A. Ramírez, E. Reynoso Lara, E. Molina, A. Zehe
Internet Electron. J. Nanoc. Moletrón. 2013, Vol. 11, N° 1, pp 1971-1982

1971

Inter*net* Electronic Journal*

Nanociencia et Moletrónica

Impact of a magnetic field in a Near-Surface Transition Layer (NSTL) on the growth of thin semiconductor films

A. Ramírez, E. Reynoso Lara, E. Molina, A. Zehe

Benemérita Universidad Autónoma de Puebla, Facultad de Electrónica,
Laboratorio de Nanotrónica, Ciudad Universitaria,72550 Puebla, Pue., Mexico
arami@ece.buap.mx

Impact of a magnetic field in a Near-Surface Transition Layer (NSTL) on the growth of thin semiconductor films

A. Ramírez, E. Reynoso Lara, E. Molina, A. Zehe

Benemérita Universidad Autónoma de Puebla, Facultad de Electrónica,
Laboratorio de Nanotrónica, Ciudad Universitaria,72550 Puebla, Pue., Mexico
arami@ece.buap.mx

Abstract
The present paper deals with the effect of a 'Near-Surface' Transition Layer (NSTL) on the growth of thin solid films. The growth kinetics of solid films is based on the well-documented phenomena of physisorption and chemisorption, as well as surface migration and particle clustering. In order to understand the effect of a NSTL on the growth kinetics, we applied an external magnetic field, polarized either vertically or horizontally to the growing surface, during the progression of cadmium sulfide films out of a chemical working solution. The CdS molecules or nanoclusters are formed by a controlled reaction in an aqueous solution. The incorporation mechanism of such neutral particles into the polymorphic CdS thin film is supposed by us to happen in a nanometer-wide transition layer via dissociation into charged constituents close to the growing interface. We found a clear effect of the external magnetic field, when the Lorentz force vector was acting parallel to the interface (the LORENTZ force is proportional to the velocity component vertical to the magnetic flux lines). Compared to the horizontal field orientation, where no effect was seen, the average grain size of the films is now reduced, the smoothness improved, and the layer thickness is increased by a factor of almost three. Band gap energy data from optical absorption measurements suggest dimorphism of the grown films, where the LORENTZ force within the NSTL turns the commonly cubic crystal modification (E= 2.38 eV) into a hexagonal polytype of a 200 meV larger energy band gap.

A. Ramírez, E. Reynoso Lara, E. Molina, A. Zehe
Internet Electron. J. Nanoc. Moletrón. 2013, Vol. 11, N° 1, pp 1971-1982

1973

INTRODUCTION

The adjustment of size dependent optical and electrical properties of metal and semiconductor cluster assemblies and ultra thin films on solid substrates is a significant problem in modern applied nanotechnology [1,2]. Interacting ions, atoms, molecules and even nanoparticles (clusters) of them, arriving on the surface may stimulate a solid to grow, which provides the dynamical aspect of this region with a fundamental importance [3-6]. In general terms, the impinging particles collide with the surface and may adsorbe to the surface or escape the surface, because the kinetic or thermal energy is insufficient to overcome the energy barrier. In the picture of adatom migration, the adatoms colliding with the covered or uncovered surface are assumed to be weakly physisorbed, therefore adatom migration can occur, even as far away as various monolayers from the surface.

Ample discussion has been given to a so-called 'Near-Surface Quasi-Gas' Transition Layer in MBE growth [7,8], which has proven a quite reasonable growth model. Such a layer, about 3 to 4 nm thick, can be compared to a thin liquid film with respect to its density, and to a gas with respect to the degree of order and mobility of the molecular or atomic species [9]. Consequently, adatom kinetics are mainly determined by such a near surface transition layer (NSTL), preceding thin film growth, which determine growth parameters such as surface mobility, surface energy, diffusion, and incorporation of adatoms. Only the material inside the more mobile interface region is able to reorganize to form clusters and modify crystal films.

