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Journal of Applied Physics
Volume 107
Number 10
Page range 104504
Year 2010
URL http://hdl.handle.net/10097/52299
doi: 10.1063/1.3399565
Theoretical calculations of hydrogen adsorption by SnO$_2$ (110) surface: Effect of doping and calcination

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(Received 26 February 2010; accepted 18 March 2010; published online 24 May 2010)

A pseudopotential plane-wave based density functional theory simulations of the hydrogen adsorption on rutile SnO$_2$ (110) surface is reported. It is found that on doping with trivalent indium, the surface becomes unstable due to the formation of bridging oxygen vacancies. At sufficiently low doping level, the surface stabilizes at an oxygen vacancy to indium ratio of 1:2. Our calculations predict that at a higher doping level of 9 at. %, this ratio becomes larger, and point out a way to synthesize $p$-type conducting SnO$_2$ thin films. The binding energy of SnO$_2$ (110) surface with adsorbed hydrogen atoms display a maximum at 3–6 at. % of indium doping. This is in good agreement with the experimental results obtained from the SnO$_2$-based hydrogen sensor’s sensitivity measurements given by Drake et al. [J. Appl. Phys. 101, 104307 (2007)]. The theoretical modeling explains that the calcinations treatment can critically affect the sensitivity of the hydrogen sensor due to the enhancement of the binding energy between the SnO$_2$ surface and the adsorbed hydrogen atoms. © 2010 American Institute of Physics. [doi:10.1063/1.3399565]

I. INTRODUCTION

Tin dioxide (SnO$_2$) is a wide band gap (3.6 eV) $n$-type semiconductor with rutile bulk structure. It is a technologically important material, which is widely used as a hydrogen gas sensor. We have reported earlier that the presence of hydrogen gas can be detected from the changes in the SnO$_2$-based hydrogen sensor’s conductivity. When SnO$_2$ based sensor is exposed to hydrogen gas it reduces the surface oxygen atoms and decreases the space charge layer thickness around the nanocrystalline SnO$_2$ grains. Doping SnO$_2$ with other elements has been a point of interest as it provides the ability to tailor its electrical and microstructural properties.

In gas-sensor devices, SnO$_2$ is used in the form of nanosized grains since the surface to volume ratio is much larger at the nanoscale. The electrical properties of the consolidated semiconductor nanoparticles show a large deviation from those of their single-crystalline or bulk polycrystalline counterparts. The variations in the electrical properties are a result of the band structure modification, the quantum confinement of the charge carriers and the predominant contribution of the largely defective and strained grain boundaries in the nanostructured materials.

The ability of a sensor to sense the presence of gas depends on the nature of the interaction between the gas molecules and the surface atoms of the sensing film. The reactivity of the surface is critically dependent on its doping and the defect structure. The surface phenomena are very important to understand the processes underlying the sensor operation. In this paper, in order to avoid the complications in electronic structure of consolidated nanoparticle arrays mentioned above, we discuss the properties of stoichiometric (defect free) pure and indium-doped SnO$_2$ slabs as a hydrogen sensing material.

Structural and electronic properties of different SnO$_2$ surfaces have been extensively studied. Electronic structure of SnO$_2$ surface was studied theoretically for both stoichiometric and reduced cases (with and without oxygen vacancies). It was found that the valence band maximum is flat at the stoichiometric surface while the conducting band minimum is strongly dispersed. The study of the structural surface relaxation reveals that the stoichiometric (oxidized) surface is stabilized by the bridging oxygen atoms, and therefore, relaxes less. For reduced surfaces, having low and intermediate concentrations of the bridging vacancies are the most stable configurations. At high concentrations of bridging vacancies, corresponding to a strongly reduced surface, the formation energies of bridging and in-plane vacancies are almost the same, so that both types should occur in thermal equilibrium. In the present contribution we study the oxygen vacancy formation energies on SnO$_2$ (110) surface as a function of In doping level. Interaction of hydrogen with the most stable configurations of indium-doped SnO$_2$ surfaces is also investigated. It is found that the binding energy of adsorbed hydrogen atoms with the slab displays a maximum at 3–6 at. % of indium doping. This observation correlates with the experimentally observed peculiarities of indium-doped SnO$_2$-based hydrogen sensors under similar conditions. At higher doping level of 9 at. % calculations predict stability of structure with $p$-type conductivity. Wide-
band-gap oxides mostly exhibit \( n \)-type conductivity, the reason for which is still widely debated and reproducible \( p \)-type doping still poses serious challenges.\(^{21-23}\)

