ORIGINAL ARTICLE

Metallicity at interphase boundaries due to polar catastrophe induced by charge density discontinuity

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The electronic properties of interphase boundaries are of basic importance for most materials, particularly when those properties deviate strongly from the bulk behavior. We introduce a mechanism that can result in metallicity at stoichiometric interphase boundaries between semiconductors based on the idea of polar catastrophe, which is usually considered only in the context of heterostructures. To this end, we perform *ab initio* calculations within density functional theory to investigate the electronic states at stoichiometric SnO/SnO₂ (110) interphase boundaries. In this system, one would not expect polar catastrophe to have a role according to state-of-the-art theory because the interface lacks formal charge discontinuity. However, we observe the formation of a hole gas between the semiconductors SnO and SnO₂. To explain these findings, we provide a generalized theory based on the idea that the charge density discontinuity between SnO and SnO₂, a consequence of lattice mismatch, drives a polar catastrophe scenario. As a result, SnO/SnO₂ (110) interphase boundaries can develop metallicity depending on the grain size. The concept of metallicity due to polar catastrophe induced by charge density discontinuity is of general validity and applies to many interphase boundaries with lattice mismatch.

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INTRODUCTION

Tin oxide has two stoichiometric phases, the monoxide (SnO) and the dioxide (SnO₂), the latter being frequently used in gas sensors, oxidation catalysts and solar cell electrodes, for example.¹ Recently, SnO has garnered interest after a record hole mobility was reported in Caraveo-Frescas *et al.*,² which opens a multitude of possible applications. Although SnO/SnO₂ interphase boundaries form during the oxidation of Sn, their properties are largely unknown,³ while in general oxide–oxide interfaces are receiving much attention due to a variety of exciting phenomena.^{4,5}

An important example is the appearance of a quantum gas at the interface between the wide-band-gap semiconductors LaAlO₃ and SrTiO₃⁶ as well as at other *n*-type interfaces,^{7–11} whereas an insulating character has been reported for the *p*-type LaAlO₃/SrTiO₃,⁶ LaVO₃/SrTiO₃¹² and NaNbO₃/SrTiO₃¹³ interfaces, likely due to O vacancies that neutralize hole carriers.^{14,15} Indeed, such defects form spontaneously at low O partial pressure.¹⁶ At an *n*-type interface, the additional charge from O vacancies, on the other hand, enhances the electron density.¹⁷ The quantum gas observed at LaAlO₃/SrTiO₃ interfaces, being well confined to the interface region, is commonly attributed to the charge discontinuity at the contact between polar LaAlO₃ and non-polar SrTiO₃. An increasing thickness of LaAlO₃ would result in potential divergence,¹⁸ the so-called polar catastrophe. Different compensation mechanisms have been proposed^{14,19,20} and are still under debate,²¹ the most famous being electronic reconstruction. Researchers have indicated

that the efficiency of electronic reconstruction is supported by multi-valent elements, as they enable charge redistribution at lower energy cost.²² The ideal number of electrons, that is, 0.5 per perovskite unit cell, as predicted by the polar catastrophe model, could not be confirmed experimentally.²¹ It has been argued that some of the charge may be localized by disorder effects or electron–phonon coupling²³ and that polarization effects in the presence of the LaAlO₃ surface reduce the expected amount of charge.²⁴

Because controlling the properties of interphase boundaries requires insight into the mechanisms leading to these properties, in the present work we investigate SnO/SnO₂ (110) interphase boundaries using density functional theory. Although the two component semiconductors SnO and SnO₂ do not give rise to a formal charge discontinuity in the (110) direction, we demonstrate the possibility of forming a hole gas at interphase boundaries (even in the absence of defects) and explain the observations by a generalization of the polar catastrophe model in terms of charge density discontinuity. Charge density discontinuity effects on charge transfer and metallicity at non-stoichiometric oxide interfaces were previously reported in Zhuang *et al.*²⁵ and Jeon *et al.*²⁶ showed that control of the charge transfer makes it possible to stabilize different stoichiometries of molecular ionic salts on metallic substrates.

