This work describes the combined use of nanocrystal water-based colloidal suspensions with spin-coating deposition in order to obtain ultrathin ceramic films. We have used tin oxide (SnO2) nanoparticles, with particle diameter sizes ranging from 1–5.5 nm, to develop the deposition approach. Films obtained under several conditions were characterized by ellipsometry and atomic force microscopy, showing that the process has the ability to produce ultrathin ceramic films, with thickness ranging from 10–100 nm, with good particle packing. Additionally, electrical measurements in the films indicate good homogeneity and potential for various applications.

1. Introduction

The ability to deposit and tailor make semiconductor and dielectric ultrathin ceramic films is of fundamental importance for the improvement of traditional solid-state electronic devices, as well as for the development of new solid-state devices based on nanotechnology. Several methods have been used to process ultrathin films for electronic applications. Usually, these techniques, which are commonly known as layer-by-layer (LbL) assembly, are based on the assembly by the electrostatic interaction between deposited alternate layers of oppositely charged organic or inorganic materials. Atomic layer deposition (ALD) is another deposition technique used to obtain ultrathin ceramic films. In the ALD process, the precursor's vapor is firstly chemisorbed at the substrate surface, where chemical reactions take place, resulting in the desired ceramic phase. Recently, a modified ALD method, which is based on the deposition of solutions, was reported; however, only amorphous ceramic oxides could be obtained.

Although the above-mentioned techniques enable the preparation of ultrathin films with good qualities, there are a number of intrinsic problems that could be related to them, such as low time efficiency, incorporation of carbon and halide elements, and, in some cases, uncontrollable reactions during processing (like formation of undesirable phases or phase segregation). In this way, a process that allows the preparation of continuous crystalline ultrathin films is still a challenge, especially if the main target is a low-cost device fabrication. In our point of view, the development of a simple solution-based deposition technique combined with spin coating is a plausible way to prepare ultrathin films. This type of deposition is commonly studied to obtain polymeric or organic–inorganic composite ultrathin films; however, this combined technique is not usual for ceramic oxide systems. Herein, we describe the spin-coating deposition of colloidal nanocrystal suspensions in order to obtain ultrathin ceramic films. In this work, we have used tin oxide (SnO2) nanoparticles to develop the deposition approach, due to our knowledge to process very stable colloidal SnO2 nanocrystal suspensions, as well as to the several technological applications of this wide band gap semiconductor.

II. Experimental Procedure

The following route was used in this work in order to obtain SnO2 nanocrystals: tin chloride (II) dihydrate (SnCl2·2H2O-Mallinckrodt Baker, Phillipsburg, NJ, purity > 99.9%) was dissolved in absolute ethanol at room temperature (tin concentration was fixed at 0.025 mol/L). A water–ethanol (0.15 mol/L) solution was added to the tin chloride (II) ethanolic solution. The solution was kept at basic pH, by adding a NH4OH ethanolic solution. A few minutes after the addition of the aqueous solution, the precipitation of a white powder occurred, because of the hydrolysis reaction of Sn2+ ions. The reaction was carried out at room temperature in a glass reactor with constant stirring (using a magnetic stirrer). After the precipitation, the Cl− and NH4+ ions were removed from the solution by a dialysis treatment versus deionized water. During the process, the pH of the suspension was continuously monitored with a pH meter (Corning model 320 Corning Inc., Corning, NY), until the suspension reached pH = 7. After the dialysis, a very stable colloidal suspension was obtained, with a volumetric relation water:ethanol ≈ 1:1. To control the solid content and to remove the ethanol used during the synthesis step, the colloidal suspension was heated (∼70°C) until complete ethanol evaporation was achieved and a residual suspension (∼10% of the initial volume) with a solid content of approximately 15 g/L was obtained. The final colloidal suspensions had pH values of approximately 7. The rheological properties of the suspensions were investigated using a coaxial cylinders rheometer (Brookfield rheometer, mod. DV III, Brookfield Engineering Labs, Stoughton, MA, with ReoCalc software), the shear rate ranging from 0 to 120 s⁻¹.

The depositions of the thin films were performed onto n- and p-type silicon (Si) substrates. The Si wafers were cleaned with a sulfochromic solution, followed by rinsing with deionized water. The deposition steps were carried out as follows: a few drops of the colloidal dispersion were placed on the top of the substrate, which was rotated with a spin coater (Chemat Tech., model KW-4B, Northridge, CA) at a fixed rotation speed for 20 s, without arrested drying. In the present work, three rotation speeds were used (3000, 5000, and 7000 rpm). After the deposition of each layer, the substrate was dried on a hot plate (∼50°C) for a few seconds. No rinsings were performed between each cycle of layer deposition. For the annealed samples, the films were heat treated at 600°C, for 2 h, in an electrical tube furnace, with fixed heating and cooling rates of 5°C/min. The annealing treatments were carried out in air or nitrogen (N2) atmospheres.

