Effects of the number of layers on the vibrational, electronic and optical properties of alpha lead oxide.

Ali Bakhtatou\textsuperscript{1} and Fatih Ersan\textsuperscript{2,3}\textsuperscript{*}

\textsuperscript{1}Laboratoire de physique des matériaux, Université 8 Mai 1945 Guelma, BP 401 Guelma 24000, Algeria
\textsuperscript{2}Department of Physics, Adnan Menderes University, 09100, Aydın, Turkey
\textsuperscript{3}Department of Physics, University of Maryland Baltimore County, Baltimore, MD 21250, USA

We have investigated the effects of number of layers on the structural, vibrational, electronic and optical properties of $\alpha$-PbO using first principles calculations. Our theoretical calculations have shown that four Raman active modes of $\alpha$-PbO tend to red-shift from bulk to monolayer due to decreasing of force constants and increasing of bond lengths. It has been shown that while bulk and multilayer $\alpha$-PbO have an indirect band gap, monolayer form has a direct band gap value of 2.59 eV. Although lead atoms have 5d states, spin-orbit coupling does not significantly affect the band structure of $\alpha$-PbO. The computed cleavage energy value (0.67 J/m\textsuperscript{2}) confirms that monolayer PbO can be easily obtained from its bulk counterpart by exfoliation methods. In addition to the band structure, we also calculated the optical properties and absorbed photon flux $J_{\text{abs}}$ of $\alpha$-PbO structures to investigate the possibility of solar absorption. Our calculations reveal that while monolayer and bilayer PbO have relatively larger band gaps and lower absorption coefficients, their $J_{\text{abs}}$ values are not ideal for solar absorption devices. In contrast, the multilayer and bulk phases of the $\alpha$-PbOs show good overlap with the solar spectrum and yield high electrical current values. Our calculations have indicated that ultrathin films of $\alpha$-PbO (such as 3nm thickness) could be excellent candidates for solar cells. We believe that our work can be utilized to improve electronic and optical devices based on lead oxide structures.

I. INTRODUCTION

The synthesis of graphene\textsuperscript{1} the first two-dimensional material (2D), has attracted a great deal of attention because of its unique electronic, optical, and transport properties. It also has opened the path to experimental and theoretical research of other materials in monolayer or few monolayer form. A significant interest has been brought to nanosheets oxide (NS) 2D by the prediction of the first metal oxide monolayer ZnO by Z. Tu \textit{et al.}\textsuperscript{2} which was synthesized later by C. Tusche \textit{et al.}\textsuperscript{3} Theoretical studies of this new material have revealed its interesting electronic and optical properties.\textsuperscript{1-3} Subsequent studies have been carried out on monolayer oxide materials in the II-VI family, exhibiting promising dynamic stability of BeO, CaO, MgO, ZnO, CdO, and HgO semiconductors in addition to revealing attractive functional properties, which could be applied to nanoelectronics, optoelectronic and spintronics.\textsuperscript{4-6} 2D MnO and NiO gain magnetization and exhibit different optical behavior from their bulk forms.\textsuperscript{7} High electronegativity of the oxygen atom causes different electronic structures for the monolayers of BO, AlO, GaO and InO, with respect to their S, Se and Te constituents.\textsuperscript{8} Recently, a stable direct band gap CO sheet with excellent mechanical properties was predicted to be a promising candidate for various applications.\textsuperscript{10} Recently, $\alpha$-PbO 2D sheets have also attracted much attention. Previous studies have confirmed this oxide as one of the most useful materials for optoelectronic sensing in the visible range.\textsuperscript{11-13} Pasha \textit{et al.} concluded that stable nanostructures of lead oxides can also be obtained at low temperatures.\textsuperscript{14} This material has an indirect band gap of about \(-1.9\) eV in its bulk form.\textsuperscript{15-17} Recent experimental findings suggest that PbO atomic sheets exhibit hydrophobicity, thermal robustness, microwave stability, anti-corrosive behaviour and acid resistance\textsuperscript{20} Theoretical studies show that impurities of 3d transition metal atoms in the $\alpha$-PbO (001) surface can induce magnetic moments to the structure.\textsuperscript{21} Similar magnetization effects can be obtained by the nonmagnetic elements in group 13 and 14.\textsuperscript{22} Possible point defects for $\alpha$-PbO has been studied by Berashevich \textit{et al.}, and their analysis shows that oxygen vacancies induce a deep donor level in the electronic band structure, while lead vacancies create a shallow level above the valence band. This implies that Pb vacancies act as an acceptor.\textsuperscript{23} In this paper, we investigate the effects of dimensionality reduction from bulk to monolayer on its structural, vibrational, electronic and optical properties. By means of density-functional theory using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)\textsuperscript{24} exchange and correlation, we calculate the structural relaxed lattice parameters for the layered structures and compare their stability by analysis of the phonon spectrum of bulk, monolayer and bilayer. To overcome the problem of band gap underestimation of GGA, we employ Quasiparticle (QP) self-consistent GW (QSGW)\textsuperscript{25} to compute and discuss the evolution of the electronic structure of monolayer, bilayer, trilayer, fourlayer and bulk $\alpha$-PbO and compare results with GGA. We find that the band gap in bulk and monolayer is significantly overestimated by this method; this is usually attributed to the underestimate of screening in the random phase approximation (RPA). To remedy the overestimation, we adopt the hybrid method QSGW (hQSGW)\textsuperscript{25} which has been shown to be an excellent predictor of electronic properties for a wide range of materials.\textsuperscript{25} Finally, optical constants of monolayer, bilayer, trilayer, fourlayer
and bulk α-PbO are computed and the absorbed solar photon flux $J_{abs}$ values (units of electrical current) are calculated.

