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Investigations on the Electrochemical Atomic Layer Growth of Bi_2Se_3 and the Surface Limited Deposition of Bismuth at Silver Electrode

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Abstract: The Electrochemical Atomic Layer Deposition (E-ALD) technique is used for the deposition of ultrathin film of bismuth (Bi) compounds. Exploiting the E-ALD it was possible to obtain high controlled nanostructured depositions as needed for the application of these materials for novel electronics (topological insulators) and opto-electronics applications. Electrochemical studies have been conducted to determine the Underpotential Deposition (UPD) of Bi on selenium (Se) to obtain the Bi_2Se_3 compound on the Ag (111) electrode. Verifying the composition with the X-ray Photoelectron Spectroscopy (XPS) emerged that, after the first monolayer, the deposition of Se is stopped. Thicker deposits were synthesized exploiting a time-controlled deposition of massive Se. Then we move to discover the optimal conditions to deposit a single monolayer of metallic Bi directly on Ag.

Keywords: Bismuth; bismuth selenide; topological insulator; E-ALD; UPD.

1. Introduction

Bismuth (Bi) and antimony chalcogenides, where the chalcogenide is selenium (Se) or tellurium, exhibit excellent thermoelectric properties, achieving ZT values of about 1 [1]. These materials commonly crystallize in the rhombohedral structure and exhibit semiconducting behavior (Band gap ~ 0.3 eV). Beyond the thermoelectric behavior, these materials show insulating response in the bulk material while exhibiting metallic conductivity at grain boundaries or surfaces; surface states in particular are protected via time reversal symmetry, such that electron scattering is not allowed [2]. Recently it has also been shown that growth of Bi_2Se_3 at low temperature results in the formation of an orthorhombic structure with higher band gap of about 1.1 eV [3], of interest in the context of light absorbers and solar cells.

The layered structure of the rhombohedral crystal, with Van der Waals interactions between the layers, encourages synthetic opportunities for the direct growth of layered structures or 2-dimensional materials. Electrochemical Atomic Layer Deposition (E-ALD) exploits Surface Limited Reactions (SLRs) such as Underpotential Deposition (UPD), thus achieving a layer-by-layer growth of various compound semiconductors. These methods are potentially suitable for the formation of such materials, both as single monoatomic layers and thin films. In this work we discuss and describe synthetic efforts towards the preparation of Bi_2Se_3 films by the alternate deposition of Bi and Se monoatomic layers.

2. Methods

The source of Se was a 1 mM Na_2SeO_3 (Alfa Aesar) solution. The Bi solution was 0.5 mM $Bi(NO_3)_3$ (Alfa Aesar) and 1 mM ethylenediaminetetraacetic acid disodium salt dihydrate ($EDTANa_2$) (Alfa Aesar). We also used 1 mM $EDTANa_2$ solution for the stripping studies of Bi. All the solutions involved in this study were prepared with NH_3 28% (Merck) and $HClO_4$ 65% (Carlo Erba), resulting in pH 9.2 ammonia (0.0918 M) buffer solution. In the case of Se stripping studies we used 0.1 M NaOH (Merck) solution. All solutions were prepared using MilliQ water (18 MΩ).

The stock solutions were stored in separated Pyrex jars filled with nitrogen and connected to a flow-cell through a circuit regulated by electro-valves. An automated deposition system connected to a computer enables the control of electro-valves to flow the desired solutions. The pressure in the jar is adjusted to a solution flow rate of 1.5 mL/s. The electrolytic cell is a Kel-F cylinder with a capacity of 1.88 mL. The working electrode is a silver (Ag) (111) monocrystalline electrode prepared and polished according to a known literature procedure [4]; polycrystalline gold was used as counter electrode and Ag/AgCl sat. KCl as reference electrode.

X-ray Photoelectron Spectroscopy (XPS) was used to evaluate the deposit composition. The instrument makes use of a non-monochromatic X-ray source (VSW Scientific Instrument Limited model TA10, Mg Kα radiation, 1253.6 eV), operating base at 120 W (12 kV and 10 mA), and of a hemispherical analyzer (VSW Scientific Instrument Limited model HA100). The analyzer was equipped with a 16-channel detector and a dedicated differential pumping system that permit to work during the acquisition with the pressure in the main chamber up to 10^{-8} mbar range. The pass energy was set to 22 eV. The measured spectra were analyzed using CasaXPS software. The inelastic background was subtracted using Shirley's method [5] and a mixed Gaussian and Lorentzian contributions were used for each component. Calibration of the spectra was obtained shifting to 284.8 eV the lowest component relative to the 1s transition of carbon for adventitious carbon [6].

