Morphology and Growth Behavior of O₂-free Chemical Bath Deposited ZnS Thin Films

Jet Meitzner^a, Brock M. Tillotson^a, Amanda T. Siedschlag^a, Frederick G. Moore^b, Stephen D.

Kevan^{a,1}, and Geraldine L. Richmond^{a,*},

^aDepartment of Chemistry, University of Oregon, Eugene, Oregon, 97403, USA

^bDepartment of Physics, Whitman College, Walla Walla, Washington 99362, USA

We investigate the role of reagent concentrations and ambient O₂ on the morphology and growth behavior of ZnS thin films grown with the chemical bath deposition method. We investigate the role of substrate on film morphology, and find significant differences between films deposited on SiO₂ versus Si. The films are also sensitive to dissolved O₂ in the bath, as it causes a layer of SiO₂ to form at the ZnS/Si interface during deposition. Degassing of solutions and an N₂ atmosphere are effective to minimize this oxidation, allowing deposition of ZnS films directly onto Si. Under these conditions, we examine film properties as they relate to reagent bath concentrations. As the reagent concentrations are decreased, both the film roughness and growth rate decrease linearly. We also observe deformation

¹Present Address: Stephen D. Kevan: Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, MS6R2100, Berkeley, CA 94720

*Corresponding Author:

Electronic mail: richmond@uoregon.edu

Tel: 541-346-4635

Address: 1253 University of Oregon
Attn: Geraldine Richmond
Eugene, OR, 97403-1253

and shifting of x-ray diffraction peaks that increases with decreasing reagent concentrations. The shifts are characteristic of lattice compression (caused by the substitution of oxygen for sulfur), and the deformation is characteristic of distortion of the lattice near crystal grain interfaces (caused by tensile stress from interatomic forces between neighboring crystal grains). At the weakest concentrations, the low roughness suggests a mixed growth mode in which both clusters and individual ZnS nanocrystallites contribute to film growth. With increasing reagent concentrations, the growth mode shifts and becomes dominated by deposition of clusters.

1. Introduction

Due to their many applications in photovoltaics [1], optical coatings [2], and photo- and electro-luminescent devices [3, 4], ZnS thin films have been fabricated by many methods, including both vapor phase and solution-based techniques. Chemical bath deposition (CBD) is solution-based and can coat large surface areas with uniform, optically smooth thin films via the controlled reaction of precursors in a solution that contains a substrate [5]. Moreover, CBD occurs at atmospheric pressure and near room temperature, thus offering economic and ecological advantages over vapor phase techniques, which are more energy intensive.

The performance of CBD ZnS thin films depends predominantly on their morphological properties (e.g. crystallinity, texture, thickness, uniformity), which are challenging to control due to competing precipitation reactions in the bulk solution (homogeneous) and on the substrate surface (heterogeneous). These two precipitation reactions give rise to the two growth mechanisms commonly reported for CBD: cluster-by-cluster and ion-by-ion growth, respectively. In practice both mechanisms occur simultaneously, leading to compact films containing embedded colloidal particles [6]. Controlling which growth mechanism dominates

(by altering growth parameters) is of primary interest, as it determines the morphological properties of films.

The growth of ZnS films by CBD is generally considered to proceed by the cluster-by-cluster mechanism, with colloidal ZnS aggregating both in solution and on the substrate [7-9]. Isolated ZnS nuclei (nanocrystallites) and aggregates of these nanocrystallites (clusters) both contribute to film growth. This mechanism was thoroughly reviewed and demonstrated by Bogush and Zukoski [10, 11] for the synthesis of silica particles, and has since been observed in the synthesis of ZnS powders and films [7, 8]. Though less common, there are also reports of ion-by-ion growth of ZnS films, which occurs upon direct interaction between surface sites and precursor species (containing Zn^{2+} and S^{2-}) [12, 13].