II. COMPUTATIONAL DETAILS

To compute the lattice constants and the relaxed internal positions of the atoms for bulk and layered structures, we used the projector augmented wave method (PAW) to deal with the electron-ion interaction and the GGA to approximate the exchange and correlation part as implemented in VASP code. For electronic calculations, the mixed basis of plane waves and muffin-tin orbitals method (PMT) was used to solve the density functional Kohn-Sham equations in the GGA, the QSGW and the hQSGW approximations as implemented in the ecalj package. For bulk as well as for layered structures, the energy cutoff parameter for self-energy calculations is set to 3 Ry. For the augmented plane waves (APWs) of the energy cutoff parameter for self-energy calculations was performed using meshes of $2 \times 6 \times 4$ for bulk, $6 \times 6 \times 2$ for bilayer and $6 \times 6 \times 1$ for monolayer. Since computing QSGW for a heavy elements like Pb (and for a number of atoms in the unit cell more than eight is very costly in time and memory), Brillouin zone meshing for GW was reduced to $3 \times 3 \times 1$ k-points for trilayer (12 atoms per unit cell) and $2 \times 2 \times 1$ k-points for fourlayer (16 atoms per unit cell). For energy bands and partial density of states calculations, the number of k-points in the three reciprocal directions was chosen roughly in proportion to the size of the reciprocal lattice: $20 \times 20 \times 16$ for bulk, $16 \times 16 \times 1$ for monolayer, $12 \times 12 \times 2$ for bilayer, $14 \times 14 \times 2$ for trilayer and $16 \times 16 \times 1$ for fourlayer. To compute the frequency dependent dielectric functions in the independent particle picture we used the VASP code, where local field effects were not implemented in our calculations. For calculations of the optical properties, we used a Γ centered $14 \times 14 \times 1$ k-points mesh and 100 extra band numbers in addition to corresponding valence band numbers of each considered PbO structure. For the all VASP calculations, the kinetic energy cutoff parameter was taken as 650 eV, the energy convergence value between two consecutive steps was chosen as $10^{-5}$ eV, and a maximum force on the each atom in the cell is allowed as 0.002 eV/Å.

III. RESULTS

A. Structural, Vibrational and Electronic Properties of α-PbO

We first carried out calculations on the bulk alpha lead oxide (α-PbO) structure, which has P4/nmm space group. Fig. 1 shows the α-PbO structures. The calculated equilibrium lattice constants are $a = b = 4.047$ Å and $c = 5.121$ Å. These values are only 2 % and 2.5 % larger than experimental results, for $a, b$ and $c$ respectively. The distance between the nearest Pb and O atoms is $d = 2.35$ Å and there is 2.72 Å between each successive PbO layer. For the sake of comparison, we calculated the phonon band structure of α-PbO and the corresponding raman spectrum as seen in Fig. 1. Our theoretical analysis indicates that the α-PbO structure belongs to the $D_{4h}^4$ point group. There are 4 atoms per unit cell, therefore it has $3 \times 4 = 12$ phonon modes (Fig. 1), of which three acoustical (translational). The remaining 9 are optical (vibrational) modes. Irreducible representations of the α-PbO at Γ, are as follows:

$$\Gamma = 4E_g + A_{1g} + 2E_u + B_{1g} + A_{2u}.$$  

We see that separately two phonon modes have the same vibration frequencies for the $E_g$ modes. Therefore, in fact $2E_g$ modes can be seen in the Raman spectrum for the α-PbO structure. Among these irreducible representations, four are Raman-active modes ($2E_g, A_{1g}$ and $B_{1g}$), while the remaining 3 are infrared-active modes ($2E_u$ and $A_{2u}$). The theoretically calculated Raman spectrum of bulk PbO is illustrated in Fig. 1 and all phonon modes are given in Table 1. The most intense Raman mode at 141.24 cm$^{-1}$ ($A_{1g}$) corresponds to lead atoms moving in opposite directions parallel to the $c$-axis. This calculated value is a bit smaller than the experimentally observed values of 145.5 cm$^{-1}$ and 150 cm$^{-1}$ or larger than 137 cm$^{-1}$ but very close the result of 140 cm$^{-1}$. These differences may be ascribable to temperature differences, since vibrational modes strongly depend on the materials temperature. The other strong intensity peak (324.47 cm$^{-1}$, $B_{1g}$) comes from the motion of oxygen atoms parallel to the $c$-axis.

