

Electrodeposition and *ab Initio* Studies of Metastable Orthorhombic Bi_2Se_3 : A Novel Semiconductor with Bandgap for Photovoltaic Applications

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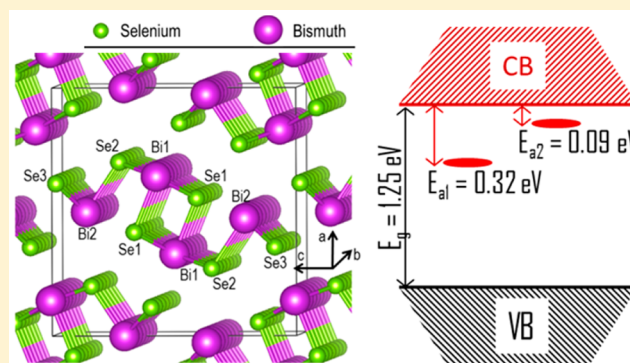
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ABSTRACT: A metastable phase of Bi_2Se_3 with orthorhombic structure has been obtained by potentiostatic electrodeposition onto Si(100) substrate. The ideal stoichiometry and single orthorhombic phase could be obtained only within a restricted potential window, where mutual underpotential co-deposition is assumed to occur. Optical and electrical characterization indicates a bandgap of 1.25 eV, close to the maximum efficiency in the Shockley–Queisser limit, and n-type semiconducting behavior with moderate electrical resistivity. Theoretical calculations using density functional theory were used to support the structural and optical results. Due to the favorable set of properties with respect to isomorphous compounds such as Bi_2S_3 , Sb_2S_3 , and Sb_2Se_3 , this material could lead to efficient and low-cost new thin film-based photovoltaic devices.



INTRODUCTION

The chalcogenide compound Bi_2S_3 and its isomorphs Sb_2S_3 and Sb_2Se_3 have recently been proposed as sensitizers for solar energy harvesting in photovoltaic cells based on quantum dots,^{1–7} solution processed materials,^{8,9} or thin films.^{10,11} These compounds share an orthorhombic crystal structure with space group $Pnma$, where the atoms are arranged in a 1-D chain along the [010] direction, generating stacked ribbon structures. A recent report indicates that this 1-D-like structure may provide for interfaces free of dangling bonds and defects,^{1,10} resulting in solar cells with efficiencies of about 5–6%.^{5,9} Additional attractive features of these chalcogenides are (i) the bandgap, usually reported to be between 1.3 and 1.7 eV,^{10–13} i.e., in the optimal range to maximize the Shockley–Queisser limit of solar conversion efficiency,¹⁴ and (ii) the high ($>10^5 \text{ cm}^{-1}$) optical absorption coefficient, minimizing the absorber layer thickness. These chalcogenide compounds are also well-suited for other technological applications such as photo-detection⁸ and photocatalysis.¹⁵

A fourth compound, Bi_2Se_3 , would ideally complete this group of isomorphs; however, Bi_2Se_3 is stable in a tetradymite (rhombohedral, $R3m$) structure,¹⁶ and synthesis of the

alternative, metastable orthorhombic phase is difficult. There is general agreement that deposition at low ($\sim$ room) temperature leads to the growth of mixed phases, while the rhombohedral phase dominates at high growth temperature;¹⁷ a pure orthorhombic phase has been rarely reported.^{18,19} As a consequence, little and confusing information on the electrical, optical, and structural properties of this material is available, in net contrast to Bi_2S_3 , Sb_2S_3 , and Sb_2Se_3 that are relatively well characterized.^{20–23} Theoretical results using *ab initio* methods suggest that orthorhombic Bi_2Se_3 should have a bandgap of approximately 0.9 eV,^{24,25} too small to enable efficient solar cells, but no experimental report was found to support this claim. Note that rhombohedral Bi_2Se_3 has been extensively studied as a prototypical system among the second generation of topological insulators,²⁶ showing a narrow bandgap of 0.35 eV^{27,28} and potential application in thermoelectric devices,^{29,30} spintronics and quantum computing.²⁶

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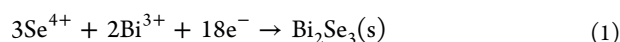
High-quality Bi₂Se₃ thin films have been grown by vacuum-based techniques, such as molecular beam epitaxy (MBE)^{31,32} and pulsed laser deposition (PLD).¹⁷ Nevertheless, only rhombohedral structures have been obtained by these procedures. Bi₂Se₃ layers have also been deposited by electrochemical methods,^{19,33} resulting in a mixture of rhombohedral and orthorhombic phases.

In this work we report the electrodeposition of Bi₂Se₃ films with a single orthorhombic phase, grown on a (100)-oriented Si substrate. Electrochemical, structural, morphological, optical, and electrical features were investigated in order to better understand the physical and chemical properties of this compound. A density functional theory (DFT) study of the crystal and electronic structure was also performed to support the experimental results. Our findings suggest that this less common phase of Bi₂Se₃ may be a suitable candidate for solar energy harvesting, such as in photovoltaic or photo-electrochemical cells.

EXPERIMENTAL DETAILS

Electrodeposition of Bi₂Se₃ was carried out in a standard three electrode cell. The substrate was a low-doped (10¹⁵ cm⁻³) n-type silicon (100) wafer, the counter electrode was a platinum foil, and a KCl saturated calomel (SCE) electrode was used as reference (all potentials in this work are referred to the SCE, 0.244 V_{SHE}). The electrolyte consisted of an aqueous solution containing 0.5 M nitric acid (HNO₃, pH about 0.7), 1 mM bismuth nitride (Bi(NO₃)₃), and 1.5 mM selenium dioxide (SeO₂), unless stated otherwise. The deposition was performed at room temperature, under potential control, with the applied voltage varying in the range -0.3 to -0.7 V. Prior to deposition, the Si substrates were immersed in a 5% HF solution, in order to remove the native oxide and induce H-termination, and then rinsed in deionized water. The deposition process and cyclic voltammograms (CVs) were monitored and recorded using an AUTOLAB 302N potentiostat.

