Surface Sol–Gel Synthesis of Ultrathin Semiconductor Films

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Ultrathin films of ZnS, Mn-doped ZnS, ZnO, and SiO2 were grown on silicon substrates using surface sol–gel reactions, and the film growth process was characterized by ellipsometry, atomic force microscopy, X-ray photoelectron spectroscopy, UV–visible absorbance, and photoluminescence (PL) spectroscopy. The Si substrates were pretreated by chemical oxidation, or by derivatization with 4-((dimethylmethoxy)silyl)butylamine. On the oxidized Si/SiO2 surface, nanoparticulate films of ZnS and Mn-doped ZnS were grown by sequential immersion in aqueous metal acetate and sodium sulfide solutions. During the first four adsorption cycles, there was little film growth, but thereafter the amount of material deposited was linear with the number of adsorption cycles. This behavior is consistent with the formation of ZnS nuclei at low coverage, followed by particle growth in subsequent cycles. PL spectra are consistent with incorporation of Mn2+ into the ZnS nanoparticles. In contrast, the growth of SiO2 films from nonaqueous SiCl4 on the same Si/SiO2 substrates was regular from the first adsorption cycle, indicating a high density of nucleation sites. On amine-derivated substrates, ZnO thin films grew as relatively smooth islands, suggesting that the interaction of Zn2+ ions or primary ZnO clusters with the amine surface priming layer was sufficiently strong to prevent the formation of isotropic nanoparticles upon exposure to aqueous base.

Introduction

There is growing interest in developing techniques for preparing ultrathin semiconductor nanoparticle films. This work is motivated by the size-dependent electronic and optical properties of semiconductors, which lead to a range of potential applications in electronic and optoelectronic devices, solar cells, photoelectrodes, photocatalysts, and sensors. The wet chemical synthesis of ultrathin semiconductor films represents, in principle, a simple and inexpensive alternative to more technologically demanding chemical vapor deposition (CVD) and physical techniques.1–3 However, the realization of practical devices from wet chemical synthesis requires the development of film growth techniques that give similar or better quality films than vapor-phase methods. In particular, precise control of film thickness, crystallinity, and morphology are significant problems to be overcome in wet chemical synthesis.

There are essentially three strategies for preparing uniform films of semiconductor nanoparticles. One is by electrochemical deposition of a compound semiconductor, either directly from a solution containing both atomic components (e.g., Cd2+ and Se),4 or by chemical reaction of a second component (chalcoogen or halogen) with an electrodeposited layer of metal particles.5 In favorable cases, particularly when there is a good epitaxial match between the substrate and the semiconductor lattice, well-crystallized films can be formed. The second method involves particle self-assembly, in which preformed colloidal particles are attached layer-by-layer to a growing surface film.6 In this case, the quality of the film depends on the properties of the nanoparticles used, as well as the attachment chemistry. The third method, which potentially offers the finest control over the film growth process, is the direct layer-by-layer synthesis from the chemical components (e.g., anion and cation) of the semiconductor. The latter method typically involves a two-step chemisorption/...
chemical activation cycle. One component is adsorbed or reacted chemically with molecules on the surface, but the reaction is self-limiting at the extent of a single monolayer. The chemisorbed monolayer is then activated in the second step, by reaction with an appropriate reagent or by redox reactions in the liquid phase. Alternatively, the activation step may occur in a gas-phase process, such as UV ozone oxidation or low-temperature plasma treatment.

When the third technique uses solution-phase activation of the surface, it is called the surface sol–gel (SSG) process. SSG can be considered as both a surface variant of the bulk sol–gel method and a liquid-phase variant of the vapor-phase atomic layer epitaxy method (ALE). A technique that is closely related to SSG and ALE is electrochemical atomic layer epitaxy (ECALE), in which either the adsorption or activation step is a Faradaic redox process. SSG is based on self-limiting surface chemical reactions between the surface and each of the film components. The first examples of SSG involved the synthesis of semiconductor particles by alternate adsorption of anions and cations from aqueous solutions, and was called SILAR (successive ionic layer adsorption and reaction). Later, Ichinose et al. generalized the technique to include molecular precursors, such as metal alkoxides, which could be adsorbed and hydrolyzed as monolayer films. The process is experimentally simple, involving alternating immersion of the substrate in solutions of the components of a compound semiconductor. Each reaction step is followed by rinsing with the appropriate solvent to remove excess reagent. SSG combines the advantages of ALE and the bulk sol–gel method: it provides film thickness control at the Angstrom level, and therefore allows one to tune the band gap and related properties through control of particle size. Like bulk sol–gel synthesis, SSG does not require high temperatures or expensive high-vacuum equipment. Another strong point of SSG is its compatibility with surface patterning techniques. This has been illustrated by the fabrication of patterned TiO2 films on Si/SiO2 substrates bearing microcontact-printed lines of an organic polysiloxane. A distinct disadvantage is that as a low-temperature synthesis technique, SSG may give low-density or incompletely crystallized films. In a previous paper, we showed low density surface oxides made by SSG can be thermally annealed to give smooth, adherent, high-density thin films.

