Size-dependent structural and electronic properties of Bi(111) ultrathin nanofilms from first principles

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Few layer bismuth nanofilms with (111) orientation have shown striking electronic properties, especially as building blocks of novel two-dimensional heterostructures. In this paper we present state-of-the-art first principles calculations, based on both density functional theory and maximally localized Wannier functions, that encompass electronic and structural properties of free-standing Bi(111) nanofilms. We accurately evaluate both the in-plane lattice constant and, by including the van der Waals interaction between bismuth bilayers, the intra/interlayer distances. Interestingly and somehow unexpectedly, the in-plane lattice constant is predicted to shrink by about 5% going from the thickest investigated nanofilm (∼80 Å) to single bilayer Bi(111), entailing a thickness dependent lattice mismatch in complex heterostructures involving ultrathin Bi(111). Moreover, quantum confinement effects, that would be expected to rule the electronic structure at this size range, compete with surface states that appear close to and across the Fermi level. The implication is that not only all but the thinnest films have a metallic band structure but also that such surface states might play a role in either the formation of interfaces with other materials or for sensing applications. Finally, the calculated electronic structure compares extremely well with ARPES measurements.

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I. INTRODUCTION

The growing interest in the search for novel two-dimensional (2D) materials with new and tunable functionalities has been driven by the possibility of van der Waals (vdW) stacking of atomic layers, realizing truly 2D electron gases with unexpected properties. While graphene is the most known example within such a family of materials, new materials such as transition-metal dichalcogenides, silicene and germanene, phosphorene, and so on are being successfully synthesized and employed in multifunctional devices [1–3]. One of the most striking opportunities offered by 2D single layer materials is the possibility of being stacked and combined (in terms of number of layers and layer type) to reach desired technological goals. As such, these materials prove to offer an unprecedented flexibility, in terms of electronic properties tunability and design (the most significant example being band gap engineering). Bismuth (Bi) deserves special attention, that can be included within the 2D materials family because its surface, with (111) orientation, shows vdW-like stacking of Bi bilayers (BLs).

The Bi(111) surface can be described with a buckled honeycomb lattice, where valleys in the surface band structure show up, that are similar to those observed in many other 2D materials with honeycomb lattice [4]. There are two fundamental issues that should be kept in mind to deeply understand the experimental observations on Bi(111) nanofilms and how theoretical insights can be linked to them: (i) the interplay between surface states and quantum confinement effects and (ii) the role of spin-orbit (SO) coupling. Bulk Bi is described by a rhombohedral Bravais lattice, with a peculiar electronic structure where very small electron and hole pockets show up at the L and T points of the Brillouin zone [5]. The resulting large Fermi wavelength (λF ∼ 30 nm) might entail important quantum confinement effects even in devices with size in the range of tens of nanometers. However, the occurrence of quantum size effects has been long debated. Indeed, the description based on the bulk band structure has to be contrasted with the appearance of surface states that strongly influence the electronic structure around the Fermi level and that might hinder or hide size-dependent features in the 2D band structure. As concerns SO coupling (SOC), the atomic 6p levels of Bi show a SO splitting as large as ∼1.5 eV [6]. On the other hand, in the bulk crystal the lowest bands (with s character) are only marginally influenced by the SOC, whereas the electronic structure around the Fermi level is strongly modified when the SOC is taken into account. However, the bands remain spin degenerate due to the crystal inversion symmetry. Let us remind that in a generic crystal E(k,↑) = E(−k,↓), the degeneration of any energy band with respect to a simultaneous flipping of k vector and spin originates from time-reversal symmetry. However, in crystals with inversion symmetry, this latter implies the additional degeneracy E(k, ↑↓) = E(−k, ↓↑) (the energy band is degenerated with respect to k vector flipping, at fixed spin). From the combination of the two symmetries, spin degeneracy, that is, E(k, ↑) = E(k, ↓), follows. In such a crystal, as it is for bulk Bi, SOC might induce splitting of band degeneracies, but SO-split bands remain spin degenerate. To get rid of spin degeneration it is necessary to break the inversion symmetry, as it might happen upon formation of a
surface and, even more evidently, when a thin film is supported onto a substrate, making the two film sides inequivalent. As such, Bi “free-standing” films have to be distinguished from substrate-supported films. The latter exhibit strong surface state SO splitting, commonly referred to as Rashba effect.

