Ab initio study of native defects in SnO under strain

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received 9 October 2013; accepted in final form 19 March 2014
published online 1 April 2014

PACS 68.43.-h - Chemisorption/physisorption: adsorbates on surfaces
PACS 73.20.-r - Electron states at surfaces and interfaces
PACS 81.05.Fb - Organic semiconductors

Abstract – Tin monoxide (SnO) has promising properties to be applied as a p-type semiconductor in transparent electronics. To this end, it is necessary to understand the behaviour of defects in order to control them. We use density functional theory to study native defects of SnO under tensile and compressive strain. We show that Sn vacancies are less stable under tension and more stable under compression, irrespectively of the charge state. In contrast, O vacancies behave differently for different charge states. It turns out that the most stable defect under compression is the +1 charged O vacancy in an Sn-rich environment and the charge neutral O interstitial in an O-rich environment. Therefore, compression can be used to transform SnO from a p-type into either an n-type or an undoped semiconductor.

Introduction. – Tin monoxide (SnO) has been known for years but has been largely ignored, because it is a metastable form of the famous tin dioxide (SnO$_2$) [1,2]. Just recently, it has gained attention as a promising transparent p-type semiconductor with high mobility, making it a candidate for applications in transparent and flexible circuits [3–5]. To control and improve its properties, it is necessary to understand the behaviour of the defects in the material. While it has been concluded from simulations that the p-type behaviour stems from Sn vacancies [6], other reports point out that complexes formed by unintentional H impurities and Sn vacancies play a major role in generating the holes [7]. Moreover, recent experimental and theoretical studies have shown that a considerable increase in the hole mobility is caused by the defects formed in an Sn-rich environment (V$_O$ and Sn$_i$) [8–10]. It has been proposed that defect engineering and an increased mobility can be achieved by both internal and external strain [11], which is more feasible for materials with low bulk modulus [12], such as SnO (35 GPa) [13], implying an urgent need to understand how the defects behave when strain is applied to SnO.

Under pressure SnO shows a phase transition into an orthorhombic structure at 1.5 GPa due to shear strain in non-hydrostatic conditions [13–15]. However, the tetragonal phase of interest is stable at hydrostatic pressures of up to 51 GPa [13,14]. In addition, SnO behaves as a metal at pressures higher than 5 GPa due to the closing of its band gap [14,16] and even is superconducting at temperatures below 1.4 K and pressures between 6 and 19 GPa [17,18]. To our knowledge, neither experiments nor simulations on defects in SnO under pressure have been reported so far. It therefore is the aim of the present work to establish an insight into the stability of SnO native defects for tensile and compressive strain.

Methodology. – Defect calculations are often challenging and time consuming for a couple of reasons. The first issue is the underestimation of the band gap in the standard density functional theory, which introduces errors in the total energy because of a wrong description of the occupied defect states inside the gap [19]. This problem often can be overcome by more sophisticated approaches, however, making the calculations more time consuming [20,21]. The second issue are spurious interactions with the jellium and with artificial images caused by periodic boundary conditions [22], which calls for large supercells. There exist various ideas to compensate for the artificial interactions in order to reduce the required size [20,21]. The correction scheme proposed by Freysoldt and coworkers models the long and short-range interactions of the defect and achieves a good formation energy convergence with respect to the supercell size [23–25].

Another important calculation aspect is whether to consider the Sn 4$d$ states as core states included in the pseudopotential or to treat them as valence states, since 10 additional 4$d$ valence electrons per Sn atom would increase the calculation time considerably. They therefore

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are usually included in the pseudopotential [6,7] with the justification of their low energy and, consequently, little influence near the Fermi level [26,27]. However, the Sn 4d orbitals mix slightly with the O 2s orbitals [28], which might affect the formation energy of defects. With these points in mind, we will first address the question as to whether the Freysoldt correction method is able to reduce the necessary supercell size and then check for differences in the formation energies when considering the Sn 4d orbitals as core or as valence states.

We employ the density functional theory as implemented in the Vienna Ab-initio Simulation Package by the projector augmented-wave method [29,30]. For the exchange-correlation potential we use the generalized gradient approximation [6,34]. To address the supercell convergence, we have calculated also using the generalized gradient approximation as parametrized by Perdew, Burke, and Ernzerhof [31]. The O 2s and 2p orbitals as well as the Sn 5s and 5p orbitals are modeled as valence states, whereas the Sn 4d orbitals are treated either as core states or as valence states where specified. Relativistic corrections are taken into account for the Sn core. All the calculations are based on an energy cutoff of 600 eV and a Brillouin zone sampling by the Monkhorst-Pack method [32] with a $3 \times 3 \times 3$ $k$-mesh. The energies and forces are converged to less than $10^{-5}$ eV and 0.02 eV/Å, respectively.