To date the SSG method has been successfully applied to the synthesis of CdS, ZnS, TiO2, Ti, Zr, Al, and B oxides and mixed Ti, Ta oxides as thin films. The related ECALE technique has been used to make a variety of II–VI semiconductors. In this work, we extend the SSG technique to the preparation of nanoparticle films of the wide-band-gap semiconductors ZnS, Mn-doped ZnS, and ZnO. SSG ZnS and SiO2 films were also studied for comparison purposes. Our interest in ZnS and (Zn,Mn)S is motivated by their commercial use as phosphors and functional layers in electroluminescent and photovoltaic devices. The oxides (ZnO and SiO2) are also useful as insulating layers. Further, a recent study has shown that certain silica sol–gels, in bulk form, are highly photoluminescent. As thin films, these organosilicate gels may also be interesting for electroluminescent display applications. We describe here the SSG synthesis of ultrathin ZnS, Mn-doped ZnS, ZnO, and SiO2 films and their characterization by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), ellipsometry, and UV–visible and photoluminescence (PL) spectroscopy.

Experimental Section

Materials. Zinc acetate dihydrate, Zn(OAc)2·2H2O, manganese acetate tetrahydrate, Mn(OAc)2·4H2O, sodium hydroxide, sodium sulfide nonahydrate, Na2S·9H2O, and carbon tetrachloride were purchased from Aldrich. Silicon tetrachloride was purchased from Acros. These compounds were used without further purification. Doubly distilled water was used in all experiments. Polished (100) Si wafers were obtained from Research and PVD Materials Company. All other chemicals were reagent grade, obtained from commercial sources, and used as received.

Film Synthesis. Si wafers were sonicated in CCI4 for 15 min and then rinsed with 2-propanol and water. OH-terminated Si surfaces (Si–OH) were prepared by 30 min sonication in “piranha” solution (4:1 concentrated H2SO4:30% H2O2) and rinsed with copious amount of water. Ellipsometric data revealed the presence of ~2 nm thick SiO2 film on the Si surface. An amine-terminated Si surface (Si–NH2) was prepared by washing Si–OH sequentially with methanol and 1:1 methanol/toluene and then reacting it with 4-((dimethylamino)ethyl)benzylamine (15 h treatment with 5% toluene solution in dry argon over KOH at ambient temperature). Quartz slides, treated in the same way, were also used as substrates.

ZnS and Mn-doped ZnS (Zn,Mn)S films were prepared as follows. Si–OH substrates were placed in a beaker (for 5 min) in an aqueous solution of Zn(OAc)2 (91 mM, pH 6.7) or a mixture (10 mL:0.2 mL, pH 6.74) of aqueous solutions of Zn(OAc)2 (91 mM) and Mn(OAc)2 (98 mM, pH 7.7), respectively. The substrates were rinsed with water and dried in a stream of Ar. The substrates then were immersed in aqueous NaN3 solution (4 mM, pH 11.05) for 2 min, rinsed with water and dried in Ar. ZnO films were prepared by alternately...

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(14) SSG can be considered as both a surface...
immersing the Si\textsubscript{NH\textsubscript{2}} substrate in the same Zn(OAc\textsubscript{2}) solution and aqueous NaOH solution (4.5 mM), rinsing and drying in the same way. For all three types of films, rinsing with water was done carefully, using a water stream directed parallel to the surface for 1 min. Experiments with longer rinsing times showed that they did not significantly affect the ellipsometric thickness of the films.