Under the supposition of electrically charged particles within the NSTL, it should be possible to influence their dynamics and mobility by means of the action of an external magnetic field. The polarization state of such a field would allow to drive ions within the NSTL, i.e. parallel to the solid surface, or affect them in a direction vertical to the surface. This makes such an experimental procedure an in-situ technique and should result in different thin film qualities.

Chemical deposition from an aqueous solution (CBD) delivers films which are homogeneous in thickness, stable, and of quality features sufficient for a number of optoelectronic applications. The method is based on a heterogeneous autocatalytic process, which occurs in two stages: catalytic decomposition of, say, thiourea to form sulfur ions on a $Cd(OH)_2$ surface followed by the interaction of sulfur ions and cadmium ions with the association of CdS molecules in the solution and subsequent film growth on the substrate surface. Nevertheless, the incorporation mechanism of molecules or even clusters of them into the film on top of the substrate is still a matter of discussion. Supposing an initial $Cd(OH)_2$ layer formation on the substrate, a following ion-by-ion condensation of Cd- and S- ions could exist. Kaur et al. [10] relate good quality CdS films with such a process. On the contrary, loosely adhered films are discussed as if the growth process is dominated by adsorption of colloidal CdS particles generated within the solution, and pushed toward the substrate by mechanical stirring. Although the model is suggestive, no direct prove is given, that the processes actually follow these lines. Pseudomorphism, i.e. crystalline regions
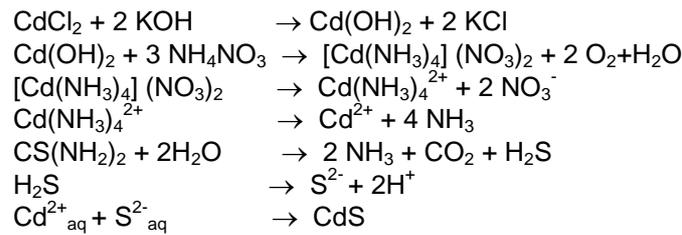
within the deposited films, are reported for both situations [11].A cluster approach of the CdS thin film growth, as proposed by Kitaev [12] since he first reported the successful preparation of CdS layers on glass substrates in the early 60's, has been motive of discussions ever since, though a CdS molecule formation within the aqueous solution prior to its arrival on the substrate surface is the most probable process to happen. An experimentally found epitaxial CdS-growth mode on single crystal substrates in a chemical bath is applied as argument and discussed as ruling out a cluster-by-cluster growth model, but should instead confirm the ion-by-ion condensation of cadmium and sulfur ions on the substrate [10]. Nevertheless does the atomistic nature involved in epitaxial layer formation not necessarily mean ion-by-ion growth in the sense as discussed by Kaur, and may not exclude at all a different mechanism. Experimental results reported up to now seem to support Kitaev's approach in some cases [13,14], and that of Kaur in others [15,16]. This hints the complexity and experimental involvement of an appearing simple experimental procedure.The growth technique of ICBD (Ionized Cluster Beam Deposition) [17], although realized under vacuum environment and not exactly comparable to CBD has proven, that small clusters are able to decay on a substrate surface, leaving behind mobile atomic species which incorporate into perfectly grown epitaxial films [7]. Mixed clusters formed from atoms of group III and group V elements, as in GaAs and InP for instance, show properties which depend upon covalent and ionic bonding [18]. Clusters in aqueous solutions are characterized by external bonds saturated with other ligands [19], but nevertheless their small size makes them reactive species. The difference between III-V and II-VI type semiconductor compounds is that in the former the cation incorporation probability is close to unity, while in the latter the anions are more easily incorporated into the crystal lattice than the cations [20]. The mobility aspect of the layer-building constituents in the immediate front of the growing film is essential. Given the electrically charged state of ions, a LORENTZ force can be exerted on them by virtue of an external magnetic field.

We chose to study the progression of thin CdS-films on glass substrates out of an aqueous chemical working solution, where neutral molecules of CdS dissociate into charged constituents close to the growing surface. It is supposed by us that due to the action of a LORENTZ force parallel to the interface inside the NSTL the mobility of the charged particles and their probability to stick to the surface is enhanced with its effect on grain size, film smoothness, layer thickness, and polymorphic growth.