The theoretical studies that have discussed the properties of Bi(111) nanofilms so far are mostly based on density functional theory, in some cases focused on specific film thickness in relation to experimental outcomes [7–11]. For example, Koroteev et al. [12] study the structural and electronic properties of Bi(111) nanofilms up to 10 BLs. The present study aims to elucidate the structural and electronic properties of Bi(111) nanofilms, as a function of their thickness. Special focus is reserved to the structural (intra- and interlayer distances, in-plane surface lattice parameter) properties, for which the inclusion of a proper description of the interlayer vdW interactions turns out to be essential and yet it lacks in the literature. The results are discussed also in light of recent experimental outcomes [13]. The evolution of the electronic properties with the film thickness brings out the emergence of a surface state that is responsible for the metallic character of the thickest films, able to disguise quantum confinement effects. While the electronic structure calculations essentially agree with those obtained by Koroteev et al. [12], we show that including vdW forces notably provides a much better agreement with experimental data on interlayer distances.

The paper is organized as follows: The theoretical framework and the methodology employed to perform the calculations are discussed in Sec. II, with a focus on how vdW interaction and SOC are dealt with. Next, the structural properties are discussed in Sec. III, with a close comparison with experimental results. Then, the electronic properties (band structure, surface related electronic states, density of states, Fermi surface) are argued in Sec. IV. The main conclusions are finally drawn in Sec. V.

II. METHODS

First principles calculations are performed using density functional theory (DFT), as implemented in the QUANTUM ESPRESSO package [14]. Bi(111) nanofilms are modeled within the supercell approach using the in-plane surface hexagonal $1 \times 1$ unit cell, with varying number of Bi BLs, from 1 to 20, corresponding to thicknesses ranging from $\sim 1.6$ to $\sim 80$ Å. In the following the nanofilm composed by $n$ BLs will be referred to as Bi(111)-$n$BL (for example, an atomistic model of Bi(111)-6BL is drawn in Fig. 1). The supercell size in the direction normal to the nanofilm surface comprises a $\sim 14$ Å vacuum space, proven to be sufficient to prevent periodic replicas from interacting with each other.

A. Structural optimization

For each nanofilm thickness both the in-plane lattice constant and the atomic positions have been optimized, the latter using the Broyden-Fletcher-Goldfarb-Shanno quasi-Newton algorithm, until all components of all residual forces were smaller than $10^{-3}$ a.u. and the total energy variation between two consecutive minimization steps was less than $10^{-4}$ a.u. SOC is not included at this stage. The projector augmented-wave (PAW) pseudopotential $\text{Bi.pbe-dn-kjpaw}_{\text{psl}}.1.0.0.\text{UPF}$ is selected from $\text{pslibrary}.1.0.0$ [15]. The plane wave basis set is truncated at an energy cutoff of 45 Ry to represent the wave functions and 455 Ry to represent the electronic charge density. The surface Brillouin zone (BZ) is sampled using a $8 \times 8 \times 1$ Monkhorst-Pack mesh. After optimization of the in-plane lattice parameter using the GGA-PBE approximation of the exchange-correlation functional, bilayer-bilayer (weak) interaction is modeled by including vdW interactions with the vdW-DF2(c09x) functional, that has been shown to provide accurate results in both long and short range interactions [16–20]. This provides accurate evaluation of the interbilayer distances.

B. Electronic properties

SOC is self-consistently included at this step, by performing total energy, band structure, and density of states (DOS) calculations on the optimized structures. For this purpose, a fully relativistic norm conserving pseudopotential has been generated using the Open-source pseudopotential code
The measurement results, together with experimental error ranges, show that the in-plane lattice constant shrinks by about 5% with respect to the bulk limit. The calculated bulk limit also fairly agrees with the literature value of 4.57 Å for the single BL nanofilm, which has been assigned zero thickness.

C. MLWF calculations

Bulk Bi band structure is characterized by two low-energy s bands, separated by a gap of several eV from the p bands. As such, the electronic structure close to the Fermi level is fully described by a set of six bands with p character for each Bi atom in the unit cell. This produces an exact description of the electronic structure around the Fermi level (see, for example, Fig. S1 in the Supplemental Material), with the advantage of allowing the interpolation of the calculated eigenvalues over very fine grids in the BZ. Such interpolation is used for both DOS calculations and the representation of the Fermi surfaces, as shown in Sec. IV. The procedure also allows an easy representation of “weighted” band structures, where the projection of a given electronic state onto a subset of MLWF orbitals is evidenced. In the present work this is used, for example, to discuss the surface character of some electronic states. The MLWF approach is implemented in the WANNIER90 code [26,27].

