Chem. Mater. **1999,** *11,* 1959−1961 1959

Kinetics of Electrophoretic Deposition of Zinc Oxide Quantum Particle Thin Films

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Received May 3, 1999
Revised Manuscript Received June 21, 1999

Zinc oxide thin films are of interest for electrical and optical applications such as the generation and detection of surface acoustic waves,[1] optical waveguides,[2] short wavelength semiconductor diodes and diode lasers,[3] and low-voltage, high-efficiency phosphors.[4] ZnO films have been deposited by a wide range of techniques including molecular beam epitaxy,[5] pulsed laser deposition,[6] sputtering,[7] and electrodeposition.[8] In this paper we show that electrophoretic deposition (EPD) can be used to deposit quantum particle thin films directly from colloidal suspensions. This technique is straightforward and can be used to fabricate films of varying thickness. While EPD has been used extensively to fabricate bulk products and films from suspensions of micrometer-sized ceramic particles,[9−11] and to deposit colloidal gold particles,[12] very little is known about the deposition of nanometer-sized semiconducting particles. Here we report on the deposition kinetics for ZnO quantum particles under constant current conditions.

The ZnO colloidal supensions were prepared from 1 mmol zinc acetate dihydrate (Aldrich, reagent grade) in 80 mL of 2-propanol (Aldrich, spectrophotometric grade) with vigorous stirring at 50 °C and subsequently diluted to a total volume of 920 mL followed by chilling to 0 °C. A total of 80 mL of a 2 × 10^{-2} M NaOH (Aldrich, reagent grade) solution in 2-propanol was then added to the zinc solution within 1 min under constant stirring.[13] Particles with mean diameters of 37, 41, and 48 Å were prepared by aging the suspension for 2 h at 45, 55, and 65 °C, respectively. The particle size was obtained from the band gap inferred from the optical absorption spectra.[14]

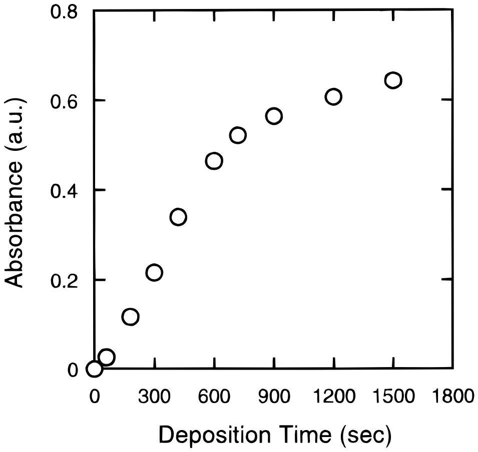

Figure 1. Optical absorbance of the deposited films measured at 340 nm as a function of deposition time.

The suspensions for EPD were prepared by rotary evaporation to a Zn concentration of 0.004 M to increase the particle concentration in the bath. The suspension was magnetically stirred for 30 min prior to deposition. No chemical additives (e.g., charging or adhesive agents) were added. A stainless steel sheet (2.5 cm × 10 cm × 0.1 mm) was used as the cathode, and a tin oxide coated glass slide (2.5 cm × 7.5 cm × 1.3 mm) with a sheet resistance of 15 Ω/□ (Libby-Owens Ford) was used as the anode. The electrodes were placed parallel to each other separated by a distance of 2 cm and immersed into the ZnO suspension which was kept in an ice bath to minimize aging of the particles. Films were deposited at a constant current of 10 mA using an HP 6209B power supply exercising the appropriate precautions for the high voltages (hundreds of volts) required. The films were then removed from the solution and allowed to dry at ambient conditions. Gas evolution was not observed at either electrode during deposition.

The deposition kinetics for the quantum particle thin films were determined from the change in the optical absorbance of the films. The absorbance was recorded at 340 nm, corresponding to the absorption peak of the ZnO suspensions, using a spectrophotometer (Shimadzu UV-2101 PC) with a tin oxide coated glass slide as reference. The absorbance was then related to the mass of ZnO deposited in the following way. Films were dissolved in 1 mL of 0.5 M HNO_3 followed by dilution to 100 mL. The Zn^{2+} concentration was then determined by atomic absorption spectrometry using a series of known solutions for calibration. Standard solutions were prepared from $Zn(NO_3)_2$ in distilled water (18 MΩ cm) with concentrations in the range 10^{-6} to 10^{-3} M.