For TEM/HRTEM analysis of the as-formed nanoparticles, a drop of the colloidal suspension was deposited on carbon-coated copper grids. A cross-section sample from a single-layer film treated at 600°C was prepared, by cutting the film in an ultrasonic cutter (Gatan mod. 601, Pleasanton, CA). A group of six pieces were attached face to face using an epoxy glue, and the set was sharpened in a dimple grinder (Gatan mod. 656) and...
finished in a precision ion-polishing system (Gatan 691). An HRTEM analysis was performed in a JEOL 3010 ARP microscope (Tokyo, Japan), operating at an acceleration voltage of 300 kV. The particle size distribution was estimated by the measurement of at least 200 particles in TEM images. Atomic force microscopy (AFM) images were obtained using a Digital Instruments model Nanoscope III equipment (Vecco Metrology Group, Chadds Ford, PA). Topographic images were recorded in the tapping mode. The thin film thickness and refractive index were determined by using an optical ellipsometer (Rudolph/Auto EL, Pennville, NJ). The measurement was performed with the 632.8 nm line of a He/Ne laser with an initial incident angle of 70°. The packing factor \( F_m \) was estimated from the refractive index measured by ellipsometry. The estimation was based on the effective medium approximation (EMA),\(^\text{16}\) considering a single-phase material. For a single-phase porous film, the EMA equation is described by

\[
\Phi_m \left( \frac{n_{\text{b}}^2 - n_s^2}{n_{\text{b}}^2 + 2n_s^2} \right) + \left( 1 - \Phi_m \right) \left( \frac{1 - n_s^2}{1 + 2n_s^2} \right) = 0
\]

where \( n_b \) is the refractive index of the bulk material and \( n_s \) is the measured refractive index. The electrical properties of the thin films were measured using a voltage source Keithley 237. In order to obtain the metal–oxide–semiconductor (MOS) configuration, Au electrodes were deposited onto ultrathin films, by means of evaporation. The electrodes were deposited in two different geometries, i.e., circular electrodes with a 0.25 mm diameter and a thickness of 40 nm, and a square-like electrode foil with a 5 mm side and a thickness of 40 nm. Use of these two geometries enabled the observation of the homogeneity of the electrical properties throughout the film and also a more accurate \( J \times E \) measurement.

### III. Results and Discussion

A water-based colloidal suspension of SnO\textsubscript{2} nanocrystals, with particle diameter sizes ranging from 1–5.5 nm, was synthesized by a process involving the hydrolysis of SnCl\textsubscript{2}. Figure 1(a) shows an HRTEM image of the SnO\textsubscript{2} particles prepared at room temperature, revealing a material that was well crystallized even without the use of heat treatments during or after particle synthesis. The presence of crystalline SnO\textsubscript{2} with a rutile-type structure was confirmed by electron diffraction analysis (Fig. 1(a), inset). As illustrated in Fig. 1(b), the processed material presented a broad particle size distribution, with a mean particle size of 3.3 nm and a distribution width of 1 nm. Figure 2 shows the \( \zeta \) potential as a function of the pH of the water-based SnO\textsubscript{2} colloidal suspension used in this work. It is possible to observe a very high value of \( \zeta \) (\( \approx -35 \) mV) for neutral pH, which is an indication that non-acidic SnO\textsubscript{2} suspensions are very stable against agglomeration and precipitation. Stable water-based colloidal suspensions in five different volumetric concentrations of SnO\textsubscript{2} nanocrystals were prepared, and stabilized by setting the pH = 7. It was ensured that the colloidal suspensions remained stable with time, and no sedimentation was observed for 12 months at room temperature. None of the suspensions showed significant initial stress to start flow. The rheological curves were fitted using a power-law equation

\[
\tau = \eta \dot{\gamma}^n
\]

where \( \tau \) is the shear stress (mPa), \( \eta \) is the apparent viscosity (mPa s), \( \dot{\gamma} \) is the shear rate (s\(^{-1}\)), and \( n \) is an index, which shows the deviation of the rheological behavior from a Newtonian fluid (\( n < 1 \) indicates a pseudoplastic fluid, while \( n > 1 \) indicates a dilatant fluid). Figure 3 shows the values of \( n \) and apparent viscosity against the volumetric concentration of the suspensions (expressed in fraction weight). The reduction in \( n \), with the increase in solid contents, indicates that the suspensions have a strong pseudoplastic behavior. However, this behavior is not normally observed in suspensions with a low solid content (lower than 0.03), as reported in the present work. This behavior can

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**Fig. 1.** Tin oxide nanoparticle characteristics: (a) HRTEM image of dried nanoparticle suspension (in the inset, the electron diffraction pattern identified as tin oxide—cassiterite is shown); (b) particle size distribution, estimated by measurements in TEM images.