Thickness measurements were performed with a contact profilometer (BRUKER Dektak XT), and the results were compared with the nominal value computed by Faraday's law. To calculate the nominal thickness, we used the overall reaction for Bi₂Se₃ formation from its ions:



which needs 18 electrons to form one stoichiometric unit of the compound. To confirm the number of electrons involved in the deposition of Bi₂Se₃, we have grown samples with different thicknesses. According to eq 1, the conversion factor of charge to thickness was 1.11 nm/mC. Experimental film thickness measurements using the profilometer and cross-sectional SEM images yielded a conversion factor of 1.08 nm/mC, very close to the nominal one, denoting an electrodeposition process with ~100% efficiency.

Film composition was determined by energy dispersive spectroscopy (EDS), using the M-edge of Bi and L-edge of Se for quantification. Imaging was carried out in a field emission gun scanning electron microscope (FEG-SEM, JEOL JSM-6701F), with an accelerating voltage of 15 kV. Cross-sectional transmission electron microscopy (TEM) images as well as selected area electron diffraction (SAED) patterns were obtained in a 200 kV, JEOL JEM2100 transmission electron microscope. XRD patterns were acquired in the Bragg–

Brentano ($\theta/2\theta$) geometry on a PANalytical X'Pert PRO MPD diffractometer with Cu K α radiation. Optical characterization was performed with a UV/vis/near-IR spectrometer (PERKIN ELMER 750), by collecting the optical transmittance spectra in the range of 800–3300 nm. The samples for optical transmittance were prepared by detaching the electrodeposited layers from the opaque silicon substrate using a Kapton tape (transparent in the range of relevant wavelengths of the Bi₂Se₃ spectrum). The band gap was determined using the Tauc plot method³⁴ for a direct band gap semiconductor. The electrical measurements were performed in a two-probe configuration by contacting the deposits using a silver epoxy. Due to heterojunction formation at the interface of Si/Bi₂Se₃, the resistivity of the Bi₂Se₃ film was calculated by extracting the device series resistance. X-ray photoelectron spectroscopy (XPS) was carried out using Al K α radiation, with the sample being cleaned with an Ar beam prior to the measurements.

COMPUTATIONAL METHODS

Ab initio DFT calculations were performed in the VASP package.³⁵ PBEsol (revised Perdew–Burke–Ernzerhof)³⁶ and HSE06 (Heyd–Scuseria–Ernzerhof)³⁷ parametrizations were used as exchange–correlation functional. Core–valence interactions were treated by the projector augmented wave method (PAW).³⁸ A plane-wave basis cutoff energy of 400 eV was used with the addition of spin–orbit coupling (SOC). The ionic relaxation with PBEsol was done with a *k*-grid containing 63 irreducible points, whereas the HSE06 total energy was calculated with a *k*-grid of 16 irreducible points, generated by the Monkhorst–Pack method.³⁹

RESULTS

Figure 1 shows the CVs measured at bare Si substrates, as well as at Si substrates covered with a selenium or bismuth film. The Se layer was deposited from an electrolyte containing 1.5 mM SeO₂ and 0.5 M HNO₃, while the Bi film was grown from 1 mM Bi(NO₃)₃ and 0.5 M HNO₃ at an applied potential of -0.5 and -0.7 V, respectively, for a total electrodeposited charge of 50 mC (~50 nm thickness). The curves in Figure 1a show the CV at a bare Si(100) electrode for the electrolytes containing only Bi or Se ions, at a scan rate of 100 mV/s. The redox potential of Bi in its solution is calculated to be 0.005 V; the current onset in the cathodic scan however is observed at about -0.5 V, suggesting a large nucleation overpotential, while in the anodic scan the reduction current for Bi falls to zero at about -0.3 V, significantly more negative than the redox potential, evidencing a possible ohmic drop through the substrate. The CV for Se shows a similar onset potential at about -0.5 V; this should be compared to the calculated redox potential of 0.44 V, indicating again a large nucleation overpotential and a hint of a nucleation loop in the returning scan, with limited hysteresis. Figure 1b displays the CVs (100 mV/s) at Si in the electrolyte containing both Se and Bi ions. Two peaks can be identified: (i) at about -0.58 V, assigned to the reduction of Bi³⁺ to metallic Bi, and (ii) at -0.65 V, due to the Se⁴⁺ (HSeO₃⁻ in strongly acidic solution) reduction to Se⁰. Distinct peaks for Bi and Se have been observed also at Au electrodes.⁴⁰ The reduction peak (iii) at -0.48 V in the return scan could be related to Bi deposition onto a fresh Se layer deposited during the scan at more negative potentials. It should be noted that much higher currents are observed during the compound deposition with

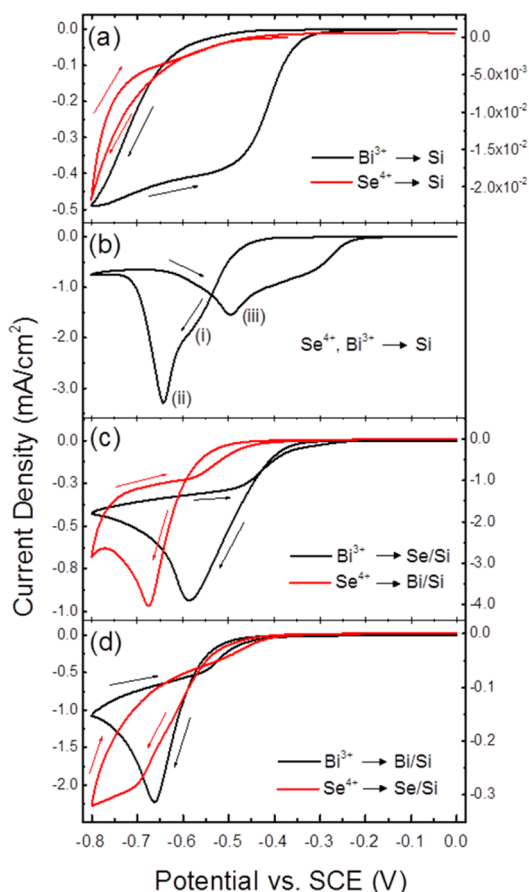


Figure 1. (a) Voltammograms at bare Si with 100 mV/s scan rate from electrolyte containing only Bi (black) and only Se (red); (b) voltammograms at bare Si using electrolytes containing both Bi and Se; (c) voltammograms for the reduction of Se ions on Bi precovered Si (black) and Bi ions on Se precovered Si (red); (d) voltammograms for the reduction of Se ions on Se precovered Si (red) and Bi ions on Bi precovered Si (black).

respect to the single elements, suggesting a synergistic effect between the Bi and Se reactions.

