

Laser-assisted spray pyrolysis process for the growth of TiO₂ and Fe₂O₃ nanoparticle coatings

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(Received 9 June 2006; accepted 30 October 2006)

We present a laser-assisted spray pyrolysis method to fabricate nanoparticle coatings of metal oxides. In this process, 1.5- μm size droplets of a titanium- or iron-containing organometallic precursor were injected into a vacuum chamber with SF₆ carrier gas. The strong absorption of a 3W CO₂ laser beam focused onto the injector tip in the presence of SF₆ increased the temperature of the gas and the droplets to about 300 °C. Films deposited on heated substrates with and without the CO₂ laser heating were studied by atomic force microscopy. The laser heating of the droplets caused the solvent to evaporate before depositing on the substrate, leading to grain sizes that are about a factor of 3 smaller than those deposited without laser heating. By controlling the concentration of the precursor in the solvent, the average particle sizes have been tuned from 80 to 50 nm.

I. INTRODUCTION

A wide range of applications associated with thin films and coatings has led to the development of a variety of growth techniques. The characteristics of the deposited films are affected by the technique used. The parameters that gauge the quality of a film include the surface morphology, the density, and the crystallinity. Among the variety of techniques available for the growth of thin films, chemical and physical vapor deposition processes are known to produce the best quality films.¹ These techniques enable precise control of the growth process, and have therefore been extensively used for the growth of films for device applications. For applications that do not require such high quality, a number of more economical techniques are available. These include electroplating,² plasma spray,³ screen-printing,⁴ and spray pyrolysis.^{5–11} The simplicity, low capital cost of equipment, and adaptability to large-scale processing make these methods attractive for coating large surface areas.

The chemical spray pyrolysis technique is particularly interesting because it can be used to form coatings of a variety of different materials. Since its initial use for the deposition of CdS films for solar cells,¹² it has been successfully implemented in the fabrication of thin films of metal oxides, chalcogenides, and high temperature superconductors.¹³ The main component of a spray pyroly-

sis system is an atomizer that generates microdroplets of a precursor solution dissolved in a relatively volatile solvent. The droplets, in the form of a fine spray, are carried out of a nozzle onto a heated substrate by a carrier gas that can be inert or reactive. The constituents of the droplets decompose and react on the hot substrate to form the chemical compound. The substrate temperature should be high enough to evaporate the volatile solvents. The spray nozzle is usually scanned continuously during the growth to coat a large area of the substrate. Laser pyrolysis techniques have also been used to generate nanocrystalline powders and coatings.¹⁴ In contrast to the thermal spray pyrolysis process where the decomposition and the reaction take place at the hot substrate, in laser pyrolysis processes, the droplets interact with a continuous wave laser beam as they come out of the nozzle. If the molecules of the precursor have a strong resonance absorption band at the wavelength of the laser beam, the molecule is dissociated. This method has been used to form amorphous nanoparticles of Si/N/C.¹⁵ However, this method is restricted to compounds that have resonance absorption bands at an available laser wavelength.

The sizes of the produced droplets depend on the technique used to atomize the solution. The simplest way to generate an aerosol spray is by a pneumatic process. In this method, the pressure drop at the orifice of a nozzle from a high flow rate of gas causes the dispersion of the solution into microdroplets. However, control of the particle size distribution produced by this method is very difficult. On the other hand, ultrasonic nebulizers (model 241CST; Sonaer Ultrasonics, Farmingdale, NY) are

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DOI: 10.1557/JMR.2007.0089

known to produce a fairly uniform distribution of micrometer-size droplets. Generally, the nebulizer is operated at a frequency of 2.4 MHz, where the precursor solution is converted into a mist of particles in a range of 1–2 μm in diameter. These particles lack sufficient inertia and thus have to be transported by a carrier gas. Because the aerosol-generating rate is independent of the gas flow rate, the transport of the droplets to the substrate can be controlled without affecting the function of the nebulizer.

When the droplets impinge upon the heated substrate, the precursor is decomposed to form the compound. The subsequent film formation and the morphology of the film are dependant on the velocity of the drop, the rate of reaction, and the rate of evaporation of the solvent. At high velocities, the droplets will flatten on the substrate, leading to large particle sizes.¹¹ If most of the solvent is evaporated when the drop gets to the substrate, the solid particle will stick to the substrate to form a crystallite that is smaller than the initial droplet. Therefore, by controlling the concentration of the solvent, the size of the particles deposited on the substrate can be controlled. In this article, we describe the growth of nanocrystalline coatings of TiO₂ in the anatase structure and Fe₂O₃ with controlled particle size distributions using this laser-assisted spray pyrolysis technique. The anatase phase of TiO₂ is widely used as a photocatalytically active material in UV,¹⁶ whereas γ-Fe₂O₃ is used in a variety of applications including magneto fluidics.^{17,18}

II. EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig. 1. A 3W continuous wave CO₂ laser was focused to a point just above the funnel tube orifice enclosed in a glass deposition chamber. Because the proposed precursors do not have resonance absorption with the CO₂ laser wavelength, sulfurhexafluoride (SF₆) is

used as the carrier gas for aerosol transport. The CO₂ laser beam of wavelength 10.6 μm was resonantly absorbed into the SF₆ molecules through vibrational excitation. Therefore, the carrier gas was heated by the CO₂ laser as the aerosol/gas mixture was injected into the chamber. The flow rate and thus the speed of the aerosol into the chamber were controlled by a gas flow meter. Nitrogen or argon gas was injected through a circular tube placed just below the nozzle to maintain a forward flow for the aerosol and the SF₆ gas. The pressure inside the chamber was kept very close to atmospheric.

Toluene was used as the solvent for the organometallic compounds used for the formation of TiO₂ and Fe₂O₃. To evaporate toluene in each drop, the laser-gas interaction time should be sufficient to increase the gas temperature above the boiling point of toluene (93 °C). At high gas flow rates, the growth rate of the film is increased while the laser energy absorbed per unit volume is decreased, leading to lowering of the gas temperature. On the other hand, a higher percentage of laser energy is absorbed at higher flow rates as the laser interacts with a larger volume per unit time. The laser power absorbed by the gas was obtained by measuring the transmitted laser energy after the laser-gas interaction. The effect of the flow rate on laser heating of the SF₆ carrier gas was studied by placing a K-type thermocouple in front of the nozzle opening just after the laser focus. The inset of Fig. 1 shows the position of the thermocouple. A thermocouple made out of thin wires was used to minimize any disturbance to the laser-gas interaction volume. Care was taken to avoid the incidence of laser beam on the thermocouple. Any direct interaction of the laser with the thermocouple would cause the temperature to rise without the presence of SF₆ gas. The organometallic compounds used for the formation of TiO₂ and Fe₂O₃ were cyclopentadiethyltitanium trichloride [(C₅H₅TiCl₃); 98%] and pentacarbonyliron [Fe (CO)₅; 99.5%], respectively. The precursors were prepared by dissolving these

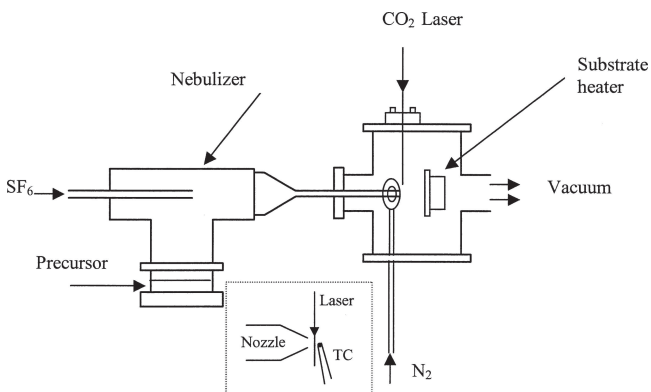


FIG. 1. Experimental setup for laser-assisted spray pyrolysis process. The inset shows the position of the thermocouple (TC) with respect to the nozzle and the laser beam.

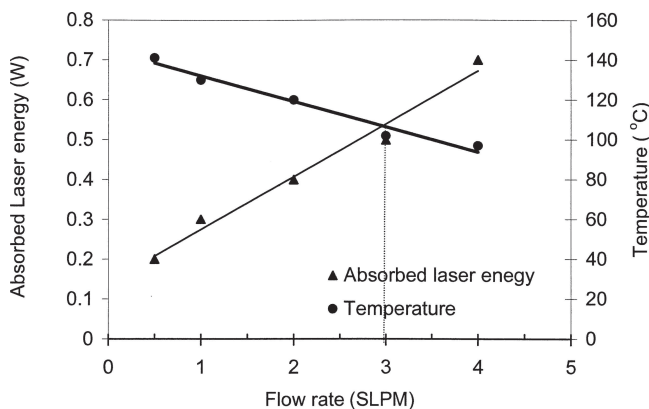


FIG. 2. Flow rate dependence of the laser energy absorbed by the gas and the measured temperature of the gas.

