

## Ternary $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ deposited on Ag (1 1 1) by ECALE: Electrochemical and EXAFS characterization

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### Abstract

This paper reports the characterization of ternary II–VI semiconductor nanocrystals, deposited by the electrochemical atomic layer epitaxy (ECALE) technique.

In particular, morphological and structural properties of the ternary compounds of formula  $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$  deposited on Ag (1 1 1) have been characterized as a function of composition. The number of the attainable  $x$  values is limited by the necessity of using well-defined ZnSe/CdSe deposition sequences. However, the quantitative analysis carried out on the basis of both electrochemical and extended X-ray absorption fine structure (EXAFS) experiments indicates that the ECALE method is a successful way of controlling the composition of  $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ . In addition, the electrochemical measurements show that the amount of deposition is minimum in correspondence to the compound with  $x = 0.5$ , thus corroborating the hypothesis of a higher degree of disorder suggested both by morphological and structural investigation. The morphology was studied by atomic force microscopy (AFM). The structure of the films is estimated by EXAFS which is a powerful technique for the analysis of the local structure around chosen atoms.

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### 1. Introduction

One of the goals of the present-day research is to decrease the size of the various components which make up electronic devices. This miniaturization is desirable not only in the electronic and optoelectronic industries, but more generally for the realization of new functional and smart materials. Such materials depend, to a large extent, on the possibility of controlling the formation of the material at the nanoscopic scale. Today electrochemistry extends to the domain of material science by developing electrochemical methods for material electrodeposition with control down to an atomic level. The advantages are mainly connected with good selectivity, low costs and low levels

of wastestreams. The drawbacks are the necessity of conductive substrates and the use of condensed media that increases the presence of impurities [1].

Electrodeposition allows for the very precise control of material deposited through, for example, Faraday's law or through the use of self-limiting phenomena such as those involved in the underpotential deposition (UPD). Underpotential deposition is the basis of the electrochemical atomic layer epitaxy (ECALE) method proposed by Stickney and Gregory [2] for the deposition of well-ordered II–VI compounds. In the ECALE procedure, the binary compounds are obtained by alternating the underpotential depositions of the metallic and non-metallic elements. One major advantage of ECALE method consists in the possibility of separately optimizing the different steps of the alternate electrodeposition by adjusting the experimental parameters.

The deposition of ternary II–VI compounds offers the possibility of tuning the bandgap to meet specific needs, but poses the challenge of controlling the film composition. As reported

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by Wang's review on the nanostructures of II–VI compound semiconductors [3], cadmium selenides quantum dots demonstrate a strong size dependence on their physical properties. In particular, it has been shown that it is possible to correlate the quantum confinement of small crystallites of CdSe to an induced higher energy shift with decreasing size [4–7]. To improve quantum efficiency, the CdSe nanocrystal core is often passivated by another semiconductor shell with a higher energy band gap, such as ZnSe [8].

Thin films of ternary compounds like  $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$  have been grown by different techniques. In particular, Han and Knoll prepared a solid solution of nanocrystals by heat treatment [9] and the mechanism for solid solution formation was elucidated by the recent work of Sung et al. [10].

In our laboratory, experience in the ECALE growth of ternary II–VI compound semiconductors was obtained by depositing  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  and  $\text{CdS}_x\text{Se}_{(1-x)}$  on Ag (1 1 1) [11–13]. Both compounds were obtained by a procedure corresponding to the alternate deposition of the corresponding binary compounds in submonolayer amounts. Thus, the compound stoichiometry depends on the ZnS/CdS or on the CdS/CdSe deposition sequence in a well-defined and reproducible way, with the limit that only certain discrete  $x$  values are attainable. However, the quantitative analysis carried out by XPS and electrochemical stripping experiments indicates that the ECALE method has good control over composition. Then, photoelectrochemical measurements confirmed that the bandgap values of the obtained compounds vary about linearly with the composition parameter  $x$  which agrees with literature data reported for bulk materials.