In Figure 1c are displayed the CVs at Se-coated Si substrates using the Bi electrolyte, *i.e.*, 1 mM $\text{Bi}(\text{NO}_3)_3$ and 0.5 M HNO_3 , and at Bi-coated Si substrates using the Se electrolyte, *i.e.*, 1.5 mM SeO_2 and 0.5 M HNO_3 . Bi reduction on Se starts at a significantly more positive potential than on Si, and also the reduction of Se on Bi is slightly depolarized with respect to the bare Si (100) surface. In both cases a well-defined nucleation loop with respect to Si is seen. The positive shift for Bi could be attributed to a stronger bond between Bi and Se than Bi to Si,^{19,41} depolarizing the deposition of Bi on Se; a similar behavior is observed for Se on Bi. Finally, Figure 1d shows the CVs for the reduction of Se^{4+} on Se-coated Si and Bi^{3+} on Bi-coated Si, respectively. Bi and Se deposition are both polarized with respect to Figure 1c, and the reduction of Se occurs with behavior similar to that in Figure 1a.

The depolarization of Bi and Se reduction with respect to the single elements, both at Si and at the heterologous component, is consistent with a mutual underpotential co-deposition (UPCD) process,^{19,42} whereby deposition of Bi would depolarize Se reduction and *vice versa*. Ideally, at a constant applied potential Bi would deposit first, inducing Se deposition by underpotential deposition, which in turn would facilitate Bi deposition, in a cyclic fashion, possibly resulting under suitable conditions in a Bi/Se multilayer. Unfortunately, due to the nucleation overvoltage and other sources of polarization, it is difficult to model the system and gain insight on the resulting deposition kinetics and the possible oscillatory behavior of reaction 1.

In order to better understand the compound deposition, Figure 2a displays CVs recorded in electrolytes with different $\text{Bi}^{3+}:\text{Se}^{4+}$ ratios, nominally 1:3, 3:3, and 4:3, in addition to 2:3 already shown in Figure 1b. In all measurements, two reduction peaks are present in the cathodic curve and one reduction peak in the returning trace. The peaks in the cathodic direction are labeled C_1 and C_2 . By increasing the concentration of Bi^{3+} ions in the electrolyte, the C_1 peak current starts to increase with respect to C_2 , confirming that C_1 peaks stand for Bi reduction. At the same time however the Se reduction current also increases upon Bi addition, due probably to a faster kinetics induced by the UPCD process. It can also be observed that an increasing Bi concentration in the electrolyte promotes the proximity of C_1 and C_2 peaks, which could eventually merge

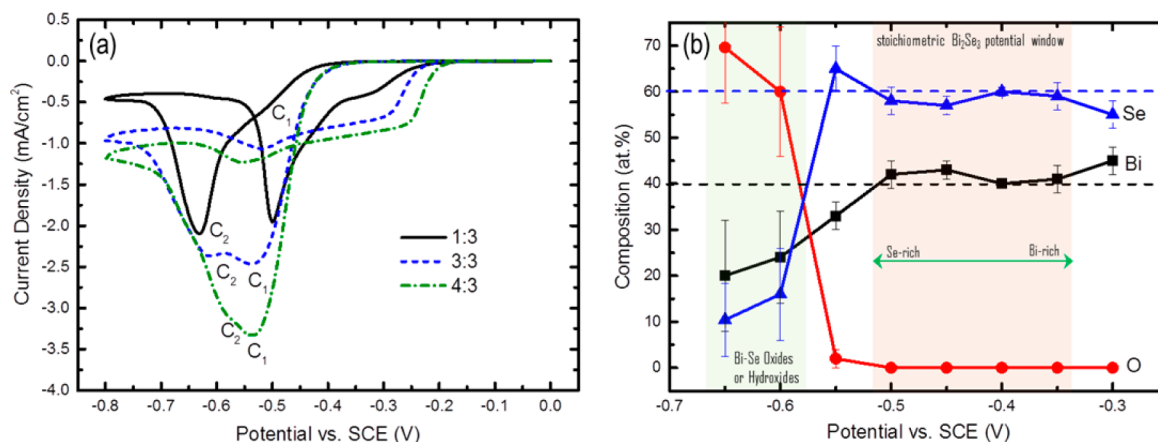


Figure 2. (a) Voltammograms obtained in Bi–Se electrolytes containing different ratios of Bi/Se concentrations: 1:3–0.5 mM $\text{Bi}(\text{NO}_3)_3$ and 1.5 mM SeO_2 (continuous line); 3:3–1.5 mM $\text{Bi}(\text{NO}_3)_3$ and 1.5 mM SeO_2 (dashed line); 4:3–2.0 mM $\text{Bi}(\text{NO}_3)_3$ and 1.5 mM SeO_2 (dotted–dashed line). All electrolytes are aqueous and contain 0.5 M of HNO_3 . (b) Elemental fraction in thin films grown at different potentials. The error bars were calculated based on sampling along different positions across the sample surface.