In this work we investigate the role of reagent bath concentrations on the growth behavior and resulting morphology of ZnS thin films deposited on Si substrates in an O_2 -free environment. Our results show that the primary building blocks of the films are nanocrystallites at low reagent concentrations and clusters at higher concentrations. We further document that this change in growth behavior is accompanied by changes in film morphology (roughness, thickness, uniformity), composition (Zn:S ratio), and grain interface stress. Finally, a comparison is made between ZnS cluster size in solution versus within the film, and the role of dissolved O_2 on oxidation of the silicon substrate is demonstrated.

2. Experimental Details

Thin film depositions utilizing microwave heating were performed using chemical bath compositions adapted from the work by Nabiyouni et al. [5]. The bath contained a mixture of zinc acetate dihydrate (ZnAc), ethylenediamine (En), and thioacetamide (TAA) with the molar ratios 1:2:4, respectively. Each chemical bath maintained this molar ratio of reagents, while

the absolute concentrations were varied. The highest bath concentration used was 0.042 M ZnAc, 0.084 M En, and 0.168 M TAA, and samples grown in this concentration were denoted type -1-. Samples deposited with concentrations reduced by two (0.021 M ZnAc, 0.042 M En, and 0.084 M TAA) were denoted type -1/2-, and so on. All depositions were performed at 80°C with stirring.

Prior to deposition, all solutions were degassed using the freeze-pump-thaw method. In order to prevent ZnS precipitation prior to film deposition, two solutions were prepared and degassed separately; one solution contained ZnAc and En, while the other contained TAA. Following degassing, the solutions were transferred to a glovebox with N₂ atmosphere. Degassed solutions and N₂ environments were used in order to minimize oxidation of the Si substrate surfaces. Indeed, the crystalline Si surfaces remained mostly un-oxidized throughout film deposition, as verified by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and transmission electron microscopy (TEM).

The substrates utilized in this study were double-side polished <111> Si wafers (1 x 1.5 cm) of high purity (undoped, R > 15000 Ωcm). The wafers were subjected to the RCA standard clean [14] followed by etching in buffered oxide etch (BOE, 20:1) for 2 minutes, and finally oxidation in a tube furnace to grow a thermal oxide of approximately 100 nm. They were then transferred to a glovebox for further preparation in a N₂ atmosphere.

Immediately prior to deposition, the Si wafers were etched again in BOE, for 24 minutes, to remove the surface oxide layer. They were then placed in a 5 mL glass vial containing the ZnAc/En solution and stir bar. After adding the TAA solution, the vial was capped and transferred to the microwave heating apparatus. Each deposition consisted of 2 hours heating time. In order to increase the thickness of the films, subsequent depositions were performed using fresh chemical bath solutions.

Zinc acetate dihydrate (J.T. Baker, A.C.S. reagent grade), ethylenediamine (Fluka, puriss. grade), and thioacetamide (Sigma-Aldrich, reagent grade) were used as received. Reaction baths were heated using a Personal Chemistry Emrys Creator microwave with a maximum heating power of 90 W. Samples were imaged using a ZEISS Ultra-55 scanning electron microscope (SEM) with 5 kV accelerating voltage. Imaging and roughness analysis were performed using atomic force microscopy (AFM; Digital Instruments Veeco Multimode with IIIa controller) in tapping mode. Elemental analyses were performed using a Cameca SX100 electron microprobe and an ION-TOF Model IV ToF-SIMS in depth profiling mode. For depth profiles, a Cs^+ sputter source (1 kV, 65 nA) was rastered over a $320\text{ }\mu\text{m} \times 320\text{ }\mu\text{m}$ area to create the sputter crater. Mass spectra were acquired from a $90\text{ }\mu\text{m} \times 90\text{ }\mu\text{m}$ area in the center of the sputter crater using a Bi^{3+} primary ion beam (25 kV, 0.3 pA). Both ion sources were operated at 10 kHz. A Titan 80-300 microscope operated at 300 kV was used for TEM cross section imaging. X-ray diffraction (XRD) measurements were performed in grazing incidence geometry using a Philips PANalytical X'Pert diffractometer with $\text{CuK}\alpha$ ($1.54\text{ }\text{\AA}$) radiation. We have estimated the deformation of grazing incidence x-ray diffraction (GI-XRD) peaks by fitting the (111) diffraction peak to the sum of 3 Gaussian curves, and comparing the integrated area under each curve. This provides only an estimate of the magnitude of peak deformation. Colloidal ZnS particle sizes were determined by dynamic light scattering (DLS) measurements using a Malvern Zetasizer Nano ZS.

