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ABSTRACT

The effect of a surface transition layer on the growth kinetics of thin solid films is investigated. We have applied an external magnetic flux during the growth of cadmium sulfide thin films from a chemical working solution. The CdS molecules or small clusters are formed by a controlled reaction in the aqueous solution. The incorporation mechanism of such neutral particles into the polycrystalline CdS thin film is supposed to happen in a transition layer via a dissociation into charged constituents close to the growing interface. We found a clear effect of the external magnetic field, when the Lorentz force was acting parallel to the surface. Band gap energy data from optical absorption measurements suggest dimorphism of the grown films, where the field application turns the commonly cubic crystal modification ($E_g = 2.38$ eV) into a hexagonal polytype of a 200 meV larger energy gap. Additionally, the average grain size of the films is reduced, the smoothness improved, and the layer thickness is increased by a factor of almost three.

KEYWORDS: CdS films; Growth kinetics; Crystal properties.

INTRODUCTION

A fundamental dynamical aspect of a solid surface is its role as a region, where interacting ions, atoms, molecules or even nanoparticles (clusters) of them may stimulate a solid to grow. Chemical methods of thin film deposition are attractive from an economical point of view. Relative simplicity allows to mass-produce large areas of films. The number of known procedures is immense, and their practical application is strongly related to the envisaged product features in a general sense. Chemical vapor deposition (CVD) on semiconductor substrates is the leading technique presently applied in microelectronics fabrication. But also 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 $\text{Cd}(\text{OH})_2$ 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 not well understood. Supposing an initial $\text{Cd}(\text{OH})_2$ layer formation on the substrate, a following ion-by-ion condensation of Cd- and S- ions could exist. Kaur et al. [1] 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 [2]. A cluster approach of the CdS thin film growth, as proposed by Kitaev [3,4] 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 [1]. 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 cluster mechanism. Experimental results reported up to now seem to support Kitaev's approach in some cases [5-8], and that of Kaur in others [9-12]. This hints the complexity and experimental involvement of an appearing simple experimental procedure. The growth technique of ICBD (Ionized Cluster Beam Deposition) [13], 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 [14]. 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 [15]. Clusters in aqueous solutions are characterized by external bonds saturated with other ligands [16], but nevertheless their small size makes them reactive species. The influence of diverse growth conditions on the incorporation kinetics of the crystal forming species was concluded from Monte-Carlo simulations [17] which have led to a quite good understanding e.g. of the GaAs-growth during molecular beam epitaxy (MBE). 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 [18]. 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. On the other hand will a mechanical stirrer motion, commonly applied in this deposition technique, also affect the mobility of neutral conglomerates, but the idea is, that these neutral particles disintegrate in front of the growing surface prior to the integration into the growing film. 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 can be 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. X-ray and optical spectroscopic data, as well as atomic force microscopy images are incorporated in the discussion.

1. 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. For instance, GaAs shows in a certain growth temperature range a wurtzite phase [19]. Such a hexagonal GaAs modification is caused by a non-equilibrium of the compound species at the growing interface, and in the cited case was related to an excess of Ga atoms. ZnS shows a wurtzite structure when grown above 1000°C, while below 900°C a cubic zincblende structure is observed [20]. GaN grown on (111)-spinell was reported to show both the common wurtzite and a cubic modification on the same substrate, proven by electron diffraction. In microscopic observation the cubic phase displayed a triangular morphology corresponding to the (111) growth mode [21]. 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. 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 [1]. Often a mixed phase is found due to the random stacking of the crystal-forming species at the growing interface.

2. TRANSITION LAYER REGION

The growth kinetics of thin films is based on the well-documented phenomena of physisorption and chemisorption, as well as surface migration and particle clustering. At the solid-liquid interface of the film prevails the interaction between its surface and the incoming particles. Chemical reactions as given in table 2 indicate, that CdS molecules are formed already in the aqueous working solution, and transported by stirring to the substrate interface. Indeed has stirring been found decisive, when a hexagonal (wurtzite) structure is stabilized, while deposition without stirring produced a large fraction of the cubic (sphalerite) phase in the film [1]. This fact suggests that the size of the cluster may be important.