One of the most favorable techniques to obtain few or monolayer structures from their layered bulk forms are liquid phase exfoliation or mechanical cleavage. Recently Kumar et al. have produced few and single layer α-PbO by using micromechanical, as well as sonochemical exfoliation, but this study holds does not provide the cleavage energy. Therefore we estimated cleavage energy of fourlayer PbO by creating a fracture in the eighth slab of α-PbO structure and systematically increasing the distance between each successive fourlayer of PbO as seen in Fig. 1. The calculated cleavage energy is 0.67 J/m$^2$, and this estimated energy value is 1.7 times larger than the exfoliation energy of graphene (0.39 ± 0.02 J/m$^2$), but smaller than many estimated 2D materials such as GeP$_3$, C$_6$N$_4$, NaSn$_3$ and C$_{20}$. Consequently, monolayers of α-PbO can be produced by using exfoli-
ation methods from its bulk form, as realized recently by Kumar et al.\textsuperscript{20} After these analyses, we created a monolayer PbO structure with the lattice constants of \(a = b = 4.022\) Å and confirmed its dynamical stability by calculating the phonon frequencies along the all directions in its Brillouin Zone (Fig. [1]). Phonon dispersion curves of monolayer PbO have only real modes over the whole BZ which indicate its stability. The highest optical frequency modes of monolayer PbO reach \(13.91\) THz. This vibration mode value is very close to that of MoS\(_2\) (14.18 THz)\textsuperscript{20} indicating the robustness of the covalent oxygen-oxygen bonds between the lead atoms. On the other hand, vibrational modes of lead atoms are under of 4.2 THz. We also checked thermal stability of the monolayer PbO by \textit{ab initio} molecular dynamic calculations for 2ps at 300K and 500K. Simulation results showed that the monolayer form of PbO can be stable at room and above temperature. In addition, we optimized the bilayer of PbO structure, which has an AA stacking order. The Raman-active modes and their corresponding intensities of monolayer and bilayer are compared with bulk PbO makes as illustrated in Fig. [1]. The \(E_g\) modes of bulk PbO at 78.50 cm\(^{-1}\), which result from the motion of lead atoms parallel to the \(xy\)-plane, are redshifted to the 76.52 cm\(^{-1}\) for the bilayer with very weak intensity. Our results indicate this mode slips to 74.56 cm\(^{-1}\) but its intensity goes nearly to zero, which probably can not seen experimentally in Raman spectrum. In addition, the \(B_{1g}\) mode tends to red-shift from bulk to monolayer PbO. The reason for these shifts can be explained by two types of interactions. First, the distance between the nearest Pb and O atoms for monolayer phase of PbO is \(d = 2.36\) Å which is slightly larger than in bulk form. In principle, for the coupled oscillators, frequency (\(\omega\)) is related to the force constant \((k)\) and the reduced mass \((\mu)\) as \(\omega = \sqrt{k/\mu}\). So, this increasing of the Pb-O bond distance appears in the Raman spectrum modes as a shift to lower frequencies due to decreased force constants of the Pb-O bonds. Second, \(\alpha\)-PbO has weak van der Waals interaction between the layers, and this vdW becomes weaker with decreasing number of layers, and disappears for the monolayer. For instance, while the perpendicular distance between the O-O atoms is 5.12 Å for the bulk, this distance becomes 5.16 Å for the bilayer PbO, so both long-range interaction and force constant decrease.

