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PAPER

Chemically Deposited PbSe Thin Films: Factors Deterring Reproducibility in the Early Stages of Growth

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The early stages of growth in chemical solution deposition of lead selenide thin films on GaAs(100) substrates were studied in detail. The deposition was found to depend strongly on substrate pre-treatment with sodium selenosulphate in an aqueous KOH solution. In cases where this stage of the process was neglected, film growth would not occur. The sequence of precursor addition and the pH of the solution were also found to be dominant factors affecting film growth. Film growth rate, grain size and the resulting roughness were all shown to increase with pH. Study of film growth kinetics revealed the selenide limited nature of the system. These factors are shown to be critical for reproducible deposition of high quality PbSe thin films.

Introduction

CBD from solution offers a simple and cost-effective route for the fabrication of high quality nanometer-sized semiconductor thin films. This without the need for high deposition temperatures, stringent vacuum or plasma generators compared to other sophisticated techniques.[1-4]

However, irreproducibility is a common issue when approaching film growth via chemical bath deposition (CBD).[1,5-7] This is true for many compounds grown through this technique but is generally not addressed. The root cause for irreproducibility is concealed in the various parameters affecting growth kinetics that are not always fully understood. Although inexpensive compared to other methods, CBD usually involves complicated reactions that can affect film growth. Therefore it is crucial to investigate and understand all reactions taking place prior to, and during film growth and not only focusing exclusively on the primary reactions which compose the final film.

Lead chalcogenide semiconductor thin films have been the subject of considerable research due to their technological importance in crystalline and polycrystalline forms as infrared radiation detectors, infrared emitters and solar control coatings. There is specific interest in nanocrystalline PbSe, mostly due to the large exciton Bohr radius (a_B) in this material (46 nm) below which quantum size effects are observed.[8-10] PbSe is widely used in optoelectronics devices, operating in the mid to near infrared range.[11] Shandalov and Golan have reported the microstructure and morphology evolution in PbSe films chemically deposited on GaAs(100) substrate.[12] Continuous transition to strong (111) texture was observed with increasing deposition temperature, along with a significant increase in crystal size. [2,3,13-16]

Control over film morphology by varying the deposition conditions e.g. temperature, pH and time is critical for obtaining high quality CBD semiconductor thin films.[12,17,18,19] The OH- concentration has an important and complex effect on the chemical reactions occurring; specifically, Osherov et al. demonstrated the importance of pH as a key factor in controlling CBD of lead sulfide thin films.[19]

Notably, Hodes and coworkers reported that by treating ZnO substrates with sulfide prior to CBD of CdS, improved surface coverage is obtained,[20] suggesting that the early stages of growth can be critical, even before the main reactions for film deposition have commenced.

In the present work we show that understanding the processes occurring in the early stages of growth is vital for controlling the composition, structure, orientation and subsequent physical properties of the incipient films.

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In particular, treatment of the GaAs substrates with sodium selenosulphate in aqueous KOH solution resulted in termination of the GaAs substrate with Se^{-2} and significantly improved the chemical compatibility of the substrate with the PbSe films. This, combined with a high $[OH^-]/[Pb^{2+}]$ solution ratio during growth provided optimized film characteristics including uniform substrate coverage, good adherence, lower density of contaminating particles on the surface and most importantly, high process reproducibility.

Experimental

Materials and Chemicals

Sodium sulfite (Aldrich, analytical 99.95 %), selenium powder (Aldrich, 100 mesh, analytical 95+ %), lead acetate trihydrate (Aldrich, analytical 99+ %) and potassium hydroxide (Frutarom, analytical) were used without further purification. Single crystal GaAs(100) substrates were purchased from AXT (epi-polished, undoped, ±0.1º miscut). The films were deposited from a solution with a final composition of 60 mM $Pb(CH_3COO)_2 \cdot 3H_2O$, 50 mM Na_2SeSO_3 and various concentrations of KOH (complexing agent for Pb) at final pH > 13. Stock solution of Na_2SeSO_3 (0.2M) was prepared with excess of sodium sulfite (0.5M), which was mixed with selenium powder in distilled water and stirred at $90^\circ C$ for 1 h. The sodium-selenosulfate (Na_2SeSO_3) solution was filtered in order to remove non-reacted selenium powder. Note that high pH is required in order to initiate strong complexation of lead to hydroxide and to avoid elemental Se decomposition from selenosulfate.