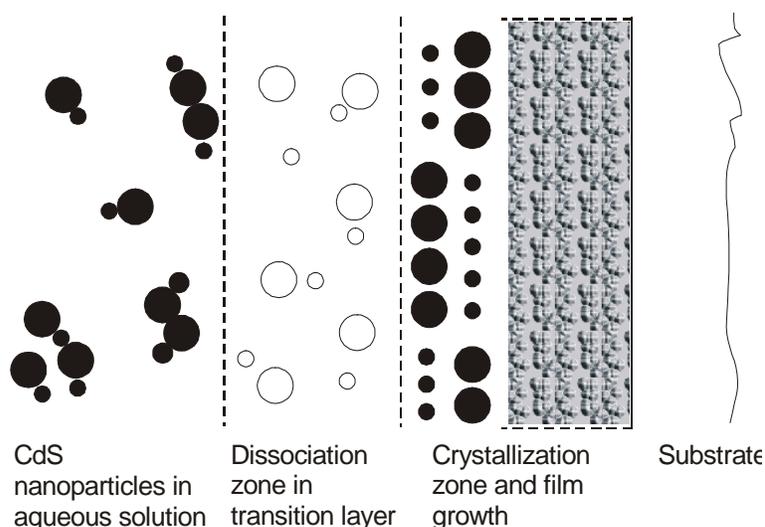


Fig. 1: Model description of the near surface transition layer

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. Small clusters entering this region could disintegrate, while for large clusters a complete integration as colloidal CdS-particles in the growing film is feasible. In this layer, surface kinetic effects of all kinds occur, dissociative chemisorption and particularly lateral migration.

Supposing a thickness of 3 to 4 monolayers 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

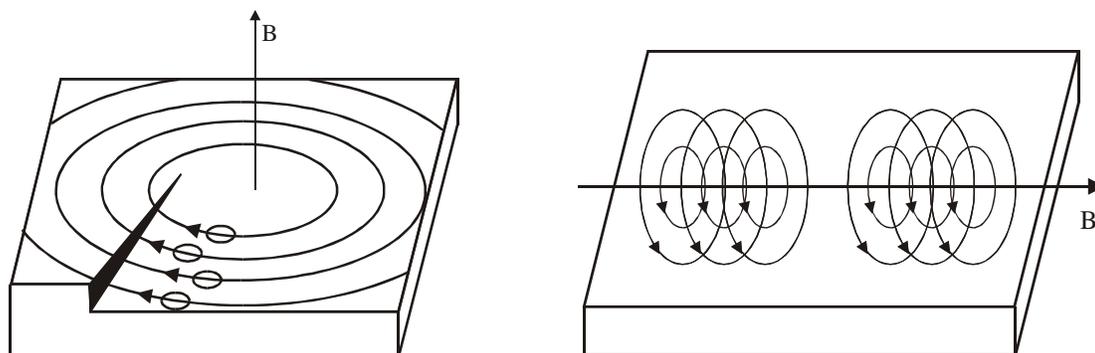
transition layer) forces mobile ions into trajectories, which lead to a specific crystal-forming behavior. The acting LORENTZ force $F = q(v \times B)$ is proportional to the velocity component v vertical to the field lines of the magnetic flux, B . The curved trajectory adopts a radius $R = mv/qB$, with q the electrical charge and m the mass of the species.

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 $\Phi^t = 0.0662$, $\Phi^l = 0.1816$, and $\Phi^k = 0.8737$, respectively [23]. In the vicinity of a surface defect, the loss of the favorable solvation energy is compensated by the greater coulombic 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. 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 $r = a\theta$, (a is a constant). The level of supersaturation, ΔG , at the growing interface determines the smallest possible value of r^* in the vicinity of the dislocation, with $r^* \sim \Delta G^{-1}$.

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. 2,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 same 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. 2,b).



(a) (b)

Fig. 2 (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

3. EXPERIMENTAL

The CdS films were fabricated by the chemical bath deposition technique on glass substrates, as suggested by Kitaev [3]. The chemical bath was an aqueous solution of (0.02M)-CdCl₂, (0.5M)-KOH, (1.5M)-NH₄NO₃, and (0.2M)-CS(NH₂)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.

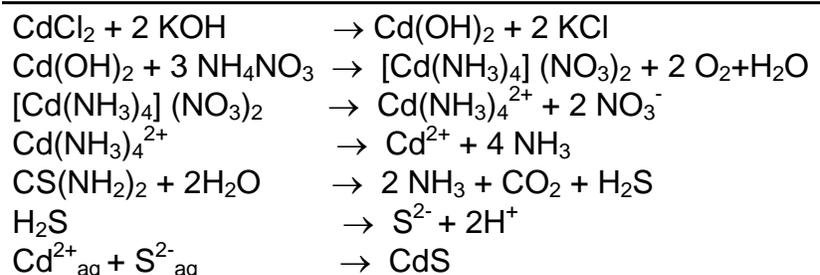


Table 1: Chemical reactions leading to the formation of CdS in an aqueous solution [24]

The temperature of the chemical bath was adjusted with a hot plate and temperature controller ($\pm 1^\circ\text{C}$). Mechanical stirring is applied to increase the particle influx onto the substrate region. The glass slides were soaked in chromic acid cleaning solution, left then for 20 minutes under ultrasonic duty in isopropyl alcohol, washed in DI water, and finally dried by blowing with dry nitrogen. The pH-value of the working solution was adjusted by a pH-meter and kept at a value of 10. The deposition time was chosen 40 minutes for all applications.