This paper deals with a discussion of a transition layer region, containing mobile ions in front of a dynamic thin film surface, where neutral molecular particles and clusters are dissociated into electrically charged species. The velocity and trajectory of such particles is influenced from outside by the application of an external magnetic field flux of different orientation. Random stacking often related to polytypism is possibly affected by this means and should prove itself by a modification of the layer morphology.

1. SAMPLE PREPARATION

The CdS films were fabricated by the chemical bath deposition technique on glass substrates, as suggested by Kitaev [12]. The chemical bath was an aqueous solution of $(0.02M)$-$CdCl_2$, $(0.5M)$-KOH, $(1.5M)$-NH_4NO_3, and $(0.2M)$-$CS(NH_2)_2$ with its molar concentrations given. CdS formation, as detailed in table 1, is achieved by a process involving a controllable chemical reaction at a low rate, by adjusting the pH-value and the temperature of the working solution, which allows to maintain the stoichiometry constant for any ratio of anions and cations.

$$CdCl_2 + 2\ KOH \quad\quad \rightarrow Cd(OH)_2 + 2\ KCl$$
$$Cd(OH)_2 + 3\ NH_4NO_3 \rightarrow [Cd(NH_3)_4]\ (NO_3)_2 + 2\ O_2 + H_2O$$
$$[Cd(NH_3)_4]\ (NO_3)_2 \quad \rightarrow Cd(NH_3)_4{}^{2+} + 2\ NO_3{}^-$$
$$Cd(NH_3)_4{}^{2+} \quad\quad\quad \rightarrow Cd^{2+} + 4\ NH_3$$
$$CS(NH_2)_2 + 2H_2O \quad \rightarrow 2\ NH_3 + CO_2 + H_2S$$
$$H_2S \quad\quad\quad\quad\quad\quad \rightarrow S^{2-} + 2H^+$$
$$Cd^{2+}{}_{aq} + S^{2-}{}_{aq} \quad\quad \rightarrow CdS$$

Table 1: Course of chemical reactions leading to the formation of CdS in an aqueous solution

The pH-value of the working solution was adjusted by a pH-meter and kept at a value of 10. The temperature of the chemical bath was adjusted with a hot plate and temperature controller ($\pm 1^oC$). The deposition time was chosen 40 minutes for all applications.
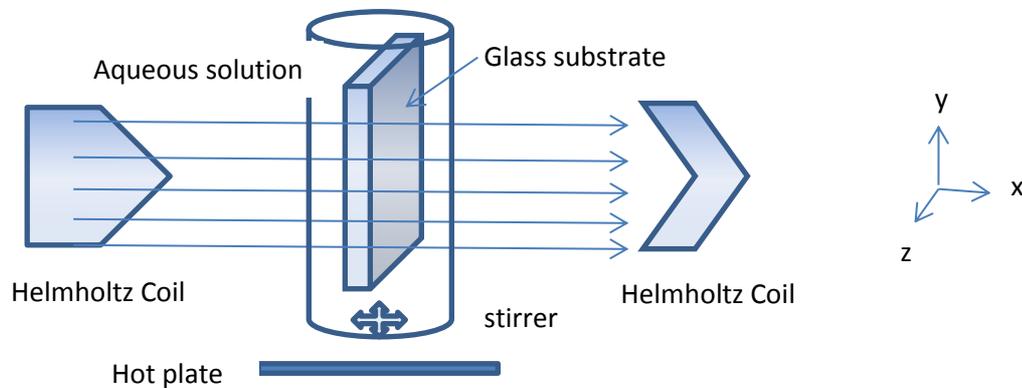
Fig. 1: Experimental arrangement for external magnetic field influenced CdS chemical-bath deposition, showing the external orientation of the magnetic flux vector B with respect to the substrate surface (y-z)

The experimental set up for the CdS deposition under the action of an external magnetic field is shown schematically in fig. 1. The container with the working solution is placed into the field space generated between two Helmholtz coils. The glass substrates are positioned such, that a parallel or vertical orientation, $B_{\parallel}$ and $B_{\perp}$ of the external field lines with respect to the growing film surface is realized. With reference to fig. 1, the vertical and parallel orientations are in line with x and y of the coordinate frame, respectively. The field strength has been varied as an additional experimental parameter, taking values of B = 0.040 Tesla, and B = 0.077 Tesla.