**Fig. 2.** \( \zeta \) potential of the water-based colloidal nanocrystal suspension.
be explained by the high surface area of the system, implicating strong particle–particle interactions. Besides observing the apparent viscosity of the suspensions, the linear behavior predicted by Einstein’s equation \( \eta = \eta_A(1 + a\phi) \) where \( \phi \) is the volumetric concentration and \( a \) is a shape factor was observed only at very low concentrations. The high viscosities developed in low volumetric concentrations also support strong particle–particle interactions, and suggest a vitreous behavior that can be explored in future works.

Ultrathin ceramic films were prepared by spin coating water-based SnO\(_2\) colloidal suspensions onto \( n \)- and \( p \)-type silicon substrates. Films with and without annealing at 600°C for 2 h were obtained. After each deposition, the residual solvent was eliminated on a hot plate at 50°C. No rinsing of the film surface or any kind of surface treatment was performed after each deposition cycle. In order to obtain a controlled thickness deposition, the colloidal suspension deposition was repeated over the previous deposited layer, after solvent evaporation. A linear increase in the film thickness as a function of the number of deposited layers (deposition cycles) was observed (Fig. 4(a)), suggesting a regular and reproducible particle deposition process from cycle to cycle, i.e., similar to an LbL process. We observed that this deposition method allowed obtaining films with thicknesses of a few nanometers (10 nm) up to thicknesses of 200 nm. This result was confirmed by cross-sectional TEM of a single-layer sample treated at 600°C—(Fig. 5)—showing a polycrystalline structure with grains of 6 nm in a film thickness of 14 nm, without neck formation—showing an absence of sintering, as expected.\(^{17}\) From the linear fit in Fig. 4(a), the growth rate by cycle was estimated, ranging from 9.8 –17 nm, depending on the rotation speed of the deposition. These results suggest that both growth rate and film thickness can be controlled by means of the rotation speed, for a colloidal suspension with a fixed particle concentration.

Figure 4(b) shows the packing factor (\( \Phi_m \)) of the thin films,\(^{16}\) as a function of the number of deposition cycles. We observed, for the different conditions studied, that \( \Phi_m \) increase up to the fourth layer. After the fourth layer, stabilization in the \( \Phi_m \) value was found. Here, it is important to point out the high value of the measured \( \Phi_m \). Values up to 0.74 were obtained, suggesting an efficient nanocrystal packing (0.74 is the highest packing factor for a monodisperse sphere). This good packing is probably decisive to avoid the redissolution of the underlying film in sequential depositions, associated with the considerable viscosity of the suspension. Random packing is expected, as the nanocrystals used presented a broad particle size distribution (as can be seen in Fig. 1(b)).

Both the regularity in the film deposition and the high values of \( \Phi_m \) suggest that during the deposition process, a sol–gel-like phase transformation occurs in the colloidal suspension. Initially, the colloidal suspension behaves as a hard sphere system, where only hydrodynamic interactions and Brownian motion affect the flow. The thin film growth rate and the nanocrystal packing will be defined during this step and will be hydrodynamically controlled. In a second step, the fast elimination of the water in the spinning process significantly increases the solid content of the colloidal dispersion during the deposition time, increasing the particle–particle interaction. Consequently, a

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**Fig. 3.** Rheological behavior of colloidal suspensions obtained: (a) \( n \) values, computed from Eq. (1); (b) apparent viscosity. In the inset, the viscosity versus shear rate curves measured are shown. The dotted lines are presented as guides to the eyes.

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**Fig. 4.** Behavior of thin film properties with the number of deposited layers (for three films): (a) film thickness as a function of number of layers; (b) packing factor, as estimated by the effective medium approximation, as a function of number of layers.
sol–gel-like transformation takes place, freezing the highly packed structure formed in the earlier stage. The high pseudo-plastic behavior of the colloidal dispersion for a higher solid content (see Fig. 3) supports the sol–gel-like transformation of the colloidal suspension with an increase in particle concentration. For instance, the apparent viscosity of the colloidal suspension increased from 3 mPa·s for a solid content of 9 g/L (volume fraction of solids of 0.0014) to 380 mPa·s for a particle concentration of 55 g/L (volume fraction of solids of 0.0079). It is important to point out that no flocculation occurred with an increase in particle concentration, indicating that the suspensions still presented a high stability. Thus, the controlled thickness deposition process described herein is different from the LbL processes commonly found in the literature, as no alternate deposition of organic and inorganic materials was performed. The process in this work is related to the assembly of nanocrystals from spin coating colloidal suspensions with a hard sphere system behavior. After the deposition process, some of the films were annealed at 600°C for 2 h. For these films, similar results were observed, i.e., no significant changes in the thickness and packing factor were observed. This result is not surprising in terms of the SnO₂ system, as this oxide does not densify during the sintering process, even for nanometric particles—as discussed for the cross-sectional HRTEM image (Fig. 5). Besides, these results suggest that the prepared ultrathin films presented a very good thermal stability.