This paper reports a detailed analysis on the growth of  $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$  by alternating the ECALE deposition of the corresponding binary compounds. The experimental conditions for the deposition of both ZnSe and CdSe on Ag (1 1 1) by ECALE, as well as some preliminary results on the attainment of  $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$  had been reported before [14,15,11].

The characterization includes the electrochemical characterization, the evaluation of composition by differential pulse anodic stripping analysis (DPASV) on hanging mercury drop electrode, the morphological analysis by atomic force microscopy (AFM) and the structural investigation by extended X-ray absorption fine structure (EXAFS) [16].

## 2. Experimental

### 2.1. ECALE film deposition

Fluka analytical reagent grade  $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ , Merck analytical reagent grade  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{HClO}_4$ ,  $\text{NH}_4\text{OH}$ ,  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  and  $\text{CH}_3\text{COOH}$  were used without further purification. Merck Suprapur  $\text{NaOH}$  and  $\text{HClO}_4$  and  $\text{NH}_4\text{OH}$  were used to prepare the pH 8.5 ammonia buffer, whereas  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  and  $\text{CH}_3\text{COOH}$  were used to prepare the pH 5.5 acetic buffer. Merck  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  was recrystallized twice from bidistilled water and then dried. The solutions were freshly prepared just before the beginning of each series of measurements. An automated deposition appa-

ratus consisting of Pyrex solutions reservoirs, solenoid valves, a distribution valve and a flow-cell was used under the control of a computer. The electrolytic cell was a Teflon cylinder with a 6.7 mm inner diameter and a 37 mm outer diameter, whose inner volume, about 0.8 ml, was delimited by the working electrode on one side and the counter electrode on the other side. The inlet and the outlet for the solutions were placed on the side walls of the cylinder. The counter electrode was gold foil, and the reference electrode was an Ag/AgCl (sat. KCl) placed on the outlet tubing. Both the distribution valve and the cell were designed and realized in the workshop of our Department [17]. The solution is pushed into the cell by applying a pressure as low as 0.3 atm which determines a flow-rate of about  $1 \text{ ml s}^{-1}$ . When the cell is filled, the pressure is no more applied, so that the flow is stopped during ECALE depositions. A simple homemade software allows filling the cell with the different solutions with the sequence necessary to obtain the compound. Binary compounds are simply obtained by alternating the underpotential deposition of the metallic element with the underpotential deposition of the non-metallic element in a cycle. Ternary compounds, such as cadmium and zinc chalcogenides, require of further alternating the cation deposition, which corresponds to alternate the deposition of the corresponding binary compounds. In other word, as better described later, cadmium and zinc selenide is obtained by alternating the deposition of CdSe and ZnSe. The silver single crystals were prepared according to the Bridgeman technique and polished by a  $\text{CrO}_3$ -based procedure preparation [18–21].

### 2.2. EXAFS measurements

EXAFS measurements at the Se–K (12658 eV) and Zn–K (9659 eV) edges were carried out at the GILDA-CRG beamline [22] of the European Synchrotron Radiation Facility in Grenoble. The photon energy selection was carried by a fixed exit monochromator equipped with a pair of Si (3 1 1) crystals running in dynamical focusing mode [23]. Two Pd-coated mirrors, set to an energy cutoff of 21 keV, were used for the harmonics rejection. The intensity of the beam impinging on the sample was monitored with an Ar filled ion chamber. The fluorescence spectra was measured using a single element Hyperpure Ge detector and the Se-K $\alpha$  and Zn-K $\alpha$  emission lines were selected for the collection of the EXAFS spectra at the related edges. 2 spectra per sample were collected and averaged in order to limit instrumental uncertainties to the data.

### 2.3. AFM measurements

Topography was measured *ex situ* in a dry nitrogen atmosphere, using a Molecular Imaging AFM (PicoSPM, Molecular Imaging) operating in contact mode, with a commercial  $\text{Si}_3\text{N}_4$  cantilever (Nanosensors, Wetzlar-Blankenfeld). The samples were characterized by non-filtered  $512 \times 512$  pixels images of  $5 \mu\text{m} \times 5 \mu\text{m}$ .

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