Two-dimensional antimony oxide

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Abstract

Two-dimensional (2D) antimony, so-called antimonene, is one of the promising novel elemental 2D materials. However it can form antimony oxide, when exposed to air. This may even be beneficial for the stability of the material and at the same time result in interesting electronic properties. Here we present different types of 2D antimony single- and few-layer oxide structures, based on density functional theory (DFT) calculations. We show that, depending on stoichiometry and bonding type, these novel antimony oxide layers have different structural stability and electronic properties, ranging from topological insulators to semiconductors with direct and indirect band gaps between 0.8 eV and 4.9 eV. Furthermore, we discuss their vibrational properties and predict Raman spectra, which allow experimental identification of the different structures. Our theoretical results are in good agreement with recent experimental findings. We suggest that oxidized few-layer antimonene forms by itself a heterostructure consisting of semiconducting antimony oxide and semimetallic few-layer antimonene.

Keywords

antimonene, 2D materials, tunable bandgap, density functional theory (DFT), Raman spectroscopy

The exfoliation of a single layer of graphene from bulk graphite unleashed an entire new field in physics and chemistry focusing on the investigation of two-dimensional (2D) layered crystals.1,2 Over the past years an increasing number of 2D materials with vastly different properties have been discovered, often driven by the search for new physical and chemical properties. Group-15 elements, also known as pnictogens, are suitable to form monoelemental 2D layered materials, which are promising candidates for a variety of applications in the field of plasmonics,3 and for sensing,4 electronic,5,6 and optoelectronic7 devices. Antimony is one of these elements and can form layered structures called antimonene. Recently, few-layer antimonene was realized experimentally by different methods such as epitaxial growth8,9 or exfoliation.10,11 Additionally, the electronic and vibrational properties of monolayer antimonene have been investigated theoretically, with a predicted band gap of about 2.4 eV.12,13 Antimonene also appears reactive to air, however, in contrast to black phosphorus,14,15 it seems...
to form new stable structures after oxidation. An oxidation process may even be favorable for certain electronic properties, for instance oxidized antimonene has been predicted to be a topological insulator.\textsuperscript{11,22}

However, the actual structure of oxidized antimonene layers is still unknown.\textsuperscript{30} In Ref. \textsuperscript{22}, for instance, the theoretical predictions are based on a monolayer antimonene with Sb=O double bonds perpendicular to the antimonene plane. However, taking into account that antimony oxides are known to exist in several different compositions\textsuperscript{31} and display polymorphism, other structures may exist, where the oxygen atoms are bound to at least two Sb atoms and are incorporated into the antimony planes. Furthermore, few-layer antimony prepared by mechanical or chemical exfoliation is likely to undergo oxidation,\textsuperscript{12–15,30} but knowledge about oxidized few-layer Sb is missing. As electronic properties of oxidized antimony depend crucially on the structure and the bonding between oxygen and antimony atoms, a precise knowledge of the atomic structure is essential for developing this new material. The ability to control the oxidation process can then be used to tailor the electronic band structure.

In this work we present several novel single- and few-layer antimonene oxide structures and antimonene/antimonene-oxide heterostructures based on density functional theory (DFT) calculations. Our results suggest that the recently proposed model\textsuperscript{22} of a double-bonded Sb=O attachment of oxygen to antimony atoms in monolayer (1L) antimonene is not dynamically stable. Instead, it relaxes into a more stable configuration, where the oxygen is absorbed into the layer and forms Sb-O-Sb bonds. We call these structures type (II). They are obtained by a frozen-phonon approach. The resulting structures have a reduced symmetry and are more stable than the type (I) structures, as will be discussed below. The different type (II) structures are shown in Figures 1(e)-(j); all structural parameters are summarized in Table S2. We note that these structures might still not be fully dynamically stable, i.e., they might relax into a slightly distorted geometry if a larger unit cell is used. Experimentally, the formation of an amorphous-like configuration exhibiting features of the idealized type (II) structures presented here might be possible as well.

