

Production and investigation about nano structures of heterogeneous ZnS/glass thin layer

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Abstract

ZnS/glass Thinlayer in high vacuum condition and 40 degree Deposition angle has been produced by resistance evaporated method with 28 nm thickness. cabin deposition temperature ZnS layer was about 50C and substrates were kept at room temperature. The Atomic Force Microscopy (AFM) and XRD analyses are perfectly accomplished for this layer.

Keywords : AFM; XRD; nanostructure.

1 Introduction

Nanostructured materials are a new class of materials, having dimensions in the 1-100 nm range, which provide one of the greatest potentials for improving performance and extended capabilities of products in a number of industrial sectors [1]. ZnS is an n-type II-VI compound with a wide band gap (3.5-3.7 eV) at room temperature [2] which is the highest value among all II-VI-based semi-conductors [3]. It has long been recognized that crystals having the wurtzite or sphalerite (zinc blende) structures are fundamentally similar despite differences between the two structures. zinc blende crystals are fcc with two atoms per primitive cell, whereas wurtzite crystals are hexagonal with four atoms per cell. The compound ZnS can crystallize in either form [4]. a cubic form (c-ZnS) with sphalerite structure and a hexagonal form (h-ZnS) with wurtzite structure [5]. It is an excellent host material for electroluminescent phosphors and is being commer-

cially used for heterojunction devices, and thin-film electroluminescent displays [6, 7]. Clean ZnS film has received great attention in recent years in the optoelectronic application, and is one of the most important materials in photonics research [8]. ZnS thin films have been prepared by a variety of techniques such as sputtering [9] spray pyrolysis [10] and Chemical deposition technique [11, 12, 13]. Depending on the process conditions, heterogeneous and or homogeneous reactions can take place [14]. The aim of this work is to produce ZnS heterogeneous nanolayers and investigate about its physical properties.

2 Mathematics Formula

2.1 Surface structure and energetic

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

$$v_i = 1/(2 * A_i)[E_i(N_{ZnS}) - N_{ZnS}\mu(ZnS, bulk) + p\Delta v - T\Delta s] \quad (2.1)$$

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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 super cell 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 [14, 15]. 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 v_i , for facets i , weighted by the factors f_i (such that $\sum_i f_i = 1$):

$$G = \Delta G_f + M/\rho(1 - 2\sum_i f_i \sigma_i / (B_0 \langle R \rangle)) \quad (2.2)$$

$$+ p_{ex}/B_0 + q\sum_i f_i v_i$$

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, $\langle R \rangle$ is the average particle radius (based on a spherical approximation) [14] and the volume dilation induced by the isotropic surface stresses and external pressure P_{ex} is included using the Laplace- Young formalism, as defined in ref [14]. In all cases we have assumed atmospheric external pressure, and have used the lattice parameter of 5.443 Å and bulk modulus $B_0 = 69.9$ GPa (calculated using the same method as above [16]) which have been shown to be in good agreement with the corresponding experimental values. [16] 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 to substrate surface, This is expressed by the following formula:

$$R = C.P/(2\pi M K_B T_Q)^{1/2} \quad (2.3)$$

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

$$\langle X \rangle^2 = 2Dt \quad (2.4)$$

In this equation $\langle X \rangle^2$ is the average square distance between the atoms at the surface at time t and D is the distribution coefficient, This distance is dependent on the energy and temperature so that the Distribution coefficient increases by increasing temperature, This increase is in accordance with the following formula:

$$D = D_0 \exp[-E_d/(K_B T_s)] \quad (2.5)$$

and

$$D_0 = a_0^2 \nu_d \quad (2.6)$$

In equation 6 ν_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 substrate temperature. After an average time Z_A Atoms are attracted to the surface and adsorption happens. The relativity of time is equal to:

$$Z_A = (1/\nu_a) * \exp[E_a/K_B.T_s] \quad (2.7)$$

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

$$R_{des} = n_1 \cdot \nu_a \exp(-E_a/K_B.T_s) = n_1/Z_a \quad (2.8)$$

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.

$$\beta(t) = (R - R_{des}(t)) / R = 1 - n_1(t) / (R \cdot Z_a) \quad (2.9)$$

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

$$\alpha(t) = 1/T \int \beta(t) \cdot dt \quad (2.10)$$

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.