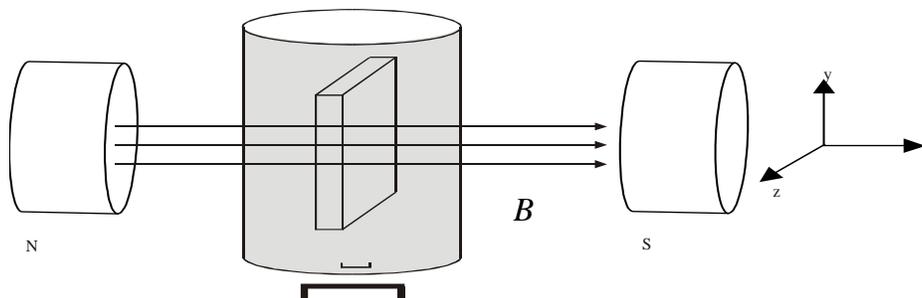


Fig. 3: Experimental arrangement for external magnetic field influenced CdS chemical-bath deposition, showing the external orientation of the magnetic flux vector B with respect to the substrate surface (y - z)

The experimental arrangement for the CdS deposition under the action of an external magnetic field is shown schematically in fig. 3. 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. 3, 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.

After deposition, the substrates were removed from the chemical bath, and cleaned several times in DI water. The film grown on the backside of the glass substrate was etched away employing a 1:10 HCl solution. 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. Atomic force microscopy (AFM) analysis was performed using a PARC Scientific Nanoprobe CP instrument in the contact mode. 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.

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.

E_g^{cub}	E_g^{hex}	Method of	Reference

determination			
2.36	2.51	Opt. Abs. Spectroscopy (compilation)	own data [34] Svechnikov [25]
2.38	2.53	Opt. Refl. Spectroscopy	Cardona et al. [26]
2.50	2.52	Opt. Abs. Spectroscopy	Vigil et al. [27]
2.35	2.51	Theoretical calcul. (OPW)	Szargan et al. [28] Dorst [29]
-	2.55	X-Ray spectroscopy (compilation)	Hadamovski [20] Nakanishi et al. [32]
2.80	2.80	Opt. Abs. Spectroscopy	Lind et al. [33]
2.59	2.59	Opt. Abs. Spectroscopy	Wu et al. [30]
2.38	2.43	Opt. Abs. Spectroscopy	RamírezBon et al. [31]
2.45	2.62	Opt. Abs. Spectroscopy	
2.41	2.48	Opt. Abs. Spectroscopy	
2.48	2.40	Opt. Abs. Spectroscopy	

Tab. 2: Published energy band gap data, E_g (in eV) at room temperature for cubic and hexagonal crystal structures of CdS. Except for data of the last line (erroneous?), the hexagonal crystal modification shows a higher band gap energy compared with the cubic one

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 [35].

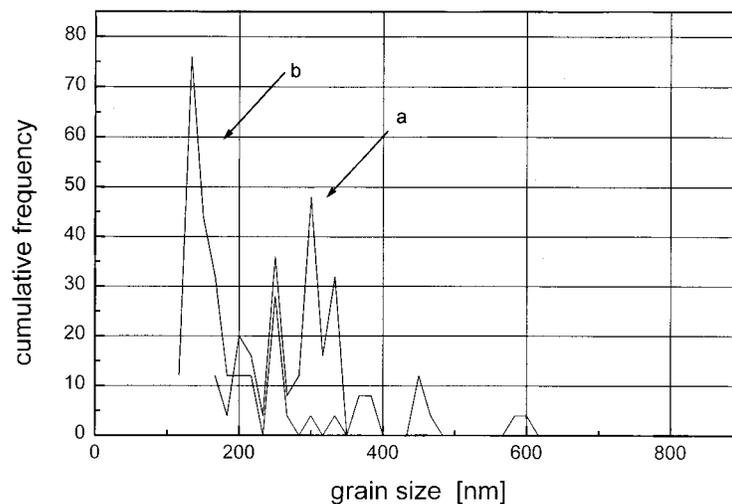


Fig. 4: Frequency of measured grain sizes of a certain grain diameter. (a) - zero-field case
 (b) - layers grown with magnetic field applied

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

Table 3: Compilation of measured properties of chemical-bath deposited CdS films under perpendicular magnetic field orientation of different strength

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

5. CONCLUSIONS

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. The spatial orientation of the field is important. Only when the field-induced LORENTZ force on charged particles acts in the plane of the growing film, a 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. While in X-ray diffraction measurements a pronounced BRAGG reflection peak is seen, the coincidence of the BRAGG angle for the cubic and the hexagonal modifications does not allow for a discrimination of the dominating crystal structure. 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 action 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 show expectantly an improved smoothness of the films. The gap energy of the field affected films is increased to 2.51 eV, a value often ascribed to a hexagonal crystal modification.

