Self-passivation of vacancies in α-PbO

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received 2 April 2013; accepted in final form 8 May 2013
published online 5 June 2013

PACS 71.20.Nr - Semiconductor compounds
PACS 71.55.Cn - Elemental semiconductors

Abstract – We introduce a self-passivation of single lead (Pb) and oxygen (O) vacancies in the α-PbO compound through formation of a Pb-O vacancy pair. With help of the first-principles methods we found that the preferential mechanism for pair formation involves initial development of the single Pb vacancy which, by weakening the covalent bonding, sets up the crystal lattice for an appearance of the O vacancy. Binding of the Pb and O vacancies occurs through the ionization interactions. Since no dangling bonds appear at the Pb-O pair site, this defect has a minor effect on the electronic properties. In such, vacancy self-passivation offers a practical way to improve the transport properties in thermally grown PbO layers.

Polycrystalline Lead Oxide (PbO) is one of the few photoconductive materials with a long —more than 60 years— history of employment in imaging devices. Although PbO is extensively used as a photoconductor, very little is known about the electronic properties and charge transport in this material. It is generally believed that transport in PbO is controlled by trapping in defects and that trapping is a cause of low mobility-time product [1]. However, the nature of defects is not fully understood. Emerging applications of PbO in the direct-conversion-flat panel radiation medical-imaging detectors revived the interest in studying defects in this material as defects can significantly affect imaging performance [2].

Our recent modeling of the native point defects in α-PbO [3] has shown that thermally deposited PbO layers should contain a significant concentration of single vacancies due to their moderate formation energies. Single vacancies are amphoteric defects appearing in the different charge states. In the neutral charge state, the O vacancy \( V_O^{(0)} \) holds two electrons and forms the deep donor level. The neutral Pb vacancy \( V_{Pb}^{(0)} \) is filled with holes, and is a shallow acceptor. It was established that the Pb vacancy prefers to appear doubly ionized, \( V_{Pb}^{(2−)} \), suggesting that the Pb and O vacancies can act as compensating centres to each other. Indeed, two compensating vacancies have a lower formation energy than neutral ones, such as \( \Delta E_f(V_{Pb}^{(0)} + V_O^{(0)}) = \Delta E_f(V_{Pb}^{(2−)} + V_O^{(2+)}) = 0.78 \text{ eV} \) [3].

The fact that vacancies prefer to appear in charge states suggests that we have to consider the ionization interactions between them and the formation of a neutral vacancy pair \( V_{Pb-O} \) instead of two separate compensating vacancies. This should further decrease the formation energy, approximately speaking, the free energy required to insert a defect in a lattice is reduced by the energy liberated due to ionization of the donor and acceptor. Indeed, the formation of the defect complexes in favor over the single defects is often observed during material deposition [4]. In this work, we present our study of the formation mechanism of the \( V_{Pb-O} \) pair in PbO layers and its effect on the electronic properties.

Analysis of the formation of the \( V_{Pb-O} \) vacancy pair was performed using the density functional theory (DFT) available in the Wien2k package [5] which utilizes the full-potential augmented plane-wave method. The Perdew-Burke-Ernzerhof parameterization [6] of the generalized gradient approximation (GGA) to DFT has been implemented. We assigned only 5p, 5d, 6s and 6p electrons of the Pb atom and 2s and 2p electrons of the O atom to the valence states, while the lower-energy electrons were included into the core shells. The supercell approach was applied, in which the supercell was taken of 120 atom size (5×3×2 array of the primitive cells shown in fig. 1 (a)). For some calculations, the supercell of 108 atom size has been used (3×3×3). The supercell has been optimized with respect to the internal degrees of freedom, for which minimization based on the forces has been applied [7]. The following parameters have been used: \( RK_{max} = 7 \) (product of the atomic sphere radius and the plane-wave cut-off in k-space), and standard Monkhorst-Pack mesh.
of size $4 \times 4 \times 2$ in $k$-space for the Brillouin zone. Assuming that PbO layers are composed primarily of $\alpha$-PbO single crystals [8], we have considered the single crystal as a model compound. The $\alpha$-PbO single crystal is of tetragonal symmetry ($129P4/nmm$), its crystal structure is layered and the layers are held together due to interlayer orbital overlap of the Pb:6s$^2$ lone pairs [9]. The detailed information on structure and parameters used in our investigation of the vacancy defects can be found elsewhere [3].

