The Production of Thin Metal Oxide Films by
Spray Pyrolysis Using Supercritical
CO₂-Assisted Aerosolization of Aqueous Solutions†

Scott P. Sellers, Bobbi A. Miles,
and Robert E. Sievers*
Department of Chemistry and Biochemistry,
University of Colorado
Ward Halverson
Spire Corporation

Abstract
Thin metal oxide films have been deposited onto various substrates, under ambient pressure, utilizing supercritical CO₂-assisted nebulization of aqueous solutions. In this process, supercritical CO₂ is contacted with an aqueous precursor solution inside a low-dead-volume tee. The resulting emulsion is allowed to expand out of a capillary restrictor, and the fine particle aerosol formed is directed toward heated substrates. Dehydration, pyrolysis and oxidation of the precursors occur at or near the surface of the substrate to form the desired metal oxide film. Thin films of zinc oxide, zinc gallate and manganese-doped zinc gallate have been prepared using this technique.

1. Introduction
Thin films of zinc oxide have recently received much attention due to their multifunctional nature. In addition to being transparent wide band-gap semiconductors, thin films of zinc oxide have piezoelectric capabilities. Potential applications of these films include transparent electrodes [1], solar cells [2, 3], surface acoustic wave devices [4] and pressure/vibration detectors [5]. Several methods have been used to deposit high quality thin films of zinc oxide, including rf sputtering [6], chemical vapor deposition [7, 8] laser ablation [9], conventional spray pyrolysis [10, 11, 12] and spray pyrolysis with ultrasonic nebulization [13, 14, 15]. In this study, it is demonstrated that the production of transparent thin films of zinc oxide is possible via a new spray pyrolysis technique using supercritical CO₂-assisted nebulization.

2. Supercritical CO₂-assisted Nebulization
Supercritical CO₂-assisted nebulization utilizes the properties of supercritical carbon dioxide (CO₂ that has been pressurized above its critical pressure (1070 psi) and heated above its critical temperature (31°C)) to assist in the production of aerosols of aqueous solutions. One of the most relevant properties is the solubility of carbon dioxide in water, with up to one to two mole percent of CO₂ dissolving in water at temperatures between ambient and 40°C and at equilibrium pressures of 1070 to 2000 psi. A diagram of the system used for supercritical CO₂-assisted nebulization is shown in Figure 1. Supercritical or near critical CO₂ is pumped into one side of a low-dead volume tee, while an aqueous precursor solution containing metal salts or other dissolved species is simultaneously pumped into another leg of the tee. The intimate mixing of the two streams generates an emulsion of aqueous droplets with dissolved CO₂ surrounded by supercritical or near-critical CO₂. The emulsion is not resident in the tee long enough to reach solubility equilibrium,
but pH indicator studies have shown that significant amounts of CO₂ become dissolved in the aqueous droplets. The resultant emulsion is then allowed to expand out of a fused silica or stainless steel capillary pressure restrictor with a very narrow diameter (50–150 μm i.d.). Upon decompression into a heating chamber containing air at atmospheric pressure, shear forces and the rapidly expanding CO₂ (CO₂ that is dissolved in the aqueous droplets and the gaseous CO₂ surrounding the droplets) produce a dense aerosol plume of very fine droplets containing the dissolved metal salts. The water droplets rapidly dehydrate to form fine particles in dry air with diameters of approximately 1 μm. The aerosol is directed toward a heated substrate, under ambient pressure, where water evaporation and pyrolysis and/or oxidation of the metal precursors occur to form the desired metal oxide thin film.

The supercritical CO₂-assisted nebulization method used for thin film deposition permits the formation of films that are chemically different from the precursors used. A wider variety of films can be formed using this method, which does not require that the precursors be volatile. Any metal-containing precursor compound or mixture of compounds that is soluble in the supercritical fluid or can form a heterogeneous emulsion in the supercritical fluid can be used as a thin film precursor. CO₂ is the supercritical fluid of choice since it is less expensive than any organic solvent, avoids the emission of organic solvent vapors, is non-flammable, and is relatively non-toxic. Sievers and coworkers have been issued several patents for this technology and have employed these methods to form thin films and powders that are potentially useful as phosphors, optical coatings, high temperature protective materials, superconductors, and electronic materials. [16] Whether one forms fine particles or thin films as a final product depends on the experimental apparatus, and heating and diluent gas dynamics. In tube heaters, with gas sheath flow to reduce particle contact with the walls of the dehydration/pyrolysis/oxidation chamber, fine particles (often spherical) are generated rather than films. [16g]