Thin film deposition

Prior to deposition, the solution contained in a Pyrex beaker was purged with pure N_2 in order to reduce levels of dissolved O_2 and CO_2, and placed in the dark in a thermostatic bath to reach the desired temperature. Growth of PbSe films on GaAs was carried out at varying temperatures, pH (KOH concentration), growth time and purging durations. The order in which reactants are added is crucial for film growth. Therefor it should be noted that prior to the purging sequence the solution contains KOH and selenosulfate. Once purging is completed the substrates are immersed in the solution until thermal equilibrium is attained. Last, the reaction is initiated by adding lead acetate.

Single crystal GaAs (100) wafer substrates were cleaved into 1×2 cm^2 rectangles and cleaned with distilled water, then with analytical ethanol and dried. Films were deposited on the bottom face of the substrates in order to prevent large particles from adhering to the growing film. Therefore, the substrates were mounted epi-side down on a custom-designed Teflon stage at an angle of < 70° with respect to the air-solution interface.

Characterization

X-RAY DIFFRACTION (XRD)

The crystallographic phase and orientation of the films were studied by XRD. A Panalytical Empyrean Powder Diffractometer equipped with PIXcel linear detector and monochromator on diffracted beam was used. Data were collected in the 2θ/θ geometry using Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 30 mA. Diffraction patterns were taken during 8 min in a 2θ range of 20-65° with step size of ~ 0.039°.

FIELD EMISSION GUN SCANNING ELECTRON MICROSCOPE (FEG-SEM)

The morphology of the films was observed using an ultrahigh resolution JEOL JSM-7400F FEG-SEM without coating of the surface. Acceleration voltage ranged from 1 to 5 kV. Film thickness was measured from cross sections (X-SEM) while surface topography was observed in plan-view.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS spectra were measured using an ESCALAB 250 spectrometer with monochromatic Al X-ray source (excitation energy 1486.6 eV) at base pressure of 1×10^{-9} mbar. Wide-scan survey spectrum for all elements and high-resolution spectra of selected elements were recorded.

Scanning Force Microscopy (SFM)

SFM was carried out in ambient conditions using an Asylum Research model NFP-3d-Bio operating in intermittent contact mode with a scan rate of 1 Hz. Roughness measurements and topography imaging was extracted using the IGORPRO 6.34A image processing software.

Results and Discussion

Chemical bath deposition of thin films involves some important, yet most often neglected processes which occur during the early stages of growth. These processes, which can be controlled by several corresponding growth parameters, can strongly affect growth rate, film morphology and in certain cases even the feasibility of growth. Among these parameters that will be discussed below are unintentional substrate surface pre-treatments (timing of substrate immersion vs. initiation time of the main CBD reaction) and the order of reactant addition.

Immersion Delay Experiments

Our standard method of deposition initially involves preparation of the deposition solution, including DI water, KOH and sodium selenosulfate (Na_2SeSO_3). The substrates are immersed in the solution until thermal equilibrium is attained, and finally the last reactant, lead acetate $(Pb(CH_3COO)_2 \cdot 3H_2O)$, is added to initiate the chemical reaction for PbSe formation. In order to examine the influence of the first stages of nucleation on the film growth, GaAs(100) substrates were immersed in the solution at different intervals after the deposition reaction has been initiated. The SEM images (Figure 1) and XRD patterns (Figure 2) show the influence of immersing the substrates into solution 10 min prior to reaction (0 min) and at varying immersion delay times (15, 30 and 60 min). It was found that film growth shows full substrate coverage only on those substrates which have been present in the solution prior to the reaction (0 min).
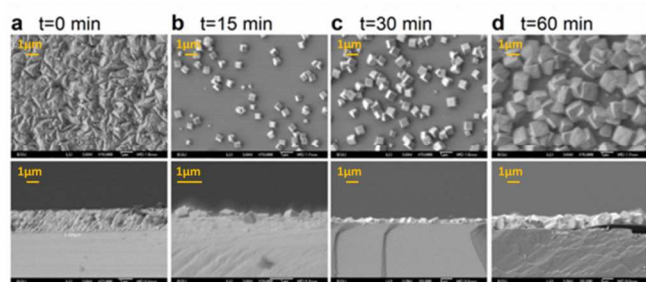
Figure 1. Plan view and cross-section HR-SEM images of films deposited at 24°C for 3 hours with 2.4M KOH. Immersion delay time was (a) 0 min. (b) 15 min. (c) 30 min. (d) 60 min.

