# New facets of CdTe electrodeposition as revealed by working under fast growth rate conditions

Catherine LEPILLER, Jamal KURDI, Philippe POIZOT*, Jacques VEDEL and Daniel LINCOT
Laboratoire d'Electrochimie et de Chimie Analytique (UMR CNRS 7575)
Ecole Nationale Supérieure de Chimie de Paris
11, rue Pierre et Marie Curie 75231 PARIS cedex 05, France

Cathodic electrodeposition of CdTe films from acidic aqueous solutions is by far the most studied case of semiconductor electrodeposition. On one side it can be considered as a case study for fundamental research in this field, as shown by numerous publications dealing with mechanistic studies and on the other side it is the main example of successful application, with industrial developments of large area CdTe deposition in the photovoltaic industry.

Standard deposition conditions both for the academic studies and for the applications involve low deposition rates, typically lower than about one micron per hour. The aim of this work was to explore the possibility of faster electrodeposition rates, which can be considered as an “historical perspective” in the field of semiconductor electrodeposition, if we look to what can be achieved for metal electrodeposition. This perspective rises a basic question : will the deposition mechanism of CdTe, based on a key UPD step of cadmium on Te sites (Kröger’s theory), allow high growth rates, up to what limit?

The experimental study has been carried out in "fast" deposition conditions based on the use of a more acidic bath formulation (about pH 1) , allowing a higher Te(IV) concentration (up to 10-3 M) which the rate limiting factor in standard conditions.  The deposition were carried out under potentiostatic conditions, under well defined hydrodynamics conditions by using of a rotating-disk electrode system. Smooth, compact and homogeneous films have been grown by this way up to 17 µm per hour on CdS substrates. This paper reports the results from the electrochemical study in these new conditions in close relation to the properties of the films.  Composition and structural characterisation of the films have been studied as a function of the main deposition parameters : Te(IV) concentration, hydrodynamic regime and potential.

The structural and compositional analysis have correlatively shown the existence of two well separated domains, which depends on the bath formulation and hydrodynamic regime. A first one is located for deposition potentials close to the E($Cd^{2+}$/Cd) potential, with a width decreasing with increasing the hydrodynamic conditions. In this range we obtained crystallised CdTe and of good optical quality, as obtained under standard conditions. The second range is located at more positive deposition potentials and/or higher hydrodynamics. In this range the film composition is systematically Te-rich with a Te/Cd ratio close to 2:1 fairly insensitive to the variation of parameters. Corresponding layers are amorphous like and present a band gap value which is lower than that of pure CdTe.

These experimental observations are typical on the new deposition conditions. They are in conflict with the usual two-step electrodeposition mechanism, which essentially predicts a continuous evolution of the deposit composition as a function of potential and rotation rate. We attributed this to the possible formation of a new phase with a stoichiometric ratio Cd/Te of ½ like "$CdTe_2$". Possible reaction mechanisms are that the compound is cadmium ditelluride, formed by the reaction of cadmium ions with ditelluride ions $Te_2^{-2}$ formed as intermediate reduction step of tellurium. This phase could be considered as an interstitial solid phase between excess tellurium and cubic CdTe, Te atoms being included in octaedric vacancies. The other possibility is that the deposition involves another element like hydrogen, with the formation of a $Cd(HTe)_2$ compound, which is similar to cadmium hydroxide in the CdO system. A complete characterisation of this phase is in progress and should allow to precise the underlying deposition mechanism.

From the chronoamperometric study it has become evident that a further kinetic limitation appears in the overall process when the potential and/or the hydrodynamic regime are increased. Strong deviations from the diffusion-limited steady-state current are supposed to be due to an internal barrier inside the growing CdTe layer, converted from n to p type during deposition. The formation of this as-grown CdTe homojunction appears to enhanced by using a fast electrodeposition approach, as compared to standard conditions for CdTe deposition.

In conclusion it appears that fast electrodeposition of CdTe is possible, with maintaining the characteristics of the self regulation mechanism observed under standard deposition conditions, but in a much narrower deposition potential window. New facets of the electrodeposition of CdTe have been revealed by working under these new conditions, in particular the formation of a defined compound with an apparent stoichiometry "$CdTe_2$".