SIZE QUANTIZATION EFFECTS IN CADMIUM SULFIDE LAYERS FORMED BY A LANGMUIR-BLODGETT TECHNIQUE

E.S. SMOTKIN, Chongmok LEE, A.J. BARD, A. CAMPION, M.A. FOX, T.E. MALLOUK, S.E. WEBBER and J.M. WHITE
Department of Chemistry, University of Texas, Austin, TX 78712, USA

Received 27 April 1988; in final form 19 August 1988

Layers of Q-state particles (< 50 Å) were prepared by exposure of Langmuir–Blodgett (LB) films of cadmium arachidate to H_2S to yield cadmium sulfide particles in a lattice of arachidic acid. The onset of absorption of this layer is blue-shifted by 0.38 eV with respect to bulk CdS. The adherence to Beer's law and insensitivity of the absorbance edge to the number of LB layers deposited (up to seven) suggest no strong electronic interactions between successive layers. Ellipsometric measurements show that exposure of the LB films of cadmium arachidic acid to H_2S gas results in an increase in thickness of about 3 Å per layer.

1. Introduction

The optical absorption edge of semiconductor particles shows a blue-shift as the particle dimensions decrease. This change in the optical properties has been attributed to the quantum size effect, a model based on the "electron–hole"-in-a-box problem. With this model, one might expect a shift on the order of $h^2/8m_c^*R^2$ due to the kinetic energy of localization in the small crystallite [1]. Such blue-shifts have also been observed in planar semiconductor lattices, with the absorption edge shifting to the blue with decreasing thickness. The equation governing the band gap shift, ΔE_g, in such anisotropic semiconductors has the form [2–4]

$$\Delta E_g = (h^2/2\mu_{xy})(2\pi^2/L_{xy}^2) + (h^2/2\mu_z)(\pi^2/L_z^2)\,, \quad (1)$$

where μ_{xy} and μ_z are the reduced effective masses of electron–hole pairs in the plane of the layers and perpendicular to the plane, respectively, and L_{xy} and L_z are the dimensions of the microcrystallite. For a thin layer of semiconductor, L_{xy} is large and the predicted ΔE_g involves only the second term in eq. (1). The photophysics of these "Q-state" semiconductors, where a gradual transition from bulk semiconductor to molecular material takes place, have been widely studied [5–12]. Q-state semiconductors can be prepared in a variety of media including micelle microemulsions [13], zeolites [11], polymers [14], solutions [5–10], and glasses [15]. These methods produce isolated, small particles. We were interested in investigating the possibility of producing thin layers of semiconductors, where there is significant lateral interaction. Such layers are analogous to the superlattices (e.g. of GaAs) produced by molecular beam epitaxy [16].

Our method of preparation is based on the widely used LB film method, as illustrated in fig. 1 and involves preparation of a "Q-layer" by depositing successive monomolecular layers of cadmium arachidate on a smooth substrate followed by exposure to H_2S gas. This produces Q-state particles in a lattice of layered arachidic acid. A monomolecular cadmium arachidate film was formed on water by the usual technique of adding 35 μl of 10 mM arachidic acid in chloroform to a clean surface of 0.3 mM cadmium chloride in a Lauda preparative film balance, model P (Brinkmann Instruments, Westbury, NY). The arachidic acid spreads rapidly to form a monomolecular film. If the *pH* of the subphase is greater than five, the carboxylate groups are complexed with the cadmium ions [17]. The cadmium arachidate film was transferred from water to glass by raising a clean glass slide slowly out of the water on which the film is spread while maintaining a constant surface

0 009-2614/88/$ 03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

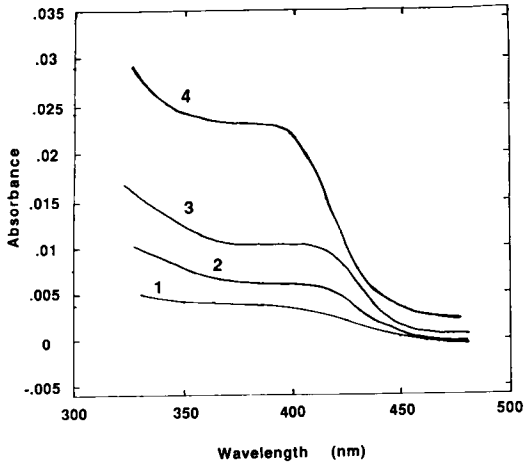

Fig. 2. Absorption spectra of CdS Langmuir–Blodgett films. (1) 1 layer, (2) 2 layers, (3) 3 layers, (4) 7 layers. Bulk CdS shows an absorption onset at 520 nm.