The XRD patterns show the loss of the crystallographic texture typical for PbSe films.[2] These patterns indicate randomly oriented deposits comprised of particles that are formed in solution and not of films formed directly onto the substrate. Moreover, XRD peak intensities vary by two orders of magnitude between the pre and post immersed substrates, due to partial coverage and lower film thicknesses on immersion delayed substrates. The observed results strongly emphasize the importance of the initial stages of nucleation which are essential in order to achieve a compact and continuous film.
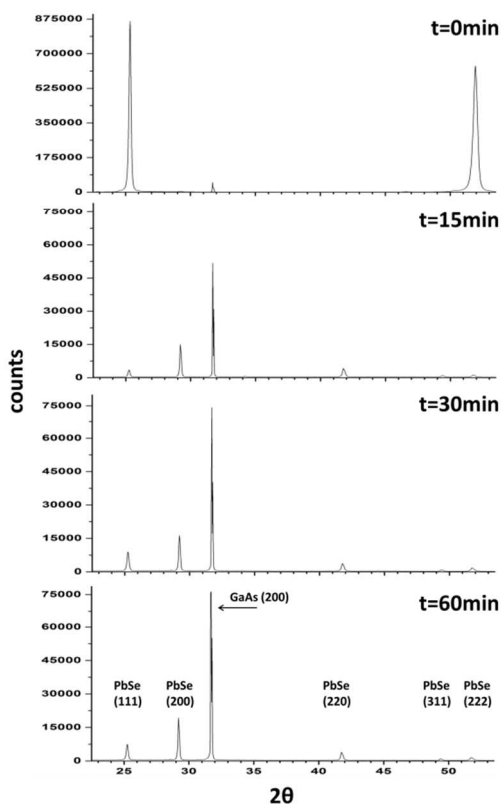

Figure 2. XRD patterns of films deposited at 24°C for 3 hours and with 2.4M KOH at varying delay periods (t = delay time).

These observations indicate that the initial stages of nucleation are critical for successful film growth. The results presented here were also obtained at shorter delay times (1, 2 and 4 min – not shown),

thus negating variations in initial concentration as the root cause for these effects. Based on these results, we hypothesized that the substrate-solution interface is likely to be the cause for hindering continuous film growth.

GaAs native oxide has been reported to be comprised of a mixture of non-stoichiometric gallium and arsenic oxides and elemental arsenic.[19] The solution prior to the reaction has two key components that can affect the native oxide and change the composition of the substrate surface. The first reactant is KOH which is responsible for the high solution pH. By exposing the substrate to harsh alkaline environment, the native oxide can be entirely or partially removed.[22] The second reactant is sodium selenosulfate, Na_2SeSO_3, which decomposes to release selenide anions in alkaline solution and has been reported to passivate substrates by replacing oxides and bonding Se^{2-} to gallium or arsenic.[23] In order to understand which of these reactants prepare the substrate for further film growth, a GaAs(100) substrate was immersed in 0.6M KOH for 10 min followed by reaction initiation and growth under standard PbSe film growth conditions (30°C, 3 hours and 0.6M KOH). The SEM plan view image in Figure 3.a shows a very thin, non-uniform film with partial surface coverage. Although this sample shows (111) texturing that is characteristic for PbSe films,[2] we note that the XRD pattern (Figure 3.b) is of very low intensity in comparison to PbSe films grown under the same conditions with standard substrate preparation (without immersion in KOH). Note that XRD shows the presence of minute amounts of basic lead carbonate (BLC) phase despite the solution purging with pure nitrogen gas.
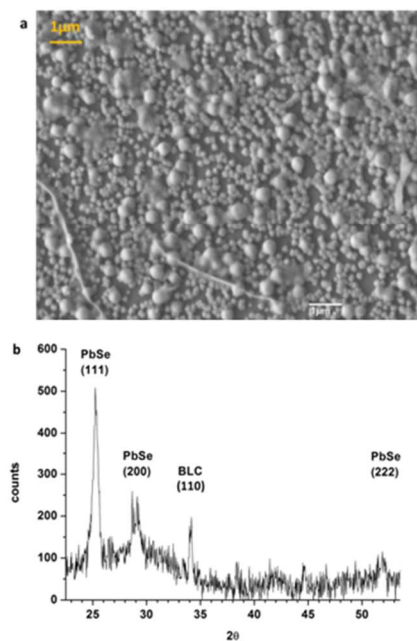