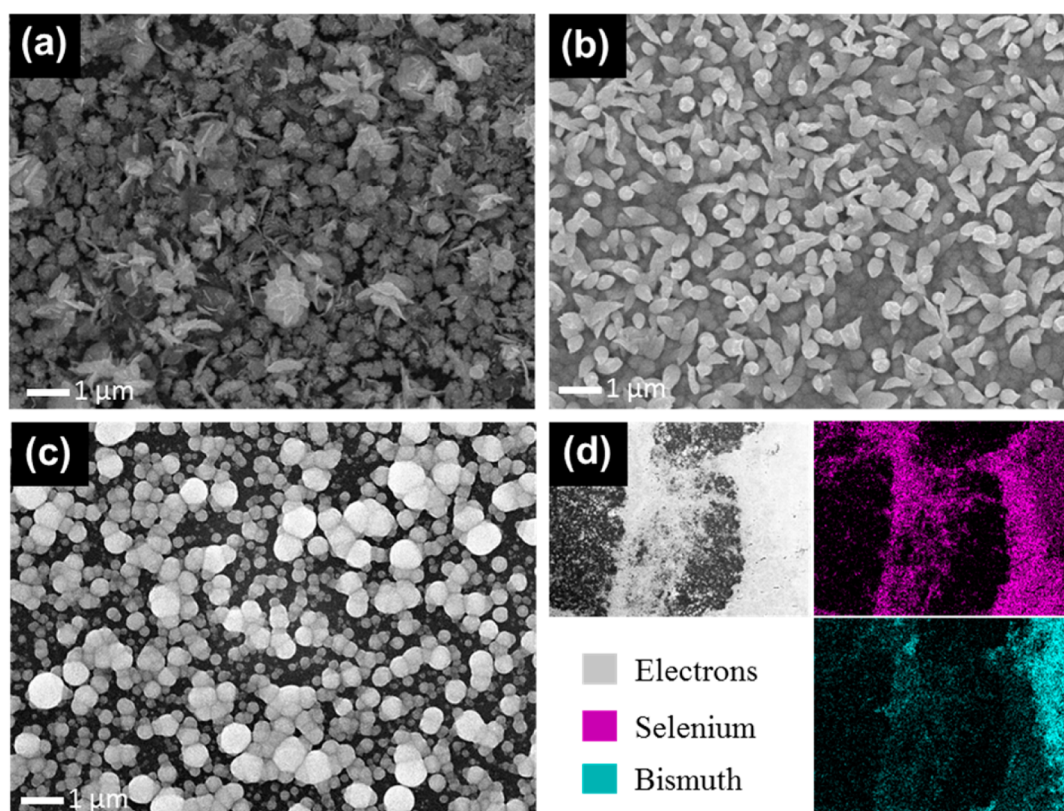


Figure 3. SEM images for samples obtained at different potentials: (a) -0.50 , (b) -0.40 , and (c) -0.30 V. (d) SEM image and the EDS compositional mapping for a sample deposited at -0.60 V enclosing regions with different concentrations of Bi and Se. All samples were deposited at the same electrochemical charge of 500 mC (deposition time approximately 2900, 4100, 9600, and 1800 s for panels a, b, c, and d, respectively).

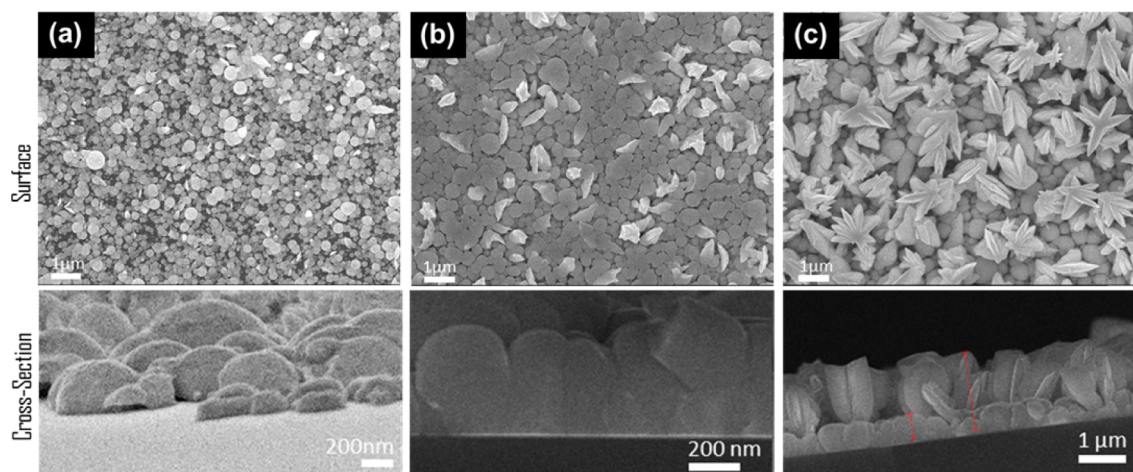


Figure 4. Surface and cross-sectional SEM images of samples grown at -0.40 V, with different thickness: (a) 108 nm, showing the initial stage of layer formation; (b) 540 nm, showing the compact morphology after the grains/clusters percolation; (c) 1080 nm, showing the transition from compact to porous layer with flower-like grains. The deposition times for the samples are approximately 820, 4100, and 8200 s, respectively.

into a single peak for higher concentrations, negating the possibility of an alternate deposition of Bi and Se.

Figure 2b summarizes the EDS compositional analysis of samples grown at different deposition potentials, ranging from -0.3 to -0.7 V. As shown, the reduction potentials more positive than -0.5 V propitiated the formation of stoichiometric Bi_2Se_3 . For potentials more negative than -0.55 V a decrease in Bi and Se fraction occurs, while the oxygen content increases, suggesting a chemical or electrochemical precipitation of oxide or hydroxide phases. The rapid fall in Se

percentage in the films below -0.55 V could be attributed to the reduction of Se^0 to Se^{2-} , occurring at more negatives potentials.⁴¹ The stoichiometric interval from -0.35 to -0.55 V would be a suitable potential window to achieve the alternating electrodeposition of Bi and Se, as discussed above. At the most negative limit of this potential window, stoichiometric deviations favoring selenium should be expected, while in the most positive limit the deviation should lean toward increasing Bi concentration, as observed indeed in Figure 2b.