MATERIALS AND METHODS

We use the projector augmented wave method with ultrasoft pseudopotentials as implemented in the Vienna Ab initio Simulation Package.²⁷ The Perdew–

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Burk–Ernzerhof generalized gradient approximation is employed together with a basis consisting of O 2s, 2p and Sn 5s, 5p orbitals and a cutoff energy of 400 eV. Wigner–Seitz radii of 1.26 and 1.59 Å are used for O and Sn, respectively; the Brillouin zone is integrated on a $5 \times 2 \times 1$ Γ -centered grid; and a Gaussian smearing of 0.06 eV width is used. The electronic self-consistency criterion is set to 10^{-5} eV, and convergence of the atomic forces is assumed for values <0.05 eV/Å.

SnO₂ has space group $P4/mmm$ with the lattice parameters $a = b = 4.737$ Å and $c = 3.186$ Å and a direct band gap of 3.6 eV.²⁸ On the other hand, SnO has space group $P4/nmm$ with the lattice parameters $a = b = 3.804$ Å and $c = 4.826$ Å²⁸ and an indirect band gap of 0.7 eV (direct band gap between 2.5 and 3 eV).²⁹ We obtain band gaps of 0.68 eV (direct) and 0.40 eV (indirect) for the relaxed SnO₂ and SnO unit cells, respectively. The significant underestimation of the band gap of SnO₂ is mainly due to the exchange contribution to the exchange–correlation potential, as it can be overcome by hybrid functional calculations.³⁰ Although the band gaps are underestimated, we have verified (using the approach of Van de Walle and Martin³¹ and Puthenkottilakam *et al.*³²) that the type of band alignment at the interface between SnO and SnO₂ agrees with the experiment,³³ see Figure 1, such that the effects of artifacts of the methodology on the results in the following can be excluded.

As the (110) growth direction is known to be preferred for SnO₂³⁴ and has also been reported for SnO,² we built interphase boundaries between the two compounds along this direction using $3 \times 4 \times 3$ SnO₂ and $2 \times 5 \times 3$ SnO supercells. This set-up minimizes the lattice mismatch (3.0% and 0.1% along the a and b axes, respectively) and avoids artificial strain effects, giving rise to the two interfaces (I and II). By construction, both interfaces have the composition of the respective bulk material on both sides. The final supercell comprises a computationally challenging number of 672 atoms, for which the positions are relaxed without imposing any restriction.

Although simple cutting would result in polar (110) surfaces for both SnO and SnO₂, there exist energetically favorable nonpolar (110) surfaces.³⁵ That of SnO₂ is obtained by removing the outermost O atoms while maintaining the bridging O atoms,³⁶ and that of SnO is obtained by removing half of the surface atomic species. In principle, therefore, polar–polar, nonpolar–nonpolar and polar–nonpolar (110) interfaces can be formed between SnO and SnO₂. The fully relaxed structures shown in Figure 2 demonstrate that the polar–polar (110) interface is favorable to the nonpolar–nonpolar (110) interface and therefore is studied in the following. This result may be surprising, as both SnO and SnO₂ favor nonpolar (110) surfaces, but is explained by the greater number of dangling bonds at the nonpolar–nonpolar (110) interface. The difference in interface binding energy between the polar–polar and nonpolar–nonpolar (110) interfaces amounts to 1.09 eV per surface unit cell of SnO (0.91 eV per surface unit cell of SnO₂).

Figure 1 Band alignment diagrams: (a) Experimental³³ and (b) theoretical.

Figure 2 Structurally relaxed (a) polar–polar and (b) nonpolar–nonpolar (110) interfaces.

RESULTS AND DISCUSSION

Polar catastrophe is usually discussed in terms of formal charge discontinuity rather than charge density discontinuity. However, the density factor becomes important when there is lattice mismatch. We analyze the density of states as a function of the atomic layer number defined in Figure 3a. To this end, partial density of states curves for selected atomic layers are presented in Figure 4a. Those next to an interface (black lines) show a metallic character, for example, Sn layer 18. We also notice that the O states of layers 5 and 17 as well as the Sn states of layer 6 shift to higher energy, which indicates that electrons are donated. In contrast, the Sn states of layer 18 shift to lower energy and accept electrons. The atomic layers in the middle of the SnO and SnO₂ slabs still show some metallic states. For thicker slabs, the semiconducting characters of the bulk materials would be fully recovered. However, even if this is not the case for our supercell size, no drawback is expected regarding the validity of our following reasoning because the two interfaces are well separated by almost 15 Å.

