Metal chalcogenide semiconductors growth from aqueous solutions

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Abstract: The chemical bath deposition of CdSe layers has been studied by means of
quartz crystal microbalance (QCM) experiments, combined with TEM, HREM
observations and EXAFS measurements. From mass vs time measurements and the
modelling of the time derivative, it is established that the nucleation/growth process
occurs via two steps : the first one corresponds to an instantaneous nucleation of
cylindrical nuclei, with a 2D-growth until a complete coverage of the substrate ; the
second one consists of a 3D-instantaneous nucleation and growth process occuring on
sites randomly distributed on the evolving surface. The addition of silicotungstic acid
to the deposition bath is shown to influence the growth kinetics of the CdSe deposit.
Nanocrystalline deposits with the cubic blende structure are obtained showing
confinement effects. After thermal treatment CdSe shows an hexagonal wurtzite
structure with a large density of defects and the grain size is increased.

INTRODUCTION

Metal chalcogenide semiconductors have attracted much attention because of potential applications in
electronics, electrooptics and solar energy conversion. Thin films can be prepared by vacuum evaporation,
spray pyrolysis, vapor deposition...(1) Nevertheless chalchogenides like sulfides, selenides and tellurides
have been also deposited from aqueous solutions: electrodeposition (2), chemical bath deposition (CBD)(3)
and Successive Ionic Layer Adsorption and Reaction (SILAR)(4) have been used. In solar energy
conversion applications, photocurrent efficiency is mainly controlled by recombination processes depending
on the crystal structure (hexagonal or cubic, grain size, defects...).
Electrodeposition allows to prepare compact polycrystalline CdTe, CdSe and mixed compounds. The
increase of the electrolyte temperature improves the crystal quality of the chalchogenide films which tend to
crystallize in the hexagonal modification ; further thermal treatments are then avoided (2).
Chalchogenide thin films of CdS, CdSe, ZnS...can be also prepared by CBD which is similar, in solution,
to the well known Chemical Vapor Deposition (CVD) in the gas phase. The film formation takes place from
two distinct mechanisms : atom by atom growth or aggregation of colloïds formed in solution by an
homogeneous reaction. Cadmium sulfide grows according to the first mechanism and films are generally
made of microcrystalline grains (size in the range 20 to 80 nm) presenting an hexagonal or cubic structure
according to the composition of the solution and the nature of the substrate (5). On the contrary CdSe and
ZnS films grow by aggregation of colloïds. The grain size is much smaller than for CdS (below 10 nm).
These semiconductor films present a large increase of the band gap which is attributed to quantum size
effects.
It has been recently shown that the addition of a heteropolyacid as silicotungstic acid (STA),$SiW_{12}O_{40}H_4$
in the deposition bath strongly improves the photoelectrochemical response of the CBD-CdSe films (6). It
was suggested that this improvement would be due to the formation of a n-CdSe/nWO$_3$ heterojunction, able
to enhance the charge transfer at the semiconductor/electrolyte interface. The aim of this work is to better
understand the growth mechanism of CBD-CdSe in the presence or not of STA by combining in situ quartz
crystal microbalance (QCM) measurements (7) and ex situ structural characterizations (SEM, TEM,
EXAFS).

EXPERIMENTAL

The CdSe layers were deposited from ammonia (4M) and triethanolamine (TEA) (1M) solutions. The pH was adjusted to 11 by adding small amounts of NH_4OH. The precursors were sodium selenosulfite and cadmium acetate. When required 10^{-5} M silicotungstic acid was added to the chemical bath. The experiments were performed at a constant temperature between 25 °C and 70 °C, mostly at 45 °C. In situ mass measurements were carried out by means of a quartz crystal microbalance using AT-cut 6 MHz quartz crystals with a gold disk electrode deposited on both sides. The quartz crystal wafers were coated by a thin F-SnO$_2$ overlayer. The quartz vibration frequency was determined with a ten-digit resolution for a 1 s measurement time. Frequency vs time data were recorded on a personal computer via an IEEE interface, owing to a lab-made software. Data files were available for further numerical treatments. This allowed the determination not only of the mass m(t) but also the instantaneous mass variation dm(t)/dt.