3. Experimental System and Procedure

The precursor solution was transported to the low-dead-volume stainless steel mixing tee (Valco) by an automated ISCO syringe pump set to a constant flow rate (0.3 to 2 mL/min). Carbon dioxide (Scott Specialty Gases, SFE grade) was added to a separate ISCO syringe pump, pressurized above the critical pressure (1100 psi), and then set to deliver at a constant pressure. The third leg of the mixing tee was fitted with either a fused silica capillary restrictor (Alltech, 50 and 75 μm i.d.), or 1/16" stainless steel tubing (100 and 170 μm i.d.) approximately 4 cm in length. The tip of the restrictor was positioned approximately 8 cm from the center of a ceramic hotplate which was used to heat the silicon substrates. Soda lime glass substrates were heated inside a horizontally mounted tube furnace in order to prevent substrate cracking. The angle of the flow restrictor tubing with the surface was varied between 90 and 180°, and the expected differences in substrate cooling and deposition shapes were noted. The details of the system used to deposit onto glass substrates are shown in Figure 2. Substrate temperatures ranged from 350 to 500°C for both silicon and glass. Common parameters and settings for this system are summarized in Table 1.

4. Analysis

The optical transparency of the films was measured with a Perkin Elmer Lambda 9 UV/Vis/NIR spectrophotometer. Coated substrates were mounted perpendicular to the light source and referenced against uncoated substrates of the same composition. Surface morphology and grain size were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Micrographs were taken with an
ISI-SX-30 Scanning Electron Microscope. Samples were coated with a thin film of gold (Polaron SEM Coating System) just prior to imaging. AFM images were taken with a Digital Instruments atomic force microscope set to contact mode using silicon nitride AFM tips (Digital Instruments). Crystal phases were identified with a Scintag PADV diffractometer using CuKα radiation. Substrates were cut to the appropriate size of 3 cm x 3 cm and mounted in the diffractometer without further preparation.

5. Results and Discussion

5.1 Deposition of ZnO films onto Glass and Silicon Substrates

Precursor solutions (0.05 M) were made using zinc acetate (99.9%, Aldrich) dissolved in deionized water with a few drops glacial acetic acid (Aldrich) to prevent precipitation. Soda lime glass substrates (Ford Glass) were placed inside a cylindrical tube furnace in order to heat the substrate uniformly and prevent substrate cracking. The aerosolized zinc acetate solution was then directed into the tube furnace for a period of 5–20 minutes. Thin films of zinc oxide deposited on glass had good adhesion and were quite transparent. Concentric birefringence rings were visible when the films were viewed perpendicularly to white light, as shown in Figure 3. The optical data shown in Figure 4 indicate 80–90% optical transparency in the region between 500 and 800 nm. A sharp decrease in transmission occurs at 380 nm indicative of a band gap of approximately 3.27 eV. This value is consistent with the literature value reported for bulk ZnO. [17]

Polished silicon substrates were heated with a ceramic block heater to approximately 450°C during the deposition. The aerosolized zinc acetate was directed onto the substrates for 5–20 minutes. The powder diffraction pattern of ZnO deposited onto silicon is shown in Figure 5. The absence of a halo in the powder pattern indicates a crystalline thin film with no observable amorphous character. One sample was deliberately broken, and a cross-sectional SEM image of the relatively thick film (>10 μm), shown in Figure 6,
indicated a structure of layered, approximately 1 μm-thick ZnO plates. Surface features of the very smooth ZnO films are not apparent with the SEM until very high magnification (60,000X), shown in Figure 7. The surface features appear to be less than 100 nm across.

