Observation of shallow-donor muonium in Ga_2O_3: Evidence for hydrogen-induced conductivity

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The electrical nature of muonium in the transparent conducting oxide material Ga_2O_3 is investigated via muon-spin rotation and relaxation spectroscopy. It is found to be a shallow donor, with an effective donor depth of $15 \leq E_D \leq 30$ meV and a hyperfine splitting of 0.13 ± 0.01 MHz. This is in contrast to the deep level observed in the majority of semiconductors but supports the recent suggestion that muonium should be a shallow donor across the class of transparent conducting oxides. These observations suggest that hydrogen will also be a shallow donor in Ga_2O_3, with important implications both for unintentional conductivity and deliberate *n*-type doping of this material. © *2010 American Institute of Physics*. [doi:10.1063/1.3309694]

A class of oxide semiconductors that can conduct electricity while simultaneously exhibiting optical transparency at visible wavelengths, so-called transparent conducting oxides (TCOs), has found obvious application in numerous devices requiring a transparent contact,[1] including flat-panel displays and solar cells. Despite their widespread use, a full understanding of the coexistence of conductivity and transparency in these materials has proved elusive. It is essential to address this if the field of transparent electronics[2] is to progress, where TCOs could be used as the active elements of device architectures,[3,4] rather than simply as contact materials. While the origin of conductivity in these materials has commonly been attributed to native defects, and in particular oxygen vacancies,[5] it has recently been suggested that hydrogen impurities should form a shallow donor state across this class of materials.[6,7] Given its prevalence in most growth environments, the incorporation of hydrogen into TCOs, whether intentional or otherwise, may therefore be expected to have important implications for the conductivity of these materials.

Ga_2O_3 has a number of appealing features for applications beyond those covered by more traditional TCO materials such as indium tin oxide. Its fundamental band gap is large, almost 5 eV,[8] making Ga_2O_3 transparent not just in the visible range of the spectrum, but also well into the ultraviolet. This spectral range covers the operating wavelength of a number of important lasers, suggesting Ga_2O_3 as a potential conductive material for use, for example, in ultraviolet laser lithography.[9] With its high melting point of $\sim 1800\ ^\circ C$, Ga_2O_3 has been proposed as a suitable candidate for high-temperature gas sensors.[10] Control has also been demonstrated over doping of this material,[11] indicating potential for the implementation of Ga_2O_3 as the active layer in novel transparent (opto)electronic devices. In general, novel changes in electronic structure and optoelectronic properties may be expected when different TCOs are combined in an alloy,[12] and there has been successful implementation of Ga_2O_3 in such schemes; indeed, a transparent field-effect transistor has already been demonstrated using $InGaO_3(ZnO)_5$ as the electron channel,[3] stimulating much work on this system.[13,14] A better understanding of the effects of doping and defects on the binary compounds, however, is still required in order to maximize performance of such devices. Finally, Ga_2O_3 has shown potential for use in both hydrogen sensing[15] and catalysis;[16] a better understanding of the electrical nature of hydrogen in Ga_2O_3 is also important for these applications.

While the electronic role of hydrogen in semiconductors can be difficult to directly assess spectroscopically, there has been significant success studying its light-isotope analog, muonium ($Mu = [\mu^+, e^-]$), via muon-spin rotation and relaxation spectroscopy (μSR).[17] This technique benefits from the ability to generate fully spin-polarized beams of muons, as well as the spin-dependent angularly-asymmetric decay of muons into positrons with a well defined half-life of 2.2 μs. Consequently, μSR allows accurate spectroscopic investigations of isolated defect centers that differ from hydrogen only by a mass factor ($m_{Mu}/m_H \approx 1/9$) and the associated small differences in zero-point energy. While conventionally, charge transition levels for muonium have been found to lie deep within the semiconductor band gap,[18,19] μSR studies of selected compounds have found shallow states. These include the TCO compounds ZnO, CdO, In_2O_3, and SnO_2.[6,20,21] Here, we present equivalent investigations into Ga_2O_3. μSR 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 of monoclinic β-Ga_2O_3 (99.999% purity obtained from Alfa Aesar). A closed-cycle refrigerator was utilized to obtain sample temperatures ranging from $\sim 5-210$ K. Measurements of the muon spin precession in an applied transverse magnetic field of 101 G were probed via the forward-backward asymmetry of the positrons emitted during the muon decay. A large number of such events was detected (at least 20 million at each sample temperature) to ensure good signal-to-noise ratio, giving confidence in the fitting results for small amplitude components.