3. Results and Discussion

The first step in order to alternately deposit monolayers of Se and Bi is to determine the condition for the SLR deposition of Bi on Ag(111) and on Ag(111)/Se_{ad} (adlayer of Se). The deposition of Se monolayers has been reported in the literature [7] and consists in biasing the potential at -0.90 V for one minute in the presence of the selenite solution and then carrying out an ammonia buffer wash while maintaining the same potential for another minute. After covering the surface of the single crystal Ag electrode with a Se monolayer, a cyclic voltammetry of the Bi solution (Figure 1) is carried out. The presence of a reductive peak that anticipates the massive deposition of the metal indicates the occurrence of an SLR.

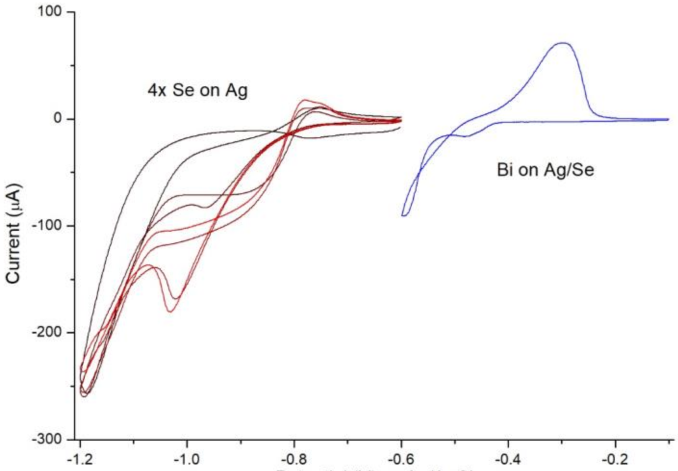

Figure 1. On the left: 4 consecutive CV of selenite (1st black – 4th red) between -0.6 and -1.2 V, scan rate 50 mV/s. On the right: CV of the Bi solution on Ag/Se_{ad} between -0.1 and -0.55 V at 10 mV/s.

Successively we proceed with a systematic study to find the best conditions for the SLR deposition of the metal. Bi depositions are carried out for one minute by varying the potential between -0.35 V and -0.48 V, and then the deposit is stripped anodically in EDTANa$_2$ solution to evaluate the actual deposited amount (Figure 2A). With increasingly negative potentials the stripping charge increases, since the deposition time is not sufficient to deposit an entire monolayer of the metal, down to -0.42 V; at a potential more negative than -0.45 V however the charge restart to grow very quickly indicating the onset of massive deposition. The optimal conditions for SLR deposition are most probably within the plateau between -0.42 V and -0.45 V. For further confirmation we repeat the depositions at -0.43 V and -0.45 V by varying the deposition time (inset in Figure 2). While at -0.43 V the charge remains practically constant, increasing the deposition time, at -0.45 V the deposit tends to grow, indicating a slow deposition of massive Bi. For this reason, -0.43 V represents the optimal SLR condition of Bi on Se.