3. Results and Discussion

3.1. O_2 -free Film Depositions

All film depositions in this work were performed with degassed solutions and under N_2 atmosphere (henceforth called 'air-free/degassed' conditions) to minimize oxidation of the

silicon substrate. To investigate the effect that O_2 (dissolved in the chemical bath) has on the resulting ZnS films, we employ ToF-SIMS, TEM, and AFM. First, we investigate the composition of the ZnS/Si interface for films deposited in the air-free/degassed case as well as under standard atmospheric conditions. Using ToF-SIMS we have obtained an elemental analysis through the depth of each sample, and observe a reduction in ZnS/Si interfacial oxygen by a factor of 19 for the air-free/degassed case compared to the film deposited under atmospheric conditions (Fig. 1). The quantity of SiO_2 remaining in the air-free/degassed case is observed in TEM cross sections of these films which show a thin, 1-2nm SiO_2 layer between the silicon substrate and ZnS film in some areas, while in other areas little to no oxide is visible (Fig. 2). Finally, we have deposited ZnS films under air-free/degassed conditions on both Si and SiO_2 substrates. As shown in Fig. 4 and discussed in detail in Section 3.2, there are significant differences due to the change in substrate composition.

Because the aqueous oxidation of silicon is catalyzed by dissolved O_2 [15], we expect that our N_2 atmosphere was contaminated with O_2 , and that superior minimization of oxidation is possible. This could be important for the fabrication of devices utilizing the ZnS/Si heterointerface, or of films that utilize the ZnS-Si lattice matching to achieve desired characteristics.

3.2. Structural Characteristics and Elemental Analysis

We have used GI-XRD to evaluate the structural characteristics of the ZnS thin films. Fig. 3 shows the GI-XRD patterns for ZnS films deposited with different reagent concentrations. In each spectrum, three peaks are evident at 2θ values of approximately 28.6, 47.5, and 56.3 corresponding to the (111), (220), and (311) planes, respectively, of the cubic form of ZnS [16].

Two trends emerge as we lower the reagent bath concentrations (trace (a) $\rightarrow$ trace (f)): each peak shifts to higher values of 2θ , and also becomes irregularly shaped with increased intensity on the low-angle side of the peak (most obvious with the (111) peak). The shift in peak positions is caused by a compression of the crystal lattice, which can be explained by the partial substitution of oxygen for sulfur in the ZnS crystals [17]. Since O has a smaller van der Waals radius than S (152 pm vs 180 pm) [18], this substitution causes a contraction of the crystal lattice, and an increase of the diffraction angle 2θ toward the value of 56.8 that would be observed for pure cubic ZnO. In order to determine elemental composition we have performed electron probe micro-analysis on each ZnS film, and summarize the results in Table 1. An increase in oxygen:sulfur and zinc:sulfur ratios with decreasing reagent concentrations is observed and consistent with this explanation. Assuming Vegard's law, which finds a linear relationship between lattice parameters and composition [19], these findings account for the observed magnitudes of GI-XRD peak shifts.

The irregular peak shapes are characteristic of a deformation of the lattice near ZnS crystal grain interfaces. Atoms near grain interfaces experience a highly asymmetrical stress field relative to those in the core of the grain, and therefore we expect their spacing to be different as well. When the number of these interface atoms is comparable to the number of atoms in the core, their altered lattice spacing can affect the shape of XRD peaks [20]. In the present case, GI-XRD intensity is shifted to lower 2θ , relative to the center of the peak, indicating that the lattice near grain interfaces is expanded (tensile strain). We have estimated the magnitude of the shifted peak intensity, relative to the main peak intensity, for each film (Table 1, 'Fractional Peak Shift').

