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Talgat M. Inerbaev
University of Central Florida

Yoshiyuki Kawazoe

Sudipta Seal
University of Central Florida

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Theoretical calculations of hydrogen adsorption by SnO₂ (110) surface: Effect of doping and calcination

Talgat M. Inerbaev,^{1,2} Yoshiyuki Kawazoe,² and Sudipta Seal^{1,3,a)}

¹NanoScience Technology Center, University of Central Florida, Orlando, Florida 32826, USA

²Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

³Advanced Material Processing and Analysis Center, University of Central Florida, Orlando, Florida 32826, USA and Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, Florida 32826, USA

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A pseudopotential plane-wave based density functional theory simulations of the hydrogen adsorption on rutile SnO₂ (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 SnO₂ thin films. The binding energy of SnO₂ (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 SnO₂-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 SnO₂ surface and the adsorbed hydrogen atoms. © 2010 American Institute of Physics. [doi:10.1063/1.3399565]

I. INTRODUCTION

Tin dioxide (SnO₂) is a wide band gap (3.6 eV) *n*-type semiconductor with rutile bulk structure.¹ It is a technologically important material, which is widely used as a hydrogen gas sensor.² We have reported earlier that the presence of hydrogen gas can be detected from the changes in the SnO₂-based hydrogen sensor's conductivity. When SnO₂ based sensor is exposed to hydrogen gas it reduces the surface oxygen atoms and decreases the space charge layer thickness around the nanocrystalline SnO₂ grains.³ Doping SnO₂ with other elements has been a point of interest as it provides the ability to tailor its electrical and microstructural properties.^{4–8}

In gas-sensor devices, SnO₂ is used in the form of nano-sized 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.⁹ 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 opera-

tion. 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 SnO₂ slabs as a hydrogen sensing material.

Structural and electronic properties of different SnO₂ surfaces have been extensively studied.^{10–20} Electronic structure of SnO₂ 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.¹² The study of the structural surface relaxation reveals that the stoichiometric (oxidized) surface is stabilized by the bridging oxygen atoms, and therefore, relaxes less.¹⁵ 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.¹⁴ In the present contribution we study the oxygen vacancy formation energies on SnO₂ (110) surface as a function of In doping level. Interaction of hydrogen with the most stable configurations of indium-doped SnO₂ 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 SnO₂-based hydrogen sensors under similar conditions. At higher doping level of 9 at. % calculations predict stability of structure with *p*-type conductivity. Wide-

^{a)}Author to whom correspondence should be addressed. Electronic addresses: sseal@mail.ucf.edu and inerbaev@yahoo.com.

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 Perdue–Burke–Ernzerhof parametrization.²⁴ The semicore Sn d states in SnO₂ 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 d levels and severely affects the band gap due to shortcomings intrinsic in the construction of DFT functionals. In order to correct the positions of d levels, the semiempirical GGA+ U scheme in the version by Dudarev *et al.*²⁹ which incorporates on-site Coulomb correlation interaction into the GGA functionals is employed. The value of self-interaction parameter U for Sn d states in SnO₂ was recently determined to be 3.5 eV.²³ The self interaction parameter for indium dopant atoms was taken as $U=7$ eV as estimated for In₂O₃ 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 (110) surface is the most stable in oxides with rutile structure such as SnO₂ and TiO₂ and it is thought to be the predominant surface in these polycrystalline samples.¹ Theoretical investigations support these data and (110) surface of SnO₂ is found to have the lowest energy.¹⁴ For these reasons, we restrict ourselves by studying the properties of this particular surface.

The (110) SnO₂ surface was simulated as a symmetric 192-atoms slab. Four-layer of SnO₂ 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 $6\times6\times1$ 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 SnO₂ 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 SnO₂ 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 SnO₂ 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 SnO₂ (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 SnO₂ 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 SnO₂ slab.