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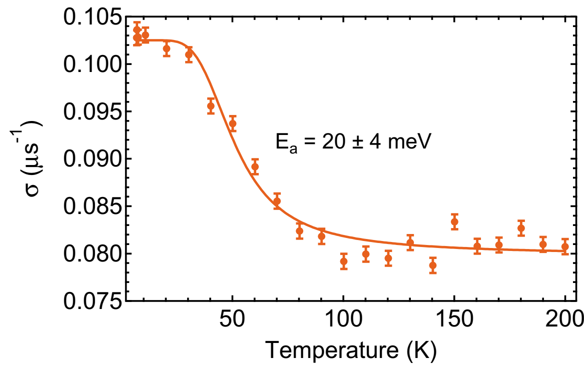

FIG. 1. (Color online) Gaussian relaxation rate, σ, of a single-component fit to time-domain μ-SR data from Ga_2O_3. Fitting to an ionization model yields an activation energy of 20 ± 4 meV.

The measured time-domain asymmetry data, proportional to the muon-spin polarization, were fitted using a single sinusoidal component to account for precession of the muon spin around the applied magnetic field at its Larmor frequency, ν_L, convolved with a Gaussian envelope. The Gaussian relaxation rate as a function of sample temperature is shown in Fig. 1. A decrease in relaxation rate is evident with increasing temperature, suggesting that the fitted relaxation rate does not simply represent a loss of the degree of spin polarization due to nuclear dipolar coupling. Indeed, in the presence of a paramagnetic Mu^0 state, hyperfine splitting yields two oscillatory components in the time-domain asymmetry data with frequencies $\nu_L \pm A/2$, where A is the hyperfine constant, in addition to the diamagnetic signal. If the hyperfine splitting is small, such components have been shown to manifest as an increase in the relaxation rate derived from a single-component fit at low temperatures,[22] as observed here. This, therefore, gives the first evidence that paramagnetic muonium is present in Ga_2O_3 at low temperatures. Indeed, fitting of the temperature dependence of the relaxation rate to an ionization model[22] yields an estimate of the activation energy of 20 ± 4 meV. Such a low value is indicative of a shallow, rather than deep, level, suggesting muonium does indeed form as a shallow center in Ga_2O_3.

To investigate this in more detail, the time-domain data was analyzed using a three-component model to explicitly account for the diamagnetic and paramagnetic fractions. The amplitudes of the components resulting from fitting to such a model are shown in Fig. 2. At low temperatures, both diamagnetic and paramagnetic components are observed, with a decrease (increase) in the paramagnetic (diamagnetic) component amplitude with increasing temperature. The sum of these amplitudes is constant to within experimental error. The temperature dependence of the amplitudes are well described by an ionization model,[22] yielding an activation energy of $E_a = 15 \pm 1$ meV, in agreement with the estimate obtained from the single-component fit. From this, an effective donor depth[6] for muonium can be estimated as $15 \leq E_D \leq 30$ meV. The fits also yield a hyperfine splitting for the paramagnetic component of only 0.13 ± 0.01 MHz, which is more than 10^4 times smaller than the hyperfine splitting of free muonium. Such a reduced value of the hyperfine splitting indicates a very extended wave function, with an effective donor radius of almost 2 nm, strongly supporting the assignment of muonium as a shallow donor in Ga_2O_3. Indeed, simple estimates for a hydrogenic shallow-donor state

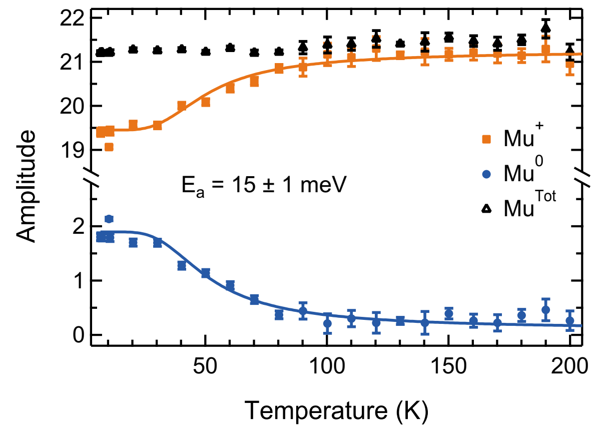

FIG. 2. (Color online) Amplitude of the paramagnetic fraction, Mu^0 (circles), diamagnetic fraction, Mu^+ (squares), and total amplitude, Mu^{Tot} (triangles), of muonium in Ga_2O_3 as a function of temperature. The amplitude variation of the components follows an ionization model, yielding an activation energy of 15 ± 1 meV.

in Ga_2O_3, using an estimated effective mass[23] and static dielectric constant[24] of $0.35m_0$ and 10, respectively, give the shallow-donor binding energy and radius as 48 meV and 1.5 nm, respectively. This is in reasonable agreement with the experimental measurements considering the band parameters for this material are still not known with great certainty.