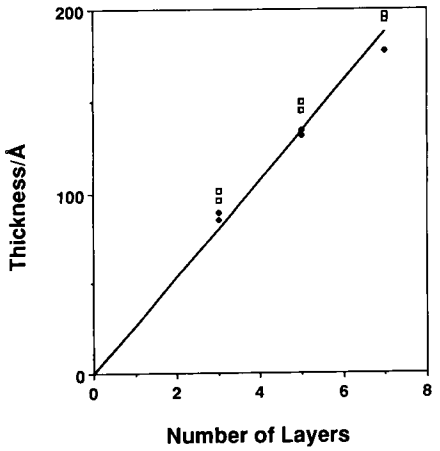

Fig. 4. Thickness of LB films versus number of layers before and after exposure to H_2S. Calculated line for thickness of cadmium arachidate films from literature values [18]. (♦) Thickness before exposure to H_2S; (□) thickness after exposure to H_2S.

layers. Although the absorption edge is independent of the number of layers, the absorbance at 380 nm is directly proportional to the number of layers of Cd arachidate originally deposited (fig. 3). Thus the particle size is independent of number of layers. For the multilayers with head to head surfaces, i.e. $n=3$, 7, one might have expected a red-shift in the absorption edge with larger particles being formed in the Cd head to head regions. Similarly, one might expect the growth of larger particles in the multilayer system compared to the monolayer one.

An alternative to 50 Å spherical particles are thin disk-like plates of domains ($d<50$ Å) of CdS. Fig. 4 shows the results of the ellipsometric measurements of the thickness of the LB films before and after exposure to H_2S versus the number of layers deposited. The solid line represents literature values for cadmium arachidate films [19]. The change in thickness for 3, 5 and 7 layers were calculated to be 11, 14 and 19 Å, respectively. Hence the average change in thickness per layer after exposure to H_2S is about 3 Å. Thus thin layers of platelets of CdS are a possibility. However, the ellipsometric measurement does not exclude the possibility of larger, more spherical, particles embedded in the arachidic acid matrix. The morphology that the CdS assumes is a function of the driving forces to minimize surface energy versus those involving movement of CdS through the hydrophobic regions of arachidic acid.

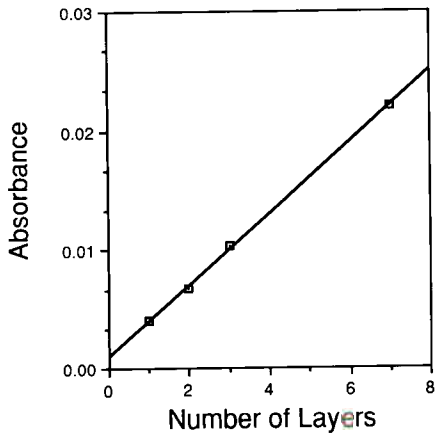

Fig. 3. Absorbance of CdS LB films at 380 versus number of layers.

3. Conclusion

Q-state particles can be prepared by exposure of LB films of cadmium arachidate to H_2S gas. The absorption onset of these Q-state particles is shifted from the bulk value by 0.4 eV and is independent of the number of layers deposited, indicating no strong electronic interactions between the particles. Preparation of semiconductor particles is especially interesting, because it would allow precise spacing between the layer distances controlled by the length

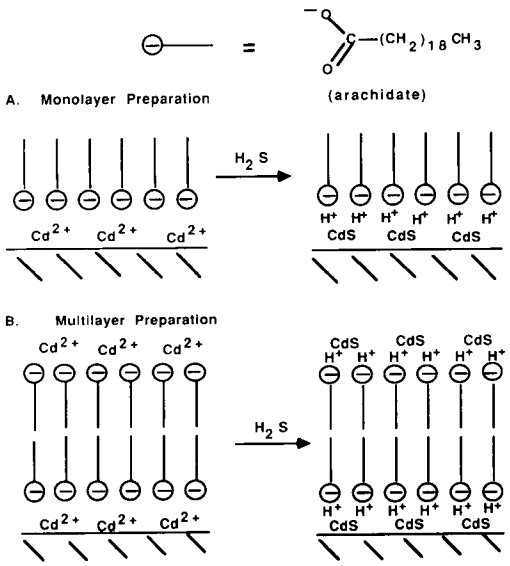

Fig. 1. (A) Formation of monolayer Q-state particles by diffusion of H_2S into Cd-arachidate LB film. (B) Formation of multilayer Q-state particles.

pressure of 30 dyne/cm. Successive layers can be overlaid by then lowering and raising the slide in and out of the aqueous subphase. Details of the above procedure have been published [17]. The Langmuir–Blodgett (LB) films were exposed to an H_2S atmosphere to yield cadmium sulfide and protonated acid.

Transmission electron microscopy (TEM) of the LB films were obtained by depositing the LB film on a 3 mm TEM disk consisting of a carbon film supported on a copper grid (Ernest F. Fullam Inc., Latham, NY, No. 10070). The disk was mounted on an aluminum sample holder and the spectrum of the supported LB film versus air was taken and stored on an HP model 8450 UV/VIS spectrophotometer (Hewlett–Packard, Palo Alto, CA). After exposure to H_2S the spectrum was taken again and the original spectrum versus air was subtracted from the latter spectrum yielding the spectrum of the CdS particles. The absorption spectrum of a monolayer on the TEM grid matched the features of the spectrum of the monolayer on quartz, although the onset was blue-shifted by 50 nm. The high magnification (200000×) image of the holey carbon film show 50 Å and smaller regions of higher apparent projected potential. The energy dispersive X-ray spectroscopy (EDS) of these regions show Cd and sulfide in approximately equal atomic concentrations, so we believe these regions represent the CdS particles. A strong peak due to the copper from the grid as well as a weak peak indicating some residual chloride from the LB trough was also present, as were Si and P, which are normal contaminants in TEM holey carbon films. In addition to the small particle of CdS, the TEM showed some sparsely distributed larger particles (approximately 700 Å across) which were cubic in shape. When a small beam was directed onto a single cube, the EDS showed a sulfur-rich region and very little cadmium. The electron diffraction pattern could not be indexed as CdS. The nature of these larger particles will be the subject of another study.