Figure 6 shows AFM images (tapping mode) of a single-layer heat-treated SnO₂ thin film (with a thickness of approximately 12-14 nm). It is possible to observe a homogeneous granular nanostructure with a smooth surface (with a mean roughness of 4.0 nm). It is interesting to observe that the mean roughness scales with the mean particle size, suggesting that the roughness is controlled by this parameter. The low-magnification AFM image (Fig. 6(a)) shows that large areas could be covered with an homogeneous SnO₂ layer. Besides, the high-magnification AFM image (Fig. 6(b)) confirms the mesoporosity and nanostructured nature of the deposited ceramic thin film.

As a tool to observe the continuity of the processed ultrathin ceramic film, and evaluate possible applications, an introductory observation of the film electrical performance was observed. Current density–electric field ($J \times E$) curves were obtained at
room temperature, using a MOS configuration. Figure 7 shows the \( J \times E \) curves for the as-deposited films and for the air- and \( N_2 \)-annealed films at 600°C for 2 h in an \( n \)-Si substrate (all films presented a thickness of 15 nm). It is possible to observe that the as-deposited ultrathin film presented higher leakage currents than the air- or \( N_2 \)-annealed thin films, probably due to the presence of \( -\)OH groups in the surface of the as-prepared nanoparticles, as the \( SnO_2 \) colloid is a water-based colloid. The leakage currents of the \( SnO_2 \) ultrathin film deposited on \( n \)-Si and \( p \)-Si substrates are described in the Table I. The films annealed in \( N_2 \) presented leakage current values similar to the ones reported for \( ZrO_2 \) thin films obtained by a modified ALD process, suggesting that the ultrathin ceramic films processed by the colloidal spin coating deposition present good electrical performances. Electrical properties are certainly affected by the packing factor; however, as no significant changes were observed in the packing factor and the thickness of the as-prepared and 600°C-annealed thin films, these effects can be neglected here. From these results, a more detailed electrical study should be performed in these films.

<table>
<thead>
<tr>
<th>Thin film</th>
<th>Substrate</th>
<th>Leakage current at 1 MV/cm (A/cm²)</th>
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<tbody>
<tr>
<td>SnO₂ as deposited</td>
<td>( n )-Si</td>
<td>( 5.4 \times 10^{-4} )</td>
</tr>
<tr>
<td>SnO₂ as deposited</td>
<td>( p )-Si</td>
<td>( 1.6 \times 10^{-1} )</td>
</tr>
<tr>
<td>SnO₂ annealed in air</td>
<td>( n )-Si</td>
<td>( 7.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>(600°C-2 h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂ annealed in air</td>
<td>( p )-Si</td>
<td>( 2.2 \times 10^{-2} )</td>
</tr>
<tr>
<td>(600°C-2 h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂ annealed in ( N_2 )</td>
<td>( n )-Si</td>
<td>( 2.2 \times 10^{-6} )</td>
</tr>
<tr>
<td>(600°C-2 h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂ annealed in ( N_2 )</td>
<td>( p )-Si</td>
<td>( 1.5 \times 10^{-6} )</td>
</tr>
<tr>
<td>(600°C-2 h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ (from ref. 9)</td>
<td>( p )-Si</td>
<td>( 1.6 \times 10^{-3} )</td>
</tr>
<tr>
<td>ZrO₂ (from ref. 9)</td>
<td>( p )-Si</td>
<td>( 9.0 \times 10^{-6} )</td>
</tr>
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</table>

These values are compared with values of ultrathin oxides films reported in the literature.

IV. Conclusions

In summary, the present article describes a controlled thickness deposition process, analogous to LbL processes, to obtain ultrathin SnO₂ films with a high \( \Phi_m \). A low-cost and convenient solution-based technique, combined with spin-coating deposition, was developed. The process developed in this work induces the assembly of nanocrystals by spin coating colloidal dispersions with a hard sphere system behavior. In fact, the colloidal dispersions used in this work presented particular properties that allowed the preparation of highly controlled and reproducible layer depositions. The desirable colloidal nanocrystal dispersion properties are: high colloidal stability at low and high solid contents and pseudo-plastic behavior at high solid contents. Nanostructured ultrathin films with homogeneous microstructures, as well as with low leakage currents, were obtained using this process. The process developed here can be applied to different ceramic oxide systems, aimed at the development of electronic devices, where ceramic ultrathin films are of considerable interest.

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References