Si\textsubscript{O} films were prepared by immersing the Si–OH substrate in a solution of SiCl\textsubscript{4} in CCl\textsubscript{4} (175 mM) for 2 min followed by rinsing with CCl\textsubscript{4} and methanol, and then drying in a stream of Ar. The substrate was then immersed in water for 1 min and dried in Ar.

By repeating these two-step adsorption cycles, multilayer films were synthesized. Each adsorption cycle was followed by ellipsometric measurements.

Characterization. Ellipsometric measurements were made with a Gaertner Scientific Corp. model L2W26D rotating polarizer ellipsometer. Si substrates were dried in an argon stream prior to the measurements. An analyzing wavelength of 632 nm was used. The film thickness of the multilayers was calculated using the Si refractive indices, n\textsubscript{Si} = 3.875 and k\textsubscript{Si} = 0.018, determined from a blank sample. The real and imaginary parts of the refractive index of the films were taken from the a blank sample.

Atomic force microscopy (AFM) images of the multilayers deposited on Si substrates were obtained with a Digital Instruments Nanoscope IIIa in tapping mode using a 3045 J VW piezo tube scanner. The 125 \textmu m etched Si cantilevers had a resonant frequency between 250 and 325 kHz and the oscillation frequency for scanning was set to \sim 0.1 – 3 kHz below resonance. Typical images were obtained with line scan rates of 2 Hz while collecting 256 x 256 pixel samples.

Transmission UV-visible absorption spectra were obtained from the films deposited on quartz substrates with a Hewlett-Packard diode array HP8452A spectrometer.

Steady-state emission spectra were recorded with a SPEX Fluorolog 1680 0.22 m double monochromator fluorimeter using a front face illumination and collection geometry. The emission spectra were corrected for the instrument response as they were obtained.

X-ray photoelectron spectra (XPS) were obtained using Kratos Series 800 spectrometer with hν = 1253.6 eV and a 4 \times 6 mm\textsuperscript{2} analyzing window. The accuracy of measured core level binding energies (E\textsubscript{B}) was \pm 0.1 eV.

Results and Discussion

Film Growth. The film growth can be schematically described by the following surface reaction sequences:

\begin{align*}
\text{Si–OH} & \xrightarrow{\text{Zn}^{2+}, \text{OAc}^-} \text{Si–O–Zn(H}_2\text{O)}_y(\text{OAc})_x \text{Si}^{2-} \\
\text{Si–O–Zn–S} & \xrightarrow{\text{NH}_2, \text{OAc}^-} \text{Si–O–Zn–S–Zn(H}_2\text{O)}_y(\text{OAc})_x \text{etc. (I)} \\
\text{Si\textsubscript{NH\textsubscript{2}}} & \xrightarrow{\text{Zn}^{2+}, \text{OAc}^-} \text{Si\textsubscript{NH\textsubscript{2}}–Zn(H}_2\text{O)}_y(\text{OAc})_x \text{OH}^{-} \\
\text{Si\textsubscript{NH\textsubscript{2}}} & \xrightarrow{\text{Zn}^{2+}, \text{OAc}^-} \text{Si–NH\textsubscript{2}–Zn–O–Zn(H}_2\text{O)}_y(\text{OAc})_x \text{etc. (II)} \\
\text{Si–OH} & \xrightarrow{\text{Si–Cl} \text{H}_2\text{O}^{-}} \text{Si–O–Si–OH} \text{etc. (III)}
\end{align*}

In the aqueous reaction sequences I and II, it is assumed that the weakly coordinating acetoate ions are easily displaced as ligands for Zn\textsuperscript{2+} or Mn\textsuperscript{2+} by the more strongly coordinating OH\textsuperscript{-} or S\textsuperscript{2-} anions. The first

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Ellipsometric thickness data for the Si–OH/SiO\textsubscript{2} (1), Si\textsubscript{NH\textsubscript{2}}/ZnO (2), Si–OH/ZnS (3), and Si–OH/(Zn,Mn)S (4) films.}
\end{figure}