## II. Computational Details

All the theoretical calculations performed in the present work are based on the density functional theory (DFT) within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof parametrization.\(^{24}\) The semicore Sn \( d \) states in SnO\(_2\) are explicitly treated as valence states through the projector augmented wave method as implemented in the VASP code.\(^{25-28}\) Unfortunately, DFT underestimates the binding energy of the rather localized states in SnO\(_2\) lattice. All these configurations could be realized with 3.5 eV.\(^{23}\) The self interaction parameter for indium dopant was taken as \( U=7 \) eV as estimated for In\(_2\)O\(_3\) compound.\(^{30}\)

An important step in modeling of gas adsorption is an appropriate selection of the crystal’s surface for calculations. It has been established experimentally, that the (110) surface is the most stable in oxides with rutile structure such as SnO\(_2\) and TiO\(_2\) and it is thought to be the predominant surface in these polycrystalline samples.\(^1\) Theoretical investigations support these data and (110) surface of SnO\(_2\) is found to have the lowest energy.\(^{14}\) For these reasons, we restrict ourselves by studying the properties of this particular surface.

The (110) SnO\(_2\) surface was simulated as a symmetric 192-atoms slab. Four-layer of SnO\(_2\) slab thickness with 8 Å of vacuum width were taken into consideration. Geometry relaxation was performed using conjugated gradient method. All calculations were performed with the \( 6 \times 6 \times 1 \) Monkhorst–Pack \( k \)-points sampling and 500 eV cut-off energy that provides surface energy convergence better than 0.2 J m\(^{-2}\).\(^{14}\)

As it was recently demonstrated, the origin of \( n \)-type conductivity of SnO\(_2\) can be consistently explained by random substitution of lattice oxygen by hydrogen and not by the native defects such as the oxygen vacancies.\(^{23,31}\) Here we consider both pure and indium-doped SnO\(_2\) surface (without any hydrogen atoms occupying the substitutional oxygen atom positions or occupying the interstitial positions). Experimentally, this case corresponds to the postpreparation annealing treatment of the SnO\(_2\) film that eliminates all the hydrogen atoms. As-prepared samples were modeled as structures where doping effect of each indium atom is compensated by a hydrogen atom placed in the oxygen site. Various levels of indium doping in SnO\(_2\) (0, 3, 6, and 9 at. \%) are considered by choosing slabs with 0, 2, 4, and 6 randomly distributed indium atoms substituting the tin atoms.

We recognize that there are several ways to distribute indium atoms as dopants at different cationic sites in the SnO\(_2\) lattice. All these configurations could be realized with a different statistical weight and experimentally observed sensor’s behavior represents by itself an averaged picture. Distribution of doping atoms can be thermodynamically unfavorable and depends on the sample preparation condition.\(^{32}\) Such metastable states are expected to appear in experiment due to the very low mobility of the indium cations in the crystal lattice at low temperature. In this study we assume the uniform distribution of indium atoms inside the SnO\(_2\) slab.