$$dn_1/dt = R - N_1/Z_A = 0 \implies n_1 = R \cdot Z_A \quad (2.11)$$

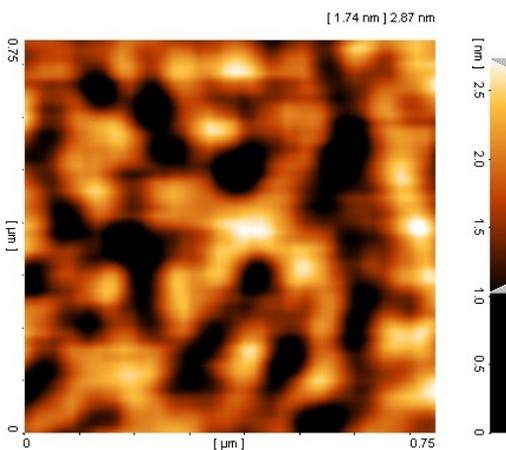


Figure 1

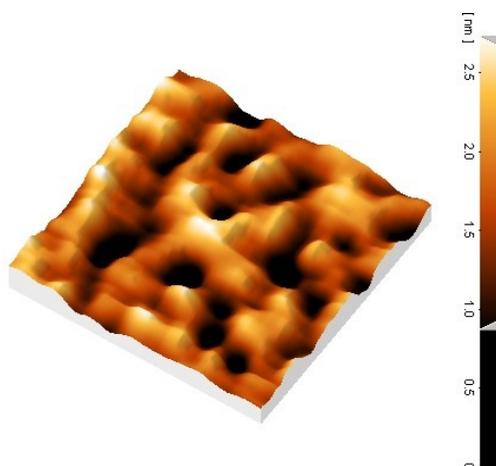


Figure 2

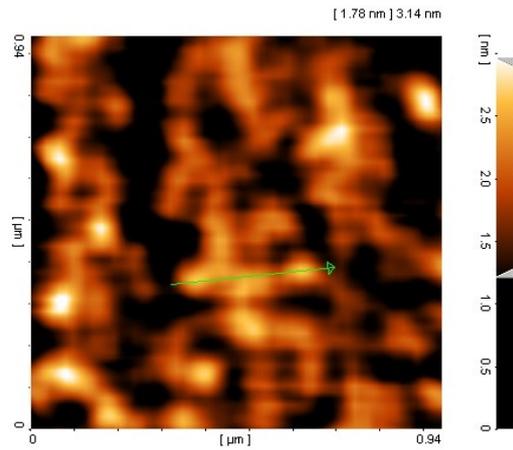


Figure 3

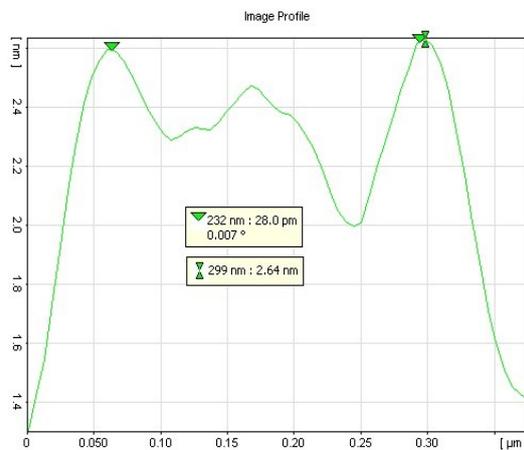


Figure 4

3 Experimental Details

Zinc sulfide nano layers were prepared on glass substrates ($1 * 20 * 20mm^3$) using an ETS 160 system with a pressure of 10^{-6} mbar. The layers were obtained in the conditions of high vacuum, using an thermal evaporation method. The deposition rate used by us was 1 A/s. The purity of zinc sulfide powder was about 97. Prior to the deposition process, the substrates were cleaned with an ultrasonic-bath technique. The temperature of the substrates was kept constant ($300K$). The thickness of the layers were about 28 nm. Deposition angle of the layers were 40 degrees that cause to produce heterogeneous layers

4 Results and Discussion

The Atomic Force Microscopy AFM and XRD analyses are perfectly accomplished for heterogeneous ZnS nanolayer and the results are men-

