UPD layer by layer growth of semiconductor thin films on Ag single crystals: effects of substrate orientation on film structure and crystallinity

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The Electrochemical Atomic Layer Epitaxy (ECALE) represents an attractive method for the production of thin films of semiconductor compounds with high grade of crystallinity. Electrodeposition can be very competitive respect to vapor phase deposition or vacuum methods for several reasons: the low cost, the possibility of room-temperature operation and the control of film composition and thickness. In the ECALE method [1] a semiconductor film can be formed on the electrode surface by an alternate Underpotential Deposition (UPD) of the elements that form the compound. UPD is a surface-limited phenomenon, so the electrodeposition in UPD conditions is generally limited to one atomic layer.
UPD processes on single crystals are substrate dependent, thus different structures of the deposited layer should be expected on substrates with different orientation. For this reason it's not clear how and if the substrate orientation may affect the structural order of the film during the ECALE growth.
Our work was focused on the deposition of CdS films on Ag(111), Ag(110) and Ag(100) substrates. Voltammetric analysis of Cd and S UPD processes present significant differences which are in relation with the different structure of the epitaxial film as shown by in-situ STM investigation [2]. So far was not clear if the epitaxial order of the first monolayers deposited on the electrode surface might contribute to the order of the film. In case of CdS two stable allotropic structures are known
: Wurtzite and Zincblende. The goal of the present work was to indentify the crystallographic structure of the film and to investigate the epitaxy of the film.

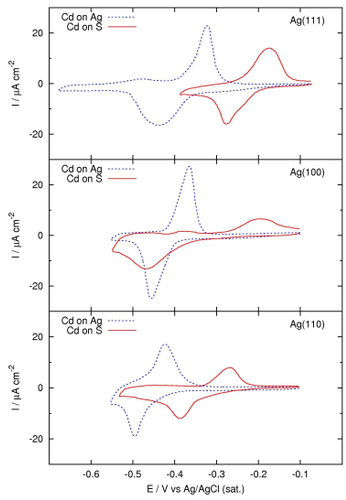

Fig. 1 Cyclic voltammograms of Cd on S-covered and bare Ag(111) Ag(100) and Ag(110), obtained from 5 mM $CdSO_4$ in ammonia buffer pH=9.6 solutions. Scan rate 10mV/sec.

Structural characterization of thin films is generally a rather complex task as it requires high brilliance x-ray sources given the small thickness of the film. Nevertheless synchrotron light sources can provide such an high photon flux to perform this kind of experiment. Surface X-ray diffraction was used to identify the crystallographic structure and to investigate the epitaxial order on the surface.

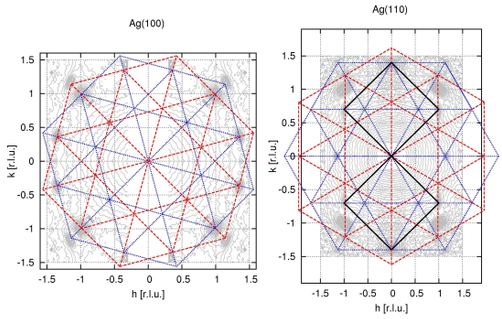

Fig 2 Mesh scans in the hk reciprocal space plane for l=0.05. Diffraction pattern show the in plane orientations of CdS domains on Ag(100) and Ag(110). In both cases two Wurtzite domain rotated by 30° can be observed. On Ag(110) CdS with a Zincblende structure is also present, this domain is rotated by 45° respect to the substrate unit cell.

The results confirm that ECALE is an effective method to grow crystalline films with high level of order. Structural analysis shows that film orientation and structure strongly dependent on the substrate lattice structure. Films present an high grade of crystallinity on all the substrates and on all facets, the growth of CdS has been proved to be epitaxial. Substrate lattice clearly influences the CdS structure, the presence of different orientation domains aligned along symmetrical direction respect to the substrate main axes is consistent on Ag(100), Ag(110) and Ag(111).
X-ray reflectivity and diffraction data are in good agreement with electrochemical analysis and confirm that film thickness can be controlled by the number of deposition cycles. The experiments clearly show that CdS with disordered or powderish structure is not present on the surface proving the ECALE method to be a versatile and powerful tool for the electrodeposition of crystalline thin films of semiconductor compounds. Conditions for CdS ECALE deposition (potential and deposition time) are similar on all the substrates analyzed. This suggest that ECALE could be successfully used for CdS deposition on substrates without a preferential orientation and the structural properties of the film should be probably unchanged. Since the method is very inexpensive, its application for the production of high crystalline semiconductor thin films represent an interesting alternative between the other techniques used in deposition of thin films of semiconductor compounds.

[1] B. W. Gregory and J. L. Stickney, J. Electroanal. Chem. 300 (1991) 543

[2] E. Lastraioli, F. Loglio, M. Cavallini, F. Simeone, M. Innocenti, F. Carla', M. L. Foresti, In Situ Scanning Tunneling Microscopy Investigation of Sulfur Oxidative Underpotential Deposition on Ag(100) and Ag(110), Langmuir 26 (2010) 17679