Tin oxide (SnO$_2$) is a wide-band-gap semiconductor with applications as a transparent conductor and in gas sensors. 1,2 With a direct band gap of 3.6 eV, it is a promising material for transparent electronics. In SnO$_2$, and transparent conducting oxides in general, the origins of n-type conductivity are not well understood. 3 Recent first-principles calculations performed by Singh et al. 4 predict that hydrogen impurities act as donors in SnO$_2$. Muonium, an analog of hydrogen, was shown to form a shallow donor state. 5 In general, hydrogen is a prevalent impurity in semiconductors, often causing drastic changes in electronic properties. 6 In zinc oxide (ZnO), for example, it has been shown theoretically 7 and experimentally 8 that the incorporation of hydrogen increases the n-type conductivity. The microscopic structure of OH donors in ZnO has been determined with infrared (IR) spectroscopy. 9 The present work was undertaken to determine the structure and electrical activity of hydrogen in SnO$_2$, and to develop insights into the behavior of hydrogen across a range of oxide materials. 10–12

SnO$_2$ can be found in nature as the mineral cassiterite. Room-temperature IR studies of cassiterite have been performed on numerous samples from around the world. 13 14 15 Hydrogen-related absorption peaks were observed at frequencies between 3200 and 3400 cm$^{-1}$ and were attributed to oxygen-hydrogen (OH) bond-stretching modes. An absorption band at 3340 cm$^{-1}$, correlated with the presence of titanium, may arise from an O-H complex with a Ti neighbor. Bands near 3255 cm$^{-1}$ are present in most samples but have not been assigned to specific defect structures. Polarized spectroscopy provided evidence that the OH bonds are oriented perpendicular to the c axis. In this Brief Report, we present results on hydrogen intentionally introduced into synthetic SnO$_2$. We also carried out first-principles calculations of hydrogen-related defects, in order to help interpret the experimental results.

Bulk, single-crystal SnO$_2$ samples used in this study were grown by the vapor-phase reaction method. The samples were then sealed in quartz ampoules filled with 2/3 atm of hydrogen or deuterium gas. The annealing was performed at 600 °C for 12 h and the sample was quenched to room temperature by immersing the ampoule in water. Since SnO$_2$ reacts with hydrogen, small metal (Sn) droplets formed on the surfaces after the annealing and were removed by mechanical polishing. IR absorption spectra were measured with a Bomem DA8 Fourier-transform IR spectrometer equipped with a Janis closed-cycle helium cryostat. An InSb detector was used and the instrumental resolution was 1 cm$^{-1}$. A spectrum from an as-grown sample was used as a reference to calculate the absorbance spectra. All spectra were obtained at a sample temperature of 10 K.

The IR absorption spectrum of a hydrogen-annealed sample is shown in Fig. 1. Three dominant peaks at 3156.1, 3261.7, and 3282.0 cm$^{-1}$ were observed. Polarized IR spectroscopy indicates that these peaks are due to dipoles aligned perpendicular to the c axis (Fig. 1, inset). Samples annealed in hydrogen or deuterium showed free-carrier absorption, consistent with the hypothesis that hydrogen acts as a donor in SnO$_2$. As-received samples did not show free-carrier absorption or the IR peaks.

Figure 1 (top) shows the absorption spectrum for a deuterium-annealed sample, where the dominant peaks are located at 2360.1, 2425.6, and 2446.6 cm$^{-1}$. The shift to lower frequencies by a factor of 1.34 is consistent with OH and OD bonds. 16 Along with the OD peaks, the deuterium-
annealed sample also showed OH peaks. The appearance of OH peaks may be due to “hidden hydrogen” in as-grown sample that is released during the annealing, similar to what is observed in ZnO. In the case of ZnO, some of the hidden hydrogen is in the form of H$_2$ molecules, which have a negligible absorption cross section in the IR. To investigate hidden hydrogen further, we annealed as-received samples in Ar, under the same conditions as for the hydrogen and deuterium anneals. These samples showed the hydrogen-related peaks, although at a lower intensity as those produced by deliberate hydrogenation.

Along with IR spectroscopy, we performed electrical measurements on (1) a sample annealed in Ar and (2) a sample annealed in Ar and then hydrogen. The sample dimensions were $3 \times 1 \times 0.3$ mm$^3$, and electrodes were placed on opposite ends with silver paint. Two-probe current-voltage measurements were carried out to determine the resistance of the two samples. Samples 1 and 2 had resistance values of 41 $\Omega$ and 9 $\Omega$, respectively, confirming the increase in conductivity upon hydrogenation.