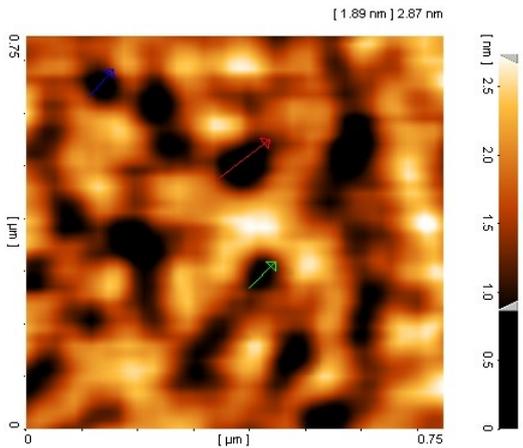


Figure 5

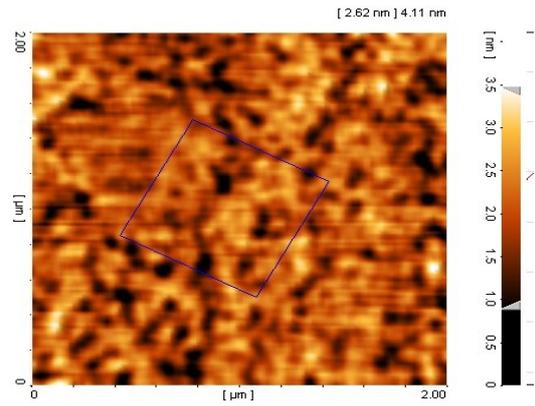


Figure 7

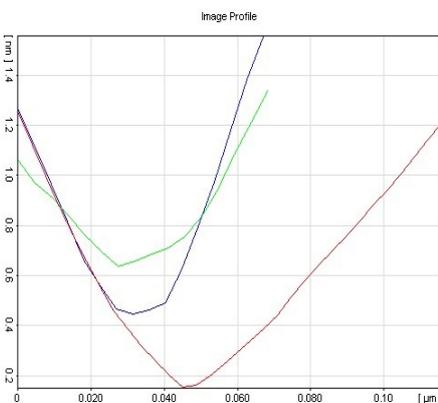


Figure 6

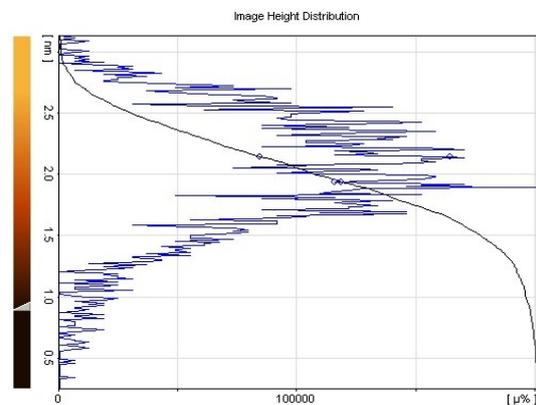


Figure 8

tioned in detail. Figure 1 shows the microscopic image of two dimension (2D) atomic force and Figure 2 show the microscopic image of three dimension (3D) atomic force of heterogeneous ZnS/glass nanolayer. Figures 1 and 2 have been taken by magnifications. surface appear as chain of hills with black holes (circle and polygon) between them. average roughness of this surface was determined 1.74 nm. The thickness of ZnS layer at room temperature is about 28 nm. Figure 3 show two dimensional atomic force microscopy image at $0.94 \mu\text{m} * 0.94 \mu\text{m}$ magnifications for heterogeneous ZnS on glass along with identified clusters. The surface appear as chain of hills with clear holes between them. Figure 4 shows image profile of identified clusters on figure 3. As it can be seen cluster is made of three clear grains and average height of grains are about 2.56 nm with about 0.35 micro meter length. Figure 5 shows two dimensional AFM image of heterogeneous ZnS nano layer taken by $0.75 \mu\text{m} * 0.75 \mu\text{m}$ mag-

nifications with identified holes on layer. Figure 6 shows image profile of holes with average depth of 0.38 nm clearly. Figure 7 shows two dimension (2D) AFM images of heterogeneous ZnS/glass nano layer with identified area. The porous structure of zinc sulfide nano layer is clearly observed from AFM images. Figure 8 shows image height distribution of identified area in figure 7. Image height distribution is following Gaussian function. Figure 9 shows X ray diffraction for ZnS/glass thin layer. ZnS nano layer produced at room temperature is amorphous. By increasing thickness of this layer alongside with heat treatment, we can get crystallized structure. XRD pattern is noisy and there is a wide peak at 20 up to 30 degree that depends on amorphous glass substrate.

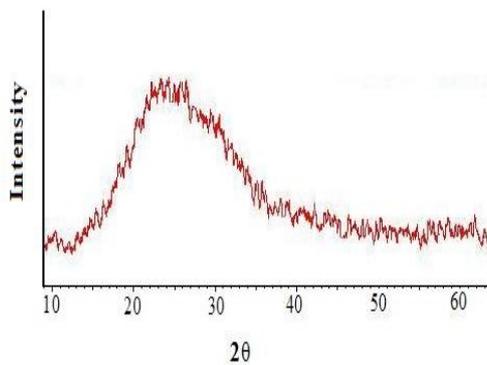


Figure 9

5 Conclusion

ZnS on glass semiconductors were produced by resistant evaporated method of 28 nano meter thickness at 50C Cabin and 28C substrate Temperature under HV conditions. Its physical properties such as atomic force microscopy and X ray diffraction, Grain and cluster height, hole depth and height distribution were determined. ZnS nanolayer had porous and amorphous structure.

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