5.2 Deposition of ZnGa₂O₄ Films onto Silicon Substrates

Precursor solutions were made by mixing zinc acetate (Zn(CH₃COO)₂, 99.99%; Aldrich) dissolved in deionized water, and an equal volume of gallium acetylacetonate (Ga(acac)₃, 99%; Aldrich) dissolved in isopropanol resulting in a 1:1 water : isopropanol single-phase solution containing 0.0125 M zinc acetate and 0.025 M gallium acetylacetonate. The precursor solution was aerosolized and directed toward a heated silicon substrate using the same parameters as with the deposition of ZnO. As deposited, the zinc gallate films are amorphous as indicated by powder X-ray diffraction. Annealing the films after deposition had the effect of increasing the crystallinity of the film, as shown in Figure 8, due to crystallization of the amorphous film or phase change. The surface morphology of the films appeared very smooth and uniform at all magnifications that could be examined in the SEM micrographs (Figure 9). An AFM image of a partially coated polished silicon substrate is shown in Figure 10. This image indicates that supercritical CO₂-assisted aerosolization and pyrolysis produces very small grain sized (60 nm) ZnGa₂O₄ films upon deposition.

The photoluminescence emission spectra of ZnGa₂O₄ films deposited on silicon had a maximum emission of approximately 435 nm, the characteristic blue emission band of zinc gallate arising from the t¹F₂ → A₂ transition. [16] Spectral intensity ranged up to 8.7×10⁻⁴ (W/sr·m²) (Table 2) for samples between one and
Table 2: Film thickness, Ga:Zn molar ratio, peak maximum and intensity for four films of zinc gallate prepared by supercritical CO$_2$-assisted deposition.

| Thickness (μm) | Ga:Zn molar ratio | $\lambda_{\text{max}}$ (nm) | Intensity (W/sr-m$^2$) |
|----------------|--------------------|-----------------------------|------------------------|
| 0.5-1          | 2.08               | 424                         | $1.8 \times 10^{-4}$   |
| 1-5            | 2.27-2.65          | 444                         | $8.7 \times 10^{-4}$   |
| >5             | 1.65-1.79          | 428                         | $5.6 \times 10^{-4}$   |

five microns thick. EDS measurements on the samples indicated a Ga:Zn molar ratio close to 2, with little variance across the surface of the film. These data indicate that the stoichiometry of the deposited films is in good agreement with the stoichiometry of the premixed precursor solution.

Five samples of ZnGa$_2$O$_4$ deposited on silicon and alumina substrates were sent to Spire Corporation for cathodoluminescence testing. The electron beam energy was 8 kV at 200 mA total current with a 3 mm estimated spot size. The cathodoluminescence data were similar for all samples and corresponded to the blue emission attributed to zinc gallate. The variation in relative intensity across the surface of each sample was too small to be detected by the eye. The sample-to-sample luminescence intensity ranged from 2.42 cd/m$^2$ for the thinnest film to 17.5 cd/m$^2$ for the thickest film measured. It should be noted that the thicker films were rougher, and it remains unclear whether brighter films are a result of differences in film thickness or surface morphology.

5.3 Manganese-doped Zinc Gallate Thin Films

In order to investigate the possibility of producing ion-doped thin films, manganese-doped zinc gallate (Mn$_x$Zn$_{1-x}$Ga$_2$O$_4$, with $x=0.006$) were deposited onto polished silicon substrates. Mn$_x$Zn$_{1-x}$Ga$_2$O$_4$ precursor solution was made by the addition of the correct volume of an aqueous stock solution of manganese (II) acetate (25 mg/100 mL) to the zinc acetate/gallium acetylacetonate solution previously described. Films were sprayed using the conditions stated for the ZnO thin films. Films were deposited onto silicon and textured silicon substrates obtained from Spire Corporation. Figure 11 shows an SEM image of a textured silicon substrate coated with Mn$_x$Zn$_{1-x}$Ga$_2$O$_4$. The substrate was masked during the deposition to determine the degree of surface coverage of the deposition (i.e., to determine whether the thin zinc gallate film would mimic the rough silicon surface upon deposition). As seen by the SEM, the films appear to have mimicked the surface perfectly with only a slight change in intensity to indicate the area of deposition.