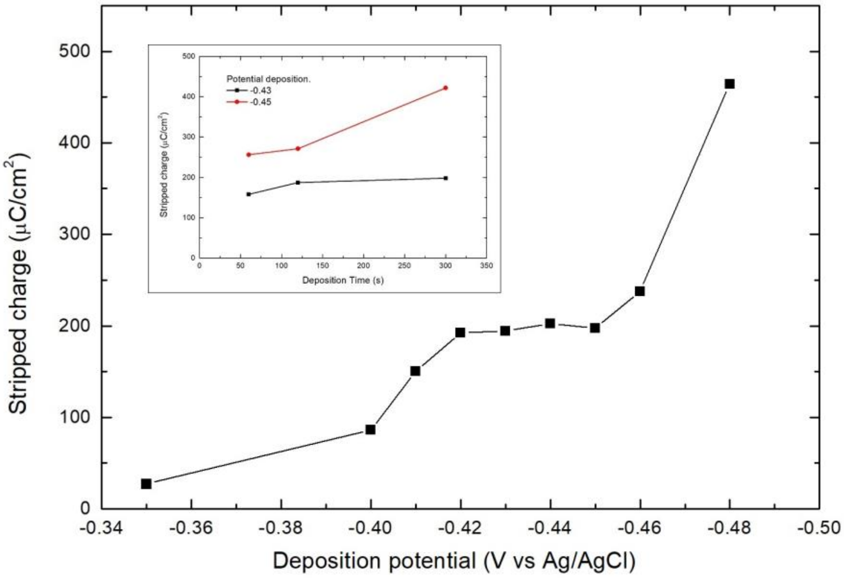

Figure 2. A) Growth of the amount of Bi deposited in one minute on Ag/Se$_{ad}$ as a function of the deposition potential. B) Amount of deposited Bi with the potential fixed at -0.43 V (black) and -0.45 V (red) as a function of the deposition time.

Once the SLR conditions have been verified for both Se and Bi, several cycles are performed to obtain a deposit thicker than a single monolayer, following the procedure below:

1. Se solution at -0.90 V for 60 s (growth of Se)
2. Buffer solution at -0.90 V for 60 s (Excess Se removal and rinse)
3. Bi solution at -0.43 V for 60 s (growth of Bi)
4. Washing with buffer solution (rinse)

A sample was prepared by performing 20 deposition cycles and then it was analyzed by XPS (Figure 3). The presence of a 4p transition of Ag from the substrate makes impossible the quantification of Se via determination of the area of the 3d transition, that is the most used transition in literature, because the two peaks overlap. For this reason, in this work, we acquire both the regions of the 3d transition and 3s transition of Se: the first feature was used to evaluate the chemical shift for the evaluation of the chemical state of this element and the second one was used for its quantification. The quantification and the evaluation of the chemical shift of Bi were obtained using the 4f transition. In Figure 3 the absence of Se was confirmed from XPS analysis: in the region from 80 to 30 eV (Se 3d transition region) only the Ag 4p transition was observed; in order to confirm this datum any signal was observed in the region from 236 to 222 eV (Se 3s transition region). The 4f transition of Bi was observed at 159.1 eV, and this position is compatible with Bi oxide (Bi_2O_3) [8]. These results reveal that the desired compound had not been formed and that the deposit had not grown as desired. In comparison, there are other examples of compounds in literature (es. InAs [9] and SnS_x [10]) which, even if they show an SLR, after a few cycles the growth spontaneously stop, perhaps because of their intrinsic semiconductor nature or due to displacement by the applied deposition potential.