The thickness d of the films was measured by a step profile technique with a Talystep Dektak 11-A. Optical transmission and absorption data in the 300…900 nm range were obtained with a uv/vis Unicam spectrometer. The crystallographic structure of the films was analyzed with a D-5000 Siemens X-ray diffractometer using the CuK_α-line (5406 Å). The average grain size in the deposited films was obtained from a Debye-Scherrer line broadening formula applied to the (111) line, as well as by direct size measurements on AFM images.

2. POLYMORPHIC GROWTH

The existence of several modifications in which a solid, and in particular a thin solid film might crystallize, brings about a variety of different physical properties. Tetrahedral configuration of nearest neighbors is the building concept of many partially ionic compounds, given a not too large ratio of the anion size to cation size. The diamond structure in which elemental semiconductors crystallize consists of two interpenetrating face-centered cubic sublattices. These sublattices differ from each other only in its spatial orientation of the four tetrahedral bonds, that connect each atom to its four nearest neighbors.
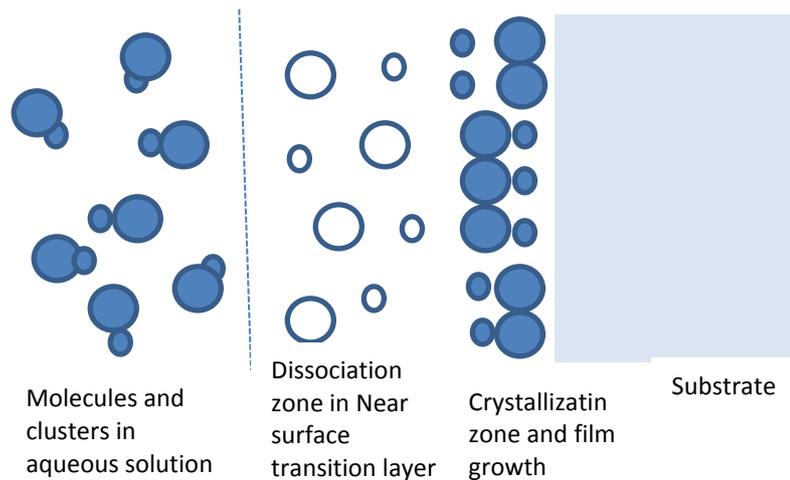
Numerous compound semiconductors, which crystallize as (cubic) sphalerite have an alternative allotropic form in the hexagonal structure known as wurtzite. In the sphalerite and wurtzite structures in which CdS crystallizes, the two sublattices are occupied by different atoms, one by Cd-atoms, the other by S-atoms. It is the different arrangement of the second-nearest neighbors which creates a hexagonal crystal instead of a cubic one. The former is true for a few III-V compounds as well as for several II-VI compound semiconductors. Generally, the conditions of crystallization determine whether a wurtzite or zincblende modification dominates. Nevertheless, polytypes are created by an initially random stacking of particles, in which the stacking sequence may be repeated several times as the layer grows thicker. This property, best known from SiC, is not caused by a far reaching force, but by the action of a moving screw dislocation with a fixed periodicity of the ledge rotating around the screw axis [21]. In very thin films certain III-V compounds, which under normal conditions crystallize in a cubic modification, have shown instead the wurtzite structure [22]. This fact is a reminder, that thin adherent physically coherent films of CdS are of hexagonal structure, while thicker powdery films show the cubic phase, as do large colloidal particle aggregations in the chemical bath. Often a mixed phase is found due to the random stacking of the crystal-forming species at the growing interface.