After the structural and stability analysis, we investigated the effects of the number of layers on the electronic properties of \(\alpha\)-PbO. For these examinations, we used two different density functional theory simulation packages (VASP and ecalj\textsuperscript{23,24}). Fig. [2] (a-d) presents the partial electronic density of states (PDOS) and band structures of bulk and layered \(\alpha\)-PbO structures, which are obtained from the ecalj package. Both VASP and ecalj packages give similar band structures and gap values for bulk or layered \(\alpha\)-PbO using the GGA method. Bulk \(\alpha\)-PbO has a 1.34 eV indirect band gap which increases to 2.20 eV by using the quasiparticle self-consistent GW (QSGW) method. We obtained good agreement with experiments (1.90, 1.95 eV\textsuperscript{11,12,14} when we used hQSGW with spin orbit coupling (1.94 eV). Spin orbit coupling (SOC) only decreases the bulk \(\alpha\)-PbO band gaps by 40 meV (see Table 2 and Fig. [2] b). As can be seen from DOS of bulk \(\alpha\)-PbO in Fig. [2] a, oxygen 2p states dominate the valence band maximum but hybridize with lead 6s states, and the lowest energy regions are occupied by Pb 6s and O 2p orbitals. The main contribution to the conduction band minimum comes from the lead \(p\) states. For the monolayer case of \(\alpha\)-PbO, the character of band structure differs from the bulk. The band gap is 2.58 eV (for GGA results) and shows direct gap character as seen in Fig. [2] d. These GGA results are in good agreement with previous studies\textsuperscript{20} Using QSGW, the band gap of the monolayer \(\alpha\)-PbO increases approximately two times from the GGA result (See in Table 2 and Fig. [2] d). The SOC effect is less important for the monolayer structure with respect to bulk \(\alpha\)-PbO; contribution of SOC only closes the band gap of monolayer PbO by 30 meV. The partial density of states also differs from bulk \(\alpha\)-PbO. The highest conduction bands are mainly Pb-6\(p\) derived, and the contribution of O-2\(p\) states is more important in monolayer than in bulk. The bands along the reciprocal directions at the edges of every subband in the valence band are flatter for monolayer than for bulk. Consequently the density of states at the edges of the four valence subbands are more significant than that of the bulk. For monolayer compared to bulk, the valence, the O-2\(p\), the Pb-6s, the Pb-5d and the O-2s bandwidths are reduced by about 1.1 eV, 1.27 eV, 1.43 eV, 0.38 eV and 0.14 eV respectively. Owing to the flatter bands at the VBM and CBM, there are several pins in the DOS graphs. In addition, the Pb 6s and 6p states give nearly same contribution to the VBM, which is different from the bulk PDOS. We calculated effective mass values for holes and electrons at the VBM and CBM using interpolation techniques to obtain the slope of each curve. Our results show that holes are \(\sim 9\) times heavier than electrons for the bulk \(\alpha\)-PbO. For monolayer this ratio is \(m^* = 63m_e^*\). These values differ from a previous study, which found holes 6 and 83 times heavier for bulk and monolayer PbO, respectively\textsuperscript{23} This difference may come from the simulation packages used. As seen in Fig. [2] e, the band gap value does not increase linearly from bulk to monolayer, and only monolayer PbO has a direct band gap while all other layered PbO have indirect band gaps. Fig. [2] f shows the lower direct band gap value at every \(k\) points in the \(\Gamma\)-X, \(\Gamma\)-M and \(\Gamma\)-\(\Gamma\) reciprocal directions for monolayer, bilayer, trilayer, fourlayer and bulk \(\alpha\)-PbO. The monolayer direct band gaps are higher than those of bulk and other layered structures except around the \(\Gamma\) point where the bulk direct band gap is the greatest. We can predict, from this figure, that the optical absorption onset of trilayer, fourlayer and bulk is approximately the same and due to direct transitions at \(\Gamma\) and \(\Gamma\) points, while the onset absorption of bilayer will be slightly above them (due to the same direct transitions), and the onset monolayer will be the highest and due only
to direct $\Gamma$ transition.

**B. Optical Properties of $\alpha$-PbO**

In this section we have investigated how the number of layers affects on the optical properties of the PbO material. Optical spectra of the materials can be revealed from the frequency dependent dielectric functions ($\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$). Detailed information can be found in literature.\cite{10,11}\ It should be noted that the excitonic effects are not included in this study. Fig. 3 illustrates the frequency dependent real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the dielectric function and related optical spectral quantities for $\alpha$-PbO structures. Due to PbO structures having a square plane unitcell in the $x$-$y$ axes, $x$ and $y$ components of the dielectric functions are equal for the same frequency, so we only plotted $x$ components of the dielectric functions. We can estimate the interior intra-optical excitations in the material by considering $\varepsilon_2(\omega)$ and the electronic DOS of the $\alpha$-PbO structures. As seen from $\varepsilon_2(\omega)$ spectra of the PbO structures, the threshold energies are comparable with the band gap values, which are given in Table 1. These threshold energy values are attributed to the interband transitions from O 2$p$ states at the VBM to the lead 6$p$ states at the CBM. Dominant peaks of $\varepsilon_2(\omega)$ around the 4 eV come from the excitations between the O 2$p$ states in the valence bands to the O 2$p$ or Pb 6$p$ states in the conduction bands for all $\alpha$-PbO structures. As seen from the reflectivity spectra, PbO is a transparent material in the visible region, while reflection coefficients increase in the ultraviolet region. However, transparence increases as layer decreases. As is known the peaks in the energy loss spectra can specify the collective excitations. Apparent peaks for the $\alpha$-PbO structures show up at around 12 eV, except for monolayer PbO where peaks exist at 7.5 eV. Refractive index of the materials decreases with the number of layers (see Fig. 3).\cite{12,13}

High absorption coefficients of the materials suggest that they can be used as highly efficient optical absorbers. As seen in Fig. 3, the $\alpha$-PbO structure has high absorption coefficients on the order of $10^6$ cm$^{-1}$, which is 10 to 100 times larger than traditional solar cell materials.\cite{14,15}\ After calculation of absorption coefficients we calculated absorbance spectra for all $\alpha$-PbO (see Fig. 3 a). The photon flux of AM1.5G solar spectrum\cite{16} shown in yellow. Monolayer MoS$_2$ can absorb up to 5-10% incident sunlight in a thickness of less than 1 nm and so could be utilized as a highly efficient solar absorber.\cite{17,18}\ Due to this knowledge we calculated the absorbance spectrum of monolayer MoS$_2$ to compare to PbO structures. Absorbance of the thin materials can be calculated as follows:\cite{19,20,21}

$$A(\omega) = \frac{\omega}{c} \varepsilon_2(\omega) \Delta z$$

where, $c$ is the speed of light, and $\Delta z$ is the length of the simulation cell in the layer-normal direction (thickness).

