

Selective Electrodesorption-Based Atomic Layer Deposition (SEBALD) of Bismuth under Morphological Control

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The development of next-generation electronics is very dependent on the discovery of materials with exceptional surface-state spin and valley properties. Bismuth has most of the characteristics required for technological development in this field. Thin films of this element have shown nontrivial topology¹⁻³ enabling their definition as a topological insulator and a distribution of spin states and valleys in the band diagram that are suitable for both spintronics and valleytronics applications.⁴ In some cases, these properties depend on the quantum confinement of the related particles or quasi-particles; hence they can be tuned by varying the thickness in the ultrathin film range.⁵ Finally, thin films of Bi can be processed by electrochemical lithographic methods.⁶

Bismuth ultrathin films can be obtained by techniques that require vapor phase with different degrees of vacuum (e.g., PVD and CVD).⁷⁻⁹ These methods are efficient for producing flat polycrystalline thin films of Bi. Similarly, Bi thin films were electrodeposited from an aqueous solution containing organic additives with multiple morphologies and textures according to the different surface effect promoted by these substances.¹⁰ These studies have demonstrated that Bi thin films are among the wide range of technologically interesting coatings that cannot be easily obtained from aqueous solutions without interference from metal oxide growth. In most cases, these processes lead to films with uncontrolled morphology.

Introduction to SEBALD

To avoid these limitations, we explored the possibility of using electrochemical atomic layer deposition (E-ALD) to deposit highly ordered ultrathin films from diluted aqueous solutions at room temperature and pressure. In the present context, we use E-ALD for the growth of metal chalcogenide films. Underpotential deposition (UPD) of metal chalcogenide is possible due to the energy gain involved in the formation of the corresponding chalcogenide, so that an adlayer of metal can be deposited at an underpotential on a chalcogenide

adlayer covering the electrode surface. The combination between the alternation of solutions containing precursor elements that form this type of compound and UPD is the basis of E-ALD. Repetition of the basic cycle of depositions leads to the growth of semiconductor materials whose thickness increases with the number of cycles, up to the ultrathin film range. Then, after selective electrodesorption of the chalcogen layer, the resulting film is constituted by a confined layer of metal, which reorganizes its shape in ordered crystalline domains. Therefore, the selective desorption of the chalcogen leaves an increasingly higher amount of metals with the number of cycles.

The combination of E-ALD with this second stage leads to a process called selective electrodesorption-based atomic layer deposition (SEBALD), which is depicted by the scheme in Fig. 1. SEBALD was successfully used to grow Cd with a control level not achievable in overpotential deposition through the application of Faraday's laws (even when deposition was limited to very low overpotentials)¹¹ and to obtain Co/Fe catalytic clusters.¹² In what follows, we show that with the SEBALD protocol it is possible to obtain the growth of a high-quality bismuth ultrathin film on the Ag (111) surface. In this way, we have overcome most of the problems derived from the electrochemical properties of bismuth at the solid-water electrified interface.

SEBALD of Bismuth Thin Films

As often happens in E-ALD,¹³ deposition during the first step plays a crucial role for the growth of the following layers. The first phase of SEBALD consisted of the deposition of (Se/Bi)_n on Ag, followed by the removal of selenium (Fig. 1). For this reason, the deposition conditions and the stability of the two elements were investigated first.

The deposition of Se is a well-known process described in literature.^{14,15} A selenide solution was used, and silver working electrode potential was set at -0.90 V versus Ag/AgCl sat. KCl

