Investigation of Hydrogen-like Muonium States in Nb-Doped SnO$_2$ Films

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(Received June 15, 2017)

Little is known about the characteristics of hydrogen states in thin films of SnO$_2$ and Nb doped SnO$_2$ (NTO) and its influence on the electrical properties in these materials, which are promising candidates for metal-oxide supports in polymer electrolyte fuel cells. Here, we used low-energy muon spin rotation/relaxation (LE-$\mu$SR) to study hydrogen-like muonium (Mu) states between 5 K and 300 K in undoped and Nb doped SnO$_2$ films with Nb doping levels of 0.1% and 2%, respectively. The films were prepared by reactive DC magnetron sputtering on undoped Si substrates. Film thicknesses varied between 75 nm and 200 nm, and muons were implanted close to the surface at a mean depth of 10 nm, in the center of the films, and in some cases close to the NTO/Si interface. Our results of transverse-field and longitudinal-field $\mu$SR show striking similarities to recent bulk $\mu$SR measurements on various zirconia systems [Vieira et al., Phys. Rev. B 94, 115207 (2016)]. This suggests that in the NTO systems the same Mu configurations exist which are the interstitial site with a deep, isotropic atomic Mu state, and, as the dominant fraction, the oxygen bound configuration with polaronic character.

KEYWORDS: muonium, hydrogen-states in doped oxide films, metal-oxides in fuel cells, low-energy $\mu$SR (LE-$\mu$SR)

1. Introduction

In recent years, one focus of research on oxygen reduction reaction catalysts for polymer electrolyte fuel cells (PEFC) has been on the investigation of metal-oxide supported platinum catalysts [1]. This interest is motivated by the potentially higher stability of the metal-oxide support in the oxidative electrochemical environment of a PEFC cathode in comparison with standard Pt/C catalysts. One of the most promising candidates so far is Nb doped SnO$_2$ (NTO) [2]. Our own studies using doped SnO$_2$ films as a catalyst support showed that they do not only act as an electronic connection between the electrode and the catalyst but are also influencing the catalytic activity [3]. On the other side, surface segregation of the dopant during operation is possible and may lead to the degradation of the electrical and electrochemical properties [4]. Therefore, bulk and surface characteristics of doped SnO$_2$ are essential for the design of durable and active catalyst systems. In the last decade theoretical calculations and first experiments confirmed the influence of hydrogen on the electrical properties of SnO$_2$, suggesting that hydrogen may produce two shallow donors, one at an interstitial site, and the other being hydrogen trapped at an oxygen vacancy [5–9]. But so far little is known about its influence on doped SnO$_2$. Distinct effects of hydrogen on the properties of transition-metal-oxide semiconductors have been observed: the neutralization of shallow impurities, removal
of deep states acting as recombination centers, catalytic enhancement of oxygen diffusion, and the change of electrical characteristics of transition metal impurities. This multitude of hydrogen related phenomena might be also relevant for understanding the origin and degradation of electrical properties in NTO. Due to the ubiquity of hydrogen the understanding of its role in NTO and its influence on the electrical properties is essential for a rational design of better electrodes. However, the experimental characterization of hydrogen impurities often turns out to be difficult. Here, the hydrogen-like muonium state in its charge states $\mu^+$, $\mu^0$, and $\mu^-$ can help to obtain detailed insights of the characteristics of hydrogen because muonium is adopting the same sites in the lattice and has essentially identical electronic structure. We investigated thin films of SnO$_2$ and NTO with different Nb doping levels. Although the temperature dependence of the transverse field depolarization rates could be interpreted as a signature of the presence of shallow Mu states, the observation of shallow Mu in these defect-rich and highly doped films seems to be very unlikely, since the presence of defects usually causes a strong suppression of the formation of shallow Mu. Instead, we find our data to be very similar to recent bulk $\mu$SR studies on various zirconia systems [10] which suggests that in the SnO$_2$ and NTO films, the dominant diamagnetic fraction is due a state with polaronic character (muon bound to an oxygen and an electron bound to the transition metal ion), and that there also exists a $\sim 15\%$ low-temperature fraction of an atomic like Mu state with a hyperfine coupling of about 1200 MHz, corresponding to 27% of vacuum Mu.

2. Experimental Details

The thin SnO$_2$ and NTO films were grown by DC reactive magnetron sputtering on undoped Si substrates, where the metal target (either a Sn target, or a Sn target with square-shaped Nb foils for NTO) is sputtered in a mixture of Ar and O$_2$ gas. To vary the Nb concentration the amount of Nb foils on the Sn target was varied accordingly. The total gas pressure during deposition was about $4 \times 10^{-3}$ mbar. The oxygen flow was adjusted to grow nearly stochiometric SnO$_2$. Post-annealing was carried out for all films at 400°C in an Ar atmosphere for four hours. The 2% NTO sample has the optimum Nb concentration/highest conductivity. After a first series of $\mu$SR experiments the 2%-doped Nb films were additionally annealed for ten hours at 800°C in oxygen ($10^{-3}$ mbar) to test if Nb segregation takes place.