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

$$E_{\text{vac}} = \frac{1}{n_{\text{O}}} \left\{ E_{\text{def}} + \frac{1}{2} n_{\text{O}} E(\text{O}_2) - E_{\text{perf}} \right\}, \quad (1)$$

where E_{def} and E_{perf} are the energies of defective (with vacancy) and perfect (vacancy free) systems, n_{O} is a number of formed vacancies and $E(\text{O}_2)$ is the energy of oxygen molecule. The binding energy between the indium-doped SnO₂ slab and the adsorbed hydrogen atoms is calculated as:

$$E_B = \frac{1}{n_{\text{H}}} \left[E(\text{slab}) + \frac{1}{2} E(\text{H}_2) - E(\text{slab} + n_{\text{H}}\text{H}) \right], \quad (2)$$

where $E(\text{slab} + n_{\text{H}}\text{H})$, $E(\text{slab})$, and $E(\text{H}_2)$ are the energy of the material slab with n_{H} adsorbed hydrogen atom, energy of the material slab without adsorbed hydrogen atoms, and the energy of H₂ 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_{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_{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_{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_{vac} for bridging

FIG. 1. (Color online) (a) (110) surface slab of rutile structure SnO_2 with tin and oxygen ions shown in unrelaxed positions. (b) Explored configurations of SnO_2 (110) surfaces with different number of bridging oxygen vacancies. Two rows of bridging oxygen sites are shown. Open circles denote occupied cites, while crosses correspond to bridging vacancies. All possible ways of vacancies arrangement in considered range of concentration are examined.

vacancies is positive for all undoped structure and is equal to 2.85 eV while the corresponding value for the in-plane vacancy is equal to 3.75 eV. Doping with indium leads to the instability of SnO_2 surface relative to the formation of bridging oxygen vacancies, i.e., in this case the value of E_{vac} is negative. The number of bridging vacancies needed for surface stabilization depends on the doping level. Thus, for 3 at. % doped SnO_2 slab, one bridging vacancy stabilizes the surface as the minimum E_{vac} . This will create a second vacancy which is positive and is equal to 0.77 eV. Similarly, two bridging vacancies can stabilize the surface for 6 and 9 at. % doped structures as E_{vac} needed to create two bridging vacancies is negative, while the energy to create a third one is again positive. In the case of the structure (2.5) in Fig. 1(b), the energy of the second bridging vacancy creation is positive, but it has a very small absolute value equal to 0.09 eV. This means that despite the formal stability at zero temperature, 6 at. % doped (110) SnO_2 surface could be stable only at very low temperatures. At any external conditions of

TABLE I. The oxygen vacancy formation energy, E_{vac} of in-plane vacancies as a function of doping level of SnO_2 with indium.

Doping level (at. %)	E_{vac} (eV)
0	3.75
3	1.70
6	1.52
9	1.41

TABLE II. Theoretical values of bridging oxygen vacancy formation energy, E_{vac} , calculated by Eq. (1) at different levels of doping SnO_2 with indium. Used configurations are shown in Fig. 2(b).

Bridging vacancy configuration	E_{vac} (eV)		
	Doping level, 3 at. %	Doping level, 6 at. %	Doping level, 9 at. %
(1.1)	−0.06	−0.19	−0.51
(2.1)	1.24	0.75	0.08
(2.2)	0.96	0.30	−0.52
(2.3)	1.34	0.84	0.04
(2.4)	0.85	0.21	−0.61
(2.5)	0.77	0.09	−0.34
(3.1)	...	0.95	0.41
(3.2)	...	1.42	0.38
(3.3)	...	0.94	0.85
(3.4)	...	0.84	0.36
(3.5)	...	0.89	0.40
(4.1)	...	...	0.77
(4.2)	...	...	0.82
(4.3)	...	...	0.72
(4.4)	...	...	0.94
(4.5)	...	...	0.82
(4.6)	...	...	0.93
(4.7)	...	...	0.83
(4.8)	...	...	0.98

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_{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 investigation has shown that even the most stable stoichiometric undoped (110) SnO_2 surface when heated above ~ 500 K reveal structure corresponding to be reduced surface.³³ In case of 9 at. % doping with indium, surface containing three bridging oxygen vacancies per unit cell is found to be strongly degenerated, i.e., there are four configurations, (3.1), (3.2), (3.4), and (3.5), which have values of E_{vac} close to each other. It means that in the framework of our model it is 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 SnO_2 slab, electronic density of states (DOS) were calculated. Results for 3 at. % doped SnO_2 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

FIG. 2. Calculated electronic DOS for 3 at. % indium-doped SnO_2 slab: (a) stoichiometric (without vacancies) and (b) with one bridging oxygen vacancy structures. Filled areas correspond to occupied electronic states. Non-stoichiometric structure is more stable since although there is an energy loss due to surface vacancy formation, it is compensated by energy gain due to elimination of hole states in electronic structure. At higher doping level of 9 at. % structures with hole states could be stable relatively surface oxygen vacancies formation.