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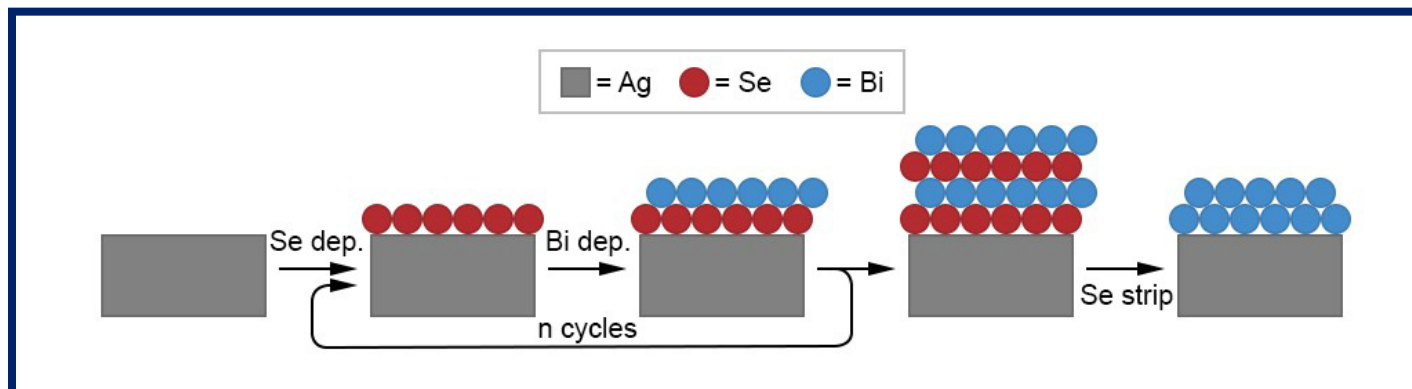


Fig. 1. Schematic operations of a SEBALD alternating a chalcogenide layer to a metal one. In our study, the chalcogenide is represented by selenium while bismuth is the metal.

reference electrode for one minute. Then, to remove the excess bulk selenium deposited, leaving only the UPD layer on silver, the working electrode was immersed in ammonia buffer solution for another minute at the same potential value. The bismuth settles to more positive potentials than selenium; therefore it is crucial for a correct E-ALD to verify the stability of Se with an anodic scan, and the results show that it does not get oxidized. Once we had ensured the stability of the Se UPD layer, we proceeded with the UPD of bismuth. The thermodynamic possibility of this deposition is justified by the presence of a cathodic peak (-0.40 – -0.50 V) slightly before the massive deposition one (over -0.50 V) in a cyclic voltammetry scan of a bismuth (III) solution (inset image in Fig. 2). After that, a conventional UPD study was carried out to evaluate the amount of metal deposited in function of the deposition potential and time.¹⁶ The optimal UPD condition to deposit bismuth on selenium consists of keeping the potential fixed at -0.43 V for one minute in the presence of the bismuth solution and then washing the sample with ammonia buffer solution.

After having optimized the UPD conditions of both the elements, the first step of SEBALD was performed by sequential automatic alternate deposition for multiple cycles, obtaining a deposit of increasing thickness. After the deposition process, SEBALD was completed by setting the working electrode potential at -2.0 V and washing the cell in the buffer solution, in order to remove all the selenium previously deposited. Anodic stripping of the remaining bismuth confirmed its growth over the number of cycles performed (Fig. 2). For the very first cycles, a typical rapid growth, due to interaction phenomena confined to the nanoscale, is present. After the fifth deposition cycle, the trend becomes linear.

A 50-cycles final bismuth deposit was morphologically characterized, revealing that this simple SEBALD process, performed at room conditions, allows obtainment of a highly ordered and crystalline deposit difficult to obtain with other techniques. From the SEM image (Fig. 3A), we can observe how the bismuth deposit obtained by SEBALD has reorganized into its typical crystalline shape,¹⁷ hard to obtain with direct bulk deposition. The EDX (Fig. 3B)

data confirm the presence of bismuth metal on the silver electrode without any traces of selenium, diagnostic of a proper SEBALD. AFM measurements (Fig. 3C) give useful information on the surface topology: the estimated RMS roughness is only 5.06 nm; moreover the image shows an overview of the sample.

Finally, the quality of the Bi thin film was quantified by XRD. The specular scan reported in Fig. 4 shows the peak of the substrate (Ag (111)) and, more importantly, peaks of Bi thin film corresponding to (102) and (204) crystalline planes. This observation indicates the growth of high-crystalline films with [102] texturing.

Conclusions and Outlook

The development of next-generation electronic devices demands specific materials that often are not simple to synthesize in the required way. SEBALD opens up the possibility of employing electrochemical processes to build, one by one, monolayers of highly pure and ordered structures. The SEBALD methodology constitutes an efficient approach to overcome the limitations of electrodepositing bismuth layers from aqueous solution. This is done by exploiting the SLRs of bismuth and selenium on Ag (111), characterized conclusively by means of electrochemical methods. The UPD experiments proved the occurrence of a SLR leading to the growth of a Bi_{ad} on Se. On this basis, multiple E-ALD cycles could be performed to grow the Bi_2Se_3 compound. Subsequent selective desorption of selenium concludes the SEBALD process and allows obtainment of the bismuth ultrathin film.