The structure of SnO is given by a lithium-type tetragonal unit cell with space group $P4/nmm$, containing two formula units. The optimized lattice parameters of the pristine unit cell at zero pressure are $a = 3.87$ Å and $c = 5.03$ Å, which are slightly higher than the experimental values of $a = 3.80$ Å and $c = 4.84$ Å [33]. Still, our values are in good agreement with previous theoretical work also using the generalized gradient approximation [6,34]. To address the supercell convergence, we have calculated the formation energies of the native defects at zero pressure for $3 \times 3 \times 3$ and $4 \times 4 \times 3$ supercells with 108 and 192 atoms, respectively. For supercells with a defect, the atomic positions are fully relaxed, while the lattice parameters of the pristine supercell are maintained. Strain effects are investigated using the $4 \times 4 \times 3$ supercell and considering the Sn 4d orbitals as valence states. For hydrostatic pressures of $+1.4$ GPa (compression) and $-1.4$ GPa (tension), we obtain pristine cell parameters of $a = 3.84$ Å, $c = 4.82$ Å and $a = 3.88$ Å, $c = 5.58$ Å, respectively. The former values agree reasonably well with the experimental results of $a = 3.79$ Å and $c = 4.71$ Å for SnO compressed by $+1.4$ GPa. Experimental values for SnO under tension could not be found in the literature. We observe that the lattice parameters change asymmetrically under pressure. Under compression, the $c/a$ ratio is slightly reduced to 1.26 from 1.30 without pressure, whereas it grows strongly to 1.44 under tension. This behavior is due to the fact that the bonding along the $c$-axis is of van der Waals type and therefore quickly weakens under tension.

We study the three most stable defects [6], namely, the Sn vacancy (V$_{Sn}$) charged from 0 to $-2$, the O vacancy (V$_{O}$) charged from 0 to $+2$, and the charge neutral O interstitial (O$_{i}$). In the latter case the interstitial atom is positioned next to the center of an Sn octahedron (shifted along the $z$-axis away from the O plane), see fig. 1. Examples of other defects are also shown in this figure. The formation energy $E^f(X^q)$ of a defect $X$ in a charge state $q$ is given by

$$E^f(X^q) = E_{\text{total}}(X^q) - E_{\text{total}}(\text{host}) - \sum_i n_i \mu_i,$$

$$+ q(E_F + E_{\text{VBM}}^\text{host}) + E_{\text{correction}}(q),$$

(1)

where $E_{\text{total}}(\text{host})$ is the total energy of the pristine charge neutral supercell of the host crystal and $E_{\text{total}}(X^q)$ is the total energy in the presence of a defect $X$ in the charge state $q$. Moreover, $n_i$ is the number of atoms of species $i$ that form the defect, where a positive (negative) value means that the atom is added to (taken from) the host structure to create the defect. The chemical potential $\mu_i$ is constrained by the equilibrium between SnO and metallic $\beta$-Sn in the Sn-rich limit, with $\mu_{Sn} = \mu_{\beta-Sn}$ and $\mu_O = \mu_{SnO} - \mu_{\beta-Sn}$, and by the equilibrium between SnO and SnO$_2$ in the O-rich limit, with $\mu_{Sn} = 2\mu_{SnO} - \mu_{SnO_2}$ and $\mu_O = \mu_{SnO_2} - \mu_{SnO}$. The chemical potentials of O, $\beta$-Sn, SnO$_2$, and SnO are obtained by calculating the total energies of the individual compounds. For Sn and O, respectively, we find $\mu_{Sn} = -3.96$ eV and $\mu_O = -7.57$ eV for the Sn-rich limit and $\mu_{Sn} = -4.21$ eV and $\mu_O = -7.32$ eV for the O-rich limit. The formation energies of SnO and SnO$_2$ are calculated to be $-2.64$ eV and $-5.04$ eV, respectively, which compares well with the values $-2.72$ eV and $-5.21$ eV of Togo and coworkers [6]. The small differences are attributed to a different approximation of the exchange-correlation potential.

The Fermi energy $E_F$ in eq. (1) ranges from the valence band maximum (VBM) up to the conduction band minimum (CBM). For setting the Fermi energy to zero at the VBM, we calculate the energy of the VBM as the
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Table 1: Formation energies of SnO native defects in the O-rich limit for different supercell sizes and for the Sn 4d orbitals treated as core or valence states (in eV).