least in the limit of zero temperature. However, in the case of 6 at. % doped SnO_2 slab, the surface is unstable with the creation of two bridging oxygen vacancies. These vacancies also eliminate the effect of p -type doping of SnO_2 with indium. At 9 at. % doping, it takes three oxygen vacancies to compensate the doping effect of one indium. But in this case, the structure is absolutely unstable due to the formation of two vacancies. The E_{vac} needed to create a third bridging vacancy is quite small but positive, and varies in the range 0.36–0.40 eV.

This theoretical result points out the possibility of synthesizing p -type conducting indium-doped SnO_2 films. To achieve this, it is necessary to prepare SnO_2 films doped with high indium concentration which also is expected to be unintentionally doped with hydrogen, i.e., n -type impurities.^{23,31} The film has to be annealed at high temperature to remove the hydrogen atoms that could be present inside the film due to its 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, increase 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.⁸ 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.⁸ 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.³⁴

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

FIG. 3. Theoretical values of binding energies per adsorbed hydrogen atom calculated using Eq. (2). Adsorption by annealed (closed symbols) and non-annealed (open symbols) indium-doped SnO_2 slab is considered as a function of doping level with indium and number of adsorbed atoms (H^{ads}). For each doping level the most stable slab structures was used except the case of 9 at. % of doping where presented results were obtained by averaging over four lowest energy configurations (see Table II). H^{ads} atoms were placed on surface bridging oxygen sites and arranged to provide the maximal average distance between them. Such ordering is the most energy favorable since minimizes interaction between H^{ads} .

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 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 crystals³⁶ 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.^{23,31} 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 mobility²³ 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 $\text{Sn}_{1-x}\text{In}_x\text{O}_{2-y}\text{H}_{y+z}$, where x is the number of indium atoms substituting tin sites, y is the number of hydrogen atoms substituting oxygen sites

FIG. 4. Schematic sketch showing the effect of calcination on the structure and sensitivity of SnO₂-based hydrogen sensor for low level of indium doping. (a) As-prepared sample has some controlled concentration of indium. Effect of *p*-type doping is eliminated by unintentional doping with hydrogen atoms and oxygen vacancies formation and resulting structure is nonconducting. Hydrogen doping atoms are expected to occupy oxygen atomic positions (see Ref. 1). These hydrogen atoms are removed by calcinations procedure and system should be *n*-type conducting since during hydrogen release there is a substitution of singly charged H⁺ defect by doubly charged oxygen vacancy. Postcalcination treatment of SnO₂-based sensor should include its exposition in oxygen-rich atmosphere. Surface oxygen vacancy sites are partially filled with atmospheric oxygen till equilibrium vacancy concentration is attained and system becomes nonconducting. (b) According to results presented in Fig. 3, calcined surface displays a better tendency for hydrogen adsorption compared to as-prepared one and gas sensor prepared by this way is much more sensitive.

in SnO₂ lattice, and *z* is a number of interstitial hydrogen atoms. During the sample preparation, indium-doped SnO₂ is unintentionally doped by hydrogen atoms occupying both interstitial and substitutional position. In the most stable state, hydrogen atoms in SnO₂ are donors donating electrons into the crystal lattice.^{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^{ads}, donating more conduction electrons into the SnO₂ lattice.

IV. CONCLUSIONS

DFT+*U* study of the hydrogen adsorption by indium-doped SnO₂ (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 at 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 SnO₂ (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.³ Sensitivity of the as-prepared and calcined SnO₂-based hydrogen sensor was also modeled. It is shown that the calcinations treatments can critically affect the sensitivity of the SnO₂-based hydrogen sensor due to the enhancement of binding energy between SnO₂ and adsorbed hydrogen atoms.