Before moving on to the discussion of the results, a central question must be remarked. Many literature studies report on the structural and electronic properties of Bi(111) nanofilms deposited on a supporting substrate, with consequent lattice mismatch. The latter might entail differences of the in-plane lattice constant shrinks by about 5% with respect to the bulk limit. The calculated bulk limit also fairly agrees with the literature value of 4.57 Å for the single BL nanofilm, which has been assigned zero thickness.

III. STRUCTURAL PROPERTIES

The in-plane lattice constants of Bi(111) films grown on a B2Te3(111) substrate have been obtained, from RHEED patterns, by Yao et al. [13], as a function of the film thickness. The measurement results, together with experimental error bars, are shown as stars in Fig. 2. In that study, a variation from 4.38 ± 0.02 Å (single BL limit, same as B2Te3(111) substrate) to 4.54 ± 0.02 Å (thickest films, bulk limit) is reported. Our numerical results, reported in Fig. 2 as empty circles, fairly agree with this picture, although obtained from free-standing films. In the figure, the solid line depicts an exponential fit of the calculated data, whereas the thin solid line, at a ≈ 4.57 Å, is its asymptotic value for large nanofilm thickness. Experimental data from Ref. [13] are included (stars), together with error bars. The inset shows the percentage deviation of the calculated values with respect to the experimental ones. The single BL nanofilm has been assigned zero thickness.

As concerns Bi(111) as a building block of complex interfaces or 2D heterostructures, it is worth pointing out that the 5% variation of the in-plane lattice constant is a significant result. Indeed, it follows that Bi(111) ultrathin films with different thickness, supported on the same substrate, are being subject to different lattice mismatch. Combined with the high sensitivity of the electronic structure to the lattice parameter, this has the implication that, depending on the material which the Bi(111) nanofilm is interfaced with, thickness-dependent mismatch-induced variations of the electronic properties and surface states around the Fermi level are expected. This paves the way to lattice mismatch-based design and engineering of the Bi(111) interfaces or heterostructures, as confirmed by some experimental evidences [28].

The structural optimization of the studied nanofilms also allows the study of the intra- and inter-BL distances and of their dependence on the nanofilm thickness. It should be remarked that it is essential to explicitly take into account the inter-BL vdW interaction for an accurate evaluation of such

FIG. 2. The optimized surface unit cell parameter as a function of the number of Bi BLs. The thick solid line shows an exponential fit of the calculated data, whereas the thin solid line, at a ≈ 4.57 Å, is its asymptotic value for large nanofilm thickness. The inset shows the percentage deviation of the calculated values with respect to the experimental one. The single BL nanofilm has been assigned zero thickness.
distances. Test calculations performed on the studied systems have revealed that, if this contribution is left out, while intra-BL distances can be overestimated by only 1–2%, the error on the inter-BL distances can become as large as 7–8%. The variation of the topmost intra-BL distance ($d_{12}$) and of inter-BL distances ($d_{23}$, $d_{45}$, $d_{67}$) with the number of BLs in the nanofilm is shown in the right panel of Fig. 3 (the distances $d_{ij}$ are defined as sketched in the left panel of the same figure). The former turns out to have a moderate dependence on the nanofilm thickness, with a maximum variation of $\sim 1%$ (corresponding to $\lesssim 0.02$ Å). The computed bulk value (shown in the figure with a dashed line) of 1.625 Å is in good agreement (within $\sim 2%$) with the experimental outcome [30] of 1.59 Å. On the other hand, the topmost inter-BL distance ($d_{23}$) exhibits a $\sim 4%$ dilatation ($\gtrsim 0.04$ Å) when moving from the thickest to the thinnest nanofilms. The dependence of the inter-BL distance on the nanofilm thickness becomes less moderate for the inner BLs, where a rapid convergence towards the computed bulk value (2.3 Å) is observed. The latter again shows a good agreement with the experimental outcome [30] of 2.35 Å.