Upon formation of the vacancy pair, the deficiency of two electrons at the Pb vacancy is compensated by two electrons occupying the O vacancy and dangling bonds appear in different layers) and each vacancy creates its own defect tails being spread within the plane of a single layer shown in interaction with each other (when defects appear in different layers) and each vacancy creates its own localized state, $V^O(0)$ and $V^Pb(0)$. The formation energy under typical growth conditions ($\mu_{Pb}^* + \mu_{O}^* = 2.92\text{eV}$) is found to be $\Delta E^f(V^O(0) + V^Pb(0)) = 5.41\text{eV}$. To initiate the interaction between vacancies, they have been placed into the same supercell, but in different layers. The interactions between such vacancies are absent (the defect tails being spread within the plane of a single layer show no interaction with each other when defects appear in different layers) and each vacancy creates its own localized state, $V^O(0)$ and $V^Pb(0)$. The formation energy of the vacancy pairs $\Delta E^f(V^Pb-O)$ as a function of the vacancy separation are presented in fig. 2(a) (in the following we assume that $\Delta E^f(V^Pb-O)$ is saturated at position 4).

The total lowering in the formation energy upon vacancy binding is found to be $E_{bind} = -1.47\text{eV}$ (vacancies are located next to each other), which suggests that $V^Pb-O$ is extremely energetically favored. There are two primary parts contributing to $E_{bind}$: interaction energy $E_{int}$ and lattice relaxation $E_{rel}$. The $E_{int}$ is the energy change induced by the electron exchange between $V^O(0)$ and $V^Pb(0)$ causing their ionization to the $V^Pb(2-)$ and $V^O(2+)$ states which is followed by lattice relaxation.
$E_{\text{lat}}$. The value of $E_{\text{int}}$ can be determined through the difference between the considered position and the point of saturation (position 4 is considered here to be the saturation point), is equal to 0.55 eV for $V^O$ in position 1. $E_{\text{int}}$ gradually decreases as the oxygen vacancy is moved away (see fig. 2(a)) thus increasing the formation energy of a pair. The magnitude of $E_{\text{int}} = 0.55$ eV is foreseen to be underestimated because the state formed by the $V^Pb$ vacancy is largely delocalized and when $V^O$ is placed at position 4, it already may interact with the periodic copies of $V^Pb$. To eliminate this effect, the supercell of larger size has to be implemented which is not computationally affordable for us. For all positions depicted in fig. 1(b), $E_{\text{lat}}$ is constant and equals 0.92 eV as the charge state within $V^Pb$ is not changed.

Although vacancy binding lowers the formation energy, its value is still high ($> 4$ eV) because the Pb and O vacancies are considered to appear simultaneously. The more realistic case appears to be settling as the compensating vacancy originates near an already existing vacancy. We introduce the notation $V^Pb-O$ when $V^Pb$ is formed nearby the existing $V^O$, and $V^O-Pb$ for the opposite case. The formation energies are

$$
\Delta E^f(V^O-Pb) = E_{\text{tot}}(D) - E_{\text{tot}}(Pb) + \mu(O), \quad (2)
$$

$$
\Delta E^f(V^Pb-O) = E_{\text{tot}}(D) - E_{\text{tot}}(O) + \mu(Pb), \quad (3)
$$

where $E_{\text{tot}}(Pb)$ and $E_{\text{tot}}(O)$ are the total energies of the system containing the single vacancy $V^Pb$ or $V^O$, respectively.

We have plotted the results on the formation energy of the vacancy pairs, $V^O-Pb$ and $V^Pb-O$, in fig. 2(b) and (c), respectively. The different growth conditions have been considered: $\mu^*_Pb = 0.0$ eV and $\mu^*_O = -2.92$ eV are defined for the Pb-rich/O-poor limit, while $\mu^*_Pb = -2.92$ eV and $\mu^*_O = 0.0$ eV for the Pb-poor/O-rich limit [3]. There is a very important trend to be observed in fig. 2(b) and (c): the values of $\Delta E^f(V^Pb-O)$ and $\Delta E^f(V^O-Pb)$ are significantly lower than the formation energy of the corresponding single vacancies in their doubly ionized state [3]. Taking into account that the binding energy is only $E_{\text{band}} = -1.47$ eV, this trend indicates that the lattice distortion induced by the single vacancy reduces the energy required to generate another vacancy nearby. The single vacancy disturbs the lattice periodicity that alters the atomic forces between atoms and weakens the covalent bonds around the vacancy site.