This equation is valid if the material has the small thickness ($\Delta z \rightarrow 0$). This formula can be obtained after a Taylor expansion\cite{20,21,22} of the equation $A(\omega) = 1 - e^{-\alpha \cdot \Delta z}$. In this study we accepted the $\Delta z$ as the polarizable electronic thickness. For this we used $d_{\text{buckling}}$ of the PbO layer as illustrated in Fig. 1 a and the van der Waals atomic radius as below:\cite{23}

$$\Delta z = d_{\text{buckling}}(\text{PbO}) + 2r_{\text{Pb}}^{\text{vdW}}$$

(2)

We only used the van der Waals atomic radius of lead atom instead of lead and oxygen atoms combined due to oxygen atoms sandwiched between the lead atoms.\cite{24}\ Fig. 1 a shows the absorbance of the $\alpha$-PbO structures and monolayer of MoS$_2$. As can be seen, visible region of the solar spectrum mostly overlaps with the absorbance curves of MoS$_2$ and bulk $\alpha$-PbO, as also indicated by their band gap values. Therefore they can absorb the incident sunlight. We remark that 2L, 3L and 4L $\alpha$-PbO structures have high absorbance value, their spectrums overlap with the low intensity flux region (ultraviolet region) of the solar spectra, due to their large band gap values. Figs. 2 a and 2 c compare the absorbed solar photon flux $J_{\text{abs}}$ in 1L, 2L, 3L, 4L $\alpha$-PbO, monolayer MoS$_2$ and bulk $\alpha$-PbO films of various thicknesses. To gauge capacity of each structure as solar absorbers, we computed $J_{\text{abs}}$ by using the calculated absorbance using the integral:\cite{25}

$$J_{\text{abs}} = \int_0^{E_g} A(\lambda) J_p(\lambda) d\lambda$$

(3)

where the integration limit $\lambda(E_g)$ is the band gap of the corresponding structure, $J_p(\lambda)$ is taken from the AM1.5G solar spectrum.\cite{26}\ All $J_{\text{abs}}$ values obtained for the in-plane absorbance and absorption coefficients of the considered materials for the out-of-plane direction are lower than their in-plane values, so their $J_{\text{abs}}$ values will be small. As mentioned before, due to expensive computational times we did not consider excitonic effects in our optic calculations, which leads to an underestimated spectrum. Therefore, the computed $J_{\text{abs}}$ value for the monolayer MoS$_2$ (for the thickness of 6.5 Å) is 1.1 mA/cm$^2$, which is smaller than calculated with using Bethe-Salpeter equation (BSE) (3.9 mA/cm$^2$).\cite{27}\ But, our calculated $J_{\text{abs}}$ value for the monolayer MoS$_2$ is comparable with the results of Tan et al.\cite{28}\ They found the $J_{\text{abs}}$ is 2.3 mA/cm$^2$, because they took the $\Delta z = 18$ Å. When we computed using the same $\Delta z$ value, we found the $J_{\text{abs}}$ equal to 2.5 mA/cm$^2$. Based on these considerations, we expect a larger $J_{\text{abs}}$ when using more sensitive for 2L, 3L, and 4L $\alpha$-PbO calculations such as BSE. On the other hand, bulk $J_{\text{abs}}$ value of the $\alpha$-PbO structure increases with increasing film thickness, reaches and exceeds the $J_{\text{abs}}$ value of the MoS$_2$ monolayer after a thickness of 30 Å. Especially, our calculations indicate that ultra-thin $\alpha$-PbO has high potential in solar cell applications.
IV. CONCLUSION

In conclusion, our first-principles calculations show that single layer \( \alpha \)-PbO is a dynamically and thermally stable material. The calculated cleavage energy value indicates that exfoliation methods can be suitable to obtain single layer \( \alpha \)-PbO. Raman active modes of \( \alpha \)-PbO are redshifted with the decreasing of the number of layers. While bulk and multilayer lead oxide structures have indirect band gaps, monolayer PbO has direct gap and it has larger band gap value. Spin-orbit coupling is not so effective on the electronic band structures, contribution of SOC is not so effective on the electronic band structures, contribution of SOC only decreases the band gaps of \( \alpha \)-PbOs by \( \sim 40 \) meV. The high absorption coefficients of the \( \alpha \)-PbO structures make this material appealing for solar absorption applications. In spite of large band gaps of mono and bilayer PbO, other band gaps of multilayered and bulk \( \alpha \)-PbO structures are in the visible region. Thereby, their obtained absorbance curves overlap with the solar photon flux spectra. The computed \( J_{\text{abs}} \) value for single layer PbO is very small and not suitable for sunlight absorption. With the increasing of the number of lead oxide layers, the \( J_{\text{abs}} \) value increases. With this increased \( J_{\text{abs}} \) we believe that ultra-thin \( \alpha \)-PbO films can be excellent solar cell candidates. These theoretical results can be helpful in designing new solar absorption devices in future optoelectronic industry.

V. ACKNOWLEDGMENTS

Computing resources used in this work were provided by the TUBITAK ULAKBIM, High Performance and Grid Computing Center (Tr-Grid e-Infrastructure) and by the "Plateau Technique de Calcul Intensif de Guelma".