These measurements suggest that the peak at 3156 cm$^{-1}$ arises from interstitial hydrogen donors (H$^+_i$) in SnO$_2$. The calculated migration barrier for interstitial hydrogen is low (0.6 eV), implying that they are unstable at room temperature. To investigate the stability of OH complexes, we compared IR spectra for samples immediately following hydrogenation and after a period of 11 days at room temperature. OH peaks may be due to “hidden hydrogen” in as-grown samples. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand 900 °C for 1 hand and 900 °C for 1 hand. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand and 900 °C for 1 hand. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand and 900 °C for 1 hand. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand and 900 °C for 1 hand. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand and 900 °C for 1 hand. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand and 900 °C for 1 hand. After the 900 °C anneal, the sample was then annealed in the air at 900 °C for 1 hand and 900 °C for 1 hand.

Similar results were obtained for deuterated samples. Figure 3 shows the disappearance of the OD vibrational mode at 2360 cm$^{-1}$ after ~1 yr at room temperature. The sample was then annealed in the air at 900 °C for 1 h and quenched to room temperature. After the 900 °C anneal, the peak at 2360 cm$^{-1}$ reappeared. This observation is consistent with the dissociation of the defect-hydrogen complexes at elevated temperatures, resulting in a recovery of the interstitial hydrogen donors.

To identify the origin of the hydrogen-related peaks in the IR spectra, we performed first-principles calculations based on a generalized Kohn-Sham scheme with the HSE06 hybrid functional and the projector augmented-wave pseudopotential plane-wave method as implemented in the VASP code. For the hydrogen interstitial, the defect formation energy is given by

$$E_F^d[H^+_i] = E_{tot}[H^+_i] - E_{tot}[SnO_2] - \mu_H + \epsilon_F,$$

where $E_{tot}[H^+_i]$ is the total energy of the supercell containing the impurity (H$^+_i$), $E_{tot}[SnO_2]$ is the total energy of the supercell without the impurity, and $\epsilon_F$ is the Fermi energy referenced to the valence-band maximum. For all defects, the chemical potentials ($\mu_H$, $\mu_O$, $\mu_{Sn}$) are referenced to the energy per atom of isolated H$_2$ and O$_2$ molecules, and the $\beta$ phase of elemental Sn, respectively.

The formation energies of native defects and complexes with hydrogen are shown in Fig. 4. O-rich and O-poor conditions. In n-type SnO$_2$, the vacancy-hydrogen complex ($V_{Sn}$-H) is lower in energy than the isolated Sn vacancy ($V_{Sn}$). For $V_{Sn}$ in the −4 charge state (the most stable state in n-type material), we calculated a migration barrier of 2.7 eV using the nudged-elastic band method. This relatively high barrier, combined with the high formation energy, suggests that $V_{Sn}$ is immobile at the temperatures probed in the current experiments. H$^+_i$, in contrast, has low formation energies (Fig. 4) and a low migration barrier. These facts make it likely that H$^+_i$ will combine with an existing $V_{Sn}$ defect to form ($V_{Sn}$-H)$^3$.

Due to the two distinct Sn-O bond lengths for each Sn site, there are two distinct ($V_{Sn}$-H)$^3$ complexes possible. Hydrogen can either bond to one of the two axial O atoms surrounding the vacancy [Fig. 5(c)] or one of the four equatorial O atoms [Fig. 5(d)]. We refer to these as the $ax$ and $eq$ configurations, respectively. The calculated formation energy for the $eq$ configuration is ~0.1 eV lower than that for the $ax$ configuration. These values indicate that, at the hydrogenation temperature (600 °C), the ratio of $eq$ to $ax$ configu-
The calculated frequencies are shown in Table I. The calculated frequencies (ω) are given by a harmonic component (ω̄) plus an anharmonic shift (∆ω). The “corrected” values, ω′, were obtained by subtracting 181 cm⁻¹ from ω.