The μSR data can also be considered in the frequency domain by performing a maximum entropy (ME) analysis of the time-domain data. The results of such an analysis performed here are shown in Fig. 3. Figure 3(a) shows ME μSR spectra as a function of temperature. At high temperatures, a single Gaussian peak is observed. However, with decreasing temperature, spectral weight is transferred to the wings of the peak, due to the presence of hyperfine-split paramagnetic components, as seen by comparing ME spectra above and below the neutral muonium ionization temperature [Fig. 3(b)]. The ME spectrum obtained at 10 K can be deconvolved into three Gaussian peaks as follows: a central diamagnetic component, and two paramagnetic components separated by the hyperfine splitting determined above, equally spaced around the diamagnetic component, as shown in Fig. 3(c). From such a fitting, the ratio of the paramagnetic

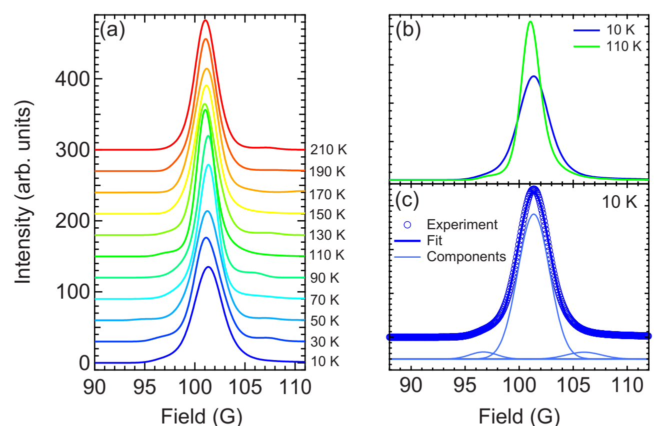

FIG. 3. (Color online) (a) Frequency-domain μ-SR spectra for Ga_2O_3, obtained from the time-domain data by a ME method, as a function of temperature from 10 to 210 K. (b) A comparison of the 10 and 110 K spectra, and (c) a spectral deconvolution of the 10 K spectrum, revealing Mu^0 satellites to the diamagnetic Mu^+ component.

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to the diamagnetic component at 10 K is obtained as 0.096, in agreement with that determined from the time-domain fitting shown in Fig. 2.

The above investigations identify muonium as a shallow donor in Ga_2O_3, as in the other TCO materials ZnO, CdO, In_2O_3, and SnO_2.[6,20,21] As the defect levels for muonium are expected to be the same as those for hydrogen except for small corrections due to differences in zero-point energy,[25] this strongly suggests that hydrogen will be a shallow donor in Ga_2O_3, with the H(+/0) donor level resonant with the conduction band. Thus, while at low temperatures the donor electron will remain bound to a hydrogen impurity in an effective-mass state, at higher temperatures (and certainly at room temperature), it becomes energetically favorable for the electron to delocalize, becoming a free-carrier in the material. Thus, hydrogen is expected to be a source of spontaneous conductivity in Ga_2O_3, suggesting that (i) hydrogen may be an effective *n*-type dopant of Ga_2O_3 to achieve high-conductivity films for use as transparent contacts, but (ii) its incorporation into the material must be eliminated as far as possible for high-quality, low carrier-density material, as required in a number of electronic device applications. This finding is qualitatively supported by first-principles investigations which find that hydrogen can be a donor in a number of other similar oxide materials,[26–28] and extends such findings to the case of Ga_2O_3 for which such calculations have not yet been performed. Furthermore, the experimental results of this work support previous discussions that the small radius and high electronegativity of oxygen tends to lead to a bulk electronic band structure that favors the existence of not only donor states of hydrogen but also donor native defects and surface states across the class of TCO materials.[6,7,29]

In conclusion, we have shown that muonium is a shallow donor in the TCO material Ga_2O_3. Muon-spin rotation and relaxation spectroscopy results indicated the presence of a paramagnetic component at low temperatures, with an ionization energy of 15 ± 1 meV, and a hyperfine constant of 0.13 ± 0.01 MHz, similar to estimates for these quantities assuming a hydrogenic shallow donor model. In contrast to its behavior in conventional semiconductors, these results suggest that hydrogen is a shallow donor in this material, and so is likely an important source of conductivity in Ga_2O_3, as in other TCOs.