References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Electric field effect in atomically thin carbon films, Science 306 (2004) 666.
2. Z. C. Tu, X. Hu, Elasticity and piezoelectricity of zinc oxide crystals, single layers, and possible single-walled nanotubes, Phys. Rev. B 74 (2006) 035434.
3. C. Tusche, H. L. Meyerheim, J. Kirschner, Observation of Depolarized ZnO(0001) Monolayers: Formation of Unreconstructed Planar Sheets, Phys. Rev. Lett. 99 (2007) 026102.
4. Q. Tang, Y. Li, Z. Zhou, Y. Chen, Z. Chen, Tuning electronic and magnetic properties of wurtzite ZnO monolayers by surface hydrogenation, ACS Appl. Mater. Interfaces 2 (2010) 2442.
5. Y. Wang, Y. Ding, J. Ni, S. Shi, C. Li, J. Shi, Electronic structures of fully fluorinated and semi fluorinated zinc oxide sheets, Appl. Phys. Lett. 96 (2010) 213117.
6. Q. Chen, J. Wang, L. Zhu, S. Wang, F. Ding, Fluorination induced half metallicity in two-dimensional few zinc oxide layers, J. Chem. Phys. 132 (2010) 204703.
7. S. Huang, H. Xu, I. Bello, R. Q. Zhang, Tuning Electronic Structures of ZnO Nanowires by Surface Functionalization: A First-Principles Study, J. Phys. Chem. C 114 (2010) 8861-8866.
8. G S Rao, T Hussain, M S Islam, M Sagynbaeva, D Gupta, P Panigrahi, R Abu, Adsorption mechanism of graphene-like ZnO monolayer towards CO\(_2\) molecules: enhanced CO\(_2\) capture, Nanotechnology 27 (2016) 015502.
9. H. L. Zhuang, R. G. Hennig, Computational identification of single-layer CdO for electronic and optical applications, Appl. Phys. Lett. 103 (2013) 212102.
10. H. Zheng, X. B. Li, N. K. Chen, S. Y. Xie, W. Q. Tian, Y. P. Chen, H. Xia, S. B. Zhang, H. B. Sun, Monolayer II-VI semiconductors: A first-principles prediction, Phys. Rev. B 92 (2015) 115307.
11. F. Shayeganfar, K. S. Vasu, R. R. Nair, F. M. Peeters, M. Neek-Amal, Monolayer alkali and transition-metal monoxides: MgO, CaO, MnO, and NiO, Phys. Rev. B 95 (2017) 144109.
12. S. Demirci, N. Avazli, E. Durgun, S. Cahangirov, Structural and electronic properties of monolayer group III monohalocogenides, Phys. Rev. B 95 (2017) 115409.
13. Z. Teng, C. Liu, X. Yan, A CO monolayer: first-principles design of a new direct band gap semiconductor with excellent mechanical properties, Nanoscale 9 (2017) 5445-5450.
14. P. Miro, M. Audiffred, T. Heine, An atlas of two-dimensional materials, Chem. Soc. Rev. 43 (2014) 6537.
15. S. Lebegue, T. Bjorkman, M. Klintenberg, R. M. Nieminen, O. Eriksson, Two-Dimensional Materials from Data Filtering and Ab Initio Calculations, Phys. Rev. X 3 (2013) 031002.
16. S.K. Khadeer Pasha, K.Chidambaram, N. Vijayan, W. Madhuri, Structural and electrical properties of nano structure lead oxide, J. Optoelectron. Adv. M. 6 (2012) 110-116.
17. R. C. Keezer, D. L. Bowman, J. H. Becker, Electrical and Optical Properties of Lead Oxide Single Crystals, J. of Appl. Phys. 39 (1968) 2062.
18. B. Thangaraju, P. Kaliannan, Optical and structural studies on spray deposited \( \alpha \)-PbO thin films, Semicond. Sci. Technol. 15 (2000) 542-545.
19. D.L. Perry, T.J. Wilkinson, Synthesis of high-purity \( \alpha \)- and \( \beta \)-PbO and possible applications to synthesis and processing of other lead oxide materials, Appl. Phys. A 89 (2007) 77-80.
20. P. Kumar, J. Liu, P. Ranjan, Y. Hu, S. S. Yamijala, S. K. Pati, J. Irudayaraj, Gary J. Cheng, Small 14 (2018) 1703346.
21. E. Arguelles, S. Amino, S. Aspera, H. Nakanishi, H. Kasai, Interstitial impurity-induced magnetism in \( \alpha \)-PbO surface,
J. Berashevich, A. Reznik, Non-magnetic impurities to induce magnetism in α-PbO crystal structure, EPL 104 (2013) 37008.

J. Berashevich, O. Semeniuk, O. Rubel, J. A. Rowlands, A. Reznik, Lead monoxide α-PbO: electronic properties and point defect formation, J. Phys.: Condens. Matter 25 (2013) 075803.

J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865.

M. van Schilfgaarde, T. Kotani, S. Faleev, Quasiparticle Self-Consistent GW Theory, Phys. Rev. Lett. 96 (2006) 226402.

A. N. Chantis, M. van Schilfgaarde, T. Kotani, Ab Initio Prediction of Conduction Band Spin Splitting in Zinc Blende Semiconductors, Phys. Rev. Lett. 96 (2006) 086405.