A more striking comparison can be made with the experimental results reported in Ref. [29], as shown in Fig. 4. Here, the percent variation (with respect to the corresponding computed bulk values) of the topmost intra-BL distance $d_{12}$ and the variation of inter-BL distance between the topmost surface BLs ($d_{23}$) are reported as a function of the number of BLs in the Bi(111) nanofilm. The results for the thickest nanofilm can be compared with the experimental measurements, showing remarkable agreement for $d_{23}$ and a satisfactory agreement for $d_{12}$, thanks to the proper treatment of the inter-BL vdW interactions. It should be pointed out that previous theoretical calculations [12,29], neglecting such interactions, estimate a 6.2% percentual variation of $d_{23}$ with respect to its bulk value. This has to be contrasted with the experimental result of 2.6% reported in Ref. [29], where the discrepancy between theoretical and experimental results is attributed to possible errors in the choice of the exchange-correlation potential and other parameters that might influence the theoretical estimation. However, if the vdW interaction is neglected, the present work result for $d_{23}$ (2.36 Å for the thickest nanofilm, in good agreement with the experimental result) becomes $d_{23} \gtrsim 2.5$ Å, in agreement with the theoretical assessment of Refs. [12,29]. This confirms that an accurate evaluation of the structural properties must take into account the vdW interaction between stacked BLs.

**Fig. 4.** The percent variation of the $d_{12}$ (top panel) and $d_{23}$ (bottom panel) distances (as defined in the left panel of Fig. 3), as a function of the number of BLs. The variation is computed with respect to the calculated bulk values, $d_{12b}$ and $d_{23b}$, respectively. The experimental results (as extrapolated at 0 K) of Ref. [29] are evidenced by the colored rectangle and can be compared with the thickest film calculation.

**IV. ELECTRONIC PROPERTIES**

The band structure calculation of Bi(111)-$n$BL nanofilms with different thicknesses reveals a metallic character starting from Bi(111)-6BL. Only the Bi(111)-1BL nanofilm shows an evident semiconducting character, with an energy gap of $\sim 0.57$ eV. On the other hand, very tiny energy gaps show up for Bi(111)-2BL ($\sim 0.06$ eV), Bi(111)-3BL ($\sim 0.06$ eV), and Bi(111)-4BL ($\sim 0.007$ eV). The calculated band structure along the $\Gamma$-$M$-$\Gamma$ path in the surface first BZ for selected Bi(111)-$n$BL nanofilms and the associated DOS (per Bi BL) are shown in Figs. S2 and S3, respectively, of the Supplemental Material [23]. While a fast convergence (on increasing the nanofilm thickness) towards the bulk limit of the DOS can be evidenced from the plots, a nonzero DOS associated to surface states determines the Fermi level pinning even in the thinnest nanofilms, thus bringing about their metallic character.

For an in-depth analysis of the metallic states crossing the Fermi level along the $\Gamma$-$M$ segment, the weighted band
FIG. 5. Weighted band structure (analogous of the weighted spectral function introduced in Ref. [28]) of selected Bi(111)-nBL nanofilms with different thickness along the $\Gamma$-$M$ segment in the first BZ of the 2D hexagonal lattice. The size of the dots is proportional to the projection of the corresponding Kohn-Sham eigenfunction on the surface MLWFs. The Fermi level is set at $E_F = 0$ eV and is represented by the dashed line.

structure for Bi(111)-nBL with $n = 4, 6, 10, 20$ is shown in Fig. 5. Here, the energy range is zoomed around the Fermi level and the size of the points is proportional to the projection of each Bloch orbital onto the MLWFs belonging to the outermost BL. It turns out that a state with marked surface character shows up close to $\Gamma$ around the Fermi energy with a dispersion that exhibits only a moderate thickness dependence starting from about 6 BLs. On the other hand, bulk Bloch orbitals at $M$ point are found, with a marked energy dependence on the nanofilm thickness. Energy and charge density distribution of such states, as revealed by a number of experimental observations, are driven by quantum confinement effects.

The reported band structure for the Bi(111)-10BL nanofilm can be easily compared with the experimental angle-resolved photoemission spectroscopy (ARPES) measurements of Ref. [8], as shown in Fig. 6 (full band dispersion along the $\Gamma$-$M$ line in the left panel and a closeup around the Fermi energy and close to $\Gamma$ point in the right panel). Here, no shift has been applied to the calculated bands with respect to the experimental ones. Although the calculated bands concern free-standing nanofilms, to be contrasted with the substrate-supported nanofilms experimentally investigated, they do show a remarkable agreement with the most intense ARPES features around the Fermi energy and close to $\Gamma$, as well as for all the branches that show up close to the $M$ point. Such an agreement is the signature of a rather weak nanofilm-substrate interaction, as concerns the ARPES results. Indeed, a significant interaction would break the inversion symmetry, giving rise to additional band splitting, as previously pointed out.