3. NEAR SURFACE TRANSITION LAYER REGION

The solid surface as seen by an approaching particle, atom, molecule or cluster, is not electroneutral, with the consequence that some distance-dependent interaction is provoked, which implies a relevant interaction energy. This makes a so-called transition layer in front of the solid film the region of an essential crystal-building mechanism (Fig.2). Small clusters entering this region could disintegrate, while for large clusters a complete integration as colloidal CdS-particles in the growing film is

A. Ramírez, E. Reynoso Lara, E. Molina, A. Zehe
Internet Electron. J. Nanoc. Moletrón. 2013, Vol. 11, N° 1, pp 1971-1982

1977

feasible. In this layer, surface kinetic effects of all kinds occur, dissociative chemisorption and particularly lateral migration.

Supposing a thickness of 3 to 4 nanometers for this transition region, with ions inside highly mobile, the action of an external magnetic field may have some specific effect on the film growth process. The field orientation with respect to the substrate surface (and thus to the transition layer) forces mobile ions into trajectories, which lead to a specific crystal-forming behavior.

Molecules and clusters in aqueous solution

Dissociation zone in Near surface transition layer

Crystallizatin zone and film growth

Substrate

Fig. 2: Model description of the near surface transition layer

The acting LORENTZ force F = q(v x B) is proportional to the velocity component v vertical to the field lines of the magnetic flux, B. The curved trajectory adopts a radius R = mv/qB, with q the effective electrical charge and m the mass of the species.

(a)   *(b)*
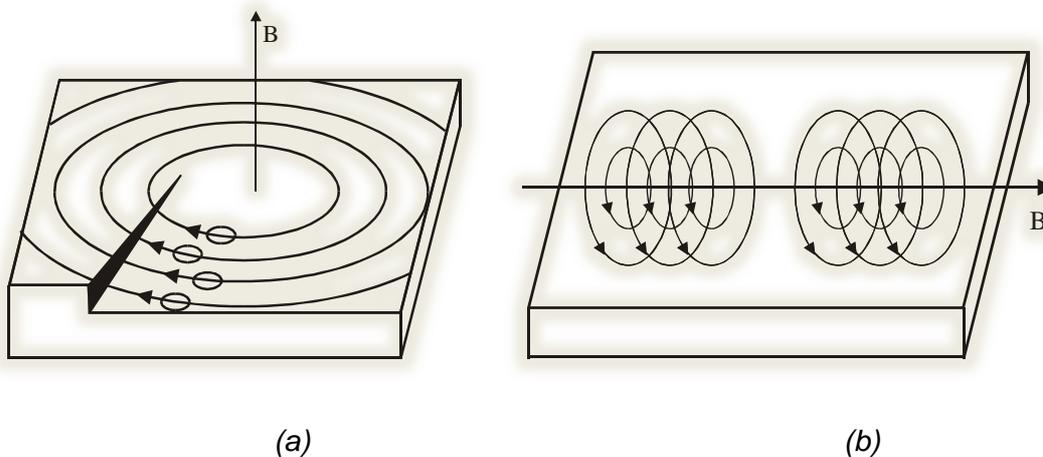
Fig. 3 (a): A rotating ledge of a screw dislocation with an increased offer of film building species, driven by a magnetic field vertical to the growing surface. (b) Particle transport in and out of the transition layer by a magnetic field parallel to the growing surface

As with any other technique are imperfections and lattice distortions on the surface of the film indispensable sites for a reasonable growth rate. There would be very little energetic advantage for an ion in solution and even within the transition layer to shed a number of its solvating molecules and stick in an exposed position on the surface. The gain of energy is proportional to MADELUNG´s constant Φ, which for a terrace, a ledge, and a kink takes values as different as Φ^t= 0.0662, Φ^l= 0.1816, and Φ^k= 0.8737, respectively [23]. Near a surface defect, the loss of the favorable solvation energy is compensated by the greater coulomb interaction between the arriving ion and several ions of a ledge, or even a kink.

