Origin of n- and p-type conductivity in undoped α-PbO: role of defects

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Received 9 August 2013, in final form 7 October 2013
Published 31 October 2013
Online at stacks.iop.org/JPhysCM/25/475801

Abstract

First-principles calculations have been applied to study the crystallographic defects in α-PbO in order to understand an origin of n- and p-type conductivity in otherwise undoped α-PbO. It was found that deposition in an oxygen-deficient environment defined in our simulations by the Pb-rich/O-poor limit stimulates a formation of O vacancies and Pb interstitials both characterized by quite low formation energies \( \sim 1.0 \) eV. The O vacancy, being occupied by two electrons, shifts the balance of electrons and holes between these two defects to an excess of electrons (four electrons against two holes) that causes n-type doping. For the Pb-poor/O-rich limit, an excess of oxygen triggers the formation of the O interstitials characterized by such a low formation energy that a spontaneous appearance of this defect is predicted. It is shown that the concentration of O interstitials is able to reach an extreme magnitude equal to the number of possible defect sites \( \sim 10^{22} \) cm\(^{-3}\). The localized state formed by the O interstitial is occupied by two holes and because there are no other defects in reasonable concentration to balance the hole redundancy, p-type doping is induced.

(Some figures may appear in colour only in the online journal)
is required. Here we apply first-principles methods for such a study (the Pb-rich/O-poor and Pb-poor/O-rich limits of the growth conditions are considered) with a focus on an analysis of the defects inherent to the α-PbO crystal structure, the appearance of the defect states inside the band gap, charged states and formation energies.

1. Methods

We study the formation of defects in α-PbO with the help of the density functional theory (DFT) provided by the WIEN2k package [8] which adopts the full-potential augmented plane-wave + local orbitals method. The generalized gradient approximation (GGA) [9] with the Perdew–Burke–Ernzerhof parametrization was used. The 5p, 5d, 6s and 6p electrons of the Pb atom and 2s and 2p electrons of the O atom have been treated as valence electrons, while lower energy electrons were assigned to the core states (the energy cutoff was −8 Ryd). We applied a supercell approach with 108-atoms size (3 × 3 × 3 array of the primitive unit cells). The geometry optimization procedure applied to a supercell containing a defect was performed based on minimization of the total energies and forces [10]. The residual forces did not exceed 0.5 mRyd/bohr, and the energy convergence limit was set to 0.0001 Ryd. The Brillouin zone was covered by a 5 × 5 × 4 k-point mesh utilizing the Monkhorst–Pack scheme. The product of the atomic sphere radius and plane-wave cutoff in k-space was equal to 7.

The tetragonal lead oxide α-PbO is characterized by a layered structure and appears in polycrystalline form upon compound growth [1]. The weak orbital overlap of the 6s2 lone pairs of Pb atoms projected out from each layer holds the PbO layers together [11, 12], while only 6p2 valence electrons participate in formation of the hetero-polar bonds with oxygen atoms [12]. GGA tends to overestimate the interlayer separation in the layered structures while bonds with oxygen atoms [12]. GGA tends to overestimate valence electrons participate in formation of the hetero-polar bonds with oxygen atoms [12]. GGA tends to overestimate the interlayer separation in the layered structures while bonds with oxygen atoms [12].

2. Crystallographic defects in α-PbO

Analysis of the literature on defect formation in semiconductors [15] and particularly in simple oxides [16] has revealed that, in addition to the vacancy defects investigated in our previous study [5], interstitials have to be considered. For crystalline materials, interstitial defects induce a large lattice distortion in their immediate neighborhood that results in their high formation energy [15]. In this regard, the crystal lattice of polycrystalline α-PbO is unique, because the distance between weakly interacting layers is large enough to accommodate a foreign atom (c0 = 5.07 Å [14]). Therefore, along with the vacancy defects, formation of the interstitials is expected to be inherent to the α-PbO lattice.