Our calculations predict stable type (II) structures for one, two, and three antimonene layers with different amounts of oxygen in the outer layers. As indicated in Figure\textsuperscript{1} they are labeled by the amount of antimony and oxygen atoms per unit cell in a single outer layer. The total energy of the stable type (II) structures for 1L and 2L is lower than the total energy of the type (I) structures with equal amount of atoms by roughly 3.9 eV and 2.7 eV, respectively. The type (I) structures seem to be in a metastable state and can be transformed into
Figures 1(a) and (b) show type (I) antimonene oxide structures with one and three layers. Corresponding to the unit cell of the top/bottom layer, we call this structure Sb$_2$O.

By increasing the amount of oxygen in the outer layers, such that the number of oxygen atoms matches the number of antimony atoms (Sb$_2$O$_2$), the structure changes even further: “chains” of alternating oxygen and antimony atoms are formed, which are each connected by three bonds to their neighbouring atoms. The chains are connected to each other by an additional bond between two antimony atoms. Such Sb$_2$O$_2$ structures are shown in Figures 1(g) and (h).

Finally, we increase the oxygen concentration in the outer layers to three oxygen atoms per two antimony atoms (Sb$_2$O$_3$), see Figures 1(i) and (j). The chain structure of alternating oxygen and antimony atoms is maintained. The additional oxygen atom is now replacing the Sb-Sb bond, forming an Sb-O-Sb bond. We note that this structure is in fact not fully dynamically stable and relaxes into a slightly distorted geometry if a larger unit cell is used (Figure S4). However, due to the small energy difference (5 meV per Sb$_2$O$_3$ formula unit), we will further use the idealized Sb$_2$O$_3$ layer shown in Figures 1(i) and (j) for reasons of convenience.

For an equal number of atoms in a given type (II) structure, the total energy decreases by roughly 1.3 eV per oxygen atom for an increasing amount of oxygen. This has been verified by calculating the energy of an O$_2$ molecule and adding or subtracting the energy, respectively.

To test the results from our geometry optimizations, which were done at zero temperature, we also performed two sets of molecular dynamics (MD) simulations at a temperature of 300 K. In the first set, we started with the hexagonal primitive cell of monolayer antimonene and added three oxygen atoms close to the antimonene layer. In the second set, we started with a 4x4 supercell of hexagonal antimonene and added an oxygen molecule at a distance of around 3 Å to the layer surface every 1 ps. The lattice vectors were allowed to relax in all calculations. In both sets of calculations, the oxygen is incorporated into the
antimonene layer and chains of Sb-O bonds are formed. In the first set, the equilibrated structure closely resembles the Sb$_2$O$_3$ structure of Figure 1(j). We refer to the supplementary material for snapshots of our MD simulations (Figures S5 and S6).

Based on the results discussed so far, we predict that type (II) structures of antimonene-oxide layers are slightly more stable than type (I) structures, in particular when considering oxidized few-layer antimonene. We expect that antimonene with more than three layers can be oxidized at the outer layers in the same way as the 3L structures shown in Figure 1. Type (I) antimonene oxide structures may exist as well, however, our calculations predict that only 1L and 2L type (I) structures may be stable.

In order to provide a guideline for identifying the different antimonene oxide structures experimentally, e.g., by Raman spectroscopy, we present their vibrational properties in the following.

The type (I) structures belong, like pristine antimonene, to the $D_{3d}$ symmetry group; therefore the vibrational modes include modes with $E_g$ and $A_{1g}$ symmetry (Figure 2). The unit cell of monolayer type (I) antimonene oxide contains four atoms, thus the number of phonon modes is twelve, see also Figure S7. All modes calculated for the type (I) structures fall into two regions, one below 180 cm$^{-1}$ and one at around 820 cm$^{-1}$, see Figure 3. The latter corresponds to stretching of the Sb=O bonds and is therefore indicative of a type (I) structure. The frequency range below 180 cm$^{-1}$ comprises the vibrations within the Sb layers, as well as rigid-layer vibrations in case of few-layer systems in all investigated structures.

However, the calculation of the phonon dispersion of the type (I) monolayer structure results in negative frequencies of the acoustic modes over a large region of the Brillouin zone. This indicates that such structures are not stable experimentally, as discussed above.