It is a well-documented experimental fact, that especially screw dislocations as one type of lattice distortions advance the crystal growth rate in a considerable measure [21]. This has been mentioned before as a mechanism of polytype formation. The surface defect formed by screw dislocations is a ledge, possibly with some kinks, where growth occurs. With continuing deposition, the ledge rotates around the screw axis, and is so steadily reproduced. If the growth rate does not depend on the direction of a ledge at the surface, the growth will take the shape of an ARCHIMEDES spiral with a radius $r = a+b\Theta$, (a,b constants). The level of supersaturation, $\varDelta G$, at the growing interface determines the smallest possible value of r near the dislocation, with $r^* \sim \varDelta G^{-1}$.

Now, the action of a vertical external magnetic field forces the electrically charged species into a circular movement parallel to the substrate surface inside the transition layer, supplying the ledges with a higher influx of more energetic atoms (Fig. 3,a). The expected effect is, that the number of layer-forming grains could grow proportional to an increasing B-field, their diameter shrink, and the roughness of the film surface diminish due to an more evenly growing interpenetration of the increased number of such growth spirals.

On the other hand should the external field vector, when oriented parallel to the substrate surface, result in a circular movement of the charged particles comparable to a rolling cylinder on a plane surface, where the cylinder axis is parallel to the growing film. The net transport of particles towards and away from the layer should then even out, and no particular effect is expected in this case under the assumption of a small capture coefficient (Fig. 3,b).

4. RESULTS AND DISCUSSION

Corresponding to expectation, only samples grown in the vertical external field mode show remarkable effects, while in the parallel field mode almost no difference to the zero-field case is found. Consequently the following results refer to the vertical field mode.

Table 2 contains published energy band gap data for two modifications of cadmium sulfide together with own results. The surprisingly large deviations of the given values

is not an effect of experimental errors, but a representation of the dimorphism contained in this material, meaning as a mixture of cubic and hexagonal modifications with different optical properties.

Given the considerable energy gap difference, optical absorption measurements provide for a quite precise result with resolution in the meV-range. As a common technique, the energy gap values are graphically determined from a representation containing optical absorption α^2 vs. photon energy $h\nu$, drawn from spectral absorption measurements [31,32].

E_g^{cub}	E_g^{hex}	Method of determination	Reference
2.36	2.51	Opt. Abs. Spectroscopy	own data [24]
2.38	2.53	(compilation)	Svechnikov [25]
2.50	2.52	Opt. Refl. Spectroscopy	Cardona et al. [26]
2.35	2.51	Opt. Abs. Spectroscopy	Vigil et al. [27]
2.38	2.43	Opt. Abs. Spectroscopy	Nakanishi et al. [28]
2.45	2.62	Opt. Abs. Spectroscopy	Lind et al. [29]
2.41	2.48	Opt. Abs. Spectroscopy	Wu et al. [30]

Tab. 2: Published energy band gap data, Eg (in eV) at room temperature for cubic and hexagonal crystal structures of CdS. The hexagonal crystal modification shows a higher band gap energy compared with the cubic one
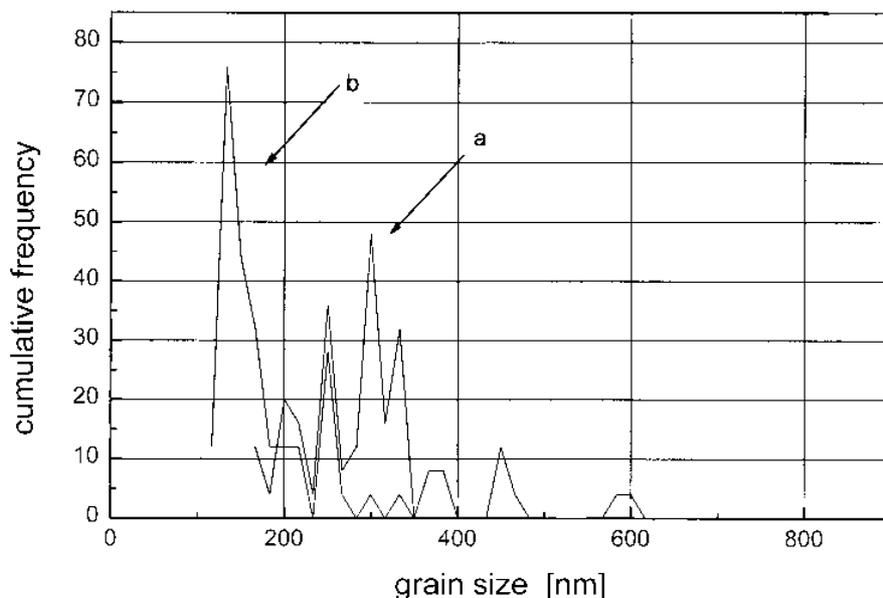
Fig. 4: Frequency of measured grain sizes of a certain grain diameter. (a) – Layers grown with horizontal magnetic field or zero-field applied; (b) - layers grown with vertical magnetic field applied