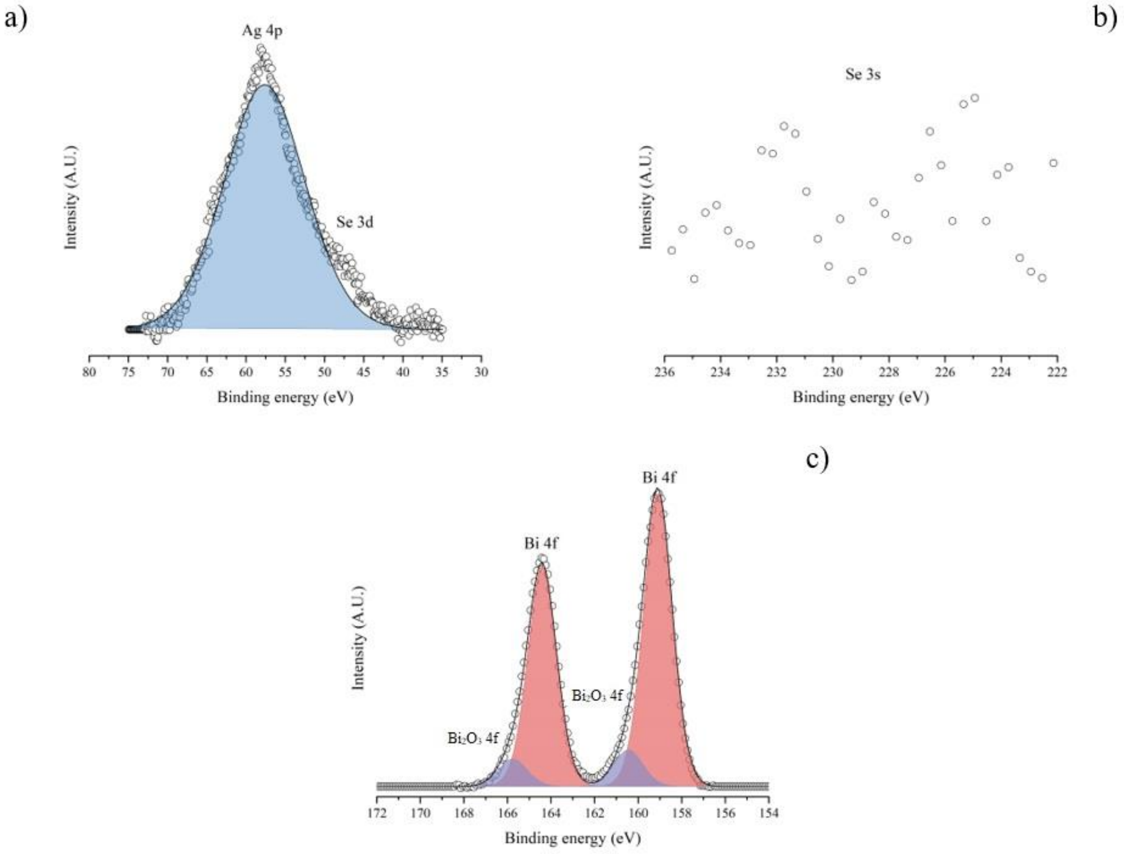

Figure 3. XPS peak of a) 3d transition region of Se (not present) and Ag 4p, b) 3s transition region of Se (not present) and c) 4f transition region of Bi in the sample prepared performing 20 deposition cycles.

To understand how the deposition process varies as a function of the number of cycles and why we do not obtain the expected quantity of Se in the 20 cycles sample we performed the stripping of multiple layers (Figure 4A). We found that, after the first Se/Bi cycle, not only the quantity of Se stops to grow but there is even a decrease of thickness to a few fractions of monolayers (Figure 4B).. On the other hand, the Bi charge continues to grow, as if the limited presence of Se was still sufficient to induce the SLR of Bi and enable formation of the subsequent layers, otherwise forbidden due to the nature of SLR deposition.

This observation suggests a SEBALD-like [11]–[13] mechanism. The Selective Electrodesorption Based Atomic Layer Deposition (SEBALD) is a method that allows the deposition of metal clusters or alloys under high morphological control. This technique consists in the E-ALD deposition of multiple layers of one or more metals alternated with an anion. The anion is then reduced and stripped out from the solid, leaving the metal deposit with shapes and/or composition not achievable with a conventional overpotential deposition. In this case seems that the SEBALD process occurs even if we actually want to avoid the chalcogenide electrodesorption.

The trend of the CV of Se on bulk Bi (Figure 4C) is similar to that one observed on Ag (Figure 1) but the current is much less and a broader peak is observed, suggesting sluggish deposition rate or disorder in the substrate. Assuming that the deposition conditions used for the deposition of the first Se layer affect the subsequent layers, a potential of -0.90 V was applied to the deposit obtained after a single Se/Bi cycle in the presence of ammonia buffer and then stripping was carried out. Instead of obtaining the typical quantity of Se_{ad}, a much lower quantity was observed; it appears thus that it is the same deposition potential (-0.90 V) of the first Se layer which, in the presence of Bi, selectively electrodesorbs the deposited Se, probably in the form of selenide.