The energy for vacancy formation \( (E_{\text{vac}}) \) in a doped structure is defined as:

\[
E_{\text{vac}} = \frac{1}{n_{\text{O}}} \left[ E_{\text{def}} + \frac{1}{2} n_{\text{O}} E(O_2) - E_{\text{perf}} \right],
\]

where \( E_{\text{def}} \) and \( E_{\text{perf}} \) are the energies of defective (with vacancy) and perfect (vacancy free) systems, \( n_{\text{O}} \) is a number of formed vacancies and \( E(O_2) \) is the energy of oxygen molecule. The binding energy between the indium-doped SnO\(_2\) slab and the adsorbed hydrogen atoms is calculated as:

\[
E_B = \frac{1}{n_{\text{H}}} \left[ E(\text{slab}) + \frac{1}{2} E(H_2) - E(\text{slab} + n_{\text{H}}H) \right],
\]

where \( E(\text{slab} + n_{\text{H}}H), E(\text{slab}), \) and \( E(H_2) \) are the energy of the material slab with \( n_{\text{H}} \) adsorbed hydrogen atom, energy of the material slab without adsorbed hydrogen atoms, and the energy of H\(_2\) molecule, respectively. All the calculations were performed at zero temperature and hence vibrational and entropic effects were not considered.

## III. Results and Discussion

### A. Effect of indium-doping on oxygen vacancy formation

We carried out a systematic series of energy calculations to elucidate the dependence of \( E_{\text{vac}} \) on the formation of vacancy sites (in-plane and bridging positions) and the concentration of indium doping atoms. Different arrangements of oxygen vacancies were examined and to distinguish the different configurations of bridging vacancies, we adopted the following notations. As it is shown in Fig. 1(a), the bridging oxygen atoms form two rows each containing four oxygen atoms. Each configuration are denoted by two numbers: first number represents the number of bridging oxygen atoms removed from the surface while the second number represents an index of the individual configuration state with the same number of bridging vacancies. All these configurations are shown in Fig. 1(b).

To investigate the surface stability relative to the oxygen vacancy formation, we calculated \( E_{\text{vac}} \) for both single bridging oxygen and in-plane oxygen vacancies using Eq. (1). Vacancy sites are considered according to the surface oxygen positions [shown in Fig. 1(b)]. The energy values calculated for in-plane vacancy formation are summarized in Table I. The corresponding energy values for bridging oxygen vacancies are presented in Table II. From the results presented in Tables I and II, it is seen that the \( E_{\text{vac}} \) for a single in-plane oxygen vacancy decreases with increase in indium doping concentration but remains positive, i.e., structures are relatively stable with an in-plane oxygen vacancy formation at all doping levels. At the same time the \( E_{\text{vac}} \) for bridging
The number of bridging vacancies needed for sur-
face stabilization depends on the doping level. Thus, for
deleted. Doping with indium leads to the
instability of SnO₂ surface relative to the formation of bridg-
ing oxygen vacancies, i.e., in this case the value of $E_{\text{vac}}$ is
negative. The number of bridging vacancies needed for
surface stabilization depends on the doping level. Thus, for
3 at. % doped SnO₂ slab, one bridging vacancy stabilizes
the surface as the minimum $E_{\text{vac}}$. This will create a second
vacancy which is positive and is equal to 0.77 eV. Similarly,
the second vacancy creation. For 9 at. % doped structure,
the $E_{\text{vac}}$ that needs to create a third bridging vacancy is
positive and has the smallest absolute value equal to 0.36 eV.
Hence, it could be easily created by sample annealing at
higher temperatures. For example, experimental investiga-
tion has shown that even the most stable stoichiometric un-
doped (110) SnO₂ surface when heated above ~500 K re-
veals structure corresponding to be reduced surface.
In case of 9 at. % doping with indium, surface containing three
bridging oxygen vacancies per unit cell is found to be
weakly degenerated, i.e., there are four configurations,
(3.1), (3.2), (3.3), and (3.5), which have values of $E_{\text{vac}}$ close
to each other. It means that in the framework of our model it
expected that at finite temperatures the equilibrium surface
structure should represent itself the superposition of all these
configurations.