SEM images showing the surface morphology of samples grown at different potentials are presented in Figure 3. The same electroplating charge of 500 mC was used, which is equivalent to a thickness of 540 nm. For potentials of -0.50 and -0.40 V, Figure 3a,b, the deposits cover the entire surface of the Si substrate, whereas for films obtained at potentials more positive than -0.30 V, Figure 3c, the surface is not completely covered and grains with size between 0.1 and 0.7 μm can be seen, in isolation or in clusters. The shape of the grains also depends strongly on the applied potential: from -0.30 to -0.50 V the grain shape changes from spherical to elongated ones and then to a mix of dendritic/needle shaped grains. At potentials where the oxide phase is formed (lower than -0.55 V), a nonuniform deposition process occurred, as shown in Figure 3d. An EDS elemental mapping of the surface of the sample electrodeposited at -0.60 V, showed that besides the nonuniformity in thickness the deposits are also nonuniform in composition.

Surface and cross-sectional SEM images of samples deposited at -0.40 V, with nominal thicknesses of 108, 540, and 1080 nm, are displayed in Figure 4a–c, respectively. For thinner samples, the Si surface is not completely covered, evidencing that the deposit grows from roughly hemispherical grains as seen in Figure 4a. For thicknesses of 200 up to 540 nm, columnar grains with round tops start to percolate forming a compact layer as seen in Figure 4b. In this figure, a few needle shaped grains are seen. For thicknesses higher than 540 nm, the formation of a relatively dense surface on top of the compact layer is observed, with large grains showing a flower-like morphology as can be observed in Figure 4c for a deposit with 1080 nm. This growth pattern for thick electroplated Bi_2Se_3 with needle-like grains and high porosity has been described previously.³³

Figure 5a shows the diffraction pattern of samples obtained at different deposition potentials with the same thickness of 540 nm. For the most positive potential, -0.30 V, five diffraction peaks are seen; however, only three of these peaks could be assigned to orthorhombic Bi_2Se_3 , notwithstanding the fact that EDS analysis indicated a composition close to the stoichiometry Bi_2Se_3 . The diamond symbols in the figure indicate peaks from the orthorhombic phase of Bi_2Se_3 , while the remaining peaks should indicate the presence of other phases. Deposits grown at -0.40 V show a series of low intensity diffraction peaks between 20° and 35° and two prominent peaks at 27.5° and 44° that clearly belong to the orthorhombic phase Bi_2Se_3 . Growth at -0.50 V results in a substantial improvement in crystallinity as seen by the significant increase in peak intensity. It should be noted that practically all diffraction peaks for the latter sample belong to the orthorhombic structure, suggesting the formation of an almost pure phase.

XRD patterns of samples with different thicknesses grown at a potential of -0.40 V are shown in Figure 5b. The intensity of the peaks corresponding to the orthorhombic phase increases significantly with increasing thickness from 0.54 to 1.08 and 3.24 μm . The positions of peaks labeled (011), (211), and (020) shift by 0.5% to higher values with increasing thickness, indicating that the structure slightly reduces its lattice parameters. The calculated values for the lattice parameters a , b , and c of the orthorhombic structure in the thickest sample are 11.71, 4.11, and 11.43 $\text{\AA}$, respectively, in agreement with those experimentally reported for mineral bulk crystals in ref 43 and very close to the theoretical values obtained by DFT, as will be discussed below. The morphologies shown in Figures 3 and

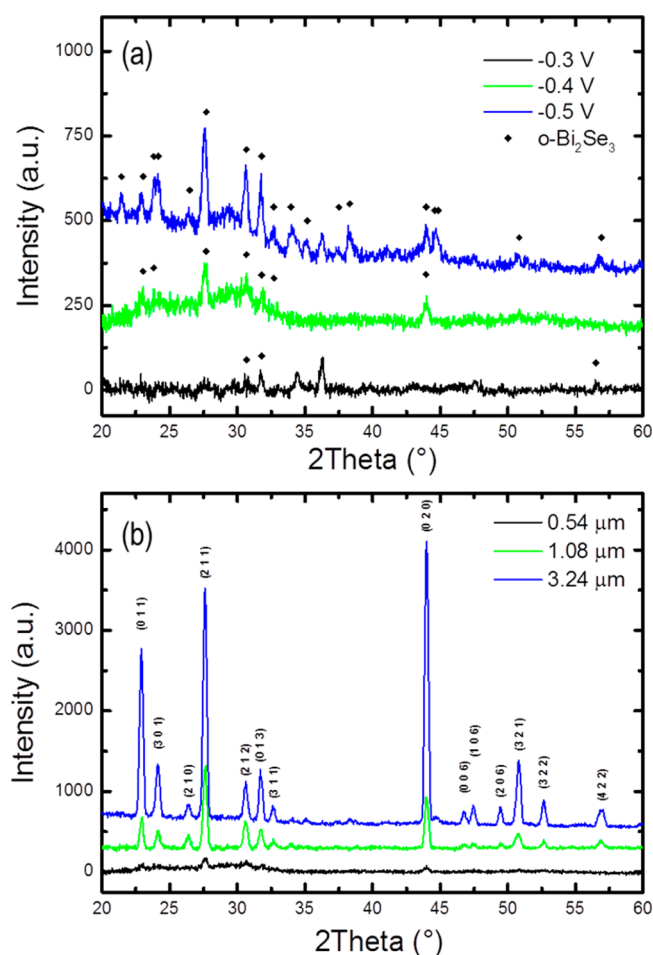


Figure 5. X-ray diffraction patterns for (a) samples electroplated at different potentials and for (b) layers with different thicknesses electroplated at -0.40 V. The diamond symbols correspond to the diffraction positions of the Bi_2Se_3 orthorhombic phase.

4 can be correlated to the crystallographic properties by relating the flower-like grains of thick films (>600 nm) with the high-intensity crystalline peaks. The compact layer with columnar grains rounded on the top observed in samples with thickness below 600 nm presented broad X-ray reflections especially at the deposition potential of -0.40 V, consistent with the formation of poor crystallinity or nanocrystallinity.