![Fig. 1. Muon stopping distributions of NTO films on undoped Si substrates, calculated with the program TrimSP [11,12]. a) For the 0.1% NTO sample with thickness 110 nm, b) the 2% NTO sample with thickness 77 nm.](image)
in the sample, which should become observable by changes of the $\mu$SR depolarization rate. The crystallite sizes in the SnO$_2$ and NTO are in a narrow range of 5.0(5) nm. Details of the sample preparation can be found in Ref. [3]. The thicknesses of the films have been determined by Rutherford backscattering spectrometry (RBS) at the Ion Beam Physics Institute at the ETH Zurich. The thicknesses were 200 nm for SnO$_2$, 110 nm for the 0.1% NTO film, and 77 nm for the 2% NTO film.

For the $\mu$SR measurements we used the low-energy $\mu^+$ beam and LE-$\mu$SR spectrometer LEM at the $\mu$E4 beam line [13] of the Paul Scherrer Insitut, Villingen, Switzerland, where the $\mu^+$ energies can be tuned between 1 and 30 keV [14] to adjust the mean implantation depth of the $\mu^+$ between a few nanometer and about two hundred nanometer. Calculated implantation profiles for the used NTO films are shown in Fig. 1.

3. Results and Discussion

The results of our LE-$\mu$SR measurements are shown in Fig. 2 where we assumed a single component signal with exponential relaxation to fit the data, using the program musrfit [16]. Implantation energies have been chosen in order to measure close to the surface (2 keV, mean implantation depth of about 10 nm), close to the center of the film (in the 0.1% NTO sample), and at the Si interface (in the 2% NTO sample). In transverse field $\mu$SR measurements we determined the diamagnetic fraction $F_D$, i.e. the fraction of muons precessing at the muon's Larmor frequency, as a function of temperature $T$, see Fig. 2 a). Whereas the undoped SnO$_2$ film shows a temperature independent diamagnetic fraction of about 85%, in the NTO films $F_D$ is about 85% below 50 K, and increases to 90% at 100 K, followed by a more gradual increase to 95% at 300 K. This is observed at the surface of all NTO samples, and close to the center of the 0.1% NTO film. In the 2% NTO film, $F_D$ is significantly lower due to the 30% fraction of muons stopping in the Si substrate, see Fig. 1 b), where most of the muons form Mu$^0$. Here, the observed increase of $F_D$ between 150 K and 300 K can be attributed to the thermally activated ionization of bond-centered Mu$^0$ in Si. In the 0.1% NTO sample the missing diamagnetic fraction below 50 K can be attributed to an atomic-like, isotropic Mu$^0$ state with a hyperfine coupling of 1200(200) MHz, Fig. 2 d). Due to a lack of data we assume that in the other systems the same Mu configuration is the origin of the missing fraction.

Above 50 K the depolarization rate $\lambda$ in Fig. 2 b) shows a monotonic decrease on increasing the temperature in all samples. A saturation of $\lambda$ below 50 K is observed for SnO$_2$, the 0.1% NTO sample at 2 keV, and the annealed 2% NTO sample at 17 keV, whereas $\lambda$ continuously increases at lower temperatures for the other data. $\lambda$ is lowest for SnO$_2$ at all temperatures, as expected, since the addition of Nb should cause an additional broadening due to the large nuclear dipole moment of 6.2 $\mu_N$ of Nb. This is also in accordance with the observation that $\lambda$ is largest for the 2% NTO sample at 2 keV (the 17 keV data of the 2% NTO sample is less "clean", because it contains a contribution from the diamagnetic fraction of $\mu^+$ stopping in Si with lower $\lambda$, and we cannot separate this contribution from the $\mu^+$ stopping in NTO; fitting a single component results in a smaller value of $\lambda$). In SnO$_2$ the estimated $\lambda$ due to the static nuclear field distribution of the 16% of Sn isotopes with nuclear moments is 0.01 - 0.02 $\mu$s$^{-1}$ [7]. This value is observed above 240 K. It is therefore evident that the increase of $\lambda$ at lower temperatures has an electronic origin. We exclude motional narrowing by muon diffusion as the origin for the decrease of $\lambda$ as a function of $T$: in the films, due to high defect concentration and presence of grain boundaries, muon diffusion is known to be suppressed [17].

On lowering the temperature the measured magnetic field at the muon site exhibits a large paramagnetic shift between 0.3% and 1.3% as shown in Fig. 2 c). An increase proportional to
1/T is observed down to about 60 K, and saturation below 50 K. The shift is largest for the samples with the highest doping level, i.e. highest concentration of free electrons. A similar dependence on the doping level/conductivity has been observed at the surface of n-doped commercial Ge and GaAs wafers [18], and it was also reported for semi-metals such as Sb [19]. A possible origin of the paramagnetic shift could be an intermittent hyperfine interaction in a localized Mu defect center where very rapid charge-exchange can lead to a 1/T dependence of the relative frequency shift Δν ≈ \frac{h A}{4 k_B T} \left( \frac{\gamma_e}{\gamma_M} \right) p_0 [19], where \hbar is the Planck constant, A the instantaneous muon contact interaction, k_B the Boltzmann constant, \gamma_e and \gamma_M the electron and muon gyromagnetic ratios, respectively, and p_0 is the fraction of time the muon spends in the neutral state. The saturation below 50 K could be explained by a temperature dependent decrease of p_0 [19]. In the higher doped films the larger electron concentration may lead to an increase of p_0, causing the larger shift at low T.