Therefore, the Pb vacancy sets up a lattice to accommodate the O vacancy, thus causing a reduction in the formation energy $\Delta E^f(V^O(2^+)) - \Delta E^f(V^O-Pb) = 4.52$ eV ($V^O$ is in position 1). Negative $\Delta E^f(V^O-Pb)$ means that the lattice containing $V^Pb$ tends to “suck in” the O vacancy and the formation of the $V^O-Pb$ pair becomes spontaneous. We expect the Pb vacancies to be completely passivated by the O vacancies, as even for the O-rich limit the formation energy $\Delta E^f(V^O-Pb)$ is close to zero. Similarly, the formation of the Pb vacancy in close proximity to the pre-existing O vacancy is energetically more favorable than single doubly ionized $V^Pb(2^-)$. However, the gain in energy is smaller than in the previous case: $\Delta E^f(V^Pb(2^-)) - \Delta E^f(V^Pb-O) = 1.96$ eV and because $\Delta E^f(V^Pb-O) > 0$, the lattice distortion induced by the O vacancy is not sufficient to make a process of origin of the Pb vacancy spontaneous.

To understand an effect of passivation on the transport properties, the next step is to examine the alteration in the electronic properties induced by the neutral vacancy pair. We found, since the uncompensated dangling bonds are absent at the $V^Pb-O$ defect site, that the vacancy pair has a little effect on the band formation, as shown in fig. 3. The vacancy pair does not seem to generate any localized state within the band gap, but rather induces a slight modification into the band behaviour. The top valence band and its dispersion are almost unaffected by the appearance of the vacancy pair and, therefore the hole microscopic mobility is predicted to remain the same (it is already low as a result of heavy holes $m^*_h = 2.44$ $m_0$ [11]). In the conduction band, the vacancy pair induces a shift of the lowest band down on the energy axis. This band is a product of the closing of the dangling bonds of vacancies on each other, i.e., its antibonding orbital. Moreover, it shows a slightly weaker dispersion at the $M^*$ point that is anticipated to cause a reduction in the electron mobility.

To gain insight into the band behaviour we have plotted the electron density map for the bottom of the conduction band ($E_C$) and the top of the valence band ($E_V$) in fig. 4(a) and (b), respectively. The O vacancy was created next to the Pb vacancy. The electron density map is plotted for the narrow energy range ($E_C + 0.076$ eV) and ($E_V - 0.076$ eV) to catch $E_C$ and $E_V$ in the vicinity of the $M^*$ and $\Gamma$ points, respectively. For the conduction band, the electron density shows a pronounced localization in

Fig. 3: (Colour on-line) Band diagram for the ideal 3×3×3 supercell (black solid line) and for the same supercell containing the $V^Pb-O$ defect (red dashed line).
The conduction band (cutting plane is perpendicular to layers and passes through the vacancy site. (a) The conduction band ($E_C + 0.076\,\text{eV}$), (b) the valence band ($E_V - 0.076\,\text{eV}$).

Fig. 4: (Colour on-line) The electron density map ($\text{e/Å}^3$) plotted with XcrySDen [12] for the $3\times3\times3$ supercell: the layer containing $V^{\text{Pb}-\text{O}}$ and, in particular, on the atoms around the defect site; continuity of the electron network is disturbed and that should affect the electron microscopic mobility. For the valence band, an alteration in the electron density is confined entirely to the vacancy site where density vanishes. Although such hole in the electron density can affect the carrier transport locally in the vicinity of the defect, density remains undisturbed, suggesting that the hole mobility is not altered.

From our study, one can conclude that Pb vacancies in PbO layers are passivated by O vacancies to form the neutral vacancy pair. It seems reasonable to assume that the negative effect of the vacancy pairs on the transport properties of PbO photoconductive layers would be minimized if the $V^{\text{Pb}-\text{O}}$ pair cannot act as trapping center (dangling bonds are absent and an extra electron or hole become delocalized). Moreover, as pair formation involves the merging of single Pb and O vacancies ($E_{\text{band}} = -1.47\,\text{eV}$) which otherwise are active traps, it is foreseen to suppress the carrier trapping. As the concentration of O vacancies is higher than that of Pb vacancies, the large fraction of $V^{\text{O}(0)}$ is left uncompensated to be filled with two electrons [3]. The experimental evidence of n-type conductivity in PbO layers [13] supports this observation. Our finding offers a practical way to improve the transport properties of thermally deposited PbO layers. The post-growth annealing (in vacuum or oxygen atmosphere) would initiate migration of the O vacancies towards Pb vacancies with driving forces defined by the vacancy interaction $E_{\text{int}} = 0.55\,\text{eV}$ and facilitates their merging.

This is expected to reduce an amount of ionized centres in PbO thus improving drift mobilities of electrons and holes as well as suppressing recombination. The improvement of the X-ray sensitivity [14] and alteration in resistivity [15] of the PbO samples observed after the thermal annealing in atmosphere of oxygen support our finding.

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