Thickness measurements of LB films of cadmium arachidic acid on single-crystal Si were made before and after exposure to H_2S (at 60 PSI, for 20 min). A Rudolph Research model 2437 ellipsometer (Rudolph Research, Flander, NJ) equipped with a model RR2000FT automatic rotating analyzer was used at an angle of incidence of 69° and a wavelength of 6328 Å. The δ (δ and ψ are the conventional ellipsometric parameters [18]) changes of samples before and after H_2S treatment were measured by fixing the sample point using detachable sample mountings. Calculations were made with the assumption that the films are isotropically stratified and the refractive index of the film before and after the H_2S treatment remains almost constant. The change in thickness of the LB layers were calculated from the change in δ using the value of $1.534-i(0.0)$ as the refractive index of the film [19].

2. Results and discussion

Fig. 2 shows the absorption spectra of a monolayer and several multilayers of CdS LB films. The absorption onset for 1, 2, 3 or 7 layers of CdS is about 450 nm (2.8 eV), which can be compared with the bandgap of bulk CdS, 2.4 eV [20]. This shift in the LB layer of CdS of 0.4 eV would correspond to spherical particles with a 50 Å diameter according to eq. (1), if the bulk values are used for the effective masses, $\mu_{xy}=\mu_z=0.154$ [21]. Such spherical particles would almost span a depth of two arachidic acid

of the organized assembly layers. By spacing the semiconductor layers from electron-transfer catalysts, details of electron transfer between these can be probed, as has been done with particulate semiconductors [23].

Acknowledgement

The support of this research by the Gas Research Institute and the National Science Foundation (CHE 8402135) is gratefully acknowledged. We thank L.K. Rabenbergus for TEM results.

References

[1] L.E. Brus, J. Chem. Phys. 79 (1983) 5566.
[2] C.J. Sandroff, D.M. Hwang and W.M. Chung, Phys. Rev. B 33 (1986) 5953.
[3] M. Shinada and S. Sugano, J. Phys. Soc. Japan 21 (1966) 1936.
[4] C.J. Sandroff, S.P. Kelty and D.M. Hwang, J.Chem. Phys. 85 (1986) 5337.
[5] L.E. Brus, J. Phys. Chem. 90 (1986) 2555.
[6] N. Chestnoy, R. Hull and L.E. Brus, J. Chem. Phys. 85 (1986) 2237.
[7] H. Weller, A. Fojtik and A. Henglein, Chem. Phys. Letters 117 (1985) 485.
[8] A.J. Nozik, F. Williams, M.T. Nenadovic, T. Rajh and O.I. Micic, J. Phys. Chem. 89 (1985) 397.
[9] J.J. Ramsden, S.E. Webber and M.J. Grätzel, J. Phys. Chem. 89 (1985) 2740.
[10] Y.M. Tricot and J.H. Fendler, J. Phys. Chem. 90 (1986) 3369.
[11] Y. Wang and N. Herron, J. Phys. Chem. 91 (1987) 257.
[12] Y. Wang and N. Herron, J. Phys. Chem. 91 (1987) 5005.
[13] M.L. Steigerwald, A.P. Alovisatos, J.M. Gibson and L.E. Brus, J. Am. Chem. Soc., submitted for publication.
[14] Y. Wang and W. Mahler, Opt. Commun. 61 (1987) 233.
[15] A.J. Ekimov and A. Onushchenko, JETP Letters 40 (1984) 1136.
[16] H.L. Stormer, A. Pinczuk, A.C. Gossard and W. Weigmann, Appl. Phys. Letters 38 (1981) 691.
[17] H. Kuhn, D. Mobius and H. Bucher, in: Physical methods of chemistry, Vol. 1, part 3B, eds. A. Weissberger and W.B. Rossiter (Wiley, New York, 1972) p. 577.
[18] R.M.A. Azzam and N.M. Bashara, Ellipsometry and polarized light (North-Holland, Amsterdam, 1977).
[19] I. Pockrand, J.D. Swalen, J.G. Gordon and M.R. Philpott, Surface Sci. 74 (1977) 237.
[20] R. Memming, Progr. Surface Sci. 17 (1984) 7.
[21] L.E. Brus, J. Chem. Phys. 80 (1984) 9.
[22] R. Rossetti, R. Hull, J.M. Gibson and L.W. Brus, J. Chem. Phys. 82 (1985) 552.
[23] A. Sobzynski, A.J. Bard, A. Campion, M.A. Fox, T. Mallouk, S.E. Webber and J.M. White, J. Phys. Chem. 91 (1987) 3316.