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Fabricating energy devices with low environmental impacts

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Techniques such as electrochemical atomic layer epitaxial deposition can be used to grow high-quality pseudo-2D layers of photovoltaic materials.

Efforts to reduce the rate of carbon emissions from industry,[1] as well as the impending economic and social problems that could arise from the depletion of fossil fuels,[2] are the two driving forces for the development of devices that can generate electric power from renewable sources. It is necessary for research and development in this field to satisfy a few major requirements. In the last few decades, the increasing demand for high-tech applications has led to increasing solicitation of mineral deposits and has brought many rare metals to the brink of irreversible depletion.[3] It is therefore necessary for new devices to be based on abundant materials that are available on a global or local scale. The whole 'life cycle' of the materials must also be environmentally friendly (i.e., the materials must be non-toxic and easily recycled). Moreover, the materials must be energetically favorable, i.e., they must involve low-energy consumption processes during all the phases of the life cycle (production, to maintenance, to decommission, to recycling). This final aspect—which can be determined accurately through a full life cycle assessment (LCA)—depends on the energy costs and energy conversion efficiency of the device itself. In a full LCA, several parameters are estimated. These include the payback time (time required to earn the energy costs of the production process), the energy return on energy investment (ratio between the energy produced by and the energy costs of the system along the whole life cycle),[4] and the net energy (the energy delivered to society for discretionary uses after all the energetic costs are subtracted from the energy produced). This last figure of merit (i.e., the net energy) is a crucial parameter for defining energy policy.[4]

All these requirements for renewable energy devices can be met satisfactorily by solar cells that are based on pseudo-ternary sulfides, such as stannite (Cu_2FeSnS_4), kuramite (Cu_3SnS_4), and kesterite (Cu_2ZnSnS_4).[5] Kesterite-type semiconductors are generally synthesized by high-temperature solidification, in the vapor phase, or under high-vacuum conditions. Other easier and cheaper methods (e.g., from aqueous solutions), however, can also be considered. Electrochemical techniques, for example, are particularly suitable for satisfying the requirements. Indeed, with these methods, a low cost can be achieved with relatively simple instrumentation, low working temperatures, and accurate control of the experimental parameters.[6] Furthermore, morphological, structural, and compositional control of the final deposited film can be obtained.

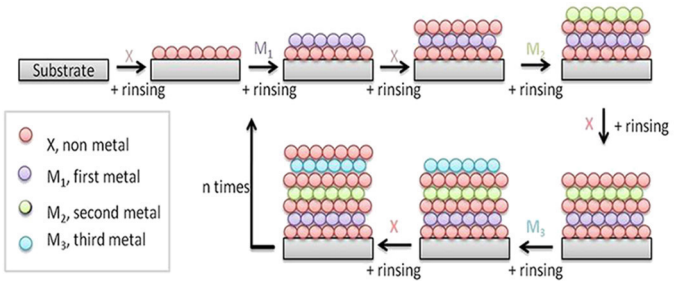

Figure 1. *Schematic illustration of the electrochemical atomic layer epitaxial deposition (ECALE) technique for the growth of quaternary metallic compound thin films.*

In our work, we use a particular electrochemical technique—known as electrochemical atomic layer epitaxial deposition (ECALE)—to manufacture high-quality monolayers and multilayers of metal sulfide materials. With ECALE, we can exploit the underpotential deposition (UPD) methodology (i.e., the property of some materials to be deposited as a monolayer before massive electrochemical deposition). In addition, ECALE allows the composition, morphology, and structure of an aqueous solution at low temperature to be controlled. When the growth from ECALE—either from UPD processes or from any surface limited reaction—cannot be rigorously considered as epitaxial, it can be referred to as electrochemical atomic layer deposition (E-ALD). The major goal of our research is to demonstrate that

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ECALE can be used to efficiently fabricate high-quality monolayers and multilayers of pseudo-2D materials.