To investigate the effect of doping and surface vacancy
formation on the electronic properties of indium-doped SnO₂
slab, electronic density of states (DOS) were calculated. Re-
sults for 3 at. % doped SnO₂ slab, in the case of a perfect
surface (vacancy-free) and surface with one bridging oxygen
vacancy are presented in Fig. 2. In case of other doping
levels, the behavior of DOS (Fig. 2) on oxygen vacancy-to-
indium ratio is qualitatively the same and is not presented
here. It is seen that in the case of a perfect surface, each
indium atom substituting tin atom in the lattice introduces
one hole state that leads to $p$-type conductivity. One surface
oxygen vacancy donates two electrons into the slab that
eliminates the doping effect of two indium atoms and as a
result the structure does not contain free charge carriers at
practical interest, i.e., at room temperature and low partial
pressure of oxygen, the surface becomes unstable relative to
the second vacancy creation. For 9 at. % doped structure,
the $E_{\text{vac}}$ needs to create a second bridging vacancy is
positive and has the smallest absolute value equal to 0.36 eV.
Hence, it could be easily created by sample annealing at
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result the structure does not contain free charge carriers at

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**TABLE I.** The oxygen vacancy formation energy, $E_{\text{vac}}$, of in-plane vacancies as a function of doping level of SnO₂ with indium.

<table>
<thead>
<tr>
<th>Doping level (at. %)</th>
<th>$E_{\text{vac}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.75</td>
</tr>
<tr>
<td>3</td>
<td>1.70</td>
</tr>
<tr>
<td>6</td>
<td>1.52</td>
</tr>
<tr>
<td>9</td>
<td>1.41</td>
</tr>
</tbody>
</table>

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**TABLE II.** Theoretical values of bridging oxygen vacancy formation energy, $E_{\text{vac}}$, calculated by Eq. (1) at different levels of doping SnO₂ with indium. Used configurations are shown in Fig. 2b.

<table>
<thead>
<tr>
<th>Bridging vacancy configuration</th>
<th>Doping level, 3 at. %</th>
<th>Doping level, 6 at. %</th>
<th>Doping level, 9 at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.1)</td>
<td>-0.06</td>
<td>-0.19</td>
<td>-0.51</td>
</tr>
<tr>
<td>(2.1)</td>
<td>1.24</td>
<td>0.75</td>
<td>0.08</td>
</tr>
<tr>
<td>(2.2)</td>
<td>0.96</td>
<td>0.30</td>
<td>-0.52</td>
</tr>
<tr>
<td>(2.3)</td>
<td>1.34</td>
<td>0.84</td>
<td>0.04</td>
</tr>
<tr>
<td>(2.4)</td>
<td>0.85</td>
<td>0.21</td>
<td>-0.61</td>
</tr>
<tr>
<td>(2.5)</td>
<td>0.77</td>
<td>0.09</td>
<td>-0.34</td>
</tr>
<tr>
<td>(3.1)</td>
<td>...</td>
<td>0.95</td>
<td>0.41</td>
</tr>
<tr>
<td>(3.2)</td>
<td>...</td>
<td>1.42</td>
<td>0.38</td>
</tr>
<tr>
<td>(3.3)</td>
<td>...</td>
<td>0.94</td>
<td>0.85</td>
</tr>
<tr>
<td>(3.4)</td>
<td>...</td>
<td>0.84</td>
<td>0.36</td>
</tr>
<tr>
<td>(3.5)</td>
<td>...</td>
<td>0.89</td>
<td>0.40</td>
</tr>
<tr>
<td>(4.1)</td>
<td>...</td>
<td>...</td>
<td>0.77</td>
</tr>
<tr>
<td>(4.2)</td>
<td>...</td>
<td>...</td>
<td>0.82</td>
</tr>
<tr>
<td>(4.3)</td>
<td>...</td>
<td>...</td>
<td>0.72</td>
</tr>
<tr>
<td>(4.4)</td>
<td>...</td>
<td>...</td>
<td>0.94</td>
</tr>
<tr>
<td>(4.5)</td>
<td>...</td>
<td>...</td>
<td>0.82</td>
</tr>
<tr>
<td>(4.6)</td>
<td>...</td>
<td>...</td>
<td>0.93</td>
</tr>
<tr>
<td>(4.7)</td>
<td>...</td>
<td>...</td>
<td>0.83</td>
</tr>
<tr>
<td>(4.8)</td>
<td>...</td>
<td>...</td>
<td>0.98</td>
</tr>
</tbody>
</table>
achieve this, it is necessary to prepare SnO$_2$ films doped with two vacancies. The compensate the doping effect of one indium. But in this case, at 9 at. % doping, it takes three oxygen vacancies to intentionally doped with hydrogen, i.e., high indium concentration which also is expected to be unintentional doping during sample preparation. After that the sample has to be exposed to oxygen-rich atmosphere to fill as much surface vacant positions as possible. Briefly summarizing, we can conclude that the doping of SnO$_2$ with indium leads to an unstable (110) surface by the formation of bridging oxygen vacancies. Concentration of these vacancies increases with doping level growth. As it is shown below, bridging oxygen sites are the most energy favorable for hydrogen adsorption. Thus, decrease in the doping level of SnO$_2$ with indium should decrease number of active adsorption sites and reduce sensor’s sensitivity.