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- ¹V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, UK, 1994).
- ²M. J. Madon and S. R. Morrison, *Chemical Sensing with Solid State Devices* (Academic, San Diego, 1989).
- ³C. Drake, S. Deshpande, and S. Seal, *Appl. Phys. Lett.* **89**, 143116 (2006).
- ⁴C. Drake and S. Seal, *Appl. Phys. Lett.* **90**, 233117 (2007).
- ⁵H. M. Yang, X. Song, X. Zhang, W. Ao, and G. Qiu, *Mater. Lett.* **57**, 3124 (2003).
- ⁶G. Xu, Y.-W. Zhang, X. Sun, C.-L. Xu, and C.-H. Yan, *J. Phys. Chem. B* **109**, 3269 (2005).
- ⁷A. P. Maciel, P. N. Lisboa-Filho, E. R. Leite, C. O. Paiva-Santos, W. H. Schreiner, Y. Maniette, and E. Longo, *J. Eur. Ceram. Soc.* **23**, 707 (2003).
- ⁸C. Drake, A. Amalu, J. Bernard, and S. Seal, *J. Appl. Phys.* **101**, 104307 (2007).
- ⁹*Handbook of Nanostructured Materials and Nanotechnology*, edited by H. S. Nalwa (Academic, USA, 2000).
- ¹⁰M. Viitala, O. Cramariuc, T. T. Rantala, and V. Golovanov, *Surf. Sci.* **602**, 3038 (2008).
- ¹¹M. A. Maki-Jaskari and T. T. Rantala, *Phys. Rev. B* **64**, 075407 (2001).
- ¹²T. T. Rantala, T. S. Rantala, and V. Lantto, *Electronic Structure of SnO₂ (110) Surface* (Elsevier, New York, 2000).
- ¹³T. T. Rantala, T. S. Rantala, and V. Lantto, *Surf. Sci.* **420**, 103 (1999).
- ¹⁴J. Oviedo and M. J. Gillan, *Surf. Sci.* **463**, 93 (2000).
- ¹⁵J. Oviedo and M. J. Gillan, *Surf. Sci.* **467**, 35 (2000).
- ¹⁶T. S. Rantala, T. T. Rantala, and V. Lantto, *Computational Studies for the Interpretation of Gas Response of SnO₂ (110) Surface* (Elsevier, New York, 2000).
- ¹⁷K. G. Godinho, A. Walsh, and G. W. Watson, *J. Phys. Chem. C* **113**, 439 (2009).
- ¹⁸M. Batzill, K. Katsiev, J. M. Burst, Y. Losovyj, W. Bergermayer, I. Tanaka, and U. Diebold, *J. Phys. Chem. Solids* **67**, 1923 (2006).
- ¹⁹W. Bergermayer and I. Tanaka, *Appl. Phys. Lett.* **84**, 909 (2004).
- ²⁰M. Batzill, K. Katsiev, J. M. Burst, U. Diebold, A. M. Chaka, and B. Delley, *Phys. Rev. B* **72**, 165414 (2005).
- ²¹A. L. Dawar, A. K. Jain, C. Jagadish, *Semiconducting Transparent Thin Films*, edited by H. L. Hartnagel (IOP, London, 1995).
- ²²D. C. Look, B. Claflin, Ya. I. Alivov, and S. J. Park, *Phys. Status Solidi A* **201**, 2203 (2004).
- ²³A. K. Singh, A. Janotti, M. Scheffler, and C. G. Van de Walle, *Phys. Rev. Lett.* **101**, 055502 (2008).
- ²⁴J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁵G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ²⁶P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ²⁷G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- ²⁸G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ²⁹S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- ³⁰P. Erhart, A. Klein, R. G. Egdell, and K. Albe, *Phys. Rev. B* **75**, 153205 (2007).
- ³¹Ç. Kılıç and A. Zunger, *Appl. Phys. Lett.* **81**, 73 (2002).
- ³²T. M. Inerbaev, R. Sahara, H. Mizuseki, Y. Kawazoe, and T. Nakamura,

[Mater. Trans.](#) **48**, 666 (2007).

³³D. F. Cox, T. B. Fryberger, and S. Semancik, [Phys. Rev. B](#) **38**, 2072 (1988).

³⁴J. Gong, Q. Chen, W. Fei, and S. Seal, [Sens. Actuators B](#) **102**, 117 (2004).

³⁵T. M. Inerbaev, R. Sahara, H. Mizuseki, Y. Kawazoe, and T. Nakamura, [Solid State Commun.](#) **150**, 18 (2010).

³⁶C. G. Van de Walle and J. Neugebauer, [J. Appl. Phys.](#) **95**, 3851 (2004).

³⁷G. Makov and M. C. Payne, [Phys. Rev. B](#) **51**, 4014 (1995).