It was determined that Mn$_x$Zn$_{1-x}$Ga$_2$O$_4$ could be deposited by the supercritical CO$_2$-assisted nebulization method. Unfortunately, the films appeared to have identical photoluminescence to the undoped films when viewed under a UV lamp. The expected result of doping manganese into the films was an increased intensity of the photoluminescence and a shift in the observed emission. It was determined that deposition in the presence of air could potentially lead to oxidation of the desired manganese (II) ions to manganese (III) (which did not produce the desired enhancement of the intensity of the luminescence), and that the addition of an annealing step (in a reducing atmosphere) might be required. The Spire collaborator was able to confirm this hypothesis by conducting the annealing experiments (for 60 sec at 800°C) and determining that the photoluminescence of the Mn$_x$Zn$_{1-x}$Ga$_2$O$_4$ films was much brighter after the annealing step. The spectral data for the best of the Mn$_x$Zn$_{1-x}$Ga$_2$O$_4$ after annealing in forming gas, appears in Figure 12. The peak of the spectrum is at 508 nm and luminance (based on eye’s spectral sensitivity) was estimated to be 16.75 candella/m$^2$.
6. Conclusion

Supercritical CO$_2$-assisted aerosolization and pyrolysis has been used to deposit smooth metal oxide films from water-soluble metal precursors. Transparent crystalline films of zinc oxide were deposited onto soda lime glass and polished silicon substrates. This study demonstrated that high quality metal oxide films can be rapidly deposited from non-volatile, as well as volatile, precursors by CO$_2$-assisted nebulization coupled with pyrolysis and oxidation. The deposition process is conducted at atmospheric pressure. The very fine aerosol droplets formed are rapidly dehydrated to form particles predominantly in the 0.1 to 5 µm diameter range, which decompose at heated (300–700°C) substrate surfaces. Crystallinity of deposited films can be increased by annealing at elevated temperatures. If annealing is conducted in the presence of a reducing gas such as forming gas, the oxidation state of metal ions can be changed; for example manganese doped in zinc gallate is reduced to Mn (II). These results indicate the ease at which multi-component thin metal oxide films and doped metal oxide films may be produced with supercritical CO$_2$-assisted nebulization and pyrolysis from water (or alcohol/water) soluble precursors.

Acknowledgements

The authors would like to thank Spire Corporation, DARPA (Grant No. DAAL01-96-K0093), NSF (Phase II SBIR Grant No. DMI-9615987), and NSF/EPA (Grant No. DMI-9615987) for their financial support of this work.

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Scott P. Sellers

Scott Sellers received his BS degree in Chemistry from the University of Southern California in 1991 and his PhD in Inorganic Chemistry in 1997 at the University of Colorado studying molecular magnetic materials. His postdoctoral research at the Cooperative Institute for Research in Environmental Sciences in Boulder, CO included the development of supercritical CO2-assisted aerosolization technology. Dr. Sellers is currently a research scientist at Coulter Pharmaceutical, Inc. (So. San Francisco, CA).

Robert E. Sievers

Professor Bob Sievers is a Professor of Chemistry and is the Director of the Environmental Program at the University of Colorado at Boulder. After completing his undergraduate work at Tulsa and his Ph.D. studies at the University of Illinois, Professor Sievers served as an officer of the U.S. Air Force and conducted research for 15 years at the Aerospace Research Lab at Wright-Patterson AFB, Ohio. He accepted a professorship at the University of Colorado in 1975, and served as Dean of the Graduate School, 1986-7. Professor Sievers has authored or co-authored approximately 190 publications dealing with powders, thin films, materials chemistry, aerosols, chromatography, and various aspects of trace analysis and environmental chemistry. In 1973, he was chosen as a Distinguished Alum by the University of Tulsa in recognition of his scientific studies, including the analysis of lunar rocks. Professor Sievers has been granted 28 U.S. and foreign patents. His most recent interests have focussed on pulmonary drug delivery and thin films produced by pyrolysis of aerosols. He has developed new patented processes for forming dense plumes of fine aerosols using supercritical carbon dioxide. He is a co-founder of Sievers Instruments, Inc., a company manufacturing innovative detectors for chemical analysis, particularly for environmental measurements, which was acquired by Ionics, Inc., in 1996.

Ward Halverson

Ward Halverson holds S.B. (1956) and Sc.D. (1965) degrees in Geophysics from the Massachusetts Institute of Technology. A post-doctorate appointment at the Centre d'Etudes Nucleares de Fontenay-aux-Roses, France, was on plasma physics and controlled thermonuclear fusion. He was a research scientist at the NASA Electronics Research Center, Cambridge, MA, for 3 years, and was then on the research staff at the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology in basic and applied plasma physics. Since 1978 he has been a Senior Scientist at Spire Corporation in Bedford, Massachusetts, where he performs applied research on thin films and surface modification of materials. He is a member of the American Physical Society and American Association for the Advancement of Science.