We start with a brief description of the vacancy defects already investigated in our previous work [5]. The O vacancy (V0) is occupied by two electrons localized on the four nearest Pb atoms with the maximum of the electron density manifesting at the vacancy site (see the electron density distribution in figure 1(a)). The O vacancy can appear in three charged states (0, 1+, 2+). The localized state generated by the O vacancy is located deep inside the band gap at ED(V0) − EV = 1.03 eV, where EV is the top of the valence band. In contrast, the Pb vacancy creates a localized state occupied by two holes and the defect level appears close to the valence band top at ED(VPb) − EV = 0.1 eV. The electron density is spread between O and Pb atoms showing long defect tails (see figure 1(b)) which is not surprising taking into account the defect level appearance close to the valence band top (see figure 2). The Pb vacancy has also three charge states (0, 1−, 2+) but its charge states would be of negative sign, i.e. ionization of the vacancy occurs through an electron gain. The effect of mismatch of the lattice parameters on location of the vacancy-induced states was examined. It is found that a position of the defect states relative to the valence band top is not affected by application of the experimental lattice parameters: since the vacancy states are localized entirely within single layer, an alteration in the interlayer interactions has almost no impact on its property [5].

There are two interstitial defects to be considered in α-PbO crystal lattice: the O and Pb interstitials. Binding of the O interstitial (I0) to the host occurs with participation of the lone pair Pb:6s2 electrons from the host (the lone pair Pb:6s2 in α-PbO is chemically active [12]): the bond is made between lone pair Pb:6s2 electrons of the host and the O:6p0 empty orbital of oxygen atom. The O:6p0 empty orbital appears upon excitation of the ground state O:2p3 1−→ O:6p0 0 state. The lowest energy state is achieved when the O interstitial is positioned just above the Pb atom (see figure 1(c), the bond length is 2.03 Å). Inside the band gap, the localized state is located above the midgap at ED(I0) − EV = 1.27 eV (see figure 2). This localized state can accommodate up to two extra electrons and, therefore, there are three charge states (0, 1−, 2+) assigned to it.
Figure 1. Schematic representation of crystallographic defects in the tetragonal $\alpha$-PbO (space group 129$P_4/\text{mmm}$) and the electron density map plotted with XcrySDen [17] for the energies $E_D \pm 0.05$ eV. (a) The O vacancy, (b) the Pb vacancy, (c) the O interstitial and (d) the Pb interstitial. The electron density maps ($\bar{e}$ Å$^{-3}$) are plotted with XcrySDen. The color scale on the left side is for the $V_O^-$, $I_O^-$, $I_{Pb}^-$, while for $V_{Pb}^+$ it should be reduced by a factor of 5.

Figure 2. Energetic location of the states induced by the various defects ($V_O^-$, $V_{Pb}^+$, $I_O^-$, $I_{Pb}^-$) within the band gap of $\alpha$-PbO ($E_G = 1.8$ eV). Electrons occupying the vacancy site are indicated by arrows while filled circles correspond to the absence of an electron.

The energetically favorable position of the Pb interstitial ($I_{Pb}^+$) in the lattice is similar to the O interstitial, i.e. on top of the Pb atom. The Pb interstitial is excited from the ground state of configuration Pb:6s$^2$6p$^2$ to the Pb*:6s$^1$6p$^3$ state thus allowing 6s$^1$ and 6p$^1$ electrons to contribute in bond formation with the host. The host Pb atom participates in bonding, again with its Pb:6s$^2$ electrons (the bond length is 2.9 Å). The originated defect state is occupied by two electrons which are Pb:6p$^1_{x+y}$ electrons belonging to $I_{Pb}^+$ (see figure 1(d)). Since each electron stays on its own orbital, Hund’s rules dictate the ferromagnetic ordering of these electrons [18]. The spin-polarization energy defined as the energy difference between the spin-unpolarized and spin-polarized states is found to be $E_{pol} = 0.235$ eV which indicates the stable triplet ground state [18]. The Pb interstitial induces a localized state inside the band gap and the spin-polarized solution separates the occupied and unoccupied states as $E_D(I_{Pb}^+) - E_V = 0.99$ eV and $E_D(I_{Pb}^+) - E_V = 1.51$ eV (see figure 2), respectively. Ionization of the defect state formed by the Pb interstitial can occur through electron gain ((1$^-$) for one electron added and (2$^-$) for two electrons) or through an excitation of existing electrons. Overall, there are five charged states ($2^+, 1^+, 0, 1^-, 2^-$) can be considered for the Pb interstitial.