B. Hydrogen adsorption by indium-doped SnO$_2$ (110) surface

The ability of pure and indium-doped SnO$_2$ slabs to adsorb hydrogen atoms is investigated. The most energy stable configurations for 3, 6 and 9 at. % of indium-doped SnO$_2$ slab, correspond to the structures (1.1), (2.5), and (3.1)–(3.4) in Fig. 1(b), respectively. According to our results discussed above, structures with 6 and 9 at. % doping with indium should formally have one and two bridging oxygen vacancies per unit cell, respectively. At such conditions these structures should be $p$-type conductors. But at the same time, in experiments it is expected of these structures to have two and three bridging vacancies which eliminate $p$-doping effect of indium and make the slab nonconducting. Such behavior is in agreement with experimentally observed high resistance of In-doped SnO$_2$-based sensor in the absence of hydrogen. These structures as well as the intact undoped one are examined to explore their ability to interact with hydrogen. In the specific case of 9 at. % doping where the ground state with three bridging vacancies is degenerated we examined all the structures with minimal energies. It is found that there are no significant differences in calculated $E_B$ within an accuracy of 0.1 eV.

The modeling of H$_2$ molecule adsorption does not reveal any strong interaction with the indium-doped SnO$_2$ surface. Hydrogen molecule does not decay by itself to atomic hydrogen and there is no change in the conduction electron density obtained. This effect is in line with the experimental observation published earlier by the authors. To make the SnO$_2$-based sensors to be hydrogen sensitive, Pt catalyst is generally used, where hydrogen molecules decays to hydrogen atoms for catalyzing the reactions.

As a first step toward the description of interaction of hydrogen atoms with (110) SnO$_2$ surface it should be recognized that the surface oxygen sites are the most energy favorable for adsorption. In this study, we consider the scenarios of hydrogen adsorption by bridge and in-plane oxygen atoms, as well as the penetration of the hydrogen inside the pure SnO$_2$ slab (with no vacancies). It is found that SnO$_2$ (110) surface is able to adsorb hydrogen only on bridging oxygen positions. Calculated binding energies are equal to 1.25 and $-0.04$ eV for adsorption by bridging and in-plane oxygen atoms, respectively. For hydrogen atoms penetrated inside the slab, $E_B$ is equal to $-0.07$ eV, i.e., this configuration is unstable. For the indium-doped SnO$_2$ structures, another possible way of hydrogen adsorption is by filling the bridging vacancy site with hydrogen atom. Calculated $E_B$ for such structures with the bridging vacancies filled by hydrogen atoms results in $E_B$ = $-1.12$ eV for 3 at. %-doped SnO$_2$ slab. The corresponding energy values for 6 at. % doped structures are equal to $-0.77$ eV (1 filled vacancy) and $-0.99$ eV (2 filled vacancies). For 9 at. % doped structure, $E_B$ of hydrogen atoms filling bridging vacancies are found to be equal to $-1.20$ eV, $-0.39$ eV, and $-0.54$ eV for 1, 2, and 3 filled vacancies, respectively. Hydrogen adsorption by in-plane oxygen atoms is energetically unfavorable and the $E_B$ for hydrogen atoms is found to be 0.03 eV, $-0.13$ eV, and $-0.07$ eV for 3, 6, and 9 at. % doping levels, respectively. We found that among all possible ways of hydrogen adsorption, bridging oxygen atoms are energetically more unfavorable.