TEM results from a sample grown at -0.4 V with 1080 nm thickness are presented in Figure 6a, showing a high-resolution image (HRTEM) of a grain close to the interface with the substrate. This image shows lattice fringes with interplanar spacing of 5.20 $\text{\AA}$ that may be attributed to stacked (201) planes, in which a separation of 5.21 $\text{\AA}$ is expected. Figure 6b shows a zoom of the image in panel a with a scheme inserted to show the molecular structure of the planes. Figure 6c finally shows an electron diffraction pattern of this grain, confirming the orthorhombic phase, where the diffraction spots related to the planes (002) and (004) are indicated.

The optical properties of electrodeposited orthorhombic Bi_2Se_3 samples were investigated by measuring the optical absorbance in the near-infrared and visible regions. Figure 7a shows the Tauc plot for two samples with different thicknesses, 540 and 1080 nm. The band gap for the sample with smaller thickness and low crystallinity is $E_g = 0.81$ eV and for the thicker one is $E_g = 1.25$ eV. The larger bandgap of the thicker

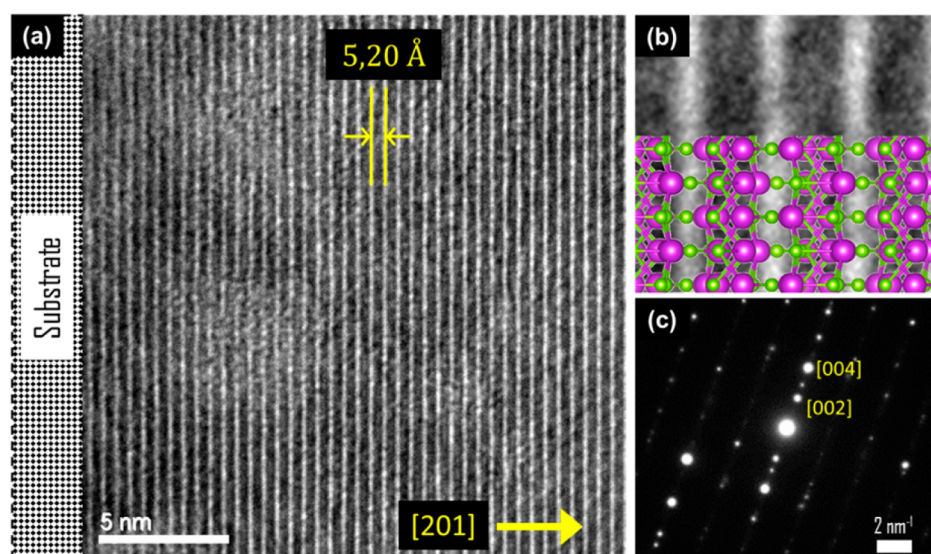


Figure 6. (a) HRTEM images of a single grain of Bi_2Se_3 at the substrate interface. (b) Zoom of the HRTEM image with a scheme showing the structure of the planes. (c) SAED pattern.

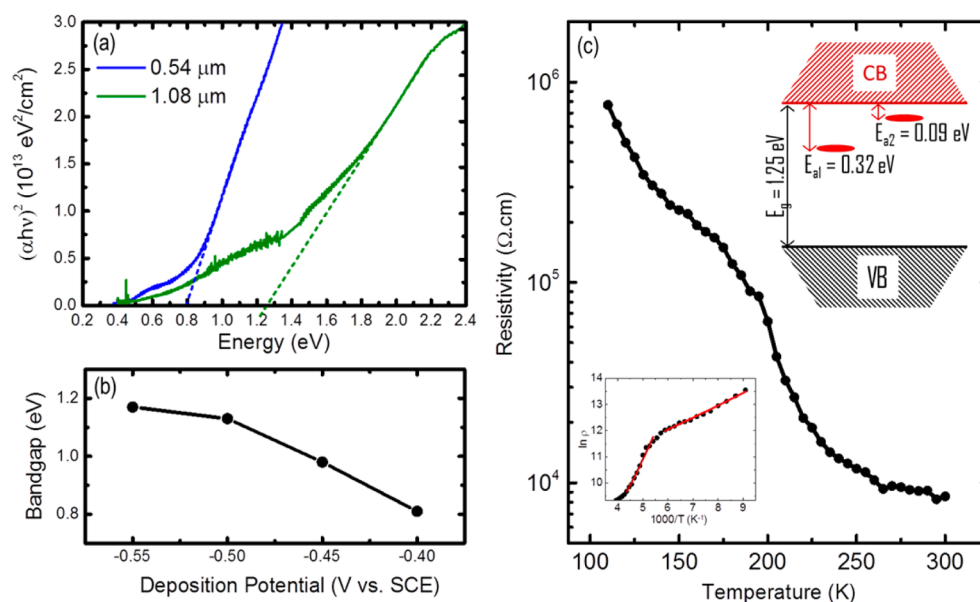


Figure 7. (a) Tauc plots for determination of the bandgap of samples with different thicknesses. (b) Bandgap values of samples grown at different potentials. (c) Electrical resistivity of Bi_2Se_3 as a function of temperature. The right inset in panel c shows a schematic of the bandgap with the two donor levels; the left inset shows a graph of the logarithm of the resistivity vs the reciprocal temperature.

sample is expected considering the lower degree of disorder and larger grain size.⁴⁴ The measured bandgap can be compared to previous experimental results on chemically sintetized Bi_2Se_3 with a value of $E_g = 1.42$ eV¹² and electrochemically sintetized $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ with E_g in the range 0.9–1.1 eV.⁴⁵ Furthermore, the bandgap of about 1.25 eV is quite close to the value of 1.19 eV, calculated below. The bandgap of samples with the same thickness of 540 nm and grown at different potentials is shown in Figure 7b; the trend for E_g reflects the improvement of crystallinity with a more negative applied potential in Figure 5a, leading to a bandgap increase from 0.8 to 1.18 eV. This result shows that the bandgap of Bi_2Se_3 can be tuned by varying the deposition potential.