D. Deguchi, K. Sato, H. Kino, T. Kotani, Accurate energy bands calculated by the hybrid quasiparticle self-consistent GW method implemented in the ecalj package, Jpn. J. Appl. Phys. 55 (2016) 051201.

G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.

T. Kotani, M. van Schilfgaarde, Fusion of the LAPW and LMTO methods: The augmented plane wave plus muffin-tin orbital method, Phys. Rev. B 81 (2010) 125117.

https://github.com/tkotani/ecalj

H. J. Monkhorst, J. D. Pack, Special Points for Brillouin-Zone Integrations, Phys. Rev. B 13 (1976) 5188-192.

E. Majima, Y. Kozuka, M. Uchida, M. Nakamura, M. Kawasaki, Band alignment and photovoltaic effect of epitaxial PbO thin films, Appl. Phys. Express 8 (2015) 074001.

J. Moreau, J. M. Kiat, P. Gamier, G. Calvarin, Incommensurate phase in lead monoxide α-PbO below 208 K, Phys. Rev. B 39 (1989) 10296.

O. Semeniuk, A. Csik, S. Kőkényesi, and A. Reznik, Ion-assisted deposition of amorphous PbO layers, J. Mater Sci. 52 (2017) 7937-7946.

M. Baleva, V. Tuncheva, Optical Characterization of Lead Monoxide Films Grown by Laser-Assisted Deposition, J. Solid State Chem. 110 (1994) 36-42.

M. Cortez-Valadez, A. Vargas-Ortiz, L. Rojas-Blanco, H. Arizpe-Chávez, M. Flores-Acosta, R. Ramírez-Bon, Additional active Raman modes in α-PbO nanoplates, Physica E 53 (2013) 146-149.

R. Yousefi, F. Jamali-Sheini, M. Cheraghizade, A. Sa‘aedí, Facile synthesis and optical properties of PbO nanostructures, Lat. Am. appl. res. 44 (2014) 159-162.

A. Hedoux, D. Le Bellac, Y. Guinet, J. M. Kiat, I. Noire, P. Garnier, Raman spectroscopy and x-ray diffraction studies on PbO and (PbO)1-x(TiO2)x, J. Phys.: Condens. Matter 7 (1995) 8547-8556.

Y. Jing, Y. Ma, Y. Li, T. Heine, GeP3: A Small Indirect Band Gap 2D Crystal with High Carrier Mobility and Strong Interlayer Quantum Confinement, Nano Lett. 17 (2017) 1833-1838.

S. Zhao, Z. Li, J. Yang, Obtaining Two-Dimensional Electron Gas in Free Space without Resorting to Electron Doping: An Electrode Based Design, J. Am. Chem. Soc. 136 (2014) 13313-13318.

Y. Jiao, F. Ma, G. Gao, J. Bell, T. Frauenheim, A. Du, Versatile Single-Layer Sodium Phosphidostannate(II): Strain-Tunable Electronic Structure, Excellent Mechanical Flexibility, and an Ideal Gap for Photovoltaics, J. Phys. Chem. Lett. 6 (2015) 2682-2687.

H. J. Terpstra, R. A. de Groot, C. Haas, Electronic structure of the lead monoxides: Band-structure calculations and photoelectron spectra, Phys. Rev. B 52 (1995) 11690.

J. Berashevich, O. Semeniuk, J. A. Rowlands, A. Reznik, Anisotropy of the carrier effective masses in bulk α-PbO, EPL 99 (2012) 47005.

C. Kittel, Introduction to Solid State Physics, 8th ed. (Wiley, New York, 1996).

M. Gajdos, K. Hummer, G. Kresse, J. Furthmuller, F. Bechstedt, Phys. Rev. B 73 (2006) 045112.

R. Chen, C. Persson, High absorption coefficients of the CuSb(Se,Te)2 and CuBi(S,Se)2 alloys enable high-efficient 100 nm thin-film photovoltaics, EPJ Photovoltaics 8 (2017) 85504.

The AM1.5G spectrum was taken from the NREL website: http://rredc.nrel.gov/solar/spectra/am1.5 and integrated with the trapezoid rule.

M. Bernardi, M. Palummo, J. C. Grossman, Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials, Nano Lett. 13 (2013) 3664-3670.

L. Yang, J. Deslippe, C.-H. Park, M. L. Cohen, S. G. Louie, Excitonic Effects on the Optical Response of Graphene and Bilayer Graphene, Phys. Rev. Lett. 103 (2009) 186802.

M. Fox, Optical properties of solids, Oxford University Press, New York, 2001.

A. Lherbier, A. R. Botello-Méndez, J.-C. Charlier, Electronic and optical properties of pristine and oxidized borophene, 2D Mater. 3 (2016) 045006.

M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, Consistent van der Waals Radii for the Whole Main Group, 2009 J. Phys. Chem. A 113 (2009) 5806.