The grown film thickness is quite sensitive to the effect of the external magnetic field. Without application, this value comes to about 120 nm, but it almost triples at the highest magnetic flux chosen. On the other hand turns the average grain size to near half of its value present in the zero-field case, as shown in fig. 4. The measured data are compiled in table 3.

Sample	Magnetic field strength [Tesla]	Grown film thickness d [nm]	Grain size g [nm]	Measured band gap energy [eV]
1	none	120	73	2.36
2	0.040	260	40	2.42
3	0.077	340	38	2.51

Table 3: Measured properties of chemical-bath deposited CdS films under the action of a perpendicular magnetic field of different strength, compared to the zero-field case

A reduced surface roughness of the films grown under the action of a perpendicular magnetic field has been observed in all the AFM images (not shown).

5. CONCLUSIONS

Experimaental data suggest the presence and involvement of a near-surface transition (NSTL) layer during the thin film growth. The formation process of thin CdS films, which are grown by CBD in a chemical working solution, is notably affected by the action of a magnetic field during growth. Expectantly, the spatial orientation of the magnetic field is important. Only when the field-generated LORENTZ force drives charged particles inside the transition layer parallel to the surface, a strong measurable effect is seen. Dimorphism of the grown films is present, which clearly displays itself in optical absorption measurements due to the modified energy band gap for cubic and hexagonal crystal modifications, influenced by the magnetic field. The existence of a reactive transition layer region next to the solid interface is a reasonable model assumption in order to explain the decomposition into ionic species of small CdS clusters formed within the chemical bath and injected by a mechanical stirring of the solution. The resulting ions in turn are acted on by the LORENTZ force due to the presence of the external magnetic field in a characteristic manner. The film thickness is found to be increased by a factor of three under otherwise identical conditions, while the medium grain size shrinks to almost half the value found without the external field. AFM images (not included here) show expectantly an improved smoothness of the films. The gap energy of the field affected films is increased to 2.51 eV, a value usually ascribed to a hexagonal crystal modification.

BIBLIOGRAPHY

[1]   Zhon Ling Wang, Yi Liu, Ze Zhang, Handbook of Nanophase and Nanostructured Materials, Kluwer Academic/Plenum Publ., N.Y., Boston, Dordrecht, London, Moscow 2002

[2]   K.D. Sattler (ed.), Handbook of Nanophysics, CRC Press, Taylor & Francis Group, Boca Raton, 2011

[3]   M. Schwartzkopf, A. Buffet, E. Metwali, K. Schlage, G. Benecke, J. Perlich, M. Rawolle, A. Rothkirch, B. Heidmann, G. Herzog, P. Mueller-Buschbaum, R. Roehlsberger, R. Gehrke, N. Stribeck, S. V. Roth, "From Atoms to Layers: In situ Gold cluster growth kinetics during sputter deposition, Nanoscale, 5, 5053-5062 (2013)