The electrical properties of the films are presented in Figure 7c, showing electrical resistivity vs. temperature for a sample grown at -0.4 V, with approximately $1 \mu\text{m}$ thickness. The

resistivity shows a thermally activated behavior typical of semiconductors, according to eq 2, where K_b is the Boltzmann constant, ρ_0 is the saturated electrical resistivity, and E_a is the activation energy.

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{2K_b T}\right) \quad (2)$$

Two activations regimes are seen in different temperature ranges. The first shows up around room temperature with an activation energy of $E_{a1} = 0.32$ eV and the other at low temperature with activation energy of $E_{a2} = 0.09$ eV, suggesting the presence of two types of defect states in the energy gap,⁴⁶ as shown in schematics in the right inset of Figure 7b. The inset in the left side of the figure is the logarithmic plot of the resistivity vs. the reciprocal temperature, where the linear regimes indicate

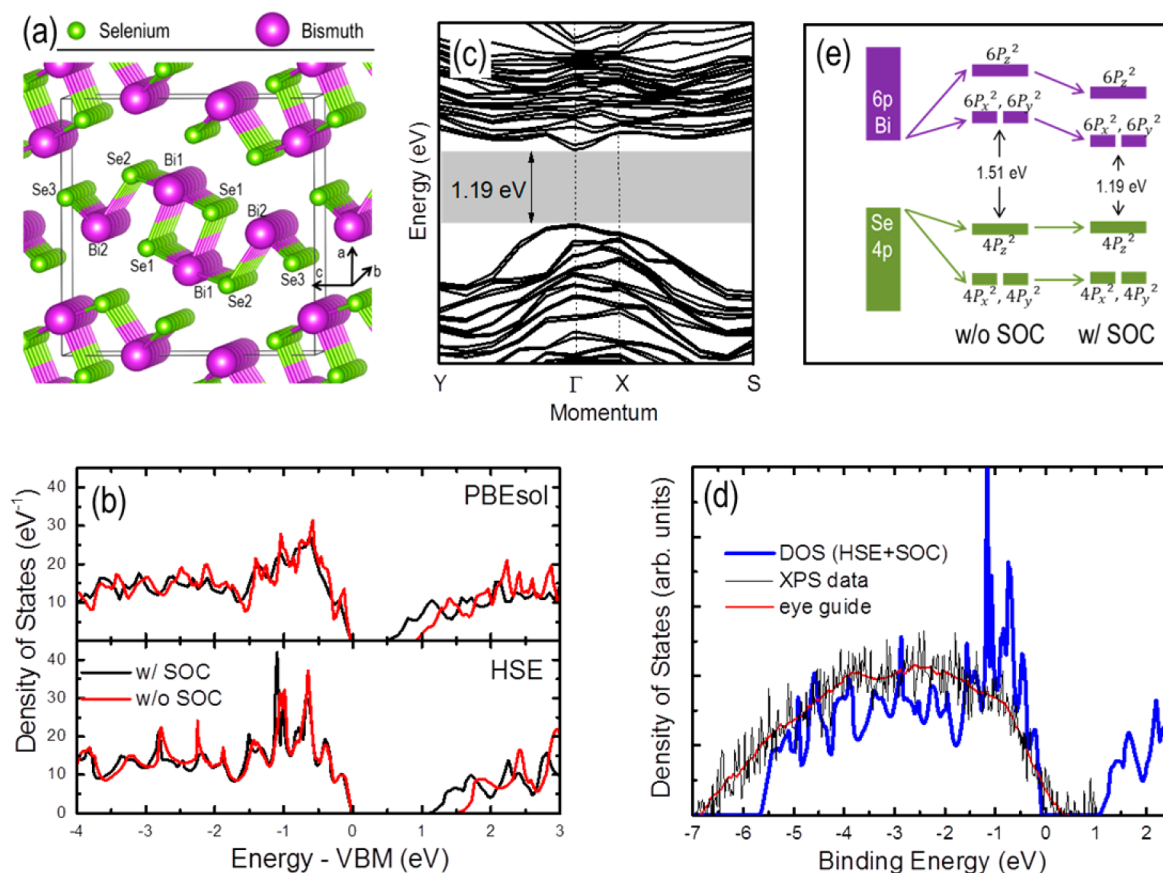


Figure 8. (a) Atomic structure of orthorhombic Bi_2Se_3 . (b) Density of states calculated with PBEsol and HSE. (c) Band dispersion using HSE functional and (d) XPS valence spectrum (sample obtained with -0.4 V deposition potential and thickness of approximately $3 \mu\text{m}$). (e) Atomic orbital resolved energy band scheme. The structure in panel a was generated with VESTA software.⁵³

the different activation energies. The high values of ρ found for Bi_2Se_3 are attributed to the large bandgap that strongly limits the electronic density in the conduction band. A previous measured value of $10^7 \Omega\cdot\text{cm}$ ⁴⁷ at room temperature has been reported for Bi_2Se_3 , but in that work no systematic structural or phase characterization was performed, resulting in an incorrect structure identification; our value of about $9 \times 10^3 \Omega\cdot\text{cm}$ is much smaller than the above one, suggesting a lower defect density and better crystallinity in our samples. Contrasting findings have also been reported with regard to the electrical and optical properties of orthorhombic Bi_2Se_3 , due to the possible presence of two distinct phases—the rhombohedral one showing semimetallic behavior (band gap 0.35 eV) and the orthorhombic being a semiconductor with band gap of 1.25 eV—the fraction, size, and topology of which are often not well characterized, possibly leading to widely different properties. n -type conductivity was observed by measuring a Seebeck coefficient of approximately $-350 \mu\text{V/K}$; this is close to the value found for Bi_2S_3 ;^{48,49} however, no previous report was found to compare the result obtained here.