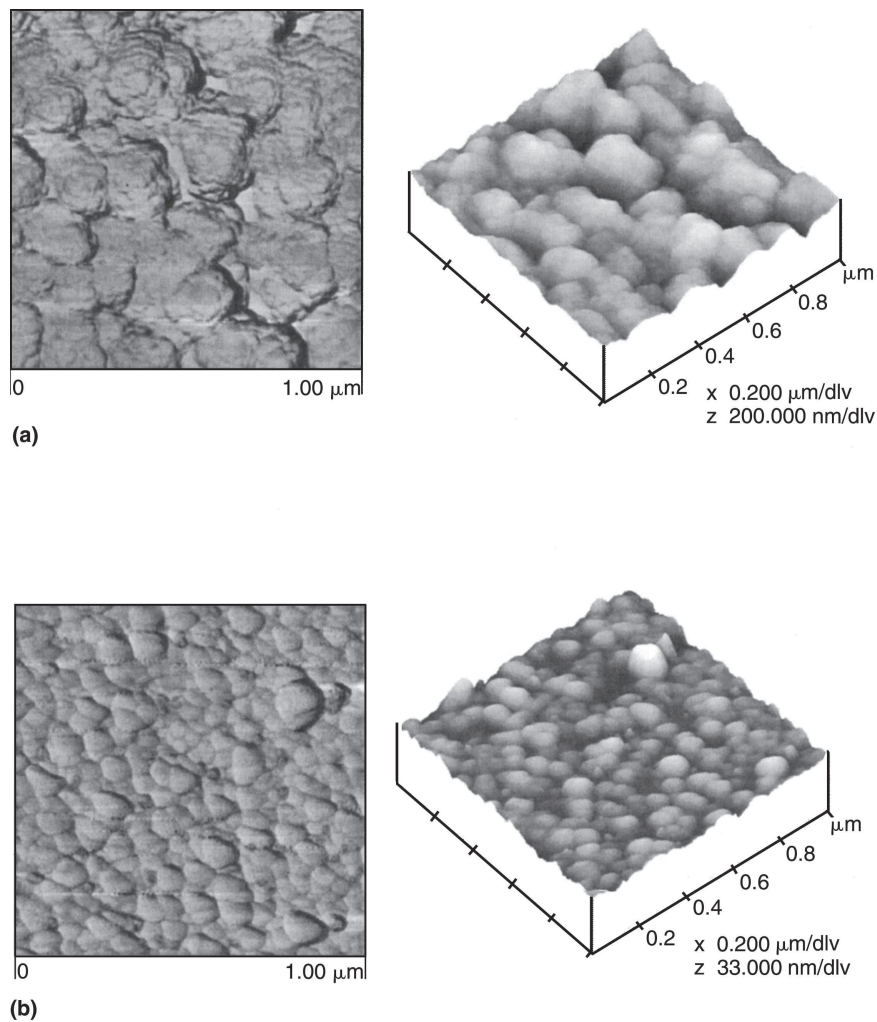


FIG. 3. In-plane and three-dimensional AFM images of TiO₂ coatings deposited by spray pyrolysis. (a) Without and (b) with CO₂ laser heating of the carrier gas.

compounds in toluene with different molar concentrations from 0.05–0.25 M. Si(100) wafers, cleaned by organic solvents and deionized water, were used as substrates. Si substrates provide a smooth surface that is advantageous for surface morphological studies of nanoparticle coatings. The substrate was mounted on a heating block that was placed 4–6 cm in front of the nozzle. Coatings were deposited at a substrate temperature of 350 °C. The morphologies of the deposited coatings were analyzed by atomic force microscopy (AFM; Dimension TM 3100; Digital Instruments, Santa Barbara, CA).

III. RESULTS AND DISCUSSION

The effect of gas flow rate on the gas temperature and the percentage of laser energy absorbed is shown in Fig. 2. To obtain a high growth rate, and at the same time to maintain the gas temperature at the nozzle above the boiling point of toluene (93 °C) while coupling a maximum

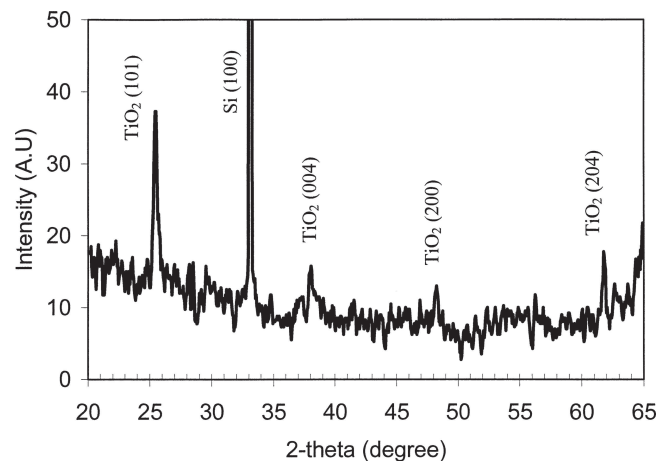


FIG. 4. The XRD patterns of a TiO₂ coating deposited with laser heating. All the indicated peaks correspond to the anatase structure of TiO₂.