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BIBLIOGRAPHY

- [1] I. Kaur, D.K. Pandya, K.L.Chopra, J. Electrochem. Soc. 127 943 (1980)
- [2] A.R. Verma and P. Krishna, *Polymorphism and polytypism in crystals*, Wiley 1966
- [3] G.A. Kitaev, Koloidni Zh. 27 51 (1965), Zh. Fis. Khim. 39 (1965) 2065
- [4] G.A. Kitaev, A.A. Uritskaya, and S.G. Mokrushin, Colloid J. (URSS) 27 (1965) 317
- [5] L.P. Deshmukh, A.B. Palme, V.S. Sawant, Sol. Energy. Mat. and Sol. Cells. 20 (1990) 34
- [6] R. Ortega, and D. Lincot, J. Electrochem. soc. 140 (1993) 3464
- [7] P.C. Rieke, and S.B. Bentjen, Chem. Mater. 5 (1993) 43
- [8] P.O. Brien, and T. Saeed, J. Cryst. Growth 158 (1996) 497
- [9] J.M. Dona, and J. Herrero, J. Electrochem. Soc. 139 (1992) 2810
- [10] S.N. Sahu, J. Mat. Sci. Mat.: Elect. 6 (1995) 43
- [11] N.G. Dhere, D.L. Waterhouse, K.B. Sundaram, O. Melendez, N.R. Parikh, and B. Patnak, J. Mat. Sci.: Mat. Elect. 6 (1995) 520
- [12] I.O. Oladeji, and I. Chow, J. Electrochem. Soc. 144 (1997) 2342
- [13] I. Yamada, J. Vac. Sci. Technol. A4 (1986) 722
- [14] B. Wolf and A. Zehe, Cryst. Res. Technol. 24 (1989) 853
- [15] S.C. O'Brien, J. Chem. Phys. 83 (1985) 5520
- [16] R. Rossetti, S. Nakahar, L.E. Brus, J. Chem. Phys. 79 (1986) 1086
ibid 80 (1984) 4430
- [17] A. Madhukar, S.V. Ghaisas, CRC Critical Rev. Sol. State Mater. Sci. 14 (1988) 1
- [18] M.A. Herman, P. Juza, W. Faschinger, H. Sitter, Cryst. Res. Technol. 23 (1988) 3
M.A. Herman, ibid 21 (1986) 1413
- [19] I.E. Davey, T. Pankey, J. Appl. Phys. 39 (1968) 1941
- [20] H.F. Hadamovski, *Halbleiterwerkstoffe*, Dtsch. Verl. Grundstoffind., Leipzig 1972
- [21] H. Seifert, A. Tempel, phys.stat.sol. (a) 23 (1978) K39
- [22] G.A. Kurov, S.T. Pinsker, J. Techn. Phys. 28 (1958) 29
- [23] G. Schultze, *Metallphysik*, Akad. Verl. Berlin 1967
- [24] A.P. Kreshkov, A.A. Yaroslavtsev, *Chemistry of Quantitative Analysis*, p.51, 332, Editorial Moscow 1985
- [25] S.V. Svechnikov, in *Optoelectronics Materials and Devices* (ed. M.A. Herman), 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 Angel, C. Vazquez López, A. Morales Acevedo, J.G. Vázquez Luna: Thin Solid Films 322 (1998) 329
- [28] R. Szargan, R. Meisel, Wiss. Zs. KMU Leipzig, Mathem. Naturwiss. R. 20 41 (1971)
- [29] M. Dorst, Ph.D. Thesis KMU Leipzig, Germ. 1964
- [30] C.W. Wu, D.C. Houghton, Mat. Res. Soc. Symp. Proc. 281 (1992) 57
- [31] R. Ramírez-Bon, N.C. Sandoval-Inda, F.J. Espinoza-Beltrán, M. Sotelo-Lerma, O. Zelaya-Angel, C. Falcony, J. Phys: Condens. Matter 9 (1997) 10051
- [32] T. Nakanishi, K. Ito, Sol. Energy. Mat. and Sol. Cells. 35 (1994) 171
- [33] L. Lind, R. Bube, J. Chem. Phys. 37 (1962) 2499
- [34] J. Vazquez, A. Zehe, and O. Zelaya, Cryst. Res. Technol. 34 (1999) 949
- [35] J. Pankove, *Optical processes in semiconductors*, Prentice Hall 1971
- [36] A. Zehe, *Herramientas Analíticas de Interfases Sólidas*, ISBN 3-8311-3262-3, Editorial LIBRIS, Norderstedt 2002