Figure 3. (a) SEM plan view image and (b) x-ray diffractogram of sample deposited at 30°C for 3 hours and 0.6M KOH. The substrate was immersed in 0.6M KOH for 10 min prior to reaction.

We can thus rule out that the behaviour observed in the immersion delay experiments described above (Figure 1) was merely due to oxide removal by the highly alkaline solution. It is therefore

reasonable to assume that Na_2SeSO_3 is the key component in substrate pre-treatment. It should be noted that although Se plays the key role in substrate preparation, the high pH is still required in order to free the Se^{2-} anions allowing them to perform the passivation. The question remaining is the mechanism that prepares the substrate for subsequent film growth.
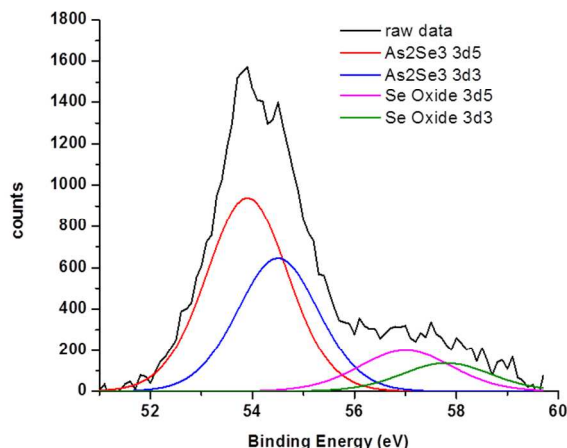

Figure 4. High resolution XPS spectra of Se 3d obtained from GaAs(100) sample immersed for 10 min in a solution containing 50mM selenosulfate and 0.6M KOH at 30°C. Black curve is as-obtained without de-convolution. Colored curves are best fitting deconvoluted spectra.

To investigate this, a GaAs(100) substrate was immersed in 60 mM Na_2SeSO_3 for 10 min and the resulting substrate surface was analyzed by XPS prior to reaction. Presence of Se on the substrate surface was unequivocally observed (Figure 4). Furthermore, a shift to low binding energy (E_B) of Se $3d^5$ compared to elemental Se (55.5 eV) is observed,[24] and the valuefound here (54 eV) matches those previously reported for As_2Se_3.[25] This result establishes that Se^{2-} ions are chemically reacting with the substrate surface prior to the reaction and suggests that the duration of immersion of the sample in solution before reaction has been initiated can strongly affect film growth. By replacing As-O bonds with As-Se, the incipient Pb and Se ions after reaction initiation will be more likely to adhere to the substrate surface, facilitating growth of continuous and adhesive films.

The Effect of Temperature and pH on Growth Kinetics

The pH of the aqueous deposition solution has two important, yet competing roles. Higher [OH⁻] increases complex formation and thus *decelerates* the deposition rate due to lower available concentration of free Pb cations. However, higher [OH⁻] also induces decomposition of Na_2SeSO_3 and thus *accelerates* the deposition rate due to higher availability of selenide anions. A schematic description of the effect of pH on film growth rate can be seen Figure 5.