The type (II) structures show frequencies up to a maximum of about 590 cm$^{-1}$ (Figure 3). This is in agreement with bulk $\beta$-Sb$_2$O$_3$: according to our calculations as well as Raman measurements in Ref. 32, it also shows a large fraction of its vibrational modes in the frequency range from 200 cm$^{-1}$ to 650 cm$^{-1}$.

Similar to the highest-frequency mode of the type (I) structures, the highest frequency in the type (II) Sb$_2$O structure at about 590 cm$^{-1}$ is an out-of-plane mode, see Figure 2. In contrast to the type (I) structure, however, the motion of the oxygen atoms is not perpendicular to the layer. A second characteristic mode of the type (II) Sb$_2$O layer, at about 315 cm$^{-1}$, is dominated by motion of the oxygen atoms (Figures 2 and 3). For the displacement patterns of all vi-

![Figure 2: Exemplary display of phonon modes of the monolayer antimonene oxide structures investigated here. The type (II) Sb$_2$O and Sb$_2$O$_2$ on the left hand side are shown from the top. All other structures are shown from the side. The green arrows indicate the displacements of the atoms and are to logarithmic scale.](image-url)
brational modes, see Figure S8. The symmetry of these structures is $C_1$ for 1L and $C_i$ for 2L and 3L.

The monolayer type (II) Sb$_2$O$_2$ structure [Figure 1(g) and (h)] can be further symmetrized such that it corresponds to the $C_{2h}$ symmetry group. Here, the frequency of the out-of-plane mode decreases to about 530 cm$^{-1}$ and the mode becomes Raman inactive. Two additional modes arise at around 590 cm$^{-1}$, which are also dominated by displacement of oxygen atoms. The highest-frequency mode is an in-plane vibration, whereas the other mode is along the bond between oxygen and antimony atoms perpendicular to the direction of the Sb-O-Sb chain, but not perpendicular to the two-dimensional crystal plane (Figures 2 and 3); see Figure S9 for all displacement patterns.

The additional oxygen atom in the type (II) Sb$_2$O$_3$ structure leads to five atoms per unit cell for 1L, i.e., 15 phonon modes, which are illustrated in Figure S10. In comparison to the previously discussed structures, the additional vibrational modes occur at roughly 300 cm$^{-1}$, 750 cm$^{-1}$, and in the range of 375 cm$^{-1}$ to 430 cm$^{-1}$ for different layer numbers (Figures 2 and 3).

Figure 3 summarizes the calculated Raman activities for the different monolayer antimony oxide structures. The characteristic $E_g$ and $A_{1g}$ Raman modes of pristine antimonene are shown in Figure 3(a). Their frequencies are at 168 cm$^{-1}$ and 206 cm$^{-1}$, respectively. In Figure 3(b)-(e), the positions of Raman active modes for the monolayer type (I) and type (II) structures with different oxygen concentration are presented. The characteristic frequencies shown in Figure 3 can be used for experimental identification of different antimony oxide structures.

Our predictions of stable type (II) antimony oxide layers are in agreement with recent experiments on the oxidation behavior of liquid phase exfoliated few-layer antimonene. Instead, predicted phonon modes of the Sb$_2$O$_3$ layers fit reasonably well to the experimentally observed spectra.

We will now discuss the simulated electronic bands associated to the different antimonene oxide structures. While bulk and few-layer antimonene are metallic due to a partial covalent bonding between the layers, first-principles calculations on the GW level predict a value of about 2.4 eV for non-oxidized monolayer antimonene. On the other hand, fully oxidized monolayer antimonene with double-bonded oxygen atoms was predicted previously to be a topological insulator with a small “bulk” band gap if spin-orbit interaction is included. Figure 4 shows the calculated electronic band structures of oxidized antimonene using the hybrid functional HSE12, based on the atomic geometries of Figure 1(a) [type (I)] and our proposed new structures [type (II)] from Figure 1(h) and (j). For type (I) Sb$_2$O$_2$, our calculations agree with the results of Ref. [22], showing a band gap of 168 meV; the system is metallic if spin-orbit interaction is neglected.
For type (II) Sb$_2$O$_2$, with the more stable chain-like configuration of the Sb-O bonds, our calculations predict the system to be a trivial insulator with a direct band gap of about 0.8 eV at the edge of the Brillouin zone [Figure 4(b)]. In the latter case, there is no discernable effect of spin-orbit coupling on the electronic dispersion. Increasing the oxygen content in the unit cell [in our slightly idealized monolayer Sb$_2$O$_3$, Figure 1(j)] causes a transition from direct to indirect semiconductor and significantly increases the band gap to 4.9 eV. This suggests that both the size and the nature of the fundamental band gap in oxidized antimonene could be tuned from the infrared to the ultraviolet range, if control over the oxidation of antimonene can be achieved. In few-layer antimonene, we expect that heterostructures of semimetallic antimonene layers sandwiched between semiconducting oxidized antimonene layers will form naturally in experiments.