We were able to grow extremely ordered bismuth layers with exquisite control on film thickness, as proven by the topography and morphology of the resulting ultrathin films. This process is a very promising candidate for the growth of metal ultrathin films and constitutes an easy way to obtain an ordered bismuth ultrathin film of controlled thickness under room temperature and pressure. The films obtained by SEBALD are highly crystalline and oriented; moreover they are characterized by low roughness. All these properties are promising for ultimate application in new-generation electronic devices. ■

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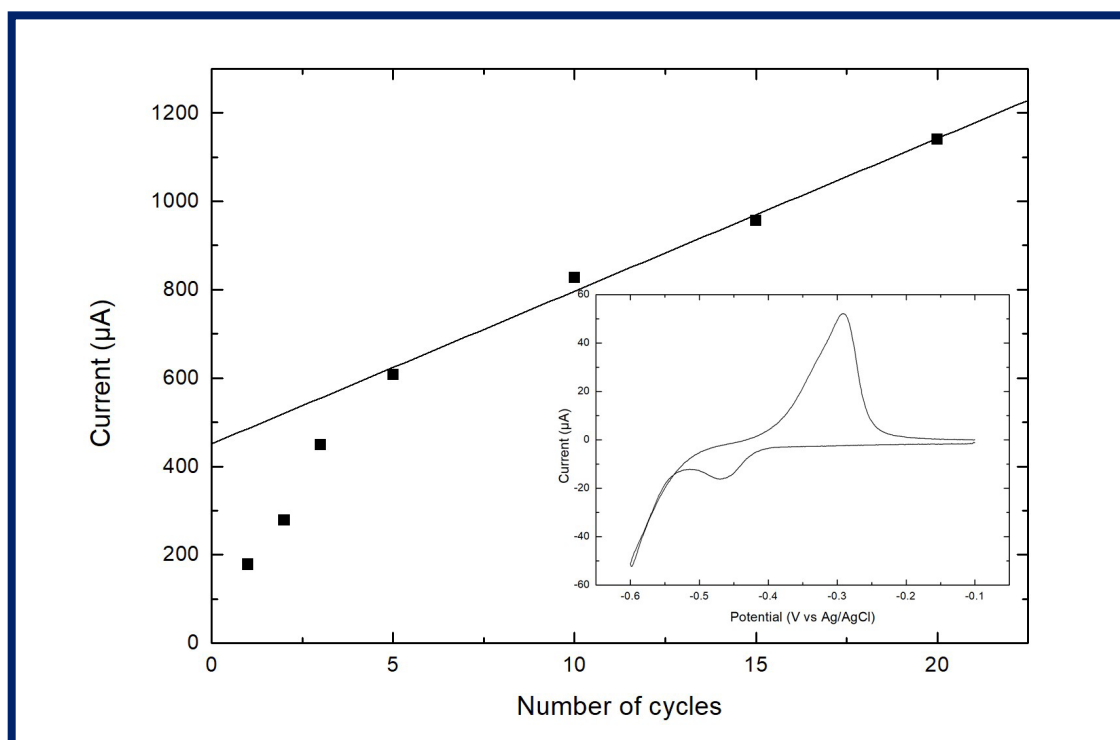


FIG. 2. Deposit growth according to the number of deposition cycles. After the first five cycles, the deposition rate becomes linear. Inset shows the cyclic voltammetry of bismuth solution on Ag/Se in which is evident the cathodic UPD peak of the metal.