| Sn 4d states | Supercell size | V\textsuperscript{−2}\textsubscript{Sn} | V\textsuperscript{−1}\textsubscript{Sn} | V\textsubscript{Sn} | O\textsubscript{1} | V\textsubscript{O} | V\textsuperscript{+1}\textsubscript{O} | V\textsuperscript{+2}\textsubscript{O} |
|--------------|----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| Valence      | 3 × 3 × 3      | 1.86            | 1.46            | 1.41           | 0.99           | 1.44           | 1.31           | 1.23           |
|              | 4 × 4 × 3      | 1.75            | 1.45            | 1.38           | 0.99           | 1.44           | 1.36           | 1.11           |
| Core         | 3 × 3 × 3      | 1.72            | 1.35            | 1.31           | 0.96           | 1.50           | 1.40           | 1.35           |
|              | 4 × 4 × 3      | 1.69            | 1.37            | 1.31           | 0.97           | 1.52           | 1.44           | 1.19           |
| Not specified | 3 × 3 × 3      | –               | –               | 1.30           | 1.02           | –              | –              | –              |
| Core [6]     | 4 × 4 × 3      | 1.42            | 1.34            | 1.30           | 0.97           | 1.35           | 1.17           | 1.01           |

Table 2: Formation energies of SnO native defects under tension and compression (in eV/GPa).

|          | V\textsuperscript{−2}\textsubscript{Sn} | V\textsuperscript{−1}\textsubscript{Sn} | V\textsubscript{Sn} | O\textsubscript{1} | V\textsubscript{O} | V\textsuperscript{+1}\textsubscript{O} | V\textsuperscript{+2}\textsubscript{O} |
|----------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| Tension  | 0.32            | 0.30            | 0.31           | 0.09           | 0.10           | -0.04          | -0.32          |
| Compression | -0.16         | -0.16           | -0.15          | -0.01          | -0.08          | -0.09          | 0.15           |

total energy difference between the 0 and +1 charged host cells, i.e., \( E_{\text{host}} = E_{\text{total}}(\text{host}^0) - E_{\text{total}}(\text{host}^{+1}) \). Considering the Sn 4d orbitals as core states, we obtain values of 4.27 eV and 4.26 eV for the 3 × 3 and 4 × 4 × 3 supercells, respectively, whereas Sn 4d valence states result in values of 6.22 eV and 6.24 eV. Independently of the treatment of the Sn 4d orbitals, we find indirect band gaps of 0.40 eV and 0.46 eV, respectively. This constitutes an underestimated band gap in compression compared to the experimental result of 0.7 eV [36], but an improvement with respect to the 0.29 eV of ref. [6]. When strain is applied the band gap of SnO is reduced significantly under compression according to the experiments in ref. [14]. The converse should be true under tension, i.e., the band gap should grow. For the 4 × 4 × 3 supercell with valence Sn 4d states, the band gap in fact decreases to 0.07 eV at +1.4 GPa (compression) and increases to 1.8 eV at -1.4 GPa (tension). These values are expected to be underestimated, because of the underestimated band gap in the calculations. Moreover, \( E_{\text{host}}^{VBM} \) changes significantly to 4.87 eV under tension and 6.93 eV under compression. The term \( E_{\text{correction}} \) of eq. (1) represents the Freysoldt correction, which is obtained for each defect using a cutoff energy of 600 eV [37] and a relative permittivity of SnO of 15 [36]. Following ref. [25], we consider the relaxed structure and use the bulk unit cell as reference for the potential alignment.

Results and discussion. – Results for the convergence analysis of the supercell size are presented in table 1, both for the Sn 4d orbitals treated as core and valence states. Comparison of the present results with the literature shows excellent agreement for the V\textsubscript{Sn} and O\textsubscript{1} defects in the charge neutral state. On the other hand, we find a significant difference of 0.17 eV (about 12%) for the formation energy of V\textsubscript{O}, which is consistent with the observation that different generalized gradient approximations cause shifts of the formation energies of metal monovacancies by up to 15% [38]. Usage of a different correction method for charged states may account for further discrepancies to ref. [6].

Table 1 demonstrates that the formation energies deviate for the two supercell sizes. The higher the charge of the system, the higher the deviation, because the interaction with periodic images is enhanced. Even with the Freysoldt correction the differences are relevant, reaching 0.12 eV (about 10%) for a doubly charged defect (Sn 4d states treated as valence states). In addition to this quantitative difference, the trend of the formation energy change is not the same for all charge states of the same defect. For V\textsubscript{O}, for example, in the larger supercell the 0 and +1 charge defects have a higher formation energy but a lower in the +2 charge state. To avoid a wrong qualitative description of the stability of this defect, thus, the larger 4 × 4 × 3 supercell has to be used. According to table 1 the results differ significantly when the Sn 4d orbitals are treated as core or valence states. Differences occur for both the V\textsubscript{Sn} and V\textsubscript{O} defects in all charge states, being often larger than the effect of the supercell size. For the 4 × 4 × 3 supercell we obtain discrepancies of up to 0.08 eV (about 7%), which is enough to affect the results qualitatively. Thus, even though the Sn 4d states are low in energy they play a role in the defect formation, probably because of their small but finite hybridization with the O 2s states [28]. The following considerations consequently are based on the 4 × 4 × 3 supercell with the Sn 4d orbitals treated as valence states.