Since the most energetically favorable surface sites which adsorb hydrogen atoms, the dependence of $E_B$ on the concentration of adsorbed atoms is to be studied. Calculated $E_B$ at different doping levels and the number of adsorbed hydrogen atoms on bridging oxygen sites are presented in Fig. 3. The $E_B$ decreases with an increase in the number of
adsorbed hydrogen atoms. It is associated with an increase in the conduction electron’s chemical potential (due to the donation of one free electron by each adsorbed hydrogen atom). This result demonstrates that the best gas sensor sensitivity could be achieved at quite low concentration of adsorbed hydrogen atoms. The active surface of a gas sensor is not expected to be fully covered by the adsorbed hydrogen atoms due to a drastic decrease in the $E_B$ with increase in the number of adsorbed atoms. It is expected that in the framework of considered model, the most energetically favorable concentration of the adsorbed hydrogen atoms is one atom per surface cell. At this particular concentration, it is observed that there exists a maximum value for the $E_B$ at 3 at. % of indium-doping (Fig. 3). At this doping level, the gas sensor is expected to have the highest sensitivity due to the maximum in the $E_B$ as a function of indium-doping level especially at the low hydrogen concentration. At other doping levels the calculated values of $E_B$ are significantly smaller. In experimental situations, adsorbed hydrogen atoms could be easily desorbed resulting an increase in the sensor resistivity. Competing effects of hydrogen adsorption and desorption will decrease the free electrons concentration, i.e., the device sensitivity. At 3 at. % of doping hydrogen atoms will strongly interact with the surface and provide a robust change in sensor resistivity. These results are in good agreement with the experimental observation for the best sensitivity of 3 at. % indium-doped SnO$_2$ hydrogen-sensor as compared to other doping concentration.$^8$

As observed from the Fig. 3, the calculated $E_B$ decreases with the surface coverage with increased adsorbed atoms. Such effect could be explained if we consider the adsorbed atoms as charged surface defects. The total energy of the system could be considered as consisting of two parts. The first is a structure part depending on the arrangement of adsorbed hydrogen atoms on the surface. The second part is an electronic energy which increases with the growth of both conducting electron concentration and Fermi energy.$^{35}$ In our particular case, there are two competing effects which govern the binding energy: (i) energy gain due to the formation of covalent bonding between the hydrogen and the bridging oxygen atoms and (ii) the energy loss due to a total energy increase caused by the energy of conducting electrons. The contribution of the latter effect becomes larger when more hydrogen atoms are adsorbed. Unfortunately, there is no general way to compensate an electrostatic energy during consideration of a charged system in the two-dimensional slab in contrast to the crystals.$^{36}$ and molecules.$^{37}$ Due to this reason, it is not feasible to perform a quantitative analysis of this effect and only some qualitative speculations could be done at this point. From our point of view, the effect of energy growth caused by the contribution of conducting electrons’ energy is responsible for the $E_B$ decrease with increase in the number of adsorbed hydrogen atoms. For our particular model the optimal coverage of the slab, i.e., when the $E_B$ has a maximal value, is at 3 at. % of indium doping and 2 adsorbed hydrogen atoms per unit cell (see Fig. 3). As mentioned earlier, any variations in the electrical properties arise from band structure modification, the quantum confinement of the charge carriers and the predominant contribution of the largely defective and strained grain boundaries in the nanostructured materials. The trend in the calculated $E_B$ with respect to the indium doping correlates with the experimentally measured sensitivity.$^8$ This observation points out that the binding between the adsorbed hydrogen and the indium-doped SnO$_2$ is the key parameter in determining the sensor sensitivity.