The temperature dependencies of \( F_D \) and \( \lambda \) are very similar to recently published data.

Fig. 2. a) Diamagnetic fraction \( F_D \) (the 2 keV data of the annealed sample (ann.) are omitted since they agree within errors with the 2 keV data of the as-grown sample), b) exponential depolarization rate \( \lambda \), and c) local magnetic field at the muon stopping site as a function of temperature \( T \), measured in a transverse magnetic field of 99 G. d) Longitudinal field (LF) repolarization curve of the NTO 0.1% sample at an implantation energy of 14 keV and a temperature of 50 K. The red (solid) line is a fit of the function \( A_{LF}(B_{LF}) = A_{Mu} \frac{1-2x^2}{1+x^2} + A_D [15] \), where \( x = B_{LF}/B_0 \) with \( B_0 \) the hyperfine field, which determines the hyperfine coupling \( \nu_0 = 1200(200) \) MHz. \( A_{Mu} \) and \( A_D \) are the asymmetries of the deep Mu state and of the diamagnetic fraction. For the LEM spectrometer setup, the maximum LF asymmetry is 0.105.

\( T \) might
on various zirconia systems [10]. Also, the LF repolarization curve in our 0.1% NTO sample with an isotropic hyperfine coupling of \( \sim 1200 \) MHz (about 27% of the vacuum value) is similar to the \( \text{ZrO}_2: \text{Ca} \) data of Ref. [10] where a larger coupling constant of about \( 3000 \) MHz was reported. These similarities suggest that the same Mu configurations as in zirconia are found in the \( \text{SnO}_2 \) and NTO films. As mentioned in Sec. 1 we can exclude the presence of shallow Mu in our thin films due to the high doping and defect concentration levels. In analogy to the zirconia data we propose the existence of two Mu configurations: i) the oxygen bound configuration with polaronic character where the electron is bound at the metal ion, accounting for the diamagnetic fraction, and ii) an atomic Mu\(^0\) state at an interstitial site with an isotropic large hyperfine coupling. The increase of the \( F_D \) in the NTO samples can then be attributed to the thermally activated transition of Mu\(^0\) from the interstitial site to the polaronic configuration. Since this transition is absent in the \( \text{SnO}_2 \) film the interstitial Mu\(^0\) appears to be more stable in \( \text{SnO}_2 \) than in the doped films.

Below 50 K the 2% NTO films actually show a two-component diamagnetic signal: a slowly relaxing as in Fig. 2 b), and a smaller, fast relaxing component with depolarization rates of about 1 \( \mu s^{-1} \) at 17 keV, and about 3 \( \mu s^{-1} \) at 2 keV. Such a fast component has been also observed in the zirconia system, where it also disappears at \( T > 50 \) K [10]. This fast component is attributed to delayed Mu\(^0\) formation at the interstitial site - which is absent (or too fast to be resolved) in the lower doped NTO and \( \text{SnO}_2 \) samples.

The annealed 2% NTO sample (ten hours at 800\(^\circ\)C in oxygen atmosphere) shows a clear reductions of \( \lambda \) at the interface to the Si substrate, see Fig. 2 b), whereas close to the surface at 2 keV implantation energy the depolarization rates are nearly the same for the as-grown and annealed samples. This reduction is expected if Nb is removed from the interface due to the annealing procedure, and is an indication of Nb segregation from the interface - but not from or to the surface region where \( \lambda \) is not changed.

4. Summary

In summary we presented a first LE-\( \mu \)SR study of hydrogen-like Mu states in \( \text{SnO}_2 \) and Nb-doped \( \text{SnO}_2 \) thin films. Our data are very similar to previously published results on zirconia [10], which suggests the presence of the same Mu states in undoped and doped \( \text{SnO}_2 \) films. These are at low temperatures a 15% fraction of Mu\(^0\) at the interstitial site with an isotropic hyperfine coupling of about 1200 MHz, and a 85% diamagnetic fraction which originates from a donor-like polaronic configuration where the \( \mu^+ \) is bound to an oxygen and an electron trapped at the next metal ion. Whereas in the \( \text{SnO}_2 \) film the interstitial configuration is stable up to room temperature in the Nb-doped films the interstitial state is transformed to the polaronic state by thermal activation. Annealing of the 2% NTO sample in an oxygen atmosphere at 800\(^\circ\)C indicates the segregation of Nb from the interface to the Si substrate, but not from the surface layer.

Acknowledgements

We are grateful for stimulating discussions with Helena Alberto, João Campos Gil, Rui Vilão, and Ricardo Vieira. We thank Max Döbeli for the RBS measurements. The LE-\( \mu \)SR measurements were performed at the Swiss Muon Source S\( \mu \)S, Paul Scherrer Institut, Villigen, Switzerland.

References

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