Since peak deformation is enhanced as we lower reagent bath concentrations, we would expect a concurrent decrease in grain size due to the changing volume/surface ratio.

1 However, the grain size within each film has been estimated using the Debye-Scherrer
2 formula [21] and the properties of the 220 diffraction peak, revealing that grain size is
3 relatively constant, within the range 3.8 - 4.5 nm, for each film (Table 1). Instead, the
4 variation in grain interface stress is related to the film morphology and composition, as
5 discussed below. There is also some GI-XRD intensity shifted to higher 2θ , however the
6 integrated magnitude is small and fluctuates randomly. Thus, we refer the reader to previous
7 reports of compressive stress in ZnS thin films [22, 23], and do not discuss it further.

8 We have observed that the identity of the substrate influences the morphological
9 properties of ZnS films. Thus, we deposited a film on oxidized Si (SiO_2) using bath conditions
10 identical to those used for a deposition on plain Si. This allowed us to observe a change in
11 film morphology that was not due to different bath conditions (Fig. 4). In the GI-XRD trace for
12 the film deposited on SiO_2 (Fig. 3.g), we observe that the peak shift and deformation are
13 similar to the film deposited on Si (Fig. 3.f). On the other hand, the film roughness and
14 growth rate vary significantly from the film deposited on plain Si (Figs. 4 and 6). This indicates
15 that the lattice strain is a result of either the change in reagent bath concentrations, or a
16 change in morphology besides roughness. The following explanation suggests that both
17 factors need to be considered.

18 According to a grain boundary model developed by Doljack [24] and extended to ZnS films
19 [22], the close proximity of crystallite grains in a film results in tensile stress due to attractive
20 interatomic forces between grains. Moreover, this effect is enhanced by the incorporation of
21 oxygen impurities due to the smaller space requirement of O relative to S. It follows that the
22 magnitude of stress depends on the inter-grain distance, and therefore on cluster size. By
23 examining SEM images of each film (discussed in section 3.2), we have estimated the cluster
24 size in each film (Table 1). We see that the peak deformation for the film deposited on SiO_2 is

greater than for films with smaller cluster sizes, and similar to the films with coalesced clusters (infinite cluster size). Based on this we conclude that grains residing in the interior of a cluster or continuous film experience tensile stress due to close proximity with neighboring grains, whereas grains residing on the interface of a cluster do so to a lesser extent.

Due to the high oxygen content in the underlying SiO_2 layer, we could not measure the oxygen content in the film deposited on SiO_2 . However, we note that the Zn:S ratio is similar to that of the film deposited on plain Si, suggesting a similar oxygen content as well.

3.3. Morphology and Growth Behavior

We have used SEM to investigate the morphology and growth rate of ZnS films via surface and cross-sectional images. Fig. 5 shows SEM surface and cross sectional images for samples -1/2- and -1/32-. For brevity we show images for only these two representative films, as the images for -1- and -1/4- are similar to the images for -1/2-, and the images for -1/8- and -1/16- are similar to the images for -1/32-. For each film, we have imaged the surface after 2 hours of growth and again once the film has reached its final thickness (≥ 40 nm, Table 1). Fig. 5.a (sample -1/2-) shows a continuous film (full surface coverage) composed of 30-40 nm clusters after two hours, and little change in appearance with further growth time (Fig. 5.b). From the cross-sectional image (Fig. 5.c), the film appears granular with non-uniform thickness. In contrast, Fig. 5.d (sample -1/32-) shows a non-continuous layer of 15-25 nm clusters after two hours. With additional growth time, surface coverage increases and the clusters appear to grow together, producing the smooth yet somewhat granular surface morphology shown in Fig. 5.e. From the cross-sectional image (Fig. 5.f), the film appears homogeneous with uniform thickness.

