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Physical properties of ZnS thin layer

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Abstract: ZnS/glass thin layer in high vacuum condition and vertical Deposition angle has been produced by resistance evaporated method with 30 nm thickness. Deposition temperature for ZnS layer was about 100°c. The Atomic Force Microscopy (AFM), optical Spectroscopy and XRD analyses are perfectly accomplished for this layer.

Key words: *AFM; XRD; Spectrophotometer; Nanostructure*

1. Introduction

Nano structured materials have attracted a great deal of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. An extremely active and prolific field in Nano materials is finding ways to control size and morphology of the Nano particles since the properties and applications of the nanoparticles are largely dependent on their size and morphology (Rossetti et al., 1984). Such properties make semiconducting nanostructures suitable for several kinds of applications, from anti reflecting coatings (Park et al., 2004) to bioelectronics (Katz and Willner, 2004) and light emitting devices (Colvin et al., 1994). In the past decade, II-VI semiconductor Nano particles attract much attention because of their size-dependent (and thus tunable) photo- and electro- luminescence properties and promising applications in optoelectronics. Among the family of II–VI semiconductors, ZnS (Dinsmore et al., 1999; Maity, Chattopadhyay, 2004), CdS (Tittel et al., 1997), ZnO (Mahamuni et al., 1999), CdTe (Rogach, 2000), etc. are the foremost candidates because of their favorable electronic and Optical properties for optoelectronic applications. Among those ZnS is a commercially important II–VI semiconductor having a wide optical band gap, rendering it a very attractive material for optical application especially in Nano crystalline form (Ghrayeb et al., 1997; Barton and Ranby , 1977).Amongst other II-VI bulk semiconductors, ZnS shows eminent prospects and opportunities for new applications in a wide variety of areas due to its direct wide band gap (3.71 eV at room temperature) with a large free exciton binding energy (~40 meV) and a small excitonic Bohr radius of ~2.5 nm (Sarkar et al., 2008; Ganeev ,2005; Brus, 1991). The aim of this work is to produce ZnS thin layers and investigate about its physical properties.

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2. Mathematical Formula

2.1. Surface structure and energetic

The surface formation energy υ_i (for a surface in orientation i), can be defined in terms of $\mu_{ZnS,\text{bulk}}$, the chemical potential of bulk ZnS (in the ZB structure) as follows:

$$\upsilon_i = \frac{1}{2A_i}\left[E_i(N_{ZnS}) - N_{ZnS}\,\mu_{ZnS,\text{bulk}} + p\Delta v - T\Delta S\right] \qquad (1)$$

where E_i (N_{ZnS}) is the total energy of a fully relaxed surface slab in orientation i (containing N_{ZnS} formula units), A_i is the explicit area of the supercell in the plane of the surface, Δv is the volume change due to surface relaxation, and ΔS is entropy change which is normally dominated by the vibrational entropy from phonons. In general $-T\Delta S$ lowers the surface free energies as T increases, but changes in the relative ordering are not expected, especially at temperatures far below the melting point.

2.2. Thermodynamics and Nano morphology

Modeling of the three dimensional polyhedral has been achieved using a shape-dependent thermodynamic model based on a geometric summation of the Gibbs free energy. A truncated version of the model has been used here, that is applicable specifically to isolated, defect-free structures in the range ~3 to 100 nm, as described in ref.[14]. In this version the total free energy G is described in terms of the specific surface free energies υ_i, for facets i, weighted by the factors f_i (such that $\sum_i f_i = 1$):

$$G = \Delta G_f + \frac{M}{\rho}\left(1 - 2\frac{\sum_i f_i \sigma_i}{B_0 \langle R \rangle} + \frac{p_{ex}}{B_0}\right) q \sum_i f \upsilon_i \qquad (2)$$

where ΔG_f is the standard bulk free energy of formation, M is the molar mass, ρ is the density, q is

the surface-to-volume ratio, $< R >$is the average particle radius (based on a spherical approximation) and the volume dilation induced by the isotropic surface stresses σ_i and external pressure P_{ex} is included using the Laplace– Young formalism. In all cases we have assumed atmospheric external pressure, and have used the lattice parameter of 5.443°A and bulk modulus B_0 = 69.9 GPa (calculated using the same method as above) which have been shown to be in good agreement with the corresponding experimental values. The bulk modulus for amorphous ZnS was also calculated to be 24.3 GPa. It is important to point out that these quantities were calculated at zero temperature.