Structural relaxation effects at interfaces, in general, are strong and therefore have to be taken into account. However, results for the unrelaxed supercell in Figure 4b show minor differences with respect to Figure 4a, at least on a qualitative level, suggesting that the physics underlying the creation of metallic states must be of electronic rather than of structural origin. The energetic shifts of the states of the O terminal layers of SnO₂ at interface I (layer 5) and SnO at interface II (layer 17) are reduced by the structural relaxation, whereas only small modifications affect the two other terminal layers 6 and 18. Minor

Figure 3 (a) Schematic representation of the SnO/SnO₂ heterostructure with the atomic layers numbered in sequence. (b) Charge density difference maps for the indicated atomic layers and for layers 0.3 Å to the left and to the right. Loss/gain of charge is indicated in red/blue.

effects of the relaxation on the electronic states, as previously reported for the KTaO₃/SrTiO₃ interface, are due to small lattice mismatch,³⁷ whereas in the present case this is an unexpected finding as the relaxation here is substantial.

To analyze the charge transfer from a spatial perspective, charge density difference maps for the unrelaxed interfaces are depicted in Figure 3b, with charge loss/gain indicated in red/blue. We show the maps for the highlighted layers as well as for layers 0.3 Å to the left and the right, to track the exact charge transfer scenario. Rather homogeneously distributed holes are observed in the two O terminal layers 5 and 17. We note that the red circular areas shown in layer 18 are related to the O atoms in layer 19, which suggests that the charge transfer is not restricted to the interface itself but reaches one atomic layer farther. Charge differences added for each atomic layer of the relaxed supercell are computed by subtracting the Bader atomic charges from the corresponding charges of the bulk compounds. The results in Figure 5 show the accumulation of 4.9 and 4.5 electrons, respectively, in layers 4 and 18, which reside in Sn 5p orbitals and thus are well localized, supporting our interpretation of Figure 3b. On the other hand, 3.9, 2.5 and 2.0 holes, respectively, are found in layers 5, 16 and 17. Furthermore, the SnO region becomes slightly hole-doped and the SnO₂ region slightly electron-doped.

The polarization at polar–polar interfaces can have valence, structural and electronic contributions.³⁸ The electronic contribution vanishes in the present case, as both SnO and SnO₂ have a centrosymmetric structure. The structural contribution is given by the rumpling shown in Figure 6. Almost negligible deviations from the bulk value of 0.5 exclude a structural origin of the metallic states. Our

next aim is to investigate the valence contribution. Along the (110) direction, SnO is composed of alternating layers of O and Sn atoms, whereas SnO₂ consists of alternating layers of O atoms and SnO layers. The formal charge thus alternates between +2 and −2 in both cases, and we have no formal charge discontinuity, that is, the electric field oscillates symmetrically around zero such that no potential can build up. Consequently, the polar catastrophe scenario appears not to be relevant in our case. However, we propose a generalized theory: In the absence of formal charge discontinuity, a charge density discontinuity, originating from lattice mismatch, can create a net dipole. This net dipole would lead to potential divergence that must be avoided by means of electronic reconstruction above a critical grain size.

In contrast to interphase boundaries between compounds with the same structure, in our case the formal charge per area is different in the SnO (110) and SnO₂ (110) planes (charge density discontinuity), which we describe in terms of a density factor G assigned to SnO; see Figure 7a. In our supercell, we count at interface I that 24 Sn⁺² ions meet 20 O^{−2} ions and at interface II that 24 Sn⁺⁴ and 24 O^{−2} ions meet 20 O^{−2} ions. The density factor consequently amounts to $G = 5/6$. Figure 7b demonstrates (exaggerated for clarity) that the charge density discontinuity leads to an asymmetric oscillation of the electric field around zero and therefore to a potential divergence; see Figure 7c. In the common polar catastrophe model, a valence change in the cations at the interface compensates for the divergence, which has been experimentally confirmed for LaAlO₃/SrTiO₃²² and La_{0.9}Sr_{0.1}MnO₃/SrTiO₃.³⁹ However, in principle, different electronic reconstruction scenarios are possible to achieve compensation. The most favorable scenario can be derived from *ab initio* calculations.