Since the properties of the interstitial defects are expected to depend on the interlayer distance, an alteration in position of the defect states inside the band gap with implementation of the experimental lattice parameters has been investigated. It was found that for the O interstitial the defect state is shifted only by 0.05 eV outwards from $E_V$. However, the effect is more pronounced for the Pb interstitial because of the larger atomic radius of Pb atom. Thus, the state occupied by electrons appears at $E_D(I_{Pb}^+) - E_V = 0.97$ eV while the empty state is at $E_D(I_{Pb}^+) - E_V = 1.25$ eV. Moreover, for a defect state like Pb interstitial, DFT is known to delocalize the defect wavefunction and underestimate the splitting between the unoccupied and occupied states that occurs due to self-interaction of the unpaired electrons [19]. Therefore, defect
wavefunction localization has been additionally applied to the Hartree–Fock (HF) approach applied directly to the unpaired electrons [19, 20] (in this way the accuracy provided by DFT is preserved). Indeed, this resulted in stronger localization and, therefore, enhanced splitting of the defect states such as $E_D (\text{IPb}) - E_V = 0.54$ eV for the occupied state and $E_D (\text{IPb}) - E_V = 1.66$ eV for the empty state. However, since the experimental lattice parameters and HF correction have an opposite effect on the defect wavefunction localization, application of both leads to a compensation effect in level splitting such that the appearance of the defect states in the band gap is $E_D (\text{IPb}) - E_V = 0.54$ eV for the occupied state and $E_D (\text{IPb}) - E_V = 1.22$ eV for the empty state. Since the band gap size is reduced by 0.22 eV [5], location of these defect states in respect to the bottom of the conduction band is very close to that found with GGA (see figure 2).

We have established that some defects can act as a donor impurity ($\text{V}^{6+}_{\text{O}}$) $\rightarrow$ $\text{V}^{5+}_{\text{O}}(1+2^+/2^-)$, and others as acceptors ($\text{V}^{5+}_{\text{Pb}}$ $\rightarrow$ $\text{V}^{4+}_{\text{Pb}}(1+2^+/2^-)$ and $\text{I}^{0}_{\text{Pb}}$ $\rightarrow$ $\text{I}^{+}_{\text{Pb}}(1+2^+/2^-)$), while $\text{I}^{0}_{\text{Pb}}$ can be both an electron donor ($\text{I}^{0}_{\text{Pb}}$ $\rightarrow$ $\text{I}^{+}_{\text{Pb}}(1+2^+/2^-)$) and an acceptor ($\text{I}^{+}_{\text{Pb}}$ $\rightarrow$ $\text{I}^{0}_{\text{Pb}}(1+2^+/2^-)$). The ability of defects to appear in several charge states encourages electron exchange between defects: the electron donor compensates missing electrons on the acceptor. The process of charge exchange defines the energetically favorable charge state for defects appearing upon compound growth.

3. Formation energy of defects

The main way to identify the formation of defects inherent to the crystal structure is to compare the formation energies of different defects, as this parameter is a particularly clear measure of the defect concentration. The formation energy of a defect $D$ in charge state $q(+2/1+0/1-1-2)$ can be defined as [15]

$$\Delta E_f(D) = E_{\text{tot}}(D^q) - E_{\text{tot}}(S) - \sum_i n_i \mu_i + q(E_F + E_V + \Delta V),$$  

(1)

where $E_{\text{tot}}(D^q)$ and $E_{\text{tot}}(S)$ are the total energy of the system containing the single defect and the defect-free system, respectively. $n_i$ indicates the number of i-atoms removed ($n_i > 0$) or added ($n_i < 0$), while $\mu_i$ is chemical potential. $(E_F + E_V + \Delta V)$ is the position of the Fermi level relative to the valence band maximum $(E_V)$ which has to be corrected by $\Delta V$ (for details see [15]).