It is understandable therefore that for a given system there is a pH value, X, that will result in maximum growth rate. Furthermore, controlling the pH can be used in order to obtain the desired growth rate. It is important to understand which of the reactants in the present system is limiting the growth rate.
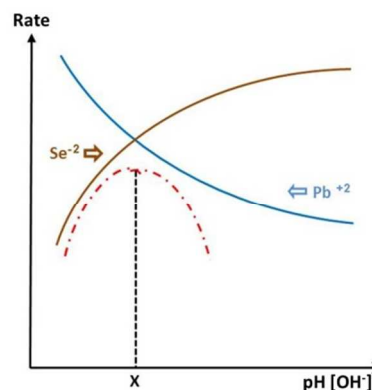

Figure 5. Schematic description of the effect of pH on deposition rate of PbSe.

To determine this, PbSe films were prepared at different [OH⁻], and their thickness was determined from SEM cross-section images. The absolute value of the thickness, presented in Figure 6, is an average value of these measurements and the error bar represents the standard deviation. Notably, the error increases with film thickness, since the roughness is increasing simultaneously with film thickness. As observed in Figure 6, increasing [OH⁻], namely increasing pH, leads to an increase in film thickness. The results shown in Figure6 correspond to pH < X (X corresponds to maximum rate in Figure 5) and therefore are clearly in the selenide limited regime. This is due to faster decomposition of (Na_2SeSO_3) resulting in greater availability of free selenide ions in the solution. Furthermore, SEM images (Figure 6a-c) show that the grain size of the films increases with higher pH values. This is also accompanied by an increase in surface roughness, as shown in the SFM images in Figures S2 and S3 in supporting information. It can thus be concluded that under these experimental conditions, the reaction rate for CBD of PbSe thin films is limited by the selenide ion concentration.
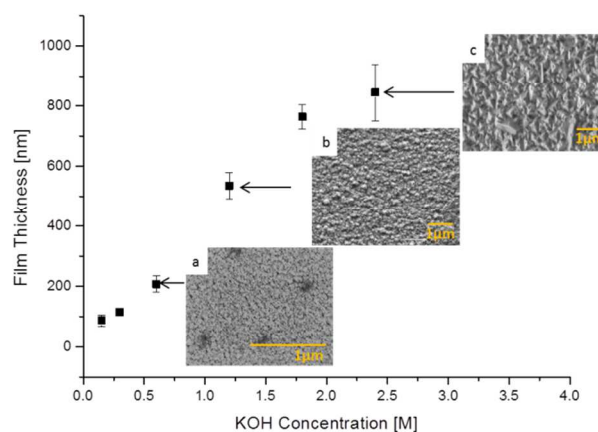

Figure 6. Film thickness plotted vs. KOH concentration for samples deposited at 20°C for 3 hours. Inset: Plan view HR-SEM images for PbSe samples grown in KOH concentrations of (a) 0.6M. (b) 1.2M (c) 2.4M.

The effect of temperature on the reaction rate is expected to be exponential according to the Arrhenius equation [1], due to the thermal energy that lowers the effective activation energy required for film growth. The effect of temperature was studied at two different pH values, 0.2M and 0.6M concentrations of KOH. Growth rate r was obtained from film thickness vs. deposition time and used for constructing Arrhenius plots. As can be observed in Figure 7b, an exponential dependence was observed for growth rate as a function of deposition temperature.
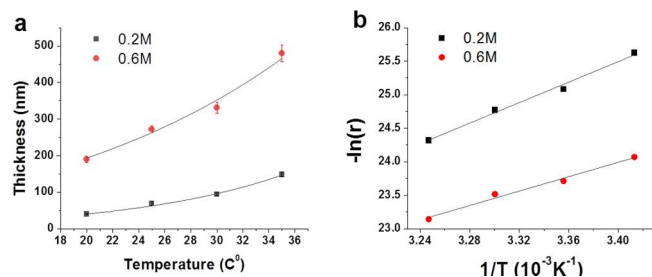

Figure 7. The effect of temperature on growth rate of films deposited using 0.2M and 0.6M KOH for 1.5h (a) Film thickness vs. temperature and (b) Arrhenius representation.