Morphology and composition of the deposits were studied with a scanning electron microscope (SEM) Leica Stereoscan 440, equipped with a tracor EDX analysis. Structural characterizations were obtained by depositing very thin CdSe layers on carbon membranes supported by gold grids or on Titanium foils before to be thinned by electropolishing. Thermal treatments are carried out on titanium substrates. Transmission Electron Microscopy (TEM) observations were performed using a Jeol 100 CX2 apparatus for routine examinations. High resolution imaging (HREM) was achieved using a 200kV Phillips CM20 microscope. EXAFS measurements were performed at LURE (Orsay) on the spectrometer XAS II in the fluorescence mode using a Si (311) monochromator.

RESULTS AND DISCUSSION

Growth kinetics
Figures 1a and 1b show the dm(t)/dt curves in the absence (1a) and in the presence (1b) of STA. The most important feature of these curves is to be characterized by a two-peak profile, an information which is difficult to get from the m(t) curves. This clearly proves that the chemical deposition process takes place via two consecutive steps. A mathematical expression has been derived (7) to represent the time behaviour of the growth rate by analogy with the nucleation/growth models proposed for the interpretation of the current transients in electrocrystallization.
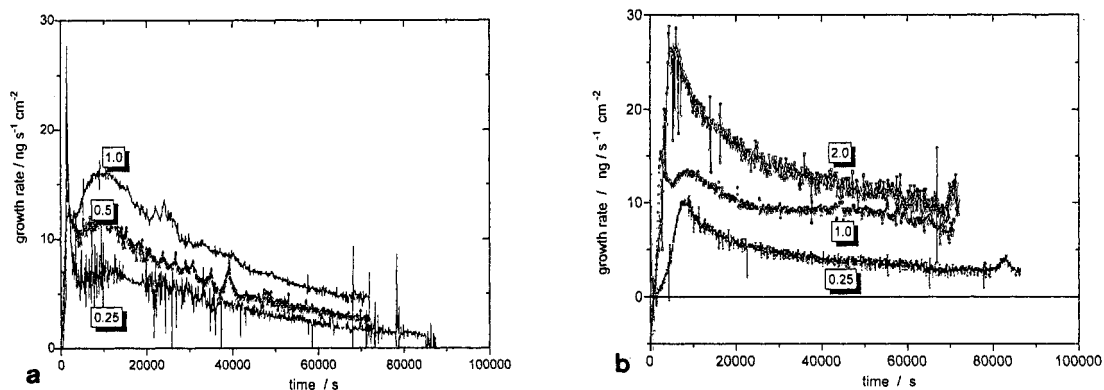

Fig. 1 Evolution against time of the growth rate obtained by numerical derivation of the m(t) curves for different values of the ration r = [Cd]/[Se] at 45 °C.
(a) in the absence of STA   (b) in the presence of STA

The first step corresponds to the instantaneous nucleation of cylindrical nuclei, followed by a 2D-growth which continues until the complete coverage of the substrate by the layer.The second step is assumed to be independent of the first one. It consists of a 3D-instantaneous nucleation and growth process occuring on sites randomly distributed on the evolving surface. In this model it is also considered that the rates of crystal growth in the directions parallel and perpendicular to the substrate are different. The SEM image (Fig. 2) shows that the vertical growth develops through the formation and coalescence of large, few dense hemispheroids.