For calculation of the formation energy of the native point defects $\Delta E_f(D)$, the supercell approach has been applied. In order to minimize an interaction between a defect and its periodic replicas, a sufficiently large supercell $(3 \times 3 \times 3)$ is used for simulation of defects. The geometry optimization procedure has been applied as for the neutral supercell (the total energy of the system corresponds to $E_{\text{tot}}(S)$) and so after defect has been charged: $E_{\text{tot}}(D^q)$ energy has been evaluated for the defects in the different charge states $q(+2/1+0/1-1-2)$ (for details see [15]). An alignment of the top of the valence band $(E_V)$ for the supercell with charged defect to that in the bulk is performed with the help of the correction term $\Delta V$ [15]. Since for accurate calculation of the formation energy of interstitial defects the mismatch in the interlayer distance $(c_0 = 5.51 \text{ Å})$ occurring for the lattice parameters optimized with GGA in comparison to the experimental data $(c_0 = 5.07 \text{ Å} [14])$ is essential, the experimental value has been used for those calculations. In this case, an application of the so-called band gap error $\Delta E_G$ [21] is required to compensate for a reduction of the band gap size [5]. For vacancies, because of their weak interactions with the opposite layer, the formation energy would be rather insignificantly affected by the interlayer distance mismatch, and the same argument works for the vacancies appearing on the surface of the single crystal (platelet). However, for interstitial defects, because of their strong interaction with the opposite layer, the formation energy would be altered upon appearance on the platelet’s surface. For defects on the surface, slabs thickness was four layers, width was $\sim 10 \text{ Å}$, while distance between slabs was $\sim 14 \text{ Å}$. To simulate the deficit and excess of oxygen, the Pb-rich/O-poor and Pb-poor/O-rich limits have been applied in evaluation of the chemical potential. The chemical potential has been found for the Pb-rich/O-poor limit as $\mu(O) = E_{\text{tot}}(O \text{ atom}) + \Delta H^D(\text{PbO})$, where $\Delta H^D(\text{PbO})$ is the standard enthalpy of formation of PbO compound, while $\mu(\text{Pb})$ is determined from $\Delta H^D(\text{PbO}) = \mu(\text{O}) + \mu(\text{Pb})$. For the Pb-poor/O-rich limit the chemical potential is $\mu(\text{Pb}) = E_{\text{tot}}(\text{Pb atom}) + \Delta H^D(\text{PbO})$ and, similarly, $\mu(O)$ is found from $\Delta H^D(\text{PbO}) = \mu(\text{O}) + \mu(\text{Pb})$. The standard enthalpy of formation of $\Delta H^D(\text{PbO}) = -2.92 \text{ eV per Pb-O pair has been calculated elsewhere [5] applying a formalism described in details earlier [15].}$

We have calculated the formation energies of the different defects in the relevant charge states and our results as a function of the Fermi level position inside the band gap. As $\mu$ deviates in a range defined by $\Delta H^D(\text{PbO})$ (in real growth conditions to be controlled by the partial pressure of reactants) it induces a shift of the formation energies. The concentration of the defects can be estimated through their formation energies as $N_{\text{defects}} \sim N_{\text{sites}} \exp(-\Delta E_f(D)/k_b T)$, where $k_b$ is the Boltzmann constant, $T = 570 \text{ K}$ is the deposition temperature and $N_{\text{sites}}$ is the concentration of sites available for defects to be formed.

For the Pb-rich/O-poor limit (see figure 3(a)), the formation energies of the O vacancy ($\text{V}^{6+}_{\text{O}}$) and the Pb interstitial ($\text{IPb}$) appear to be much lower than that for other defects and, therefore, these defects are expected to dominate. The defect concentrations estimated for their zero charge states are $10^{15} \text{ cm}^{-3}$ for the O vacancy and $10^{14} \text{ cm}^{-3}$ for the Pb interstitial. For the Fermi level assigned to the midgap, the $(0, 1+)$ and $(0, 1-)$ states are energetically preferable for the O vacancy and the Pb interstitial, respectively. Since the thermodynamic transition $\text{V}^{6+}_{\text{O}}$ $\rightarrow$ $\text{V}^{4+}_{\text{O}}(1+)$ is found to occur almost at the midgap, this indicates a potential for both states
Figure 3. Formation energy as a function of the Fermi level position ($E_F$ varies from 0 to $E_F = 1.8$ eV [22]). (a) Oxygen deficit (Pb-rich/O-poor limit). (b) Oxygen excess (Pb-poor/O-rich limit).