Thickness values for each film have been estimated from the SEM cross-section images and used to calculate growth rates, which are plotted in Fig. 6. Also plotted is film roughness, as determined by AFM, which follows the same trend: increasing linearly with reagent bath concentrations. The most striking result is the low roughness observed for films deposited at the lowest reagent bath concentration. Examining film -1/32-, we observe that growth begins with ~20 nm particles dispersed across the Si surface (Fig. 5.d). If the final film consisted of these 20 nm (spherical) particles stacked side-by-side, to form the smoothest film possible, the RMS roughness would be 3.1 nm. If instead we consider the constituent particles to be 4.0 nm (and again spherical), which is the grain size determined by GI-XRD, we calculate an RMS roughness of 0.63 nm, which is slightly below the actual value of 1.3 nm. These calculations suggest that at low bath reagent concentrations we have a mixed growth mode, in which both clusters and individual ZnS nanocrystallites contribute to film growth. At higher reagent bath concentrations, however, the high roughness and granular appearance suggest film formation predominantly from clusters of nanocrystallites that have aggregated in solution before attaching to the substrate.

3.4. Comparison with Homogeneous Precipitation

We have used DLS to investigate the size of colloidal particles in each chemical bath after 2 hours of film deposition. The results, summarized in Table 2, indicate an enhanced degree of aggregation for higher reagent bath concentrations. For the concentrations $\geq 1/4$, we see particle sizes of 5-8 μm in solution, but these large particles were not observed in SEM imaging of the film surfaces. For relative concentrations $\leq 1/8$, we see smaller particle sizes of 0.4-1.5 μm in solution, which were observed in SEM imaging of the film surfaces. In every case, some 0.1 – 1.5 μm particles have adhered to the substrate surface, and sit atop the

compact film underneath. Thus, higher reagent bath concentrations result in larger colloidal particles, but the size adhered to film surfaces does not increase beyond about 1.5 μm . This is due to the decreasing surface energy with increasing particle size, which limits the size of particle that will attach to the film [25].

4. Conclusions

We have documented the changes in growth behavior, morphology, composition, and interface stress that result from changing reagent concentrations in the O_2 -free CBD of ZnS thin films. As reagent concentrations are changed, we observe a shift in growth behavior that accompanies changes in each of these film characteristics. This demonstrates a simple way of tuning these important film properties. We have also shown that O_2 dissolved in the chemical bath solution causes a layer of insulating SiO_2 to form at the ZnS/Si interface, which affects film growth rate and morphology. Degassing of the solutions and an N_2 environment is effective to minimize this oxidation; we observed a reduction in ZnS/Si interfacial oxygen by a factor of 19 for the air-free/degassed case compared to the film deposited under standard (atmospheric) conditions. Thus, control over O_2 content in the chemical bath environment is important not only for control over film properties, but also for the fabrication of devices utilizing the ZnS/Si interface.

Acknowledgements

The authors gratefully acknowledge the National Science Foundation (Award No. DMS-1035513) for support of this research.

References

- [1] S. W. Shin, S. R. Kang, K. V. Gurav, J. H. Yun, J.-H. Moon, J. Y. Lee, and J. H. Kim, A study on the improved growth rate and morphology of chemically deposited ZnS thin film buffer layer for thin film solar cells in acidic medium, *Sol. Energy*, 85 (2011) 2903.
- [2] I. Tapan, M. A. Ahmetoglu, and F. Kocak, A ZnS–Si isotype heterojunction avalanche photodiode structure for scintillation light detection, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 567 (2006) 268.
- [3] M. Bredol and J. Merikhi, ZnS precipitation: morphology control, *J. Mater. Sci.*, 33 (1998) 471.
- [4] R. Mach and G. O. Müller, ZnS:Mn in polycrystalline electroluminescence thin film display, *J. Cryst. Growth*, 86 (1990) 866.
- [5] G. Nabiyouni, R. Sahraei, M. Toghiani, M. H. M. Ara, and K. Hedayati, Preparation and characterization of nanostructured ZnS thin films grown on glass and n-type Si substrates using a new chemical bath deposition technique, *Rev. Adv. Mater. Sci.*, 27 (2011) 52.
- [6] P. O'brien and J. Mcaleese, Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS, *J. Mater. Chem.*, 8 (1998) 2309.
- [7] K. Yamaguchi, T. Yoshida, D. Lincot, and H. Minoura, Mechanistic Study of Chemical Deposition of ZnS Thin Films from Aqueous Solutions Containing Zinc Acetate and Thioacetamide by Comparison with Homogeneous Precipitation, *J. Phys. Chem. B*, 107 (2002) 387.
- [8] A. Eshuis, G. R. A. van Elderen, and C. A. J. Koning, A descriptive model for the homogeneous precipitation of zinc sulfide from acidic zinc salt solutions, *Colloids Surf. A*, 151 (1999) 505.
- [9] A. Goudarzi, G. M. Aval, R. Sahraei, and H. Ahmadpoor, Ammonia-free chemical bath