In summary, we present new layered antimonene oxide structures with the oxygen atoms being incorporated into the antimonene sheet [type (II)]. They are more stable than configurations with Sb=O double bonds perpendicular to the antimonene plane [type (I)]. Distinct differences in the vibrational frequencies between type (I) and the different type (II) antimonene oxides allow an experimental identification of the structures via Raman spectroscopy. This is also in good agreement with recent experimental findings on liquid-phase exfoliated few-layer antimonene. All type (II) single-layer antimonene oxides presented here are semiconductors with stoichiometry-dependent band gaps ranging from approximately 0.8 eV to 4.9 eV. Our results thus pave the way for tailoring the electronic band structure of antimonene flakes via controlled oxidation and will guide future development of antimonene-based 2D materials and heterostructures.

**Methods**

All calculations are performed using density functional theory (DFT) as implemented in Quantum Espresso. We apply a local density approximation (LDA) for the exchange-correlation, since it has been leading to results which are in good agreement to previous phonon calculations. Ultrasoft pseudopotent-

![Figure 4: Electronic band structures and density-of-states calculated using the hybrid functional HSE12 and inclusion of spin-orbit interactions (SOI) for (a) type (I) Sb$_2$O$_2$, (b) type (II) Sb$_2$O$_2$, and (c) type (II) Sb$_2$O$_3$ monolayers. Grey dashed lines are the results without inclusion of spin-orbit interactions and are almost congruent with the bands with SOI for (b) and (c). The zero-of-energy is set to the Fermi energy.](image)
tials with 6 and 15 valence electrons, which are taken from the GBRV library are utilized for O and Sb, respectively. The energy cutoff is set to a value of 60 Ry (816.34 eV). A Monkhorst-Pack grid with $14 \times 14 \times 1$ $k$ points is used for the structural optimization, which is performed until the forces on every atom are less than 0.005 eV/Å. To ensure that interaction between the structures is negligible, unit cells with a size ranging from 22 Å to 30 Å in the direction perpendicular to the layers are used.

The phonon spectra were calculated through a density functional perturbation theory (DFPT) approach. For the phonon dispersions, we interpolated the frequencies along the high-symmetry directions from the explicitly calculated vibrations on a regular $6 \times 6 \times 1$ $q$ point grid. The Raman calculations require norm-conserving pseudopotentials which are taken from the Pseudo-Dojo database, and utilize 6 and 15 valence electrons for O and Sb, respectively. The energy cutoff is set to a value of 80 Ry (1088.46 eV).

The norm-conserving pseudopotentials were also used for calculations of the electronic band structures including spin-orbit-interaction. In this case, we employed the hybrid functional HSE12 in order to guarantee a better description of the electronic band gap sizes compared to LDA simulations.

For the molecular dynamics (MD) calculations, we used the SIESTA code with a $k$ point grid of $15 \times 15 \times 1$ $k$ points, normconserving pseudopotentials and a double-zeta polarized (DZP) basis set. The lattice vectors were allowed to change during the MD runs by virtue of the Parrinello-Rahman variable cell dynamics scheme.

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Supporting Information Available

The following files are available free of charge.
Information about the structural parameters including images of all structures, snapshots of MD calculations, of all vibrational modes, displacement patterns, phonon dispersion relations of the monolayer structures, and atomic positions used for the phonon dispersion calculations.

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