to be formed during the compound growth. However, to be ionized, V$^{0(0)}_O$ has to dispose of its electron and therefore the appearance of the V$^{0(1+)}_O$ charge state would naturally depend on the presence of the electron acceptor. For the Pb interstitial, we have calculated the formation energy for the five states ($2^- + 1^-, 1^+, 0^-, 1^-, 2^-$). Since the formation energy of the ($1^-$) state occurs when an extra electron is added is significantly lower than that when an electron is removed ($\Delta E^f(\text{I}^{1+}\text{Pb}) = 3.98$ eV for $E_F$ at midgap), the ($1^+$) and ($2^+$) states have been disregarded. The thermodynamic transition $\text{I}^{0(0)}_{\text{Pb}} \rightarrow \text{I}^{1-}_{\text{Pb}}$ occurs close to the midgap and therefore the charge states (0, 1−) appear to be the preferable states. To become ionized to the ($1^-$) state, $\text{I}^{0(0)}_{\text{Pb}}$ has to gain an electron (electron acceptor).

Therefore, the charge exchange between $V^{0(0)}_O$ and $\text{I}^{0(0)}_{\text{Pb}}$ is possible as one of them can work as an electron donor and the other as an acceptor. The concentration of ionized states manifesting upon charge exchange could be limited by the defect of lower concentration, i.e. by the Pb interstitial (10$^{11}$ cm$^{-3}$). It is important to emphasize that the balance of electrons and holes occupying both defect sites in either combination of the charge states ($V^{0(0)}_O/\text{I}^{0(0)}_{\text{Pb}}$ or $V^{0(1+)}_O/\text{I}^{1+}_{\text{Pb}}$) is always shifted to a higher population of electrons (four electrons against two holes). Therefore, with respect to the conductivity type, redundant electrons induced by the O vacancies would cause n-type doping of $\alpha$-PbO at the Pb-rich/O-poor limit to be in agreement with our previous studies [5]. In the non-equilibrium electron gas (photogenerated or injected carriers), the ionized O vacancies $V^{0(1+)}_O$ and the Pb interstitials in both charge states $\text{I}^{0(0)}_{\text{Pb}}, \text{I}^{1-}_{\text{Pb}}$ work as trapping centers for electrons in the conduction band.

For the Pb-poor/O-rich limit, only the O interstitial $\text{I}^0_O$ possesses a low formation energy, while the formation energies of other defects ($\text{I}^{+}_{\text{Pb}}, V^{0}_{\text{O}}$ and $V^{+}_{\text{Pb}}$) are higher than 3.0 eV. In fact, the formation energy of $\text{I}^0_O$ being so close to zero implies the spontaneous appearance of this defect such that the defect concentration can become equal to the concentration of the possible defect sites ($N_{\text{sites}} \sim 10^{22}$ cm$^{-3}$). The O interstitial in its neutral charge state $\text{I}^{0(0)}_O$ misses two electrons and, to be ionized to the charge states ($1^−/2^-), has to acquire electrons. Since the thermodynamic transition $\text{I}^{0(0)}_O \rightarrow \text{I}^{0(2-)}_O$ occurs close to the midgap, $\text{I}^0_O$ potentially can be formed in the charge states ($1^−, 2^−$). However, because the concentration of centers of the donor type ($\text{I}^{+}_{\text{Pb}}, V^0_{\text{O}}$) is negligible, the O interstitial is expected to occur primarily in its $\text{I}^{0(0)}_O$ state. The $\text{I}^{0(0)}_O$ state would act as a trap for the non-equilibrium electrons in the conduction band. Therefore, under growth conditions corresponding to oxygen excess, the high concentration of $\text{I}^{0(0)}_O$ defects each occupied by two holes would cause p-type doping. Moreover, the state formed by the O interstitial is characterized by a quite delocalized nature (see figure 1(c)): the long defect tails in combination with the high defect concentration results in strong defect–defect interaction potentially leading to formation of the defect band.