- deposition of nanocrystalline ZnS thin film buffer layer for solar cells, Thin Solid Films, 516 (2008) 4953.
- [10] G. H. Bogush and C. F. Zukoski Iv, Studies of the kinetics of the precipitation of uniform silica particles through the hydrolysis and condensation of silicon alkoxides, J. Colloid Interface Sci., 142 (1991) 1.
- [11] G. H. Bogush and C. F. Zukoski Iv, Uniform silica particle precipitation: An aggregative growth model, J. Colloid Interface Sci., 142 (1991) 19.
- [12] G. L. Agawane, S. W. Shin, A. V. Moholkar, K. V. Gurav, J. H. Yun, J. Y. Lee, and J. H. Kim, Non-toxic complexing agent Tri-sodium citrate's effect on chemical bath deposited ZnS thin films and its growth mechanism, J. Alloys Compd., 535 (2012) 53.
- [13] A. Bayer, D. S. Boyle, and P. O'brien, In situ kinetic studies of the chemical bath deposition of zinc sulfide from acidic solutions, J. Mater. Chem., 12 (2002) 2940.
- [14] W. Kern, The Evolution of Silicon Wafer Cleaning Technology, J. Electrochem. Soc., 137 (1990) 1887.
- [15] Y. J. Chabal, G. S. Higashi, and R. J. Small, Surface Chemical Composition and Morphology, in: K. A. Reinhardt, W. Kern (Eds.), Handbook of Silicon Wafer Cleaning Technology, 2nd edition, William Andrew Publishing, Norwich, NY, 2008, p. 523.
- [16] H. E. Swanson and R. K. Fuyat, *Standard x-ray diffraction powder patterns*. National Bureau of Standards Circular 539. Vol. 2. 1953, [Washington, DC]: National Bureau of Standards.
- [17] B. J. Skinner and P. B. Barton Jr., The Substitution of Oxygen for Sulfur in Wurtzite and Sphalerite, Am. Mineral., 45 (1960) 612.
- [18] A. Bondi, van der Waals Volumes and Radii, J. Phys. Chem., 68 (1964) 441.
- [19] L. Vegard, Die Konstitution der Mischkristalle und die Raumfüllung der Atome,

- 1 Zeitschrift für Physik, 5 (1921) 17.
- 2 [20] B. Palosz, E. Grzanka, S. Gierlotka, S. Stel'makh, R. Pielaszek, W. Lojkowski, U.
3 Bismayer, J. Neuefeind, H. P. Weber, and W. Palosz, Application of X-ray Powder
4 Diffraction to Nano-materials - Determination of the Atomic Structure of Nanocrystals
5 with Relaxed and Strained Surfaces, Phase Transitions, 76 (2003) 171.
- 6 [21] S. M. Salim, A. H. Eid, A. M. Salem, and H. M. Abou El-Khair, Nanocrystalline ZnS thin
7 films by chemical bath deposition method and its characterization, Surf. Interface
8 Anal., 44 (2012) 1214.
- 9 [22] H. Pulker and J. Maser, The origin of mechanical stress in vacuum-deposited MgF₂
10 and ZnS films, Thin Solid Films, 59 (1979) 65.
- 11 [23] J. A. Ruffner, M. D. Himel, V. Mizrahi, G. L. Stegeman, and U. J. Gibson, Effects of low
12 substrate temperature and ion assisted deposition on composition, optical
13 properties, and stress of ZnS thin films, Appl. Opt., 28 (1989) 5209.
- 14 [24] F. A. Doljack, *The Origins of Stress in Thin Nickel Films. AEC Technical Rep. No. 76.*
15 Case Western Reserve University, Cleveland, OH, 1971.
- 16 [25] S. Gorer and G. Hodes, Quantum size effects in the study of chemical solution
17 deposition mechanisms of semiconductor films, J. Phys. Chem., 98 (1994) 5338.