Turning to the stability of SnO native defects under strain, we study tension by applying a pressure of -1.4 GPa and compression by applying a pressure of +1.4 GPa. The variation of the formation energy under strain is summarized in table 2. For O\textsubscript{1} we find almost the same value for compression and a slight increase for tension, whereas for V\textsubscript{Sn} there is a clear increase (decrease) for
Fig. 2: (Colour on-line) Formation energies of SnO native defects under tensile strain (top row), no strain (middle row), and compressive strain (bottom row) for the Sn-rich (left column) and O-rich (right column) limits. Each colour represents a different type of defect and dots represent changes of the excitation state. The coloured bars on the bottom of the graphs give the defects with lowest formation energy.
tension (compression). In the latter defect the variation is similar for all charge states, whereas for $V_O$ the different charge states behave differently. The charge neutral $V_O$ resembles the behaviour of $V_{Sn}$, but with lower magnitudes. On the contrary, a $V_O^{+2}$ defect shows a similarly strong variation as $V_{Sn}$, but is more stable under tension and less stable under compression, probably because of the enhanced interaction with the lone pair trapping an electron. Finally, for $V_O^{+1}$ the formation energy is reduced for both tensile and compressive strain.

To visualize how these variations modify the relative stability of the defects, we show in fig. 2 the formation energy as a function of the Fermi energy, which depends on external factors such as the temperature. The curve for zero strain agrees well with ref. [6]. In the Sn-rich limit the most stable defects are $V_{O}^{+2}$ from the VBM to 0.17 eV, charge neutral $V_O$ from 0.17 eV to 0.40 eV, and $V_{Sn}^{-2}$ at higher Fermi energy. In the O-rich limit, the $O_i$ and $V_{Sn}^{-2}$ defects are most stable below and above a Fermi energy of 0.38 eV, respectively. Under tension the formation energy of $V_{O}^{+2}$ is lowered significantly to make it the most stable defect near the VBM, even in the O-rich environment. On the other hand, in the Sn-rich limit we obtain no qualitative change under tension, because $V_{O}^{+2}$ was already the most stable defect without strain. Under compression the formation energy of $V_{O}^{+2}$ increases while that of $V_{O}^{-1}$ decreases, so that the latter becomes the most stable defect in the Sn-rich limit. In addition, because the band gap is reduced, $V_{Sn}$ is no longer preferable near the CBM. Therefore, the most stable defect is always $V_{O}^{+1}$, which renders an n-type character to SnO under these conditions. In order to make sure that this conclusion does not depend on the underestimation of the band gap in the generalized gradient approximation (the band width of the mid-gap states of the $V_{O}^{+1}$ defect is 0.2 eV), we have taken into account an onsite interaction of 2.5 eV for the Sn $p$ states. In this case the band gaps without pressure and under compression increase from 0.46 eV to 0.53 eV and from 0.07 eV to 0.20 eV, respectively, for the defect-free system. According to fig. 3, the n-type character is maintained. In the O-rich limit, see fig. 2, the formation energy of $V_{Sn}$ throughout the band gap is higher than that of charge neutral $O_i$, giving rise to an undoped semiconductor. As a consequence, control of the growth conditions in combination with compressive strain can be used to tailor the dominating defects and, thus, to transform SnO from a p-type to either an n-type or an undoped semiconductor.

**Conclusion.** We have studied the stability of the native defects in SnO under pressure. From the methodology point of view, we find that a $4 \times 4 \times 3$ supercell is required and sufficient for a corrected description of the system. The Freysoldt correction method for improving the convergence with respect to the supercell size turns out to be inefficient for SnO. Our results demonstrate significant variations in the formation energies when the Sn 4$d$ states are treated as core or valence states. Therefore, we have been able to quantitatively improve the description of the native defects in unstrained SnO as compared to the existing literature, though the qualitative situation remains the same. For the first time we have analyzed the effects of strain on the defects in SnO. While an applied strain of $\pm 1.4$ GPa (tensile and compressive) does not alter the charge states of the $V_{Sn}$ and $O_i$ defects, different charge states of $V_O$ behave very differently under strain. Under tension the formation energy of $V_{O}^{+2}$ is reduced so that this defect becomes most stable near the VBM even in an O-rich growth environment, whereas under compression it increases to leave $V_{O}^{+1}$ the most stable defect in an Sn-rich environment. In the O-rich limit under compression charge neutral $O_i$ becomes the most stable defect in the full Fermi energy range, due to a reduction of the band gap. Our results show that SnO can be modified from a p-type to either an n-type or an undoped semiconductor by means of the growth conditions and applied pressure, without affecting the transparency.

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