The parameters of the growth have been deduced from the simulation of the experimental dm/dt data according to the mathematical expression of the model (7). In the absence of STA, the time constants of the first and the second steps differ by a factor 3 and, therefore, are relatively well separated on the time scale. The thickness of the layer developed during the first step lies in the range 50-85 nm. The surface

density of active sites is around 10^{10} cm^{-2}. In agreement with the SEM observations a better representation of the second peak is obtained by considering flattened hemispheroids (density 10^9 cm^{-2}). In the presence of STA, the thickness of the first layer is lowered by a factor 2 and the time constant of the first step is larger. In the case of step 2, the effect of STA is to reduce the growth rate.
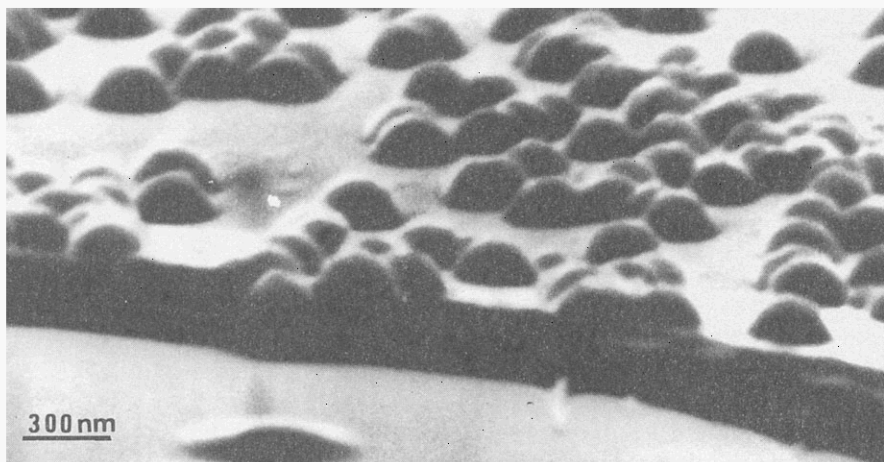

Fig. 2 SEM image of a CdSe deposit on a glass sustrate in the absence of STA; [Cd]/[Se] = 2; T = 60°C; deposition time = 20 min. The image shows the step between the glass substrate and the deposit.

Structural organization of CBD-CdSe

TEM observations bring complementary informations concerning the growth mechanism specially during the first stages. Low magnification images (Fig. 3a) obtained before the coalescence correspond to flat platelets with a surface density approximately 10^{10} cm^{-2}. Each platelet is, in fact, formed by the very aggregation of a large number of elementary CdSe grains, as shown by the microdiffraction pattern (Fig. 3b) which corresponds to the cubic structure (8).
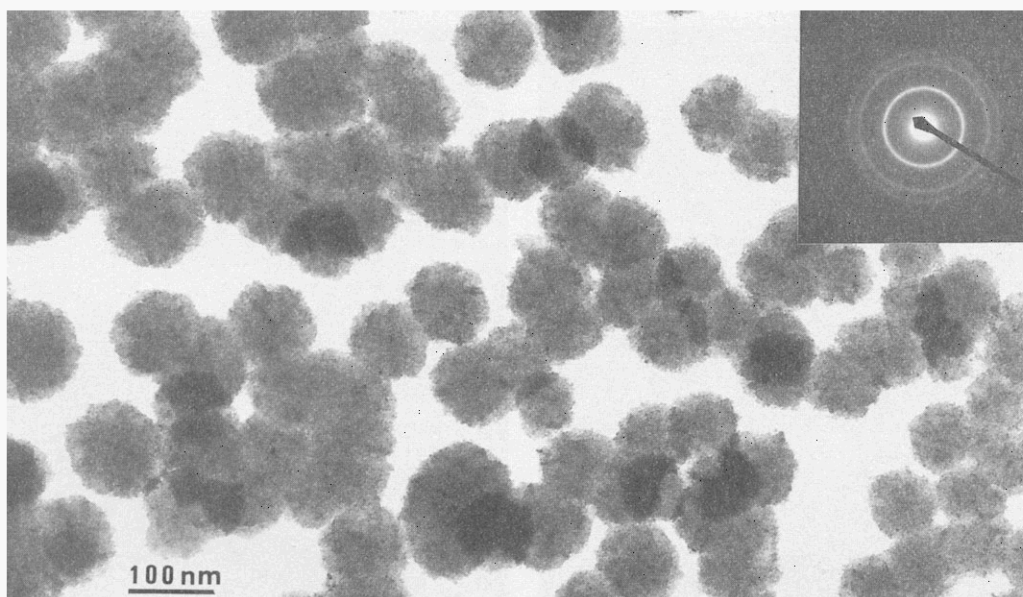

Fig. 3 TEM image of a CdSe deposit on a carbon membrane in the presence of 10-5 M STA. [Cd]/[Se] = 2 ; T = 56°C ; deposition time = 10 min. Insert : Microdiffraction pattern.