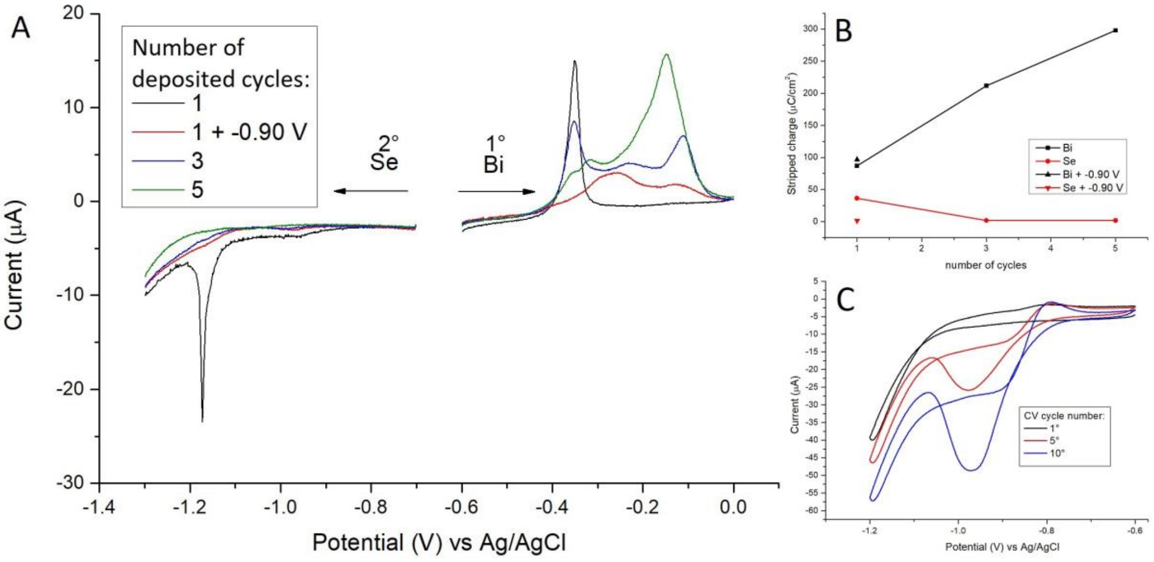

Figure 4. A) Stripping of the Se/Bi_n, with n equal to the number of the cycles performed (from 1 to 5), first removing the metal and then the non-metal element, 10 mV/s scan rate. B) Charge calculated integrating the stripping curves. C) Consecutive CVs cycles of selenite on bulk Bi: 1st black, 5th red, 10th blue, 50 mV/s scan rate.

After performing further experiments, it emerged that, although it was not possible to deposit SLR layers of Se on Bi, the deposition of massive Se remained unaltered and did not interfere with the already deposited underlying Se. This behavior is probably due to the fact that bulk Se is deposited at a lower potential (-0.8 V), without occurring in the reduction and desorption of the underlying layers. In order to deposit an amount of massive Se equivalent to the amount of a Se_{ad} we found that the potential should be kept at -0.8 V for around 3 minutes (time-controlled deposition). Deposits up to 10 cycles were thus made (Figure 5) and subsequent stripping confirms the presence of both elements, even if the ratio Se:Bi is not exactly 3:2 probably due to the uncontrollable nature of the massive deposition.

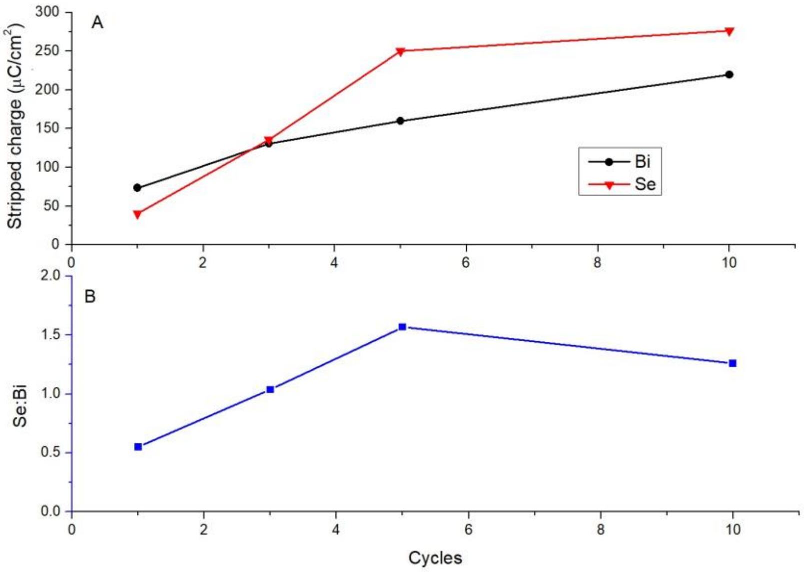

Figure 5. A) Stripped charge, from samples with up to 10 layers, before of the Bi (black) and then of the Se (red). B) Ratio between the quantity of Se and the Bi (ideal 1.5).

XPS measurements (Figure 6) were also performed on a sample on which 20 cycles have been grown using the bulk Se deposition method. In Figure 6 the presence of Se is confirmed in both the regions. In particular, the peak relative to the 3d transition is well defined over the Ag 4p transition peak and the position was determined at 53.6 eV, compatible with the expected value for this element in selenide (52.9 eV, [14]). The position of the 4f transition peak of Bi was unchanged and located at the energy expected for Bi_2O_3 and not of Bi_2Se_3 (156.8 eV, [14]). It is possible that we did observe the formation of Ag_2Se instead of Bi_2Se_3. On the other hand, the amount (ratios of the XPS areas) of Bi 4f (42 %) and Se 3s (58 %) in the sample are compatible with the stoichiometry (2:3) of the desired compound.