<table>
<thead>
<tr>
<th>Type</th>
<th>Configuration</th>
<th>ω₀ (cm⁻¹)</th>
<th>ω′ (cm⁻¹)</th>
<th>ω (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>Interstitial</td>
<td>3604</td>
<td>3156</td>
<td>3156</td>
</tr>
<tr>
<td>(V_Sn-H)⁻³</td>
<td>eq</td>
<td>3638</td>
<td>3262</td>
<td>3262</td>
</tr>
<tr>
<td>(V_Sn-H)⁻³</td>
<td>ax</td>
<td>3604</td>
<td>3280</td>
<td>3282</td>
</tr>
<tr>
<td>H₂</td>
<td>Interstitial</td>
<td>4826</td>
<td>4246</td>
<td>4246</td>
</tr>
</tbody>
</table>

The calculated frequencies for the two (V_Sn-H)⁻³ complexes. Furthermore, the IR peak attributed to the eq configuration is stronger than that for the ax configuration, in qualitative agreement with theory.

We can also characterize the stability of these complexes by their binding energy, defined as the energy difference between the complex and the isolated constituents. The binding energy between H⁺ and VSn⁻ is given by

\[ E_b = E[V_{\text{Sn}}^-] + E[H^+] - E[(V_{\text{Sn}}-H)^-], \]

where \( E[(V_{\text{Sn}}-H)^-] \) is the formation energy of the complex. The (V_Sn-H)⁻ complexes are characterized by large binding energies of 3.5 and 3.4 eV for the eq and ax configurations, respectively, signifying a strong preference for the formation of the complex over the isolated constituents. Combined with the migration barrier of 0.6 eV for H⁺, we can estimate an activation energy for dissociation of ~4 eV for the complex. We therefore predict that the complex would dissociate at a temperature around 1000 °C.³² Annealing at 900 °C will result in the majority of the complexes being present with the ax complex more likely to dissociate and release H⁺ as compared to the eq complex. These theoretical findings are consistent with the results of annealing the deuterated sample (Fig. 3).

Finally, we investigated several defects that might be responsible for the hidden hydrogen that gets released upon annealing. Candidates include H₀ donors and interstitial H₂ molecules. Figure 4 shows that H₂ has a high formation energy and is therefore unlikely to be a major source of hidden hydrogen. The H₀ center, however, does have a low enough formation energy to account for the appearance of H⁺ upon annealing of as-grown samples. We find the binding energy of H₀⁺ to be 0.78 eV with respect to the H⁺ and V₀⁻ constituents. The activation energy for dissociation is ~1.4 eV, which corresponds to a dissociation temperature of ~200 °C.³² H₀⁺ is therefore more stable than H⁺ at room temperature but can release trapped hydrogen during high-temperature annealing. The highest vibrational mode for H₀⁻ was calculated to be 1114 cm⁻¹ in the harmonic approximation, which lies within the strongly absorbing two-phonon region of SnO₂ and is “hidden” from our experiments.

In conclusion, we have discovered interstitial hydrogen donors in SnO₂. These donors give rise to OH vibrational...
modes in the IR and are unstable at room temperature. When combined with prior research on hydrogen in ZnO, the present work suggests that interstitial hydrogen may behave as an unstable donor in a range of transparent oxides. In SnO₂, Ḥ⁺ is mobile at room temperature and has an associated vibrational frequency of 3156 cm⁻¹. Two additional peaks at 3262 and 3282 cm⁻¹ are observed. Based on first-principles calculations, we attribute these peaks to hydrogen bound in two distinct configurations within Sn vacancies, (V₈Sn-H)⁻³. The high stability of these acceptor complexes explains the persistence of these peaks after annealing. We also find that Ḥ⁺ can form and is a plausible source of hidden hydrogen present in the as-grown samples.

The authors thank R. Helbig for providing the samples. This work was supported by NSF under Grant No. DMR-1004804, DOE under Grant No. DE-FG02-07ER46386, by the NSF MRSEC Program under Award No. DMR-0520415, and by Saint-Gobain Research. It made use of the CNSI Computing Facility under NSF under Grant No. CHE-0321368, and the Ranger supercomputer from the Teragrid computing resources supported by NSF under Grant No. DMR-070072N.

8mattmcc@wsu.edu
9vandewalle@mrl.ucsb.edu
22The as-received samples had resistance values ≈1 Ω.
27The O-poor limit is characterized by μSn⁰=0, μO²⁺=1/2 ΔH²(SnO₂). The O-rich limit is defined by μO⁺=0, μSn⁰=ΔH²(SnO₂). The solubilities of H-related species are limited by the formation of H₂O only under O-rich conditions; i.e., μO²⁺+2μH²<ΔH²(H₂O). SnO and SnO₂H₂ were found not to affect the results.
32Estimation based on a hopping rate Γ=Γ₀ exp(-βE₀) of one per minute, and Γ₀=100 THz.