The HREM image shows that the grain size is around 3-5 nm (Fig. 4a) The Fourrier transform diffraction pattern corresponding to this figure, confirms the cubic structure (Fig. 4b). Figure 5 corresponds to the inverse Fourrier transform image with a more important magnification than Fig. 4 and using a filtering.
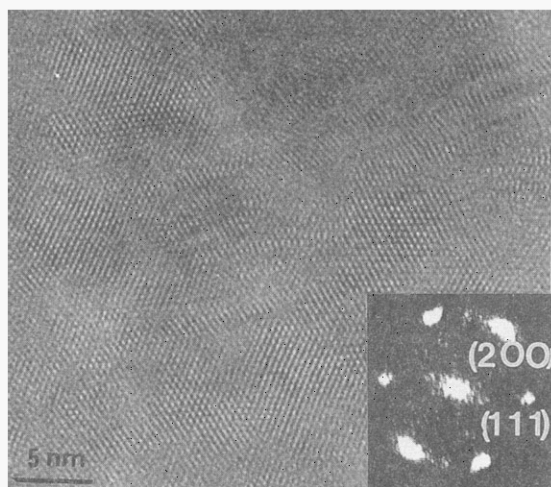

Fig. 4 HREM image of a CdSe deposit obtained in
the same conditions as Fig. 3
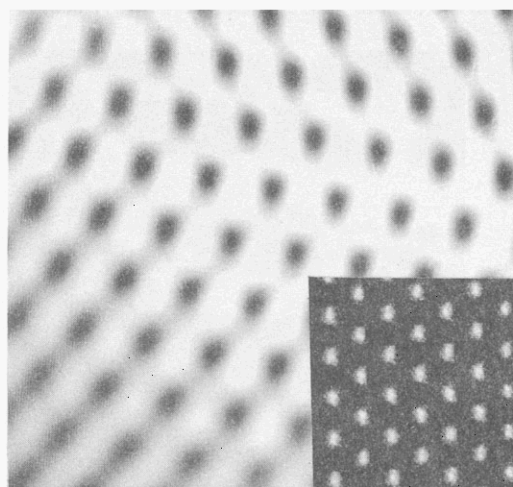Insert : Fourrier transform diffraction pattern

Fig. 5 Inverse Fourrier transform of Fig. 4
Insert : simulated image of [110] CdSe

It corresponds perfectly to the projection of atomic columns along [110] of a blende structure.This nanostructure is the same in the presence of STA in the solution ; this means that tungsten is probably concentrated in the grain boundaries.The low grain size is responsible for the red colour of the deposit which corresponds to a blue-shift of the band gap from 1.7 eV (bulk CdSe) to 2.1 eV (nanosized CBD CdSe)(8).

Thermal treatments induce an important transformation of the CdSe structure. Figure 6 corresponds to a low magnification image of CdSe deposited on titanium. It can be seen that annealing induces the increase
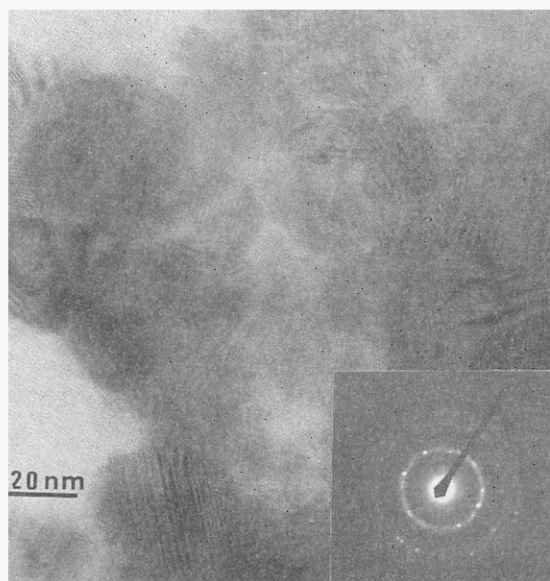