The metallic character of the thickest nanofilms is evident from 2D Fermi surface visualization. The Fermi surface possesses hexagonal symmetry and the multiple crossings of the bands with the Fermi level result in the appearance of electron and hole pockets at different $k$ points in the hexagonal first BZ. More specifically, moving along the $\Gamma$-$M$ direction, a hole pocket at $\Gamma$, an hexagonal electron pocket around $\Gamma$, a hole pocket at about 1/4 of the $\Gamma$-$M$ line, and an electron pocket close to $M$ are found. These are highlighted in Fig. 7.

The Fermi surfaces are shown in Fig. 8 for the Bi(111)-6BL, Bi(111)-10BL, and Bi(111)-20BL nanofilms. As also revealed in the experimental measurements [10], the surface states, which the Fermi surface originates from, possess thickness dependence. While the basic features (position of the electron

FIG. 6. (left) The Bi(111)-10BL nanofilm band structure of Fig. 5 (solid lines and circles) compared with the ARPES measurements of Ref. [8] (shaded regions). (right) A closeup of the band dispersion along the $\Gamma$-$M$ line around the Fermi energy and close to $\Gamma$ (experimental data are reported as shaded regions where different colors distinguish the highest but different intensities of the photoemission results). The Fermi level is set at $E_F = 0$ eV. No relative shift of the theoretical data with respect to the experimental ones has been applied.

FIG. 7. Hole (purple) and electron (yellow) pockets in the Fermi surface for the Bi(111)-20BL nanofilm are evidenced in the band structure along the $\Gamma$-$M$ direction. The Fermi level is set at $E_F = 0$. No relative shift of the theoretical data with respect to the experimental ones has been applied.
FIG. 8. The Fermi surface for the Bi(111)-6BL (top panel), Bi(111)-10BL (middle panel), and Bi(111)-20BL nanofilms. The Fermi level is set at $E_F = 0$ and depicted in blue. Yellow (purple) regions correspond to states below (above) $E_F$. The color bar labels are in eV.

and hole pockets) remain the same for the different films, the dimensions of the Fermi surface do show a moderate thickness dependence.

V. CONCLUSIONS

Several recent experiments have revealed striking features of Bi(111) nanofilms, such as topologically nontrivial electronic properties [13], the observation of a two-dimensional spinful massless electron gas in Bi(111)/Sb heterostructures [31], as well as strain-induced topological phase transition [28]. From these experiments, Bi(111) can be recognized not only as a material of interest for its peculiar electronic properties (e.g., emergence of electron and hole pockets at the Fermi level) but as a possible building block in engineered 2D nanostructures obtained from the stacking of different 2D materials. Quantum confinement effects, that are expected to fully explain the density of states and electronic structure in ultrathin nanofilms, compete in such structures with the presence of surface electronic states crossing the Fermi level and for the metallic character of all but the thinnest films. As such, the electron and hole pockets markedly characterize the Fermi surface, giving it a moderate (but visible) dependence on the nanofilm thickness. These surface states are of utmost interest, since they might play a fundamental role in both bismuth-based heterostructures (driving possible band offset and charge transfer effects) and sensors (being the associated electronic charge available to the interaction with an external environment).

Along with the electronic properties, the results of the present work elucidate the thickness dependence of the structural properties, bringing out significant variations of both the in-plane lattice parameter and of the interlayer distance (the latter, driven by the vdW interaction). The results, that fairly match the available experimental results, open up avenues to bismuth-based heterostructures design, when combined with the high sensitivity of the bismuth nanofilms electronic structure with respect to the structural parameters. Moreover, from a theoretical point of view, they elucidate to what extent inclusion of vdW forces affects the properties of the Bi(111) surface, nanofilms, and heterostructures, namely, structural ones significantly and electronic ones marginally.

Quantum confinement effects are revealed by quantum-well-like states, observed in several experiments, particularly evident at the $M$ point, whereas the Fermi level is pinned by metallic surface states. Those also originate the peculiar Fermi surface, where electron and hole pockets alternate going from $\Gamma$ to $M$ point.

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[4] The [111] direction is referred to the rhombohedral notation, related with the bulk crystal minimal unit cell. This has to be contrasted with the [0001] hexagonal indexing [32], related with a description of the bulk crystal with an hexagonal lattice, with a threefold unit cell volume, compared to that of the rhombohedral unit cell.