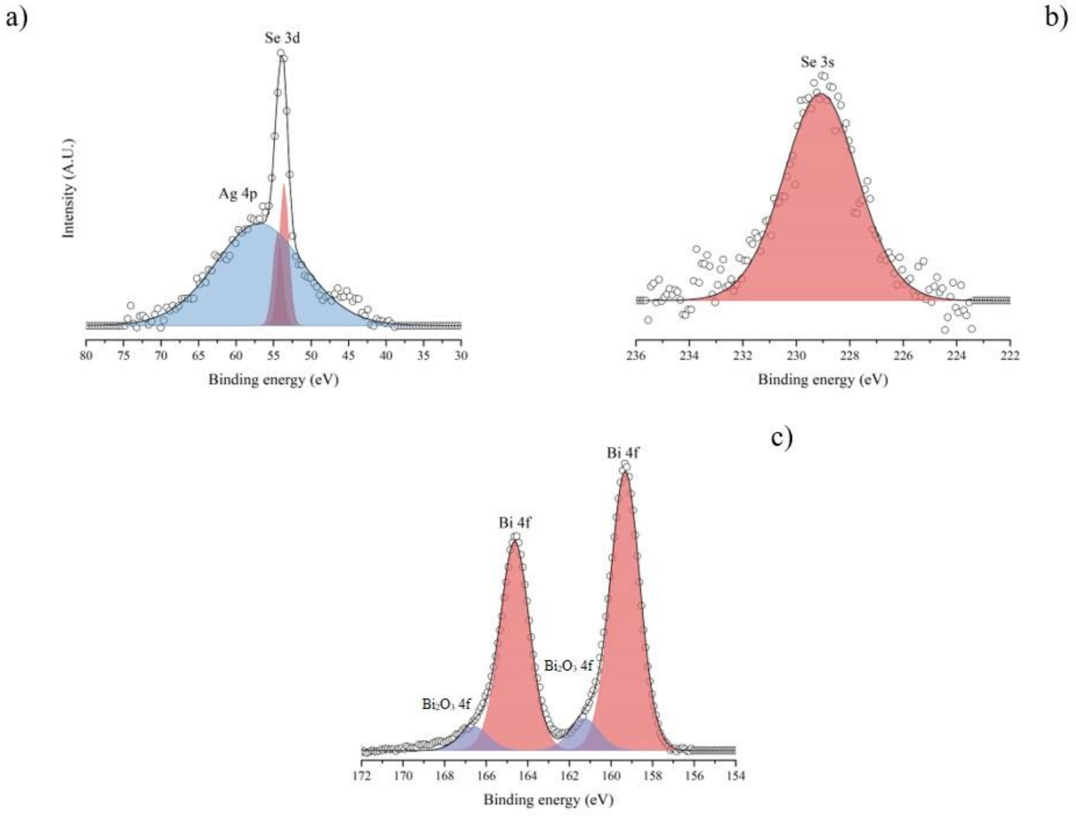

Figure 6. XPS peak of a) 3d transition region of Se and Ag 4p, b) 3s transition region of Se and c) 4f transition region of Bi in the sample prepared performing 20 deposition cycles with the time-controlled bulk Se deposition method.

The shape and the position of the Bi stripping peaks in Figure 4A are very different whether in presence or not of Se (with a shift towards more positive potentials), suggesting a strong Bi interaction with the Ag substrate and a probable alloy formation. On this basis we evaluate the possibility of depositing a single Bi monolayer directly on the Ag electrode. From the voltammetry of the Bi solution on the Ag electrode (Figure 7), not only it seems possible to deposit a metal monolayer through SLR, but the deposition peak appears much more sharp and distant from the massive deposition than in the presence of Se. This could be an additional indication for the formation of an Ag/Bi alloy.