\begin{equation}
\text{Stability Constants of Metal-Ion Complexes; Special Publications 17 and 25; The Chemical Society; London, 1964 and 1971.}
\end{equation}
in MeOH/HOAc\(^{13}\)). Apparently, there is sufficiently strong coordination of Zn\(^{2+}\) ions in EtOH/HOAc that the surface interaction is weak or easily reversed in the washing step. It should also be noted that no ZnO film formation was achieved on Si-OH substrates during six adsorption cycles. This implies that the ZnO film growth requires stronger linking of Zn\(^{2+}\) ions to the surface via coordination to NH\(_2\) groups. An essential condition for a successful SSG process is that the binding of the chemisorbed monolayer is irreversible, or sufficiently strong to prevent desorption in the subsequent rinsing/activation step. Thus proper choice of film growth parameters, such as the chemical composition of the surface and solvent used, is necessary for the successful formation of surface-bound nanoparticles. It has been shown previously that the chemical composition of the anion in a metal salt precursor and its concentration affect the rate of film growth.\(^{12}\) Similarly, temperature has been shown to be an important factor in controlling the kinetics of SSG reactions\(^{13}\) and the thermodynamics of metal coordination reactions on surfaces.\(^{28}\)

**Morphology of the Films.** Typical AFM images of the sulfide and oxide films prepared are shown in Figure 2a–d. The images of both Si–OH/ZnS and Si–OH/(Zn,Mn)S films grown in 10 adsorption cycles (Figure 2a,b) reveal close-packed layers of well-resolved rounded features about 10–30 nm in diameter and 4–9 nm in height. CdS layers deposited by SSG on TiO\(_2\) surfaces had similar morphologies.\(^{11}\) For the Si–OH/(Zn,Mn)S film (Figure 2b) a part of the image containing the uncovered substrate surface was selected in order to estimate the approximate film thickness. The thickness is about 4.2 nm, which is in good agreement with the average thickness found by ellipsometry, 4 nm (Figure 1.4). This value is also consistent with the height of the rounded features and suggests crystal growth immediately on the Si–OH surface. The surface coverage is estimated to be ~90% and 75% for the Si–OH/ZnS and Si–OH/(Zn,Mn)S films, respectively. An image of the films...
the Si–OH/ZnS film deposited in five adsorption cycles (not shown) also shows evenly distributed rounded features of approximately the same diameter, but their average height is lower (1–7 nm). The surface coverage in the latter case was estimated at about 80%. These data suggest that the sulfide nanoparticles form on the surface from well-separated crystal nuclei, rather than data suggest that the sulfide nanoparticles form on the surface, with the case in ALE,20 or in ECALE films nucleated by surface from well-separated crystal nuclei, rather than in the latter case was estimated at about 80%. These average height is lower (1 nm).

Features of approximately the same diameter, but their features also shows evenly distributed rounded features of about 30–60 nm in diameter, which form aggregates. The average roughness of the film is about 3.2 nm.

The surface morphology of the Si–OH/ZnO film grown in four adsorption cycles is quite different from those described above. No well-resolved rounded features are observed. Instead, the film consists of extended (50–500 nm) and rather flat separate islands of different thickness, which cover about 70% of the surface. Figure 2c shows an area of the surface that is covered with relatively thin (3–5 nm) and quite smooth islands. The average roughness of these islands is about 0.85 nm.

Although the mechanism of the SSG film growth process is still not understood in detail, the significant difference in the morphology of the ZnO film and the other films makes us believe in the existence of at least two possible descriptions of the main events of the films growth. The first one, which is consistent with the formation of three-dimensional, rounded features, involves continuous particle growth from nuclei, and approximately follows the Ostwald model for colloids: (ZnS)$_{m-n}$ + Zn$^{2+}$ + S$^{2-}$ → (ZnS)$_{m+n+1}$, etc. In this case, the strength of bonds within the particle is greater than that of the bonds anchoring the particle to the substrate. This is the case for ZnS, and also apparently for SiO$_2$.