2.3. Formation of thin layer and formulas

Individual atoms are evaporated by source with a rate R reaches the substrate surface this is expressed by the following formula

$$R = C.P/(2\pi MK_B.T_Q)^{\frac{1}{2}} \quad (3)$$

Where P Vapor pressure, M the molecular mass, C is a geometrical factor, K_B Boltzmann constant And T_Q is the temperature of the source. After sitting on the surface atoms due to thermal energy will begin to spread over the surface The relationship between the average square spread in time is obtained from the following equation

$$\left\langle X^2 \right\rangle = 2D.t \quad (4)$$

In this equation $< x^2 >$ the average square distance between the atoms at the surface is t And D is the distribution coefficient, This distance is dependent on the energy and temperature so that the Distribution coefficient increases with increasing temperature This increase is in accordance with the following formula:

$$D = D_0 \exp\left[\frac{-Ed}{k_B.T_s}\right] \quad (5)$$

$$D_0 = a_0^2.V_D \quad (6)$$

In equation (6) γ_d is the oscillation frequency of atoms on the surface. In equation 5 E_d is the activation energy, a_0 is the distance of a jump and T_s is the substrate temperature. After an average time Z_A Atoms are attracted to surface the vacuum may be back again The relativity of time is equal to

$$Z_A = \frac{1}{r_d}\exp\left[\frac{E_a}{K_B.T_S}\right] \quad (7)$$

Here γ_a is the oscillation frequency of the atoms are attracted to surface, and E_a The adsorption energy. Re-evaporation rate can be expressed by the following formula.

$$R_{des} = n_1.\gamma_a \exp\left(\frac{-E_a}{K_B.T_S}\right) = \frac{n_1}{Z_A} \quad (8)$$

Among the sticking coefficient is used to describe the thin film growth, Absorption rate is defined as the ratio of the collision rate. Viscosity coefficient is expressed as follows; coefficient indicates that surface probability of joining the nuclear deal.

$$\beta(t) = \frac{R - R_{des}^{(t)}}{R} = 1 - \frac{n_1(t)}{R.Z_A} \quad (9)$$

Adhesion coefficient is the integral average and is defined as follows.

$$\propto (t) = \frac{1}{T}\int \beta(t).dt \quad (10)$$

Under certain conditions, the balance between absorption and evaporation occurs in a short and alternating time where the collision rate remains constant when n_1 is equal to a constant value.

$$\frac{dn_1}{dt} = R - \frac{n_1}{Z_A} = 0 \rightarrow n_1 = R.Z_A \quad (11)$$

3. Experimental work

Substrate was made from glass (laboratory smear) in (2.54 * 7.62) mm and thickness of (1-1.2) mm. substrate has been cleaned by ultra-sonic bath for 15 minutes in pure acetone and then 15 minutes in absolute alcohol. Supported Rotary pump used for vacuum up to 10^{-3}tor then with main pump reached to 10^{-6}tor. Layer deposition angle was optimized and vertical. Distance between boats to substrate was about 45 cm and the diameter of supported substrate was 50 cm. I used molybdenum both for evaporating ZnS powder. ZnS powder was in white color. Deposition temperature for Zns thin layer was 100 degree Celsius. Thickness of Zns was about 30 nm.

4. Result and discussion

The Atomic Force Microscopy (AFM), Spectrophotometer and XRD analyses are perfectly accomplished for this layer and the results are mentioned in detail.

Fig. 1 shows the microscopic image of two dimension (2D) atomic force and Fig. 2 shows the microscopic image of three dimension (3D) atomic force of Zns/glass thin layer.

Fig. 1 and Fig. 2 have been taken by $2.44\mu m \times 2.44\mu m$ magnifications. Surface appears as chain of hills with black holes (circle and polygon) between them. Indelicacy average of this surface was determined 2.47 nm. Deposition temperature for ZnS

sample is about 100˚c. The thickness of ZnS layer at 100°c is 30 nm.

Fig. 3 shows the microscopic image of atomic force at 0.53 µm × 0.53 µm magnifications for ZnS made for this project. The median curve measuring for surface was 2.24 nm, surface appear as chain of hills with holes between them It is obvious when magnification of the surface get deeper connection of points and their relation with holes get clearer.

Fig. 4 shows the size of the points of these dots with red, blue and green arrows. Fig 5 show the profiles of these three points, red point has maximum thickness of 6.2 nm, blue point with maximum 5 nm and green point with maximum 5.3 nm heights.

Fig. 6 shows the X ray diffraction for ZnS/glass thin layer. In general, the typical is amorphous (without form). In addition, in some area peaks are more obvious which show the start of crystallisation due to ZnS grains. By increasing the thickness of this layer alongside with heat treatment, we can get better crystallization.

Fig. 7 shows the transmittance of ZnS thin layer with a thickness of 30 nm. Transmittance for Zns is about 69%. This is due to the porous structure that was clearly observed from AFM images