It is important to emphasize that all investigated defects $V^0_O, V^+_{\text{Pb}}, I^0_O$ and $\text{I}^{+}_{\text{Pb}}$ considered in bulk $\alpha$-PbO would be inherent to the surface of a single crystal (platelet). For some defects, the formation energy is found to be lowered when they are placed on the platelet surface. The strongest effect is observed for the Pb interstitial for which the formation energy drops by $\sim 1.0$ eV. For the vacancies, the formation energy is only affected provided they appear at the edge of the platelet (for example, it is reduced by 0.3 eV for oxygen vacancy). The reduction of the formation energy at the platelet edge is a result of surface reconstruction leading to the formation of Pb–O double bonds instead of single bonds. Since the balance of electrons and holes occupying the defect sites is not affected by the formation of surface states, the considered phenomenon of the n- and p-doping remains valid. There is one more interesting feature to be examined, which is defect pairing. For the Pb-rich/O-poor conditions, pairing may occur between $V^0_O$ and $\text{I}^{0(0)}_{\text{Pb}}$, and is promoted by a lowering of the formation energy by 0.84 eV. Such a $V^0_O\text{I}^{0(0)}_{\text{Pb}}$ pair results in the disappearance of the triplet state at $\text{I}^{0(0)}_{\text{Pb}}$ and forms three defect levels; one is empty at $E_D (V^0_O\text{I}^{0(0)}_{\text{Pb}}) - E_V = 1.77$ and two are occupied at $E_D (V^0_O\text{I}^{0(0)}_{\text{Pb}}) - E_V = 1.22$ and $E_D (V^0_O\text{I}^{0(0)}_{\text{Pb}}) - E_V = 0.66$. For the Pb-poor/O-rich conditions, the interaction between $\text{I}^0_O$ and $\text{I}^{+}_{\text{Pb}}$ can potentially occur but because each localized state is occupied by two holes, such interaction is repulsive. Under equilibrium growth conditions, the formation energy of $V^0_O$ and $V^0_O$ would become comparable, indicating a possibility of their pairing as well [23]. This combination of defects is unique as it induces vanishing of the dangling bonds and, therefore, occurs without generation of a defect state inside the band gap. Moreover, because the formation energy is lowered by 1.47 eV upon defect pairing, this indicates the pairing to occur not only during the compound growth but also as a post-growth migration of the O vacancy towards the Pb vacancy.

1 The standard procedure has been applied to determine $N_{\text{sites}}\text{N}_{\text{sites}} = N_A\rho/M$, where $N_A$ is Avogadro’s number, $M$ is the molar mass and $\rho$ is the density found for $\alpha$-PbO at http://en.wikipedia.org/wiki/Lead(II)oxide.
4. Conclusion

Our study on the formation of defects in single crystal α-PbO has revealed that some defects under certain growth conditions appear in significant concentration causing n- or p-type doping of the compound. In particular, for the Pb-rich/O-poor limit the formation of V\textsubscript{O} and I\textsubscript{Pb} defects is found to dominate with concentrations of $10^{15}$ cm\textsuperscript{-3} and $10^{11}$ cm\textsuperscript{-3}, respectively. The obtained defect concentrations are in good agreement with the concentration of localized states estimated experimentally ($10^{14}$–$10^{15}$ cm\textsuperscript{-3} [2]). It was established that the accumulation of electrons on the sites of the V\textsubscript{O} and I\textsubscript{Pb} defects results in n-type doping of α-PbO.

For the oxygen excess created during the compound growth (Pb-poor/O-rich limit), another defect is found to manifest which is the O interstitial. The concentration of I\textsubscript{O} is predicted to approach the highest limit because its formation energy is around zero, i.e. the defect concentration may become equal to the number of the possible defect sites. Since each I\textsubscript{O(0)} is occupied by two holes, its high concentration would result in p-type doping of α-PbO. Moreover, such a low formation energy of the O interstitial might be a problem for post-growth procedures such as annealing. We predict that annealing in an atmosphere of oxygen in order to heal O vacancies would generate new defects such as O interstitials. The negative impact of the dominant defects I\textsubscript{O}, V\textsubscript{O} and I\textsubscript{Pb} would become apparent because these defects induce the states close to the midgap: severe trapping of non-equilibrium electrons from the conduction band is expected.

Acknowledgments

The financial support of the Ontario Ministry of Research and Innovation through a Research Excellence Program Ontario network for advanced medical imaging detectors is gratefully acknowledged.

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