[4]   Sivasankar Reddy Akepati, Hyun-chul Cho, Kee Sun Lee; "Growth of ultrathin Ag films on TaN_x Layer and their optical Properties", Electronic Materials Letters, 2013, vol. 9, 231-235, (2013)

[5]   Kai Shinotzuka, V.N. Bliznyuk, H.E. Assender, "Near Surface crystallization of PET", Polymer 2012, vol. 53, 5554-5559, (2012)

[6]   Wolf, B. Bantz, T, Zehe, A., "On cluster Kinetics and MBE growth" Cryst Res Technol. 24, 853-858 (1989)

[7]   M.A. Herman, "The Problem of Near Surface Quasi Gas Transition Layer in MBE", Cryst. Res. Technol. 21, 1413-1420 (1986); DOI 10.102, (2006)

[8]   Artioukov, A.I., Asadchikov, V.E., Koshevnikov, I.V., "Effects of a Near Surface Transition Layer on X-Ray Reflection and Scattering, J.XRay Sci. Technol. Vol.6, 223-243, (1996)

 [9]   Wolf, B., Zehe, A., "Are in.growth surface reactions during MBE controlled by a Quasi-Gas Transition Layer?", Cryst. Res. Technol. 22, 903-909, (1987)

[10] I. Kaur, D.K. Pandya, K.L.Chopra, J. Electrochem. Soc. 127 943 (1980)

[11] A.R. Verma and P. Krishna, Polymorhism and polytypism in crystals, Wiley 1966

[12] G.A. Kitaev, Koloidni Zh. 27 51 (1965), Zh. Fis. Khim. 39 (1965) 2065

[13] L.P. Deshmukh, A.B. Palme, V.S. Sawant, Sol. Energy. Mat. and Sol. Cells. 20 (1990) 34

[14] P.O. Brien, and T. Saeed, J. Cryst. Growth 158 (1996) 497

[15] S.N. Sahu, J. Mat. Sci. Mat.: Elect. 6 (1995) 43

[16] I.O. Oladejl, and l. Chow, J. Electrochem. Soc. 144 (1997) 2342

[17] I. Yamada, J. Vac. Sci. Technol. A4 (1986) 722

[18] S.C. O´Brien, J. Chem. Phys. 83 (1985) 5520

[19] R. Rossetti, S. Nakahar, L.E. Brus, J. Chem. Phys. 79 (1986) 1086 ibid 80 (1984) 4430

[20] M.A. Herman, P. Juza, W. Faschinger, H. Sitter, Cryst. Res. Technol. 23(1988)3

[21] R. Gómez, A. Ramírez, A. Zehe "Crecimiento epitaxal de nanoestructuras sobre SiC" Nanocs. Moletron.8, 1531-1548 (2010)

[22] G.A. Kurov, S.T. Pinsker, J.Techn. Phys. 28 (1958) 29

[23] G. Schultze, Metallphysik, Akad. Verl. Berlin 1967

[24] J. Vazquez, A. Zehe, and O. Zelaya, Cryst. Res. Technol.34 (1999) 949

[25] S.V. Svechnikov, in Optoelctronics Materials and Devices, p.141, PWN, Warszawa 1981

[26] M. Cardona, M. Weinstein, G.A. Wolf, Phys. Rev. 140 (1965) A633

[27] O .Vigil, Y. Rodriguez, O. Zelaya, C. Vazquez, A. Morales, J.G. Vázquez: TSF 322 (1998) 329

[28] T. Nakanishi, K. Ito, Sol. Energy. Mat. and Sol. Cells. 35 (1994) 171

[29] L. Lind, R. Bube, J. Chem. Phys. 37 (1962) 2499

[30] C.W. Wu, D.C. Houghton, Mat. Res. Soc. Symp. Proc. 281 (1992) 57

[31] J. Pankove, Optical processes in semiconductors, Prentice Hall 1971

[32] A. Zehe, Herramientas Analíticas de Interfases Sólidas, ISBN 3-8311-3262-3, Editorial LIBRIS, Norderstedt 2002