CHEMISTRY OF MATERIALS

VOLUME 18, NUMBER 16 AUGUST 8, 2006

Communications

Real Time Monitoring of the Deposition Mechanism in Chemical Solution Deposited PbSe Films Using Light Scattering

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Received April 30, 2006
Revised Manuscript Received June 25, 2006

Chemical solution deposition (CD) is an effective and low-cost way to grow high quality semiconductor poly- (or single) and nanocrystalline thin films without the need for high deposition temperatures, stringent vacuum, or plasma generators. Particular interest in nanocrystalline PbSe is due to its near-IR band gap and exceptionally large exciton radius (a_B) of about 46 nm, following which significant quantum size effects are readily observed in relatively large nanoparticles.[1] Earlier studies on CD of nanocrystalline PbSe films have been reported.[2−7] Notably, Gorer et al. investigated the influence of different complexing agents on PbSe.[8,9] These authors also used qualitative laser light scattering (LS) for determining the pH at which $Cd(OH)_2$ precipitation occurs in chemical deposition from solutions containing Cd^{2+} and potassium nitriloacetate.[10] Recently, amplified emission from nanocrystalline PbSe was reported, demonstrating the potential of this material for devices emitting in the technologically useful 1.5 μm range.[11]

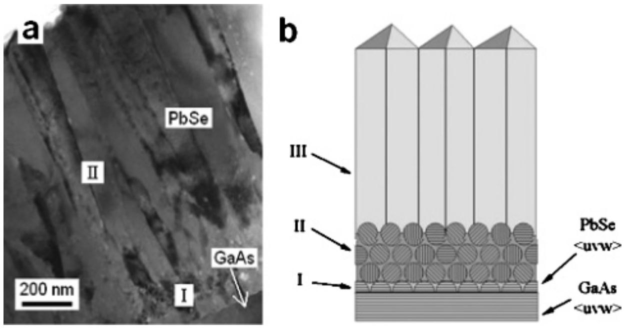

Figure 1. (a) TEM cross section of PbSe on GaAs showing the two distinct regions present in the film; (b) schematic illustration showing the morphology evolution in PbSe films on GaAs as a function of thickness. The ⟨*u*,*v*,*w*⟩ indices denote the substrate orientation and the corresponding direction of the PbSe film growth. (Reprinted with permission from ref 14. Copyright 2005 EDP Sciences.)

We have previously reported on the chemical deposition of PbSe films on GaAs substrates.[12−14] Three distinct layers have been identified as a function of thickness: (I) The first layer of nanocrystals strongly interacts with the substrate. The orientation of these crystallites is governed by the orientation of the underlying GaAs substrate. (II) Subsequent layers of nanocrystals are present in which the ⟨111⟩ texture develops with increasing thickness. (III) Abrupt transition

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(1) Wise, F. *Acc. Chem. Res.* **2000**, *33*, 773.
(2) Grozdanov, I.; Najdoski, M.; Dey, S. K. *Mater. Lett.* **1999**, *38*, 28.
(3) Pramanik, P.; Biswas, S.; Basu, P. K.; Mondal, A. *J. Mater. Sci. Lett.* **1990**, *9*, 1120.
(4) Biro, L. P.; Candea, R. M.; Borodi, G.; Darabont, A.; Fitori, P.; Bratu, I.; Dadarlat, D. *Thin Solid Films* **1988**, *165*, 303.
(5) Kainthla, R. C.; Pandya, D. K.; Chopra, K. L. *J. Electrochem. Soc.* **1980**, *127*, 277.
(6) Candea, R. M.; Dadarlat, N.; Turcu, R.; Indrea, E. *Phys. Status Solidi A* **1985**, *90*, K91.
(7) Kitaev, G. A.; Khvorenkova, A. Z. *Russ. J. Appl. Chem.* **1999**, *72*, 1520.
(8) Gorer, S.; Albu-Yaron, A.; Hodes, G. *Chem. Mater.* **1995**, *7*, 1243.
(9) Gorer, S.; Albu-Yaron, A.; Hodes, G. *J. Phys. Chem.* **1995**, *99*, 16442.
(10) Gorer, S.; Hodes, G. *J. Phys. Chem.* **1994**, *98*, 5338.
(11) Schaller, R. D.; Petruska, M. A.; Klimov, V. I. *J. Phys. Chem. B* **2003**, *107*, 13765.
(12) Shandalov, M.; Golan, Y. *Europhys. J.: Appl. Phys.* **2003**, *24*, 13.
(13) Shandalov, M.; Golan, Y. *Europhys. J.: Appl. Phys.* **2004**, *28*, 51.
(14) Shandalov, M.; Golan, Y. *Europhys. J.: Appl. Phys.* **2005**, *31*, 27.