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[1]T. Minami, Semicond. Sci. Technol. **20**, S35 (2005).
[2]G. Thomas, Nature (London) **389**, 907 (1997).
[3]K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, and H. Hosono, Science **300**, 1269 (2003).
[4]A. P. Ramirez, Science **315**, 1377 (2007).
[5]S. Samson and C. G. Fonstad, J. Appl. Phys. **44**, 4618 (1973).
[6]P. D. C. King, R. L. Lichti, Y. G. Celebi, J. M. Gil, R. C. V. ao, H. V. Alberto, J. P. Duarte, D. J. Payne, R. G. Egdell, I. McKenzie, C. F. McConville, S. F. J. Cox, and T. D. Veal, Phys. Rev. B **80**, 081201(R) (2009).
[7]P. D. C. King, T. D. Veal, P. H. Jefferson, J. Zúñiga-Pérez, V. Muñoz-Sanjosé, and C. F. McConville, Phys. Rev. B **79**, 035203 (2009).
[8]H. H. Tippins, Phys. Rev. **140**, A316 (1965).
[9]N. Ueda, H. Hosono, R. Waseda, and H. Kawazoe, Appl. Phys. Lett. **70**, 3561 (1997).
[10]M. Bartic, C.-I. Baban, H. Suzuki, M. Ogita, and M. Isai, J. Am. Ceram. Soc. **90**, 2879 (2007).
[11]E. G. Víllora, K. Shimamura, Y. Yoshikawa, T. Ujiie, and K. Aoki, Appl. Phys. Lett. **92**, 202120 (2008).
[12]A. Walsh, J. L. F. D. Silva, Y. Yan, M. M. Al-Jassim, and S.-H. Wei, Phys. Rev. B **79**, 073105 (2009).
[13]J. K. Jeong, J. H. Jeong, H. W. Yang, J.-S. Park, Y.-G. Mo, and H. D. Kim, Appl. Phys. Lett. **91**, 113505 (2007).
[14]G. H. Kim, B. D. Ahn, H. S. Shin, W. H. Jeong, H. J. Kim, and H. J. Kim, Appl. Phys. Lett. **94**, 233501 (2009).
[15]A. Trinchi, W. Wlodarski, and Y. X. Li, Sens. Actuators B **100**, 94 (2004).
[16]W. Jochum, S. Penner, K. Föttinger, R. Kramer, G. Rupprechter, and B. Klötzer, J. Catal. **256**, 268 (2008).
[17]S. F. J. Cox, Rep. Prog. Phys. **72**, 116501 (2009).
[18]S. R. Kreitzman, B. Hitti, R. L. Lichti, T. L. Estle, and K. H. Chow, Phys. Rev. B **51**, 13117 (1995).
[19]R. L. Lichti, H. N. Bani-Salameh, B. R. Carroll, K. H. Chow, B. Hitti, and S. R. Kreitzman, Phys. Rev. B **76**, 045221 (2007).
[20]S. F. J. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Vilão, J. Piroto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irvine, Phys. Rev. Lett. **86**, 2601 (2001).
[21]S. F. J. Cox, J. S. Lord, S. P. Cottrell, J. M. Gil, H. V. Alberto, A. Keren, D. Prabhakaran, R. Scheuermann, and A. Stoykov, J. Phys.: Condens. Matter **18**, 1061 (2006).
[22]S. F. J. Cox, J. L. Gavartin, J. S. Lord, S. P. Cottrell, J. M. Gil, H. V. Alberto, J. P. Duarte, R. C. Vilao, N. Ayres de Campos, D. J. Keeble, E. A. Davis, M. Charlton, and D. P. van der Werf, J. Phys.: Condens. Matter **18**, 1079 (2006).
[23]H. He, R. Orlando, M. A. Blanco, R. Pandey, E. Amzallag, I. Baraille, and M. Rérat, Phys. Rev. B **74**, 195123 (2006).
[24]M. Passlack, N. E. J. Hunt, E. F. Schubert, G. J. Zydzik, M. Hong, J. P. Mannaerts, R. L. Opila, and R. J. Fischer, Appl. Phys. Lett. **64**, 2715 (1994).
[25]R. L. Lichti, K. H. Chow, and S. F. J. Cox, Phys. Rev. Lett. **101**, 136403 (2008).
[26]C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[27]K. Xiong, J. Robertson, and S. J. Clark, J. Appl. Phys. **102**, 083710 (2007).
[28]S. Limpijumnong, P. Reunchan, A. Janotti, and C. G. Van de Walle, Phys. Rev. B **80**, 193202 (2009).
[29]P. D. C. King, T. D. Veal, D. J. Payne, A. Bourlange, R. G. Egdell, and C. F. McConville, Phys. Rev. Lett. **101**, 116808 (2008).

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