Figure 1 shows a typical plot of absorbance as a function of deposition time. The absorption initially increases linearly with time and then saturates after

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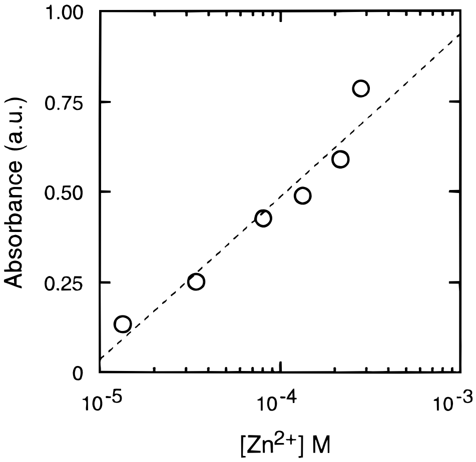

Figure 2. Reference curve relating the optical absorbance of the films at 340 nm with the concentration of Zn^{2+} obtained from atomic absorption spectrometry measurements.

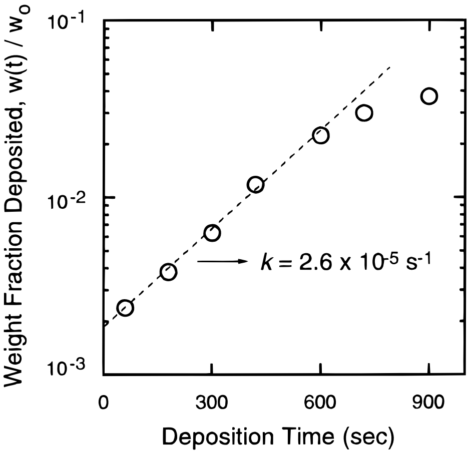

Figure 3. Semilog plot of the mass fraction of ZnO deposited from solution as a function of deposition time at 10 mA showing the extrapolation of the kinetic parameter, *k*, in the linear region.

about 15 min deposition. According to the Beer–Lambert Law, the optical transmittance of the film is given by

$$I/I_o = \exp(-\alpha x) \tag{1}$$

where I is the transmitted light intensity, I_o is the incident light intensity, α is the absorption coefficient, and x is distance. The absorption coefficient for bulk ZnO[15] is $3.17 \times 10^5\ cm^{-1}$, corresponding to an absorption length of ~0.03 μm. The absorbance of the film is expected to approach 1 at about three absorption depths, or ~0.1 μm for a fully dense film.

The relationship between the film absorbance and the Zn^{2+} concentration in the film is shown in Figure 2. From this figure it can be seen that the Zn^{2+} concentration in the films increases from about 10^{-5} M to about 3×10^{-4} M at the point where the absorbance begins to saturate. For a film deposited for 10 min, corresponding to the time where the absorbance saturates, the thickness of a fully dense film calculated[16] from the deposition mass was determined to be ~0.33 μm, in good agreement with the value inferred from the absorption coefficient.

A general expression for the weight, w, deposited during electrophoretic deposition can be obtained by integrating over the deposition area and time. For an electrode with constant deposition area, S, on which weight of particles dw has been deposited in time dt, the mass is given by[9]

$$\int \mathrm{d}w = Sfv \int C(t)\,\mathrm{d}t \tag{2}$$

where f is the efficiency factor and is equal to 1 when all particles arriving at the surface are incorporated into the film, v is the average velocity of the particles, and $C(t)$ is the concentration of particles in the suspension at time t. Assuming that the suspension is homogeneous and there is no decrease of particle concentration due to sedimentation or any other process (i.e., the only change of concentration is due to deposition), then from mass balance at time $t = 0$, $C(0) = w_o/V$ and at time $t = t$

$$C(t) = \frac{w_o - w(t)}{V} \tag{3}$$

where V is the volume of the suspension, w_o is the initial weight of the particles in suspension, $w(t)$ is the deposition mass at time time t, and t is the time duration of deposition. By combining eqs 2 and 3, we obtain the following expression:

$$\int_0^w \frac{\mathrm{d}w}{w_o - w(t)} = k \int_0^t \mathrm{d}t \tag{4}$$

where k is a kinetic parameter given by

$$k = \frac{Sfv}{V} \tag{5}$$

Evaluating eq 4, the expression for the weight deposited under constant current deposition conditions with a time dependent particle concentration is given by