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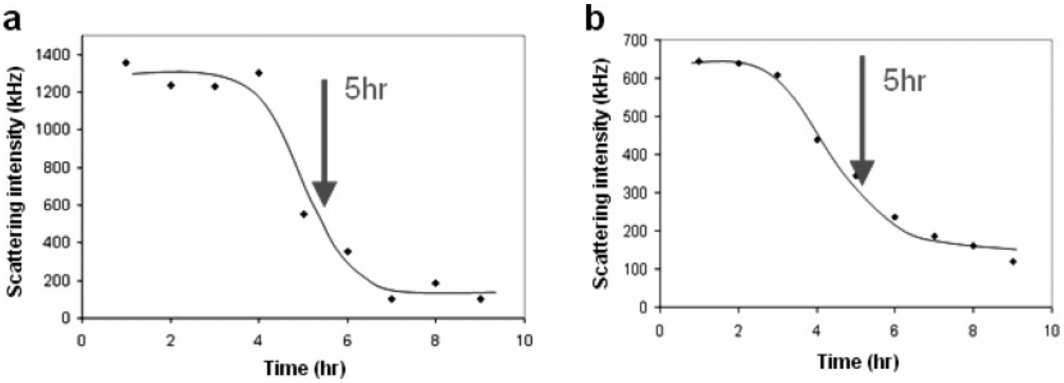

Figure 2. Time-resolved LS data obtained at 27 °C showing the mechanism transition point at ca. 5 h: (a) $\theta = 30°$ and (b) $\theta = 60°$.

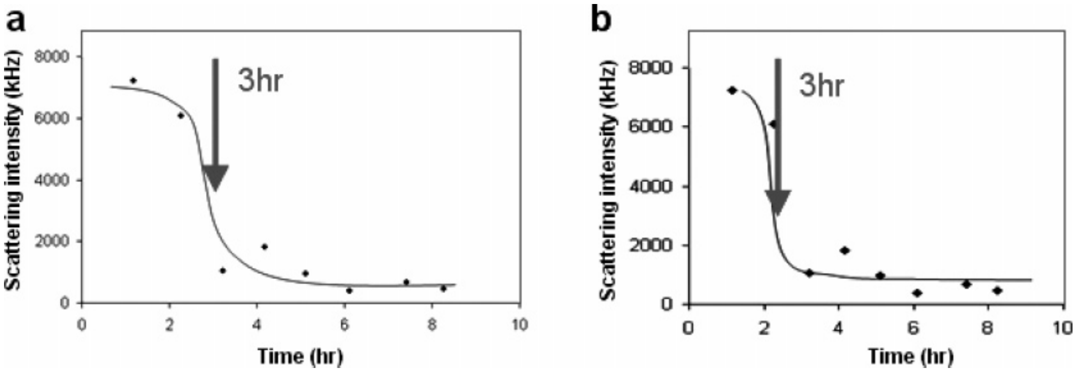

Figure 3. Time-resolved LS data obtained at 30 °C showing the mechanism transition point at ca. 3 h: (a) $\theta = 30°$ and (b) $\theta = 60°$.

to ⟨111⟩ columnar crystal growth occurs.[12,13] These stages in the morphology evolution of PbSe films on GaAs are schematically illustrated shown in Figure 1b. The transition from the nanocrystal growth mode to the columnar crystal growth mode was assumed to occur because of a transition from the cluster growth mechanism in the initial stages of growth to ion-by-ion growth, which has been previously reported to result in large crystals.[15] Our recent studies confirmed this assumption and showed that *single crystal* PbSe films were obtained under conditions in which the ion-by-ion deposition mechanism is exclusively active (Shandalov and Golan, manuscript submitted). This time dependent transition from the cluster to the ion-by-ion growth mechanism is expected as a result of depletion of lead ions in solution (e.g., increase in complex-to-metal ion concentration ratio) as the reaction proceeds. Hence, the characteristic growth rate, film morphology, and physical properties directly depend on the active deposition mechanism. Therefore, it is essential to gain control over the active deposition mechanism for obtaining various film morphologies upon demand. This paper describes for the first time studies using time-resolved LS measurements to identify the active mechanism during deposition. Verification of the transition point obtained by LS was achieved by correlating the data with structural characterization of the resulting films.

Each of the two mechanisms has a distinct LS behavior. The cluster mechanism shows strong scattering intensities which strongly depend on particle size in solution, while the scattering intensity sharply decreases once the clusters settle and the deposition proceeds in the ion-by-ion mechanism.