Another way to improve the gas sensor’s sensitivity is by calcination at high temperature. To date it is established that the origin of SnO$_2$ conductivity is due to its unintentional doping with the hydrogen atoms substituting the oxygen atoms in the crystal lattice.$^{33,34}$ Calcination in air removes these hydrogen atoms from the lattice structure and some of the vacancies are filled by the atmospheric oxygen till an equilibrium vacancy concentration is reached. Thus, all the structures considered above correspond to the modeling of the calcined samples. As-prepared samples are modeled as indium-doped slab, where the effect of $p$-type doping by indium is compensated by the hydrogen donor atoms substituting oxygen atoms. These hydrogen atoms, which come from unintentional doping of SnO$_2$, possess quite large mobility$^{23}$ and could be removed from the lattice during calcinations. Oxygen vacancies appearing during calcination are filled by oxygen atoms from the air according to the conditions discussed above. The equilibrium bridging oxygen surface vacancy concentration depends on the In doping concentration. The results for calculated $E_B$ are presented in Fig. 3. It is seen that the effect of sample calcination is critical for the sensor sensitivity. $E_B$ as a function of doping level for as-prepared sample is a monotonic steadily decreasing function, i.e., there is no sensitivity improvement with doping.

The effect of calcination in air on the structure and sensitivity of indium-doped SnO$_2$-based hydrogen sensor is schematically summarized in Fig. 4. We assume that as-prepared sensor has a chemical formula Sn$_{1−x}$In$_x$O$_2$-$x$H$_y$+$\gamma$, where $x$ is the number of indium atoms substituting tin sites, $y$ is the number of hydrogen atoms substituting oxygen sites.
in SnO$_2$ lattice, and $z$ is a number of interstitial hydrogen atoms. During the sample preparation, indium-doped SnO$_2$ is unintentionally doped by hydrogen atoms occupying both interstitial and substitutional position. In the most stable state, hydrogen atoms in SnO$_2$ are donors donating electrons into the crystal lattice.\textsuperscript{23,31} Calcination leads to the removal of unintentionally doped hydrogen atoms from the crystal lattice. Oxygen vacancies appearing on the surface after the removal of those hydrogen atoms are partially filled by oxygen atoms from the air. Sensitivity behavior of the as-prepared and calcined sensor, according to $E_B$ is presented in Fig. 3. Perfectly calcined sensor is able to adsorb much larger number of hydrogen atoms, H$_{\text{abs}}$, donating more conduction electrons into the SnO$_2$ lattice.

IV. CONCLUSIONS

DFT+$U$ study of the hydrogen adsorption by indium-doped SnO$_2$ (110) surface was performed. It was found that doping with trivalent indium dopant makes the (110) surface unstable relative to the formation of bridging oxygen vacancies while vacancies in-plane positions are not energetically favorable. At doping levels of 3 and 6 at. % of indium, the surface stabilizes at oxygen vacancy-to-indium ratio equal to 1:2. DFT+$U$ calculations predict that at higher doping level of 9 at. %, this ratio becomes larger and suggests a way to overcome the problem of reproducible synthesis of $p$-type conducting oxide thin films. Binding energy of SnO$_2$ (110) surface with adsorbed hydrogen atoms has a maximum at 3–6 at. % of doping level with indium, and is in good agreement with the experimental results obtained from the hydrogen sensors sensitivity measurements.\textsuperscript{3} Sensitivity of the as-prepared and calcined SnO$_2$-based hydrogen sensor was also modeled. It is shown that the calcinations treatments can critically affect the sensitivity of the SnO$_2$-based hydrogen sensor due to the enhancement of binding energy between SnO$_2$ and adsorbed hydrogen atoms.

ACKNOWLEDGMENTS

We thank the National Science Foundation (Grant No. EECS-0801774) for funding this work. We would like to thank the Information Science Group of the Institute for Materials Research, Tohoku University for their continuous support of the SR11000-K2/51 supercomputing system and Stokes HPCC facility at UCF Institute for Simulation and Training (IST).

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