In the case of the ZnO films, the formation of islands is consistent with the formation of ZnO at islands of Si–NH$_3$ on an otherwise unreactive surface, or with growth from sparse amine nucleation sites with the primary growth direction being horizontal. On the basis of our experience with priming layers of organosilanes, we favor the former explanation. That is, the priming monolayer formed from 4-(dimethylmethoxy)silyl)butylamine is relatively patchy, and it nucleates the growth of the ZnO film. There are two possible explanations for the unusual smoothness of the ZnO films grown on the amine islands. The first one involves strong coordination of Zn$^{2+}$ ions by the amine monolayer. Subsequent reaction with base converts this to a surface Zn–OH film, which coordinates more Zn$^{2+}$ ions in the next adsorption cycle, etc., to form a smooth film. This model assumes dense packing of the amine groups within the surface islands, allowing the formation of continuous surface Zn–O–Zn–O surface layers. In this case one might expect that the films formed would be dense, and perhaps would show a preferred crystallographic orientation. However, it is more likely that the tethered butylamine groups within the islands are disordered and disordered at a distance from each other, in which case the nucleation of separate (ZnO)$_n$ primary clusters would occur. A smooth film could result if these small clusters have some lateral mobility on the amine surface and can aggregate to form a film. In this case, one would expect a disordered or polycrystalline film. We observed that the ZnO film could be partially removed from the surface if the washing steps were not done carefully. This suggests that the second model is probably operative. Unfortunately, the ZnO films shown in Figure 2 were too thin to obtain Bragg diffraction peaks by X-ray diffraction, which might have distinguished between the two models for smooth film growth.

Chemical Composition of the Films. The surface chemical compositions of the Si–OH/ZnO, Si–OH/ZnS and Si–OH/(Zn,Mn)S films were determined by XPS. The position of the Zn 2p$_3/2$ line in the spectra of the ZnO film (1022.5 eV) and both of the ZnS-containing films (1021.8 eV) is characteristic of bulk ZnO and ZnS respectively.29

For Si–OH/(Zn,Mn)S film, the Mn 2p XPS spectrum reveals a photoelectron line at 639.8 eV, which is accompanied by two shake-up satellites at 651.3 and 657.1 eV. This spectrum is characteristic of isolated paramagnetic Mn$^{2+}$.29 The Zn:Mn surface ratio was found to be 1:0.064:0.61 (see Table). It is interesting to note that Zn:Mn ratio in the film is about 3 times higher than in starting solution, consistent with the much lower solubility product of ZnS (4.5 × 10$^{-24}$) relative to MnS (3 × 10$^{-13}$).30

In each of the three XPS spectra, the intense C 1s line from adventitious carbon is asymmetrical and has a shoulder at 288.1–288.3 eV, indicating the presence of O=C=O bonds, and hence acetate groups.29 By integrating the area of the deconvoluted peaks, the approximate percentages of acetate groups in the films were determined to be 3.3%, 4.8%, and 3.1% for Si–NH$_3$/ZnO, Si–OH/ZnS, and Si–OH/(Zn,Mn)S, respectively. Residual precursor molecules suggest incomplete sulfidization or hydrolysis. Similar residual ligands have been detected in ZnO colloids,31 metal oxide films prepared by SSG,12 and in ZnS nanoparticles grown on SiO$_2$ by sonochemical reactions.32

An Si 2p$_3/2$ line, which originates from the uncovered substrate, is observed for all the samples. Its envelope exhibits two distinct features: bulk silicon at 99.1 eV and oxidized silicon at 102.2–102.9 eV. The latter peak appears at lower energy than that observed for SiO$_2$ (103.3–103.7 eV),29 and is characteristic of the Si(=O) oxidation state in different inorganic environments (e.g., SiO$_2$, SiO$_x$ (x < 2), and SiO$_2$(OH)$_2$). The approximate percentages of the oxidized silicon species in the samples


and SiO₂/ZnS nanoparticles. This emission results from Mn²⁺-based transitions. Band gap energies estimated from the spectra (5.17 and 5.07 eV for ZnS and (Zn,Mn)S, respectively) are consistent with quantum size effects, as expected from the small particle sizes (Zn₂⁻ Mn)S clusters, and hence the introduction of Mn²⁺ ions into ZnS host lattice.

In the PL spectrum of the ZnO film, a broad emission centered at 440 nm is observed (Figure 4b). As has been previously found for ZnO colloids, the position of the emission peak is strongly dependent on particles size and falls within the range of 420–560 nm. 31,38,39 Freshly prepared ZnO sols exhibit blue emission, which changes to blue-green within 1 h. 39 Green emission around 450 nm is also observed in ZnO colloids prepared in alkaline alcohol solutions. 39 The emission band around 450 nm29 observed in our experiments implies that the ZnO film is composed of very small ZnO grains with a size close to that of colloidal particles in freshly prepared sols (<3 nm). This result is consistent with the smooth, featureless films observed in the AFM image. The broad emission spectra observed for both ZnS and ZnO nanoparticle films can be explained as follows. Photogenerated charge carriers, which have been trapped in shallow traps, are slightly red shifted, a shoulder at 330 nm appears in the photoluminescence of doped ZnS:Mn nanoparticles33,36,37 and assigned to the Mn²⁺ 4T₁⁻→6A₁ transition. It is known that the Mn²⁺ ion d electron states act as luminescent centers because of strong interaction with the s–p electronic states of the ZnS nanocrystals, which are excited by band gap absorption. The yellow emission in the PL spectrum of the (Zn,Mn)S film indicates the existence of an energy-transfer pathway that arises from electronic interaction in the (Zn,Mn)S clusters, and hence the introduction of Mn²⁺ ions into ZnS host lattice.