Arrhenius representation provided the deposition activation energies from plot slopes: 44.5 KJ/mole for the 0.6M bath and 63.3 KJ/mole for the 0.2M bath, in good agreement with the activation energy of 60 KJ/mole reported for CBD PbSe from a selenourea bath.[1] It is important to note that these values refer to the total energy required for film deposition. Considering this, it can be stated that the lower pH bath (0.2M) shows higher activation energy values i.e., the Se^{2-} anions have less tendency to dissolve from their Na_2SeSO_3 source, resulting in lower deposition rate. This result further confirms that the deposition system is indeed selenide limited. Moreover, lower activation energy (increased pH) will result in higher Se^{2-} concentration which in turn increases ionic surface diffusion, resulting in fewer nucleation sites and larger crystals. This can be seen in Figure 7.a by the standard deviation in film thickness due to larger crystal size.

Order of Reactant Addition

In light of the results described above, we investigated the effect of the order of reactant addition on film growth. In alkaline solutions, increasing [OH⁻] facilitates the formation of metal hydroxide complexes and at the same time, affects the rate of selenide anion generation due to decomposition of selenosulfate. Two sequences of reactant addition were studied and compared – (i) addition of Se^{2-} followed by addition of Pb^{2+} ("Pb^{2+} last") and (ii) addition of Pb^{2+} followed by addition of Se^{2-} ("Se^{2-} last"). It was found that adding the components "Pb^{2+} last" results in the formation of a continuous film, as can be seen in the SEM images, while "Se^{2-} last" resulted in a discontinuous film and in much slower growth rate as can be seen in Figure 8c,d. This is due to surface passivation of the substrate with selenide ions, resulting in enhanced chemical compatibility of the substrate, in light of the discussion above (Figure 9b). Moreover, the lead cations that are added last are free to react with the Se ions, that are present in high effective concentrations since under "Pb^{2+}

last" conditions the selenosulfate precursor is left for ample time to decompose in the highly alkaline solution. For the scenario in which Pb^{2+} source is added first, the GaAs substrate lacks the required surface passivation, thus inhibiting film growth (Figure 8).
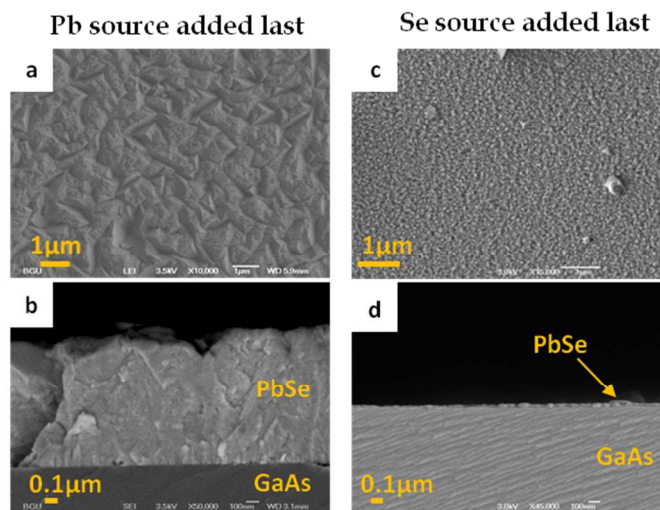

Figure 8. HR-SEM images of PbSe films deposited at 20°C for 3 hours with 1.8M KOH (a) XSEM Plan view image - Pb added last. (b) X-SEM image - Pb added last. (c) Plan view image - Se added last. (d) X-SEM image - Se added last.