Fig. 6 TEM image of a CdSe deposit after an annealing
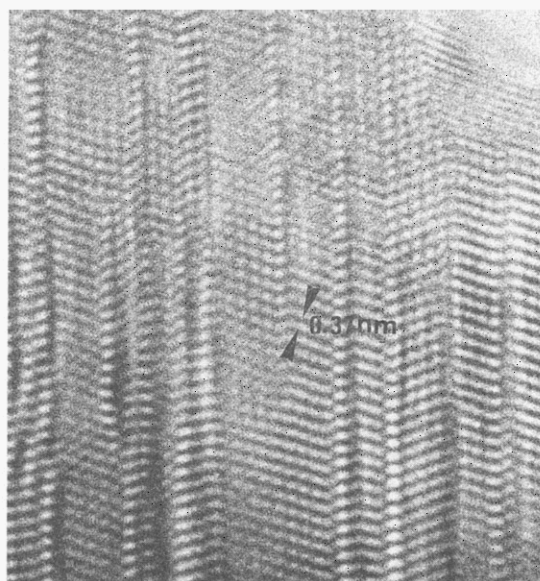of 1 hour at 400°C.Insert : microdiffraction pattern.

Fig. 7 Formation of defects in annealed CdSe.
HREM image.

in the grain size (10-30 nm). As shown by Fig. 7 some grains contain an important density of planar defects (stacking faults, microtwins). These defects are correlated with the cubic/hexagonal phase transformation, occuring in these conditions. It is well known that the bulk CdSe crystallizes in the wurtzite structure. However as the crystal becomes smaller the effects of the surface become important, so, as the fraction of atoms at the surface becomes larger, the arrangement of the nuclei changes in order to minimize the number of pending bonds. Consequently a transformation occurs from the bulk structure to a more closed-packed arrangement (9). That is so, after a thermal treatment, accompanied by an increase of the grain size, the hexagonal struture is observed on the microdiffraction diagram (Fig. 6, insert). HREM observations (Fig. 8) reveal large areas where the image can be interpreted as the projection of the atomic columns on the (0001) basal plane.
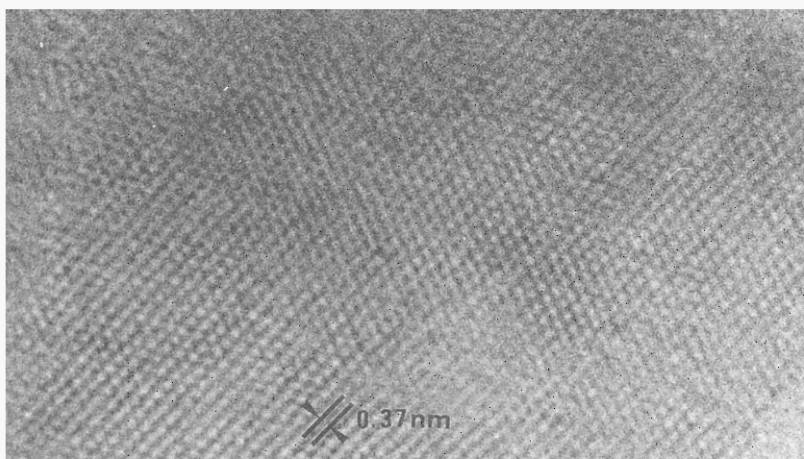

Fig 8 CdSe deposit after an annealing of 1 Hour at 400°C. HREM Image.

Tungsten incorporation and chemical structure.