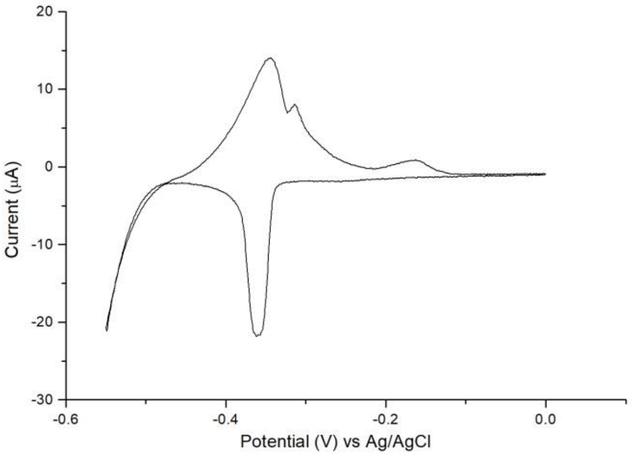

Figure 7. CV of the Bi solution at Ag (111) electrode between 0.0 and -0.55 V at 2 mV/s.

At this point we proceed to the SLR study quantifying the amount of Bi deposited in one minute as a function of the potential (between -0.30 V and -0.55 V) (Figure 8A). The presence of a plateau at intermediate potentials confirms that what is shown in the CV is actually an SLR peak. Holding the potential fixed at -0.45 V, the amount of charge deposited as a function of the deposition time was measured (Figure 8B). The charge tends to grow in the first three minutes, confirming that the monolayer is formed relatively slowly (generally few tens of seconds are sufficient) and by applying less negative potentials the growth is even slower. Over three minutes of deposition the amount of Bi remains stable, reaching a plateau indicating that bulk Bi is not deposited. Subsequently, Se deposition tests were performed on this Ag/Bi_{ad} layer, but we have had no evidence of any SLR.

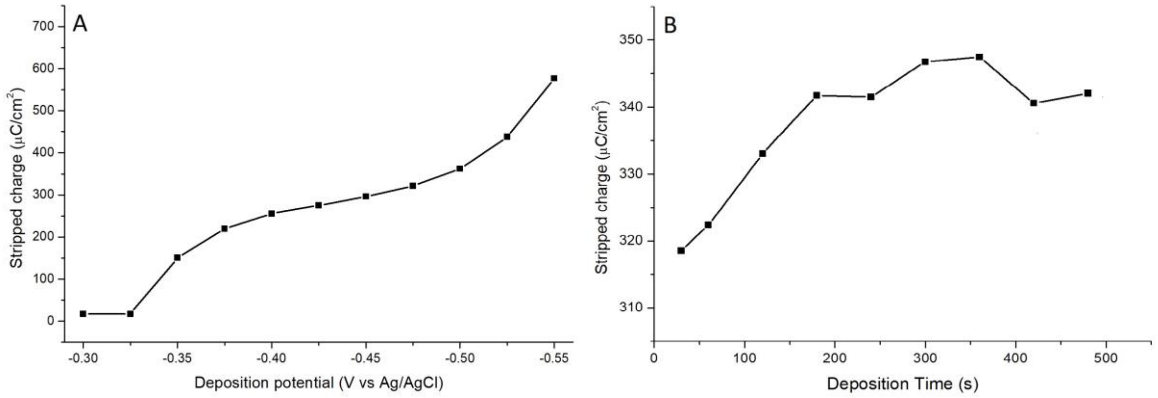

Figure 8. A) Growth of the amount of Bi deposited in one minute on Ag electrode in function of the deposition potential. B) Amount of deposited Bi with a potential fixed at -0.45 depending on the deposition time.

4. Conclusions

In this article various aspects of Bi thin films grown under SLR conditions were explored. First of all, the possibility of depositing the metal under controlled conditions on a Se monolayer was investigated, looking for the most appropriate potential that was found to be -0.43 V. Thus a single Bi_2Se_3 monolayer could be synthesized. Proceeding with the successive layers, it has been noticed that the growth of the compound is limited to the first monolayer but the Bi growth is still evident, highlighting the possibility of obtaining multilayers of the metal by means of a SEBALD process. Operating a time-controlled deposition for Se at the bulk potential we obtain both elements in the final sample, but it is not clear if the Bi_2Se_3 is formed because. Even if the 2:3 stoichiometry ratio between the two elements is confirmed, the observed XPS energy levels do not match with the ones available in literature for Bi_2Se_3, and for this reason more investigation must be performed in future.

Subsequently, the SLR deposition of Bi directly on Ag was also investigated, resulting in a likely formation of an alloy at a potential of -0.45 V. As expected from the previous measurements, however, we did not observe any deposition of Se on this type of deposit.

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