Table 1

Sample	Zn:S ratio	O:S ratio	220 Peak Position	Fractional Peak Shift (arb.)	Grain Size (nm)	Thickness (nm)	Particle Size (nm)
-1-	1.05	0.11	47.66	0.36	4.5	200	40
-1/2-	1.14	0.20	47.91	0.34	3.8	100	35
-1/4-	1.13	0.40	48.04	0.46	4.0	50	30
-1/8-	1.23	0.42	48.33	0.86	4.3	50	30/coalesced
-1/16-	1.23	0.49	48.49	0.96	4.0	50	25/coalesced
-1/32-	1.22	0.59	48.60	0.95	4.0	40	coalesced
-1/32- on SiO ₂	1.21	n/a	48.47	0.96	3.8	80	85

Table 2

Bath Concentration	Particle size in solution (μm)	Particle size in film (μm)
1	6.5	0.1 – 0.5
1/2	7.5	1.0 – 1.5
1/4	5.6	0.5 – 1.5
1/8	1.3	0.5 – 1.5
1/16	0.4	0.1 – 0.5
1/32	0.7	0.1 – 1.0

Figure 1 _ colorforonline

Figure 1 _ greyscaleforprint

Figure 2 - TEM

Figure 3 - XRD_color

Figure 3 - XRD_greyscale

Figure 5

Figure 6 _ color

Figure 6 _ greyscale

Figure and Table captions

Figure 1. ToF-SIMS data showing SiO₂ levels at the ZnS/Si interface for samples grown under conditions identical in all ways except that one was deposited under atmospheric conditions (red circles) while the other was deposited under air-free/degassed conditions (under N₂, blue triangles). Reagent concentrations were 1/32 in both cases. The integrated area under the SiO₂ peak is 19 times larger for the film deposited under atmospheric compared to air-free/degassed conditions.

Figure 2. TEM cross section images of film -1/32- showing a 1-2nm oxide layer between the silicon substrate and ZnS film in some areas (a), while in other areas little to no oxide is visible (b).

Figure 3. Grazing incidence x-ray diffractograms for samples (a) 1, (b) 1/2, (c) 1/4, (d) 1/8, (e) 1/16, (f) 1/32, and (g) 1/32 on thermally oxidized Si. The vertical dashed line is a guide to the eye, showing the shift in peak position.

Figure 4. Atomic force micrographs of films deposited using 1/32 reagent bath concentrations on (a) silicon and (b) thermally oxidized silicon. All bath conditions were identical, thus the differences in morphology are due to the change of substrate.

Figure 5. Scanning electron microscope images of sample -1/2- (a) after 2 hours growth time, (b) after 4 hours growth time, and (c) cross sectional image after 4 hours growth time, and sample -1/32- (d) after 2 hours growth time, (e) 12 hours growth time, and (f) cross sectional image after 12 hours growth time.

Figure 6. Film growth rate (circles) and RMS roughness (triangles) increase linearly with reagent bath concentrations. The shaded shapes are for films deposited on Si, while the open shapes are for the film deposited on SiO₂.

Table 1.
Properties of ZnS thin films deposited at various reagent bath concentrations.

Table 2.
Particle sizes in solution and within films.