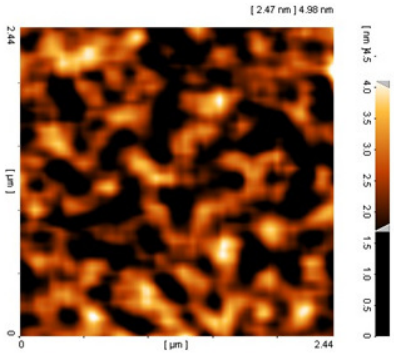

Fig. 1: two dimension (2D) AFM images of ZnS/ glass thin layer

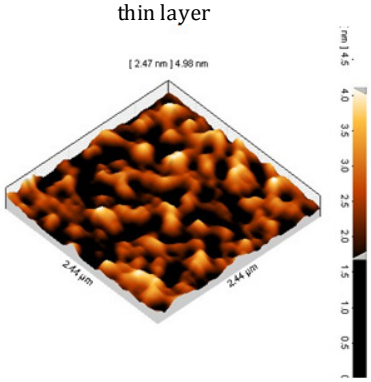

Fig 2: three dimension (3D) AFM images of ZnS/glass thin layer

5. Conclusions

ZnS on glass semiconductors were produced by resistant evaporated method of 30 Nano meter thickness at 100˚C Temperature under HV conditions. Its physical properties such as atomic force microscopy, X ray diffraction, grain height, and transmittance were determined. ZnS thin layer had porous structure with high transmittance and amorphous structure.

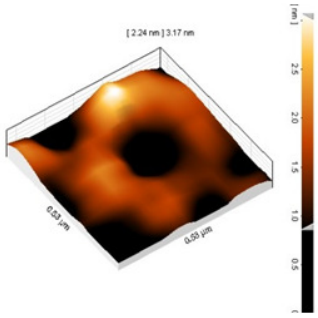

Fig. 3: three dimension (3D) AFM images of ZnS/glass thin layer

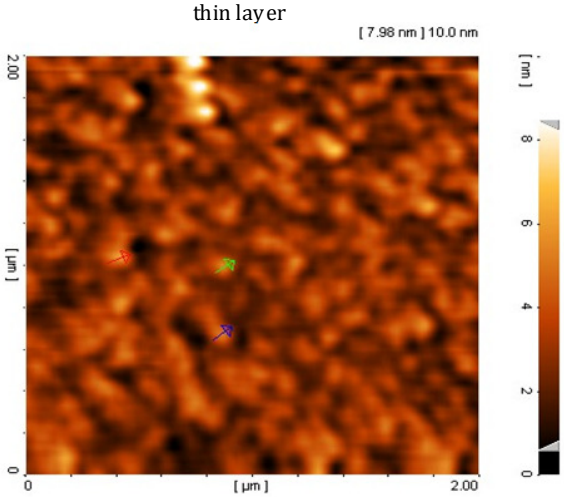

Fig. 4: two dimension (2D) AFM images of ZnS/ glass thin layer

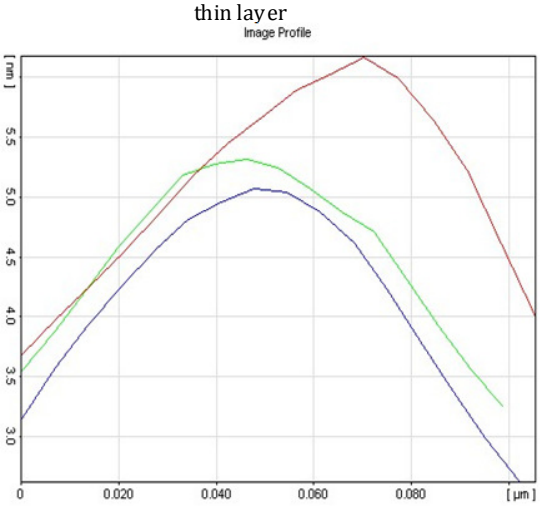

Fig. 5: Image profile of the ZnS/ glass thin layer

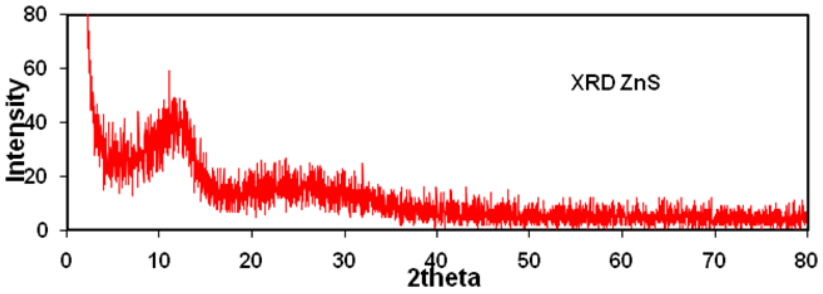

Fig.6: x-ray diffraction diagram

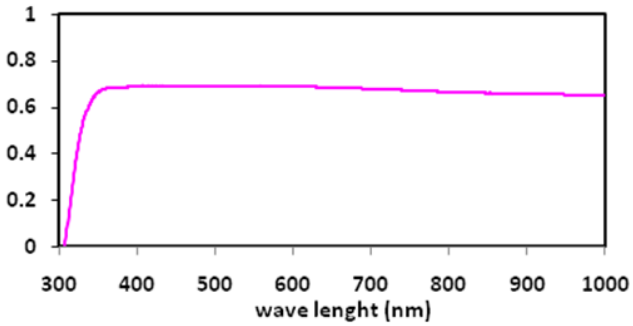

Fig. 7: Transmittance diagram of ZnS/glass thin layer.

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