component was observed, although in this case only up to  $\sim 30$  K, indicating a more weakly bound state than in  $\text{In}_2\text{O}_3$ . The hyperfine constant was determined to be  $0.09 \pm 0.02$  MHz, also slightly smaller than for  $\text{In}_2\text{O}_3$ . Fits to an ionization model yield an activation energy of  $18 \pm 3$  meV, corresponding to an effective donor depth of  $18 \leq E_d \leq 36$  meV. Estimates

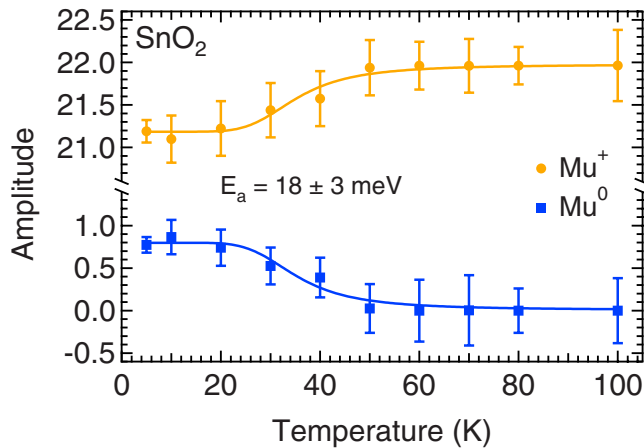


FIG. 3. (Color online) Amplitude of the paramagnetic fraction,  $\text{Mu}^0$  (squares), and diamagnetic fraction,  $\text{Mu}^+$  (circles), of muonium in  $\text{SnO}_2$  as a function of temperature. The fits to an ionization model give an activation energy of  $18 \pm 3$  meV.

from a hydrogenic model give a donor binding energy of approximately 40 meV and a scaled hyperfine constant of  $\sim 0.1$  MHz, in excellent agreement with the experimental results. This again supports the assignment of the shallow-donor state of muonium in  $\text{SnO}_2$ .

Thus, in both  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ , as well as in  $\text{ZnO}$ ,<sup>18</sup> muonium forms a shallow donor. By analogy, therefore, hydrogen also forms a shallow donor in  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . This is in agreement with the results of recent first-principles calculations for hydrogen in  $\text{SnO}_2$ .<sup>12,27,28</sup> Moreover, it seems to be emerging as a rather general feature of the TCOs. As hydrogen is a common impurity in many growth environments, it is certainly plausible that it may be present as an unintentional dopant in these materials. These results indicate that hydrogen must therefore be considered as a potential source of  $n$ -type conductivity in TCOs, consistent with the CNL position in these materials as discussed below.

It should be noted that isolated interstitial hydrogen in  $\text{ZnO}$  is mobile even at low temperatures.<sup>9</sup> In order to contribute to conductivity in this material following the high temperatures involved in growth, annealing treatments or even device-operating temperatures, it must either be trapped at other defects<sup>9</sup> or occur substitutionally. Janotti and Van de Walle<sup>10</sup> showed that hydrogen can substitute for an oxygen atom in  $\text{ZnO}$ , becoming fourfold coordinated. This donor defect center has a very similar formation energy to that of the interstitial hydrogen donor in  $\text{ZnO}$ , while being much more thermally stable than interstitial hydrogen, and exhibiting a dependence on oxygen partial pressure. Recent first-principles calculations have suggested similar behavior for threefold coordinated substitutional hydrogen in  $\text{SnO}_2$ .<sup>12</sup> Although we are not aware of any such calculations for hydrogen in  $\text{In}_2\text{O}_3$ , we would expect a similar effect to occur, and so it may be substitutional, rather than interstitial, hydrogen which constitutes the main unintentional donor impurity in these TCOs.

The fact that hydrogen acting as a shallow donor seems to be a general feature of these TCOs can be understood with reference to Fig. 4. In all cases, the CNL of the TCO, and

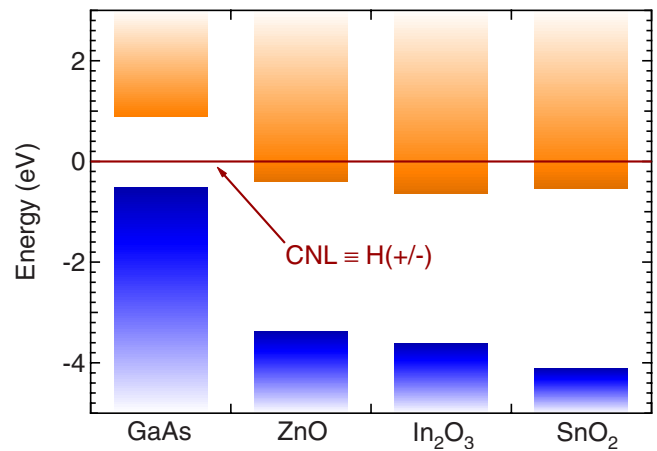


FIG. 4. (Color online) Valence band (blue [dark gray]) and conduction band (yellow [light gray]) alignment relative to the CNL of GaAs and the TCO compounds  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$ , and  $\text{SnO}_2$ . The CNL position is located from experimental investigations for GaAs (Ref. 29),  $\text{ZnO}$  (Refs. 30 and 31), and  $\text{In}_2\text{O}_3$  (Refs. 22 and 32), and from calculations for  $\text{SnO}_2$  (Ref. 23).

consequently the  $\text{H}(+/-)$  level, lies within the conduction band, and so the charge state of hydrogen will be governed by formation energies of the form shown in Fig. 1(b). For these materials, the combination of the small size and low  $2s$  orbital energy of the oxygen atom with the relatively large size and comparatively electropositive nature of the cation leads to a single low-lying  $s$ -like conduction band at  $\Gamma$ , where the CBM lies well below the conduction band edge across the rest of the Brillouin zone. This also means that the electron affinity of these TCOs is high. As hydrogen is a very localized impurity, its charge state is influenced by the character of the electronic band structure across the Brillouin zone, rather than just close to  $\Gamma$ .<sup>20</sup> Consequently, the  $\text{H}(+/-)$  level, as is the situation for the CNL, lies close to the midgap energy when averaged across the Brillouin zone, and therefore above the CBM in these TCO materials. In addition to the resulting shallow-donor nature of hydrogen, this also suggests that native defects will tend to be donors in these materials,<sup>33</sup> and so it may be a combination of native defects and hydrogen impurities which ultimately give rise to their unintentional conductivity.

In conclusion, we have used muon spin rotation and relaxation spectroscopy to probe the electrical behavior of muonium in  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . In both cases, a shallow-donor center was observed with an activation energy of  $47 \pm 6$  meV and  $18 \pm 3$  meV, respectively, and a hyperfine splitting of  $0.17 \pm 0.02$  MHz and  $0.09 \pm 0.02$  MHz, respectively. These quantities are all within a factor of two of values estimated from a simple hydrogenic model, strongly supporting the shallow-donor assignment. By analogy, these results suggest that hydrogen will form a shallow-donor center in  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  and so may make an important contribution to unintentional conductivity in these materials. This behavior of hydrogen was argued to be a common feature of all transparent conducting oxide materials due to their low-lying  $\Gamma$ -point conduction band minima, which conse-

quently lie below the H(+/-) transition level. Similar effects would be expected in other compound semiconductors consisting of a large cation and small electronegative anion.

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