DFT methods, as described in **Computational Methods**, were used to understand the crystallographic and electronic structure of orthorhombic Bi_2Se_3 . The crystal structure is shown in **Figure 8a**, where the unit cell contains three Se and two Bi non-equivalent sites, respectively. The repetition of the cell along the “ b ” axis, indicated in the figure, leads to the formation of the 1-D ribbon already discussed in the **Introduction**.^{10,25} In the calculations, the lattice parameters were relaxed to values that minimize the total energy of the cell; the resulting lattice

constants were $a = 11.711$, $b = 4.102$, and $c = 11.404 \text{ \AA}$, in good agreement with the experimental values found above. The relaxation was performed using the PBEsol functional, that usually predicts precisely the values of lattice parameters.³⁶

Figure 8b presents the density of states for orthorhombic Bi_2Se_3 , with and without SOC. The upper curves were obtained by using the PBEsol functional, while the lower curves were calculated with the HSE functional. The spin–orbit interaction decreases the bandgap by approximately 0.35 eV, through a rigid shift of the conduction band (CB) to lower energies. The CB is mainly formed by Bi $6p$ orbitals, while the valence band is formed by Se $4p$ orbitals (independent from the spin–orbit interaction). The band gap calculated with PBEsol is about 0.90 and 0.55 eV for the case without and with spin–orbit, respectively. Once the HSE functional is used, however, these values increased to 1.51 and 1.19 eV, respectively. Due to the high atomic weight of Bi, including the SOC in the calculations is necessary. The HSE functional is extensively used for the calculation of bandgaps in semiconductors, providing precise correspondence between theoretical and experimental values.³⁷ Indeed, PBEsol leads to a highly underestimated value compared to the experimental bandgap of about 1.25 eV, while the values found using HSE, about 1.19 eV, are in much better agreement, supporting the experimental results. Furthermore, from the band dispersion⁵⁰ in **Figure 8c** it was found that orthorhombic Bi_2Se_3 has a direct bandgap at the Γ point, confirming the potential applicability of this compound in efficient thin films or quantum dots solar cells. These results

are in contrast to those discussed in ref 24, where an indirect bandgap of 0.91 eV was found using GW methodology.

In Figure 8c an orbital-resolved energy band scheme is presented, showing the atomic orbital configuration of the conduction and valence band. As commented on in the Introduction, another phase of Bi_2Se_3 having a rhombohedral ($R\bar{3}M$) structure, is a topological insulator due to an inversion of the bandgap of 0.35 eV.²⁷ The inversion occurs due to the strong SOC of Bi, reducing the energies of the $4p_z$ Bi orbital and forming the valence band. In the case of the orthorhombic structure; no bandgap inversion is found, as can be seen in Figure 8c, probably due its large value, much higher than the SOC energy, meaning that this phase is a trivial insulator and therefore no protected conductive surfaces should be expected. Figure 8d displays the DOS calculated using HSE functional (with SOC) and a XPS spectrum of the valence band. The measured and calculated valence bands are in good agreement, with a width of approximately 6 eV, supporting the use of HSE for the electronic structure description of orthorhombic Bi_2Se_3 .

DISCUSSION

The growth of a single-phase orthorhombic Bi_2Se_3 by electrodeposition is an important achievement, since only a few reports have been published on this phase. X. L. Li et al.,³³ showed the presence of a mixture of phases in thin films grown on Ti substrates. J. Y. Li et al.⁴⁵ showed that by replacing Bi atoms with Sb a transition from rhombohedral to orthorhombic phase is achieved in films grown over ITO substrates, since the most stable phase of Sb_2Se_3 is the orthorhombic one. However, no report was found on the electrodeposition of films with a single orthorhombic phase of Bi_2Se_3 . A sluggish phase transition from rhombohedral to orthorhombic for Bi_2Se_3 has been reported upon compression and release of the applied pressure;⁵¹ this suggests that internal stresses evolving during growth may be responsible for the formation of an otherwise metastable structure. In particular, the presumed alternating deposition of Bi and Se layers at constant potential could lead not only to low-crystallinity deposits during the initial stages of electrodeposition but may be responsible for the onset of compressive internal stresses. A previous report on a layer-by-layer growth of Bi_2Se_3 using ECALE also showed low crystallinity in the XRD pattern.¹⁹

Previous theoretical estimates of the bandgap for the orthorhombic phase has led to a value of 0.9 eV.^{24,25} In this work, we show that the bandgap of crystalline orthorhombic Bi_2Se_3 is higher than those estimates, about 1.25 eV, and confirmed by our HSE functional DFT calculations. This result is important in the context of solar cells, since in a previous theoretical analysis by Filip et al.²⁴ for V_2VI_3 compounds, Bi_2Se_3 was out of the optimal bandgap range. By taking the value obtained in this work, the same material becomes an excellent candidate for future application in solar cells. A direct comparison to Bi_2S_3 that has a bandgap of 1.4 eV, slightly higher than Bi_2Se_3 , and higher resistivities, of about $10^5 \Omega\text{-cm}$,⁵² suggests that Bi_2Se_3 could provide a better performance than Bi_2S_3 in photovoltaic devices.⁹

CONCLUSIONS

In conclusion, we successfully prepared by electrodeposition thin films of Bi_2Se_3 with orthorhombic phase, over Si(100) substrates. The formation of what is recognized to be a metastable phase may be explained in terms of internal stresses

generated during growth. Alternate deposition of Bi- and Se-rich layers may occur in the underpotential co-deposition regime at constant applied potential and could account for the growth of an initial layer with low crystallinity. Cyclic voltammetry experiments evidenced that initially Bi and Se reduction occur separately over the silicon substrate, and the coverage of the substrate by one of these two elements facilitates the deposition of the other one, due to favorable interatomic interactions. Films obtained at more negative potentials show better crystallinity, but tend to give a less compact and nonuniform morphology. The increase in film thickness leads to larger crystalline grains. Optical characterization indicates a direct bandgap of about 1.25 eV for the crystalline and about 0.8 eV for low-crystallinity samples. A moderate electrical resistivity of about $8 \text{ k}\Omega\text{-cm}$ with n-type conductivity was measured. DFT calculations of the bandgap are close to the measured value. The low bandgap and electrical resistivity compared to other prominent V_2VI_3 orthorhombic semiconductors set the Bi_2Se_3 as a relevant material for future developments in photovoltaics, photocatalysis, and optoelectronics.

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Notes

The authors declare no competing financial interest.

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