For dispersed particle systems, the main scattered signal is due to the difference in refractive index between the dispersion medium and the dispersed particulate phase. In a typical experiment, a dispersion of particles is illuminated with a collimated laser beam. The radiation scattered under an angle θ with respect to the incident beam is registered with a highly sensitive single photon counter detector. The obtained signal is proportional to the scattered light energy flux averaged over observation times on the order of 10 ns to 1 ms. The particle scattering function $P(\theta)$, which is defined as the ratio between the intensity of scattered light at angle θ and the intensity at zero angle, depends on θ and the radius of gyration R_g of the particles:

$$P(\theta) = \frac{I(\theta)}{I(0)} \approx 1 - \frac{q^2 {R_g}^2}{3} \qquad (1)$$

where q depends on the scattering angle θ and the wavelength of incident light λ,

$$q = \frac{4\pi \sin(\theta/2)}{\lambda} \qquad (2)$$

In a polydispersed solution, the scattering intensity depends on the size of the particles; at low scattering angles most scattered light comes from large particles, and at higher angles most scattered light comes from small particles.[16]

In these experiments a CGS3 LS system (ALV Co., Ltd.) was used. Preparation of the deposition solutions was described previously.[12,13] Measurements were taken every hour from the beginning of the deposition reaction. The

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(15) Hodes, G. *Chemical Solution Deposition of Semiconductor Films*; M. Dekker, Inc.: New York, 2003.

(16) Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley & Sons, Inc.: New York, 1961.

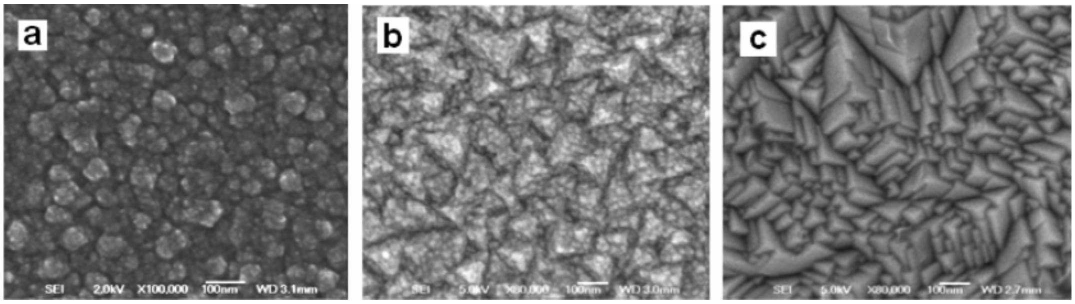

Figure 4. UHR-SEM images showing the surface morphology of films deposited at 30 °C for (a) 2 h, (b) 3 h, and (c) 6 h.

detected counts per second (expressed in kHz) were normalized and plotted versus time.

LS from deposition solutions was carried out in an attempt to detect the point in which the deposition mechanism transition occurs at temperatures of 27 °C and 30 °C. These temperatures were chosen for practical reasons to avoid very slow, as well as very fast, deposition reactions because reaction rates vary exponentially with deposition temperature. Scans of the samples at 27 °C and 30 °C are shown in Figures 2 and 3, respectively.

LS clearly showed the transition regions which appeared as an abrupt reduction in LS intensity after approximately 5 h for a deposition temperature of 27 °C and 3 h for a deposition temperature of 30 °C, as marked with arrows in the figures. The large differences in transition time and in film morphology (see Supporting Information) obtained upon a small variation in the deposition temperature suggest a large activation energy, in agreement with previous reports.[7]

In the beginning of the reaction, the deposition proceeds via the cluster mechanism, where a large amount of clusters and cluster aggregates in solution give rise to strong scattering intensity. Subsequently, most particles settle down and the solution becomes transparent to light. Under these conditions, a transition to an ion-by-ion deposition mechanism is expected. To verify this assumption, an interrupted growth series of chemically deposited PbSe films was deposited on GaAs(100) with growth terminated before, at, and after the transition point observed using LS. Ultrahigh-resolution scanning electron microscopy (UHR-SEM) images taken using a JEOL JSM-7400F are shown in Figure 4 for interrupted growth runs deposited at 30 °C. Film growth that was interrupted well before the transition point indeed showed a distinct nanocrystalline structure (Figure 4a), while films left to grow up to the transition region showed a mixed nature, where pyramidal edges of large columnar crystals coexist together with nanocrystals (Figure 4b). Finally, film growth that was interrupted well after the transition region exclusively showed large, facetted crystals, as shown in Figure 4c. As expected, the transition point shifted to shorter times and grew sharper at higher temperature because of the strong dependence of the reaction rate on the deposition temperature.

In summary, time-resolved LS measurements were used for the first time to monitor the active deposition mechanism in real time during chemical deposition of PbSe on GaAs(100). The abrupt reduction in scattering intensity was unequivocally correlated with the transition from the cluster to the ion-by-ion growth mechanism using UHR-SEM. Firm control over the active deposition mechanism in real time allows the deposition of PbSe films with well-defined morphologies and physical properties upon demand. In general, this quantitative LS method can be applied to many other thin film materials grown using CD.

Acknowledgment. The authors thank Dr. Sharon Vaanunu for expert assistance in LS measurements. This work has been partially supported by the European Commission FP-6 Project SEMINANO under Contract No. NMP4-CT-2004-505285.

Supporting Information Available: Additional UHR-SEM images showing morphology evolution at 27 °C and 30 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM061000M