Additionally, when lead is added first, a lead complex is readily formed by reaction with the OH⁻ ions.[1] Thus, fewer free OH⁻ ions are available to decompose the Na_2SeSO_3 and release selenide anions. This deficiency results in low effective concentrations of Pb^{2+}, as well as of Se^{2-} ions which inhibits the growth of continuous, high quality films (Figure 9d).
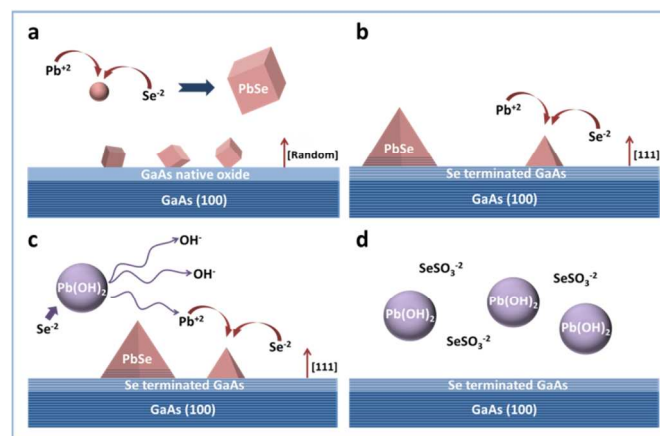

Figure 9. Schematic illustration depicting various growth mechanisms operating under the following conditions: (a) Se pre-treatment was not performed. Faceted particles are formed in solution and adhere to the substrate with random orientations. (b) Pre-treatment performed and "Pb^{2+} last" sequence. Ion-by-ion growth mechanism at relatively slow deposition rates. (c) Pre-treatment performed, "Se^{2-} last" sequence and high [OH⁻]/[Pb^{2+}] ratio. Optimal conditions for ion-by-ion thin film growth. (d) Pre-treatment performed, "Se^{2-} last" sequence and low [OH⁻]/[Pb^{2+}] ratio. Film growth is not obtained under these conditions.

In order to test this hypothesis a high [OH⁻] solution (2.4M) deposition bath was prepared in the "Se last" sequence order. GaAs

substrates were added, only some of which was pre-treated with selenosulfate. Film growth was initiated by the addition of the last reagent (selenosulfate). The substrates that were not treated with Se^{2-} anions showed bad adhesion and peeling as predicted (not shown). On the other hand, the Se^{2-} treated substrates showed uniform and mirror-like PbSe films, as shown in the XRD and X-SEM image in Figure 10.a,b. These results confirm our hypothesis regarding Se passivation and free OH^- ions as critical factors for film growth (Figure 9c).
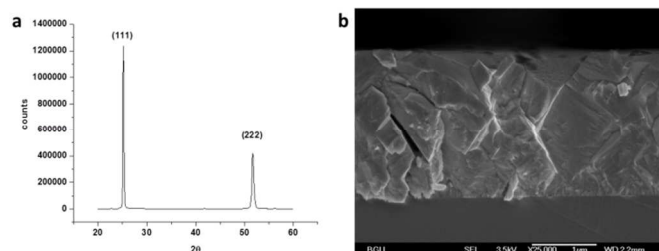

Figure 10. (a) x-ray diffractogram and (b) **X-SEM** image of sample deposited at 30°C for 100 min. and 2.4M KOH. The substrate was Se treated prior to deposition.

Both growth methods described in Figure 9b and 9c result in (111) oriented PbSe films. The method which includes separate pre-treatment of the substrate followed by "Se^{2-} last" growth sequence (Figure 9c), results in much better quality films in terms of lower film particle contamination density and better adhesion - resulting in increased maximum film thickness.

Conclusions

Chemical bath deposition of PbSe involves a complex series of intricate reactions, some of which are subtle and previously unknown. Each individual reaction can dramatically affect the resulting films. Immersion delay experiments have shown the critical role of substrate – solution interactions prior to the main CBD reaction. This is due to the Se^{2-} passivation effect on the substrate that replaces As-O bonds with As-Se, thus strongly facilitating chemical compatibility with the incipient PbSe films.
The importance of reactant addition order was clearly demonstrated. Addition of the reactants in the appropriate sequence and substrate pre-treatments are likely to be crucial for CBD of other metal selenides on GaAs, such as ZnSe, CdSe, etc., and likely to be relevant to other substrates as well, as has been demonstrated for ZnO substrates.[20] We have also demonstrated the effect of pH on film growth rate and identified the deposition under these growth conditions to be selenide limited. Furthermore, based on Arrhenius plots, activation energies for two different solution pH were calculated and were found to be in agreement with the selenide limited nature described above.

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