T. L. Tan, M.-F. Ng, G. Eda, Stable Monolayer Transition Metal Dichalcogenide Ordered Alloys with Tunable Electronic Properties, J. Phys. Chem. C 120 (2016) 2501-2508.
Table I. Raman-active (R.A) and Infrared-active (I.A) phonon frequencies in cm$^{-1}$: α-PbO bulk, bilayer and monolayer. Comparison of the frequencies with the experimental, previously reported (Theoretical) and present study.

| Mode (R.A) | Present Study | Experimental | Theoretical | Present Study | Present Study |
|-----------|---------------|--------------|-------------|---------------|---------------|
| $E_g$     | 79.41         |              |             | 78.50         | 76.5 (9)      |
| $E_g$     | 78.50         | 81 (9)       | 74.50       | 76.54         | 74.57         |
| $A_{1g}$  | 141.24        | 145.2 (9)    | 140.37      | 22.91, 141.63, 458.94 | 140.49       |
| $E_u$ (I.A) | 233.58      |              |             | 234.51        | 232.75       |
| $E_u$ (I.A) | 233.59        |              |             | 234.54        | 232.76       |
| $B_{1g}$  | 324.47        | 331 (9)      | 330.38      | 322.80        | 322.48       |
| $A_{2u}$  | 378.50        |              |             | 371           | 388.65       |
| $E_g$ (I.A) | 388.38        |              |             | 392.44        | 388.67       |
| $E_u$ (I.A) | 388.39        |              |             | 392.42        | 457.20       |
Table II. LDA, GGA, one-shot GW, hQSGW and QSGW gaps (with (w) and without (wo) spin-orbit-coupling (SOC) effects) and absorbed solar flux $J_{abs}$ (converted to units of equivalent electrical current (mA/cm$^2$)) of bulk, monolayer, bilayer, trilayer and fourlayer $\alpha$-PbO. The label one-shot means the 1shot GW calculation from the LDA result. The $J_{abs}$ for bulk in table is for a thickness of 50 Å.

|       | LDA | GGA | one-shot GW | hQSGW | QSGW | Gap Values (eV) |
|-------|-----|-----|-------------|-------|------|-----------------|
|       | wo-SOC | w-SOC | wo-SOC | w-SOC | wo-SOC | w-SOC | wo-SOC | w-SOC | wo-SOC | w-SOC | wo-SOC | w-SOC | wo-SOC | w-SOC | $J_{abs}$ |
| Bulk-PbO | 1.32  | 1.27 | 1.36  | 1.31  | 2.07  | 2.03  | 1.98  | 1.94  | 2.20  | 2.16  | 1.51  |       |       |       |       |
| 1L-PbO  | 2.55  | 2.45 | 2.59  | 2.54  | 4.79  | 4.76  | 4.57  | 4.54  | 5.11  | 5.08  | 0.05  |       |       |       |       |
| 2L-PbO  | 1.94  | 1.89 | 1.99  | 1.94  | 3.78  | 3.73  | 3.59  | 3.54  | 4.06  | 4.01  | 0.27  |       |       |       |       |
| 3L-PbO  | 1.68  | 1.62 | 1.72  | 1.68  | 2.99  | 2.94  | 2.86  | 2.85  | 3.26  | 3.22  | 0.39  |       |       |       |       |
| 4L-PbO  | 1.52  | 1.46 | 1.56  | 1.51  | 2.77  | 2.73  | 2.65  | 2.60  | 2.98  | 2.93  | 0.49  |       |       |       |       |
Figure 1. (Color online) a) Top and side views of the optimized bulk $\alpha$-PbO structure. Primitive unit cell with the lattice constants a, b, and c is delineated by lines. Considered length for the buckling parameter illustrated as $d_{\text{buckling}}$ in the structure. b) Calculated phonon dispersion curves for the bulk $\alpha$-PbO, c) Estimated cleavage energy curve, d) phonon dispersion of monolayer PbO, e) Computed Raman spectrums for the bulk, bilayer and monolayer forms of PbO structures and f) Vibrational modes of Pb and O atoms at the center of the Brillouin Zone (Γ).
Figure 2. (Color online) a), d) Electronic energy band structures and corresponding orbital projected densities of states of the bulk and monolayer PbO structures. e) Variation of the energy band gap with the number of layer of PbO. f) Variation of lower direct band gap value at every k-points through the Γ to Γ'.
Figure 3. (Color online) a) Real $\varepsilon_1(\omega)$ and b) imaginary $\varepsilon_2(\omega)$ parts of the dielectric response function, c) reflectivity $R(\omega)$, d) absorption coefficient $\alpha(\omega)$, e) energy-loss spectrum $L(\omega)$, and f) refractive index $n(\omega)$ of $\alpha$-PbO structures as a function of photon energy. All optical spectrum curves obtained for the $x$ component of the dielectric response functions.
Figure 4. (Color online) a) Absorbance (Derived from equation 1) of the α-PbO and monolayer MoS$_2$ structures along x direction. The photon flux of AM1.5G solar spectrum is shown in yellow. b) Variation of $J_{abs}$ as a function of the number of PbO layer. $J_{abs}$ value of monolayer MoS$_2$ is illustrated by red dot for the comparison. c) Computed $J_{abs}$ values for the bulk α-PbO for various thicknesses.