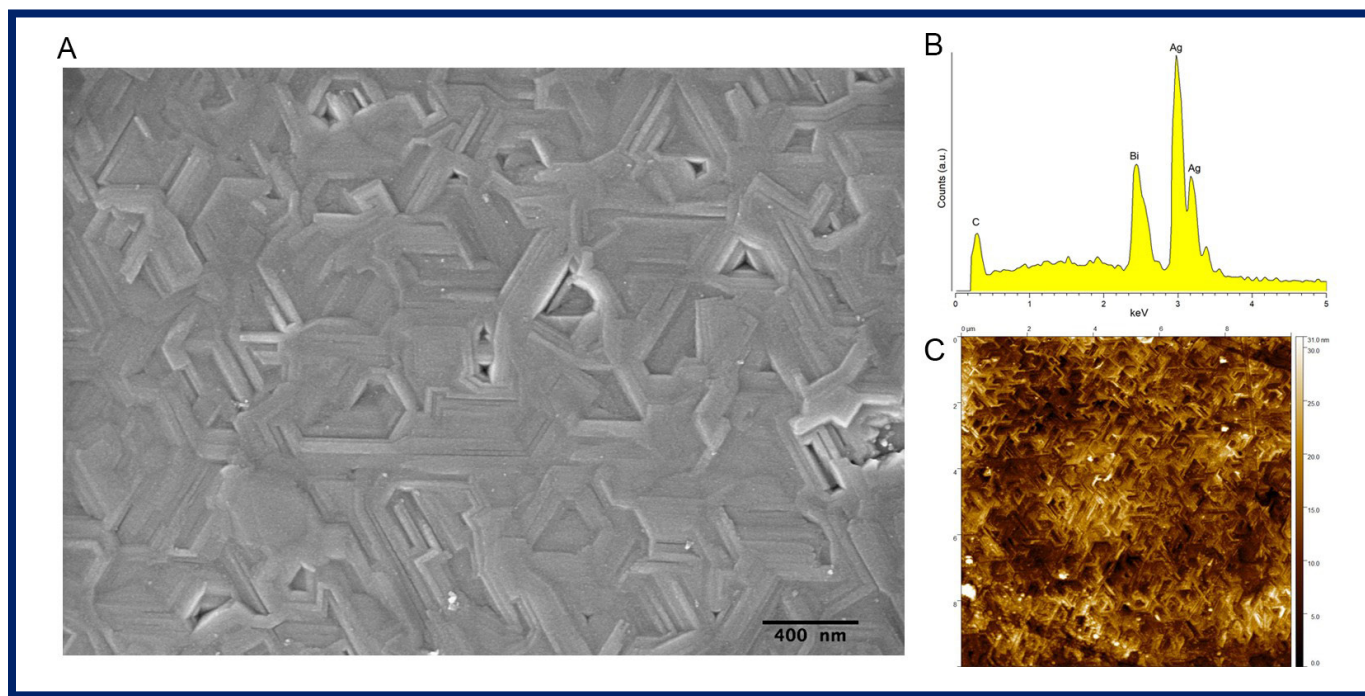


FIG. 3. A) Secondary electrons SEM image of the 50-layers bismuth sample, showing the shape and morphology of the deposit. B) EDX spectrum collected on the same area, with an accelerating voltage of 10 kV that confirms the absence of selenium. C) AFM image of the same sample.

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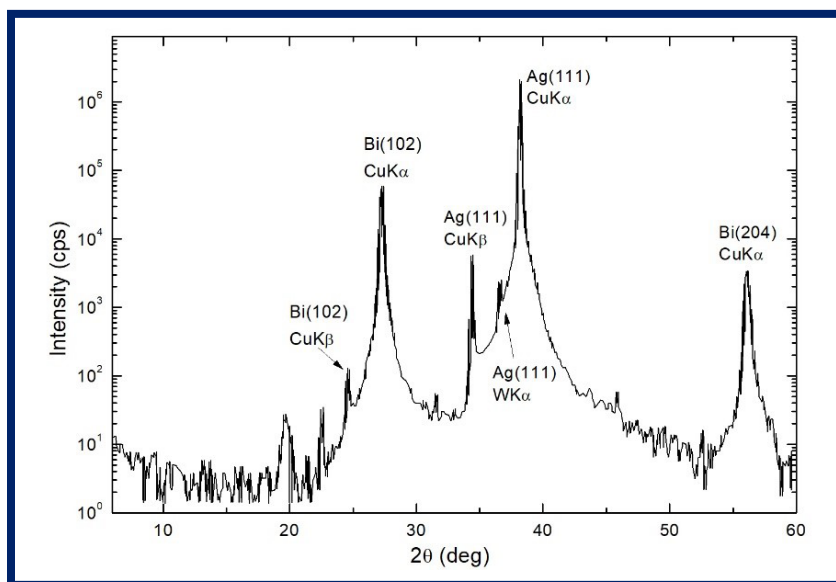



FIG. 4. XRD measurement of the 50-layers bismuth sample to prove the crystallinity of the deposit.

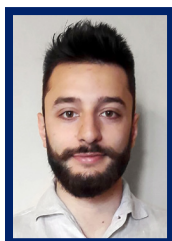
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