Figure 4 Partial density of states for selected atomic layers in the (a) relaxed and (b) unrelaxed supercells.

Figure 5 Charge difference per atomic layer calculated by subtracting the Bader atomic charges of the relaxed supercell from those of the bulk compounds. The dashed lines are results obtained for a force convergence criterion of $0.35 \text{ eV } \text{\AA}^{-1}$. The small deviations from the full lines ($0.05 \text{ eV } \text{\AA}^{-1}$) indicate that the observed effect is robust against structural details.

Figure 6 Rumppling of the crystal structure across the supercell.

Figure 7 (a) Schematic representation of the atomic layer charges before electronic reconstruction. (b) Electric field and (c) the corresponding potential.

Figure 8 (a) Schematic representation of the atomic layer charges after electronic reconstruction, where δ is the compensation charge. (b) Electric field and (c) the corresponding potential.

According to Figure 5, at interface I, δ electrons (polarization discontinuity³⁸) are accommodated in the Sn $5p$ orbitals in layer 4 (Sn valence $+4-\delta$), and at interface II, $\delta/2$ holes reside in the Sn $5p$ orbitals of layer 16 as well as in the O $2p$ orbitals of layer 17 (Sn valence $+2+\delta/2$, O valence $-2+\delta/2$). The electronic reconstruction is illustrated schematically in Figure 8a. We note that the generated electric field in this situation, see Figure 8b, indeed does not give rise to a potential divergence; see Figure 8c. The band alignment diagrams of SnO and SnO₂³³ show that the valence band maximum of SnO₂ is

Figure 9 Charge difference per atomic layer in the presence of an O vacancy on the SnO side of interface I (solid line), SnO₂ side of interface I (dotted line), SnO side of interface II (dashed line) and SnO₂ side of interface II (dash-dotted line).

approximately 2.5 eV lower than that of SnO. Therefore, charge transfer from SnO to SnO₂ is possible, which fits perfectly with our results, as at interface I the Sn states on the SnO₂ side are occupied by δ electrons and at interface II the Sn and O states on the SnO side are occupied by $\delta/2$ holes; see Figure 8a. It is thus the band alignment between the two oxides that results in the specific electronic reconstruction. The formal amount of compensation charge, $\delta = 4/24 = 1/6$, agrees with the numerical results in Figure 5. Minor deviations can be attributed to partial screening. We note that the proposed mechanism can be generalized directly to other polar–polar interfaces without formal charge discontinuity as long as there is lattice mismatch.

To investigate the effect of O vacancies on our predictions, we calculate the O vacancy formation energy for different possible sites with respect to the bulk value and find that O vacancies favor location at the interfaces. We obtain preferences of 0.85 eV for the SnO side of interface I, 0.85 eV for the SnO₂ side of interface I, 1.15 eV for the SnO side of interface II and 1.32 eV for the SnO₂ side of interface II. Figure 9 summarizes results for the charge density difference per atomic layer in the presence of an O vacancy, showing that there is no qualitative difference in the electronic reconstruction relatively to the case without an O vacancy.

CONCLUSION

In conclusion, *ab initio* calculations reveal the existence of metallic states at (110) interphase boundaries between the semiconductors SnO and SnO₂. This observation is unexpected from the perspective of the common polar catastrophe model that can explain the creation of quantum gases between semiconductors. We therefore propose a generalized model based on charge density discontinuity and demonstrate that it is able to explain electronic reconstruction even at polar–polar interfaces with the same formal charges of the atomic layers on both sides. The introduced mechanism is expected to have an important role at interphase boundaries between polar materials.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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