We grow the compound materials on metallic surfaces by depositing (using the UPD process) alternating monolayers of the different components (see Figure 1). We are also involved in developing a method to grow homostructures (i.e., monolayer and multilayers) and heterostructures (multilayers made of different layers of pseudo-2D materials). These techniques are being optimized in several laboratories. Indeed, we have used ECALE to successfully obtain a number of binary and ternary semiconductor thin films. These compounds include cadmium sulfide (CdS),[7–11] cadmium telluride (CdTe),[12] cadmium selenide (CdSe),[13] zinc sulfide (ZnS),[14] zinc selenide (ZnSe),[14] nickel sulfide (NiS),[15] lead sulfide (PbS),[16–18] copper sulfide (CuS),[19,20] and indium arsenide (InAs).[21]

A specific need in our field of work is for the structural characterization—with the use of opportunistic analytical techniques—of the ultra-thin films that are obtained from the electrochemical deposition techniques. We have thus performed in situ surface x-ray diffraction (SXRD) measurements to investigate the growth of CuS films. We conducted our experiments at the ID03 beamline at the European Synchrotron Radiation Facility in Grenoble, France. In these tests, we monitored the growth of the film by examining the evolution of the Bragg peaks after each E-ALD step. The results of our SXRD measurements are illustrated in Figure 2. These highlight the occurrence of a self-standing film, with a definite crystal structure, after 15 E-ALD cycles. After the first observation of the Bragg reflections, we registered only minor subsequent changes to the structural arrangement of the film.

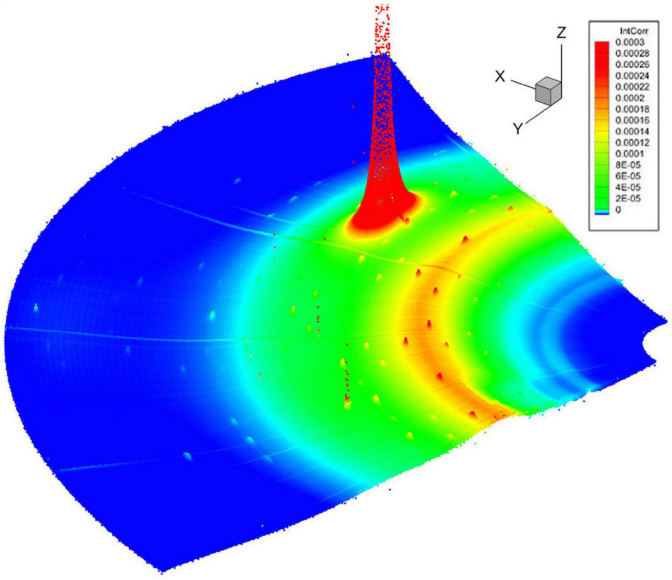

Figure 2. *Results from surface x-ray diffraction measurements of a copper sulfide film. The 2D intensity map illustrates the reciprocal space where the Bragg reflections of the sample and the reference silver substrate are apparent. The self-standing film is clearly indicated by the high-intensity peak.*

We also conducted additional SXRD measurements to monitor the influence of the applied electric potential on the stability of the electro-deposited crystal structure. We performed these SXRD measurements during the switch-off of the potential. Our results showed that a structural change was indeed registered. Furthermore, we found that this structural change was correlated with the occurrence of the stable phases under conventional laboratory conditions.

Our research involves the use of the ECALE deposition technique for the growth of ultra-thin films of metal sulfide,[22–25] and other, materials. So far we have been able to successfully develop several films of materials, including CdS, CdTe, CdSe, ZnS, ZnSe, NiS, PbS, CuS, and InAs. Such films can be used for the manufacture of semiconductors for solar cells. Our electrochemical approach can meet the requirements for low-cost and efficient fabrication methods. We have also experimentally demonstrated that SXRD can be used to successfully characterize the structure of the fabricated films.[26,27] Our future research will be aimed primarily at the construction of an entire solar cell, as well as electrodeposition of p and n semiconductors via the E-ALD technique.

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