$$w(t) = w_o(1 - e^{-kt}) \tag{6}$$

Figure 3 shows the weight fraction of ZnO particles deposited as a function of deposition time. The linear region on the semilog plot shows that the rate law derived for large particles is also applicable for nanometer-sized particles. The deviation from linearity at longer times is due to the very small transmittance in the films at longer times, as described above. The rate constant, k, obtained from the slope of the linear region of this curve is $2.6 \times 10^{-5}\ s^{-1}$. Taking $S = 3.75\ cm^2$, $V = 100$ mL, and assuming $f = 1$ (i.e., all particles reaching the anode are deposited), we obtain a value for the average particle velocity under the influence of the field of 7 μm/s. This can be compared with typical values of 10 to 20 μm/s for micrometer-sized particles deposited at slightly lower current conditions (5 mA).

The differences in the particle velocity can be further examined by considering the velocity of the particles as

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(16) True thickness measurements of deposited films were made using profilometry techniques; however, significant scatter within the data was found. Therefore, calculations of expected thickness were made based on the deposition mass.

expressed by the Stokes equation:[17]

$$v = \frac{zeE}{6\pi\eta r} \qquad (7)$$

where z is the charge on the particle, e is the elementary charge, E is the electric field, η is the viscosity of the solution, and r is the particle radius. If we consider the case where the electric field and solution viscosity are constant, the particle velocity should be proportional to the particle charge and vary inversely with the particle size. The mean particle diameter is 5 nm for the quantum particles and ~3 μm for the commercial phosphor material. From this, we calculate a normalized charge, q/e, of -0.03 for the nanoparticles and $+44.2$ for the micrometer-sized particles. The particle diameters differ by a factor of about 600 such that the nanoparticles would be expected to move much faster; however, the net charge on the larger particles is over 1000 times greater such that the surface charge dominates the particle movement in this comparison and the quantum particles move slower by a factor of about 3.

To compare the optical properties of the ZnO quantum particles in colloidal suspensions and in the thin films, a series of films was prepared at 10 mA constant current for 15 min from suspensions with mean particle diameters of about 38, 43, and 49 Å. The band gap[18] for bulk ZnO is 3.35 eV corresponding to 371 nm and quantum effects are observed for particle diameters smaller than about 55 Å. The optical absorbance spectra of these films are shown in Figure 4. It can be seen that there is a progressive red shift of the absorption onset with increasing particle size, illustrating that the optical properties of the films are derived from the optical properties of the particles.[19] A small red shift in the absorption onset was observed for each film due to the slight coarsening of the particles that occurred during electrophoretic deposition.

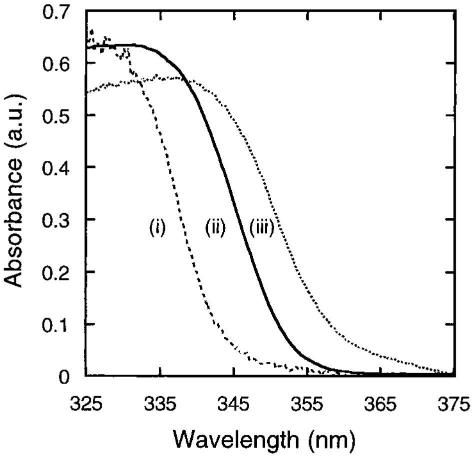

Figure 4. Absorbance spectra of deposited films prepared by aging the nanocrystalline particle suspensions for 2 h at (i) 45 °C ($\bar{d} = 38$ Å), (ii) 55 °C ($\bar{d} = 43$ Å), and (iii) 65 °C ($\bar{d} = 49$ Å), illustrating the red shift of the optical absorbance onset with increasing particle size.

In summary, we have demonstrated that quantum particle thin films can be obtained by EPD from colloidal suspensions. Measurements of the inherently small film mass were made by relating the optical absorbance of the films to Zn^{2+} concentration determined by AAS after dissolving the films. The semilogarithmic relationship of deposition mass with deposition time shows that the EPD of quantum particles follows the rate law derived for micrometer-sized particles. The optical properties of these thin films originated from those of the particle suspensions, showing that the EPD process did not significantly alter the material properties.

Acknowledgment. This work was supported in part by the NSF Materials Research Science and Engineering Center on Nanostructured Materials at JHU. E.M.W. acknowledges support from the JHU Materials Initiative Fellowship.

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