XRD measurements show a weak incorporation of STA or of its decomposition products (W concentration < 2-3 at. %). EXAFS measurements have been performed to know the chemical structure of the incorporated products. Figure 9 shows Fourier-transform magnitude spectrum of χ (k)*k^2. On these curves, the peak position is representative (with a shift due to the phase factor) of the distance of the neighbours. The first peak is relative to the W-O bonds : it is the same as the standard one. The second peak at 0.32 nm, relative to W-O, W-Si, W-W bonds, is slightly smaller than the standard one.
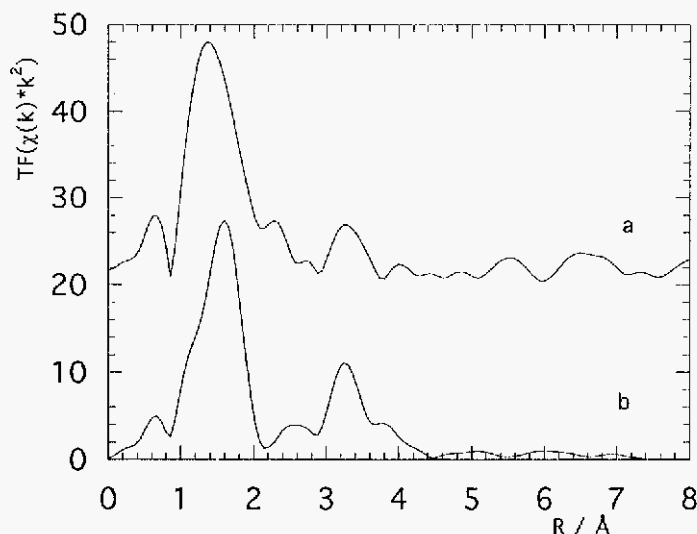

Fig. 9 Fourrier-transform magnitude spectrum at the W edge (uncorrected for phase shift) of CdSe deposited in presence of STA (curve a) and STA powder used as standard (curve b)

A more precise an alysis of the second peak shows that the W-W bonds are the same in the standard and the chemical deposit. Then, the decrease of the second peak could be attributed to a loss of correlation in the W-Si bonds. It results that tungsten is dispersed at the periphery of the CdSe grains in the same form but with disorder.

CONCLUSIONS

- The formation of CdSe films by chemical bath deposition is well described by considering the 2D growth of a layer followed, after coalescence, by a 3D nucleation growth process. The addition of small amounts of silicotungstic acid strongly influences the growth kinetics of the CdSe deposit.
- Electron microscopy observations (SEM, HREM) support this growth mechanism and show the chemical deposit of CdSe occurs through the aggregation of colloids.
- Thermal treatments provoque the cubic/hexagonal transformation coming with an increase in the grain size and the formation of extended defects (stacking faults, twins).
- The improvement of the CdSe photoelectrochemical or photovoltaic properties, in presence of silicotungstic acid, could be attributed to the catalysis of the charge transfer to the redox species by the presence of tungsten containing groups incorporated in the CdSe grain boundaries.

ACKNOWLEDGMENT

REFERENCES

1. T. Gruszecki and B. Holmström, *Solar Energy Materials and Solar Cells* **31**, 227 (1993)
2. Z. Loizos, A. Mitsis, N. Spyrellis, M. Froment and G. Maurin, *Thin Solid Films* **235**, 51 (1993)
3. S. Gorer and G. Hodes, *J. Phys. Chem.* **98**, 5338 (1994)
4. Y.F. Nicolau and M. Dupuy, *J. Electrochem. Soc.* **137**, 2915 (1990)
5. D. Lincot, R. Ortega-Borges and M. Froment, *Philosophical Magazine B* **68**, 185 (1994)
6. O. Savadogo and K.C. Mandal, *J. Electrochem. Soc.* **141**, 2871 (1994)
7. H. Cachet, H. Essaaidi, M. Froment and G. Maurin, *J. Electroanalytical Chem.* under press.
8. G. Hodes, A. Albu-Yaron, F. Decker and P. Motisuke, *Physical Review,* **36,** 4215(1987)
9. D. Manno, R. Cingolani and L. Vasarelli, *Electron Microscopy 1994,* **1**, p. 977, Editions de Physique (1994)