The photoluminescence spectra of (a) sulfide films Si–OH/ZnS (1) and Si–OH/(Zn,Mn)S (2) deposited in 10 adsorption cycles; (b) oxide films Si–NH₂/ZnO (1) and Si–OH/SiO₂ (2) deposited in 4 adsorption cycles. Excitation wavelengths were 290 nm in (a) and 340 nm in (b). The PL spectrum of the (Zn,Mn)S film (Figure 4a) reveals blue-green and yellow emissions at about 438 and 580 nm. This Mn²⁺-based yellow emission has been observed in the photoluminescence of doped ZnS:Mn nanoparticles31,37 and assigned to the Mn²⁺ 4T₁⁻→₆A₁ transition. It is known that the Mn²⁺ ion d electron states act as luminescent centers because of strong interaction with the s–p electronic states of the ZnS nanocrystals, which are excited by band gap absorption. The yellow emission in the PL spectrum of the (Zn,Mn)S film indicates the existence of an energy-transfer pathway that arises from electronic interaction in the (Zn,Mn)S clusters, and hence the introduction of Mn²⁺ ions into ZnS host lattice.

The photoluminescence (PL) spectrum of the ZnS film excited a 290 nm displays a broad emission centered at 445 nm (Figure 4a). Photoluminescence in this spectral region is attributed to the presence of sulfur vacancies in the lattice, as previously found for ZnS colloids 33,35 and SiO₂/ZnS nanoparticles. 32 This emission results from the recombination of photogenerated charge carriers in shallow traps. 33,34

Table 1. Relative Integrated XPS Peak Areas, Corrected for Atomic Sensitivity, for Si–NH₂/ZnO and Si–OH/(Zn,Mn)S Films

<table>
<thead>
<tr>
<th>Element</th>
<th>Si–NH₂/ZnO</th>
<th>Si–OH/(Zn,Mn)S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>9.1</td>
<td>31.3</td>
</tr>
<tr>
<td>S</td>
<td>56.7</td>
<td>31.1</td>
</tr>
<tr>
<td>C</td>
<td>0.79</td>
<td>22.42</td>
</tr>
<tr>
<td>O</td>
<td>10.5</td>
<td>9.0</td>
</tr>
<tr>
<td>Mn</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>10.5</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Figure 3. Transmission UV–visible spectra of ZnS (1) and (Zn,Mn)S (2) films deposited in 10 adsorption cycles on quartz slides.

Figure 4. Photoluminescence spectra of (a) sulfide films Si–OH/ZnS (1) and Si–OH/(Zn,Mn)S (2) deposited in 10 adsorption cycles; (b) oxide films Si–NH₂/ZnO (1) and Si–OH/SiO₂ (2) deposited in 4 adsorption cycles. Excitation wavelengths were 290 nm in (a) and 340 nm in (b).

shallow and deep surface states, tunnel to each other to recombine. Emission from recombination of short-distance pairs (in shallow traps) appears at lower wavelength than that from long-distance pairs (in deep traps). Broad emission bands represent a superposition of the wide distribution of trap distances.31

The SiO₂ film shows a broad emission band centered at 415 nm when excited at 340 nm (Figure 4b). Photoluminescence in this spectral region is due to oxygen vacancies associated with electrons localized on the bridge oxygen atoms of siloxane linkages.40

Conclusions

We have shown that the surface sol–gel technique can be used to make ultrathin films of ZnSₓ, Mn-doped ZnSₓ, and ZnOₓ nanoparticles from aqueous precursor solutions. The thickness of the films is controlled by the number of adsorption cycles, and dense coverage of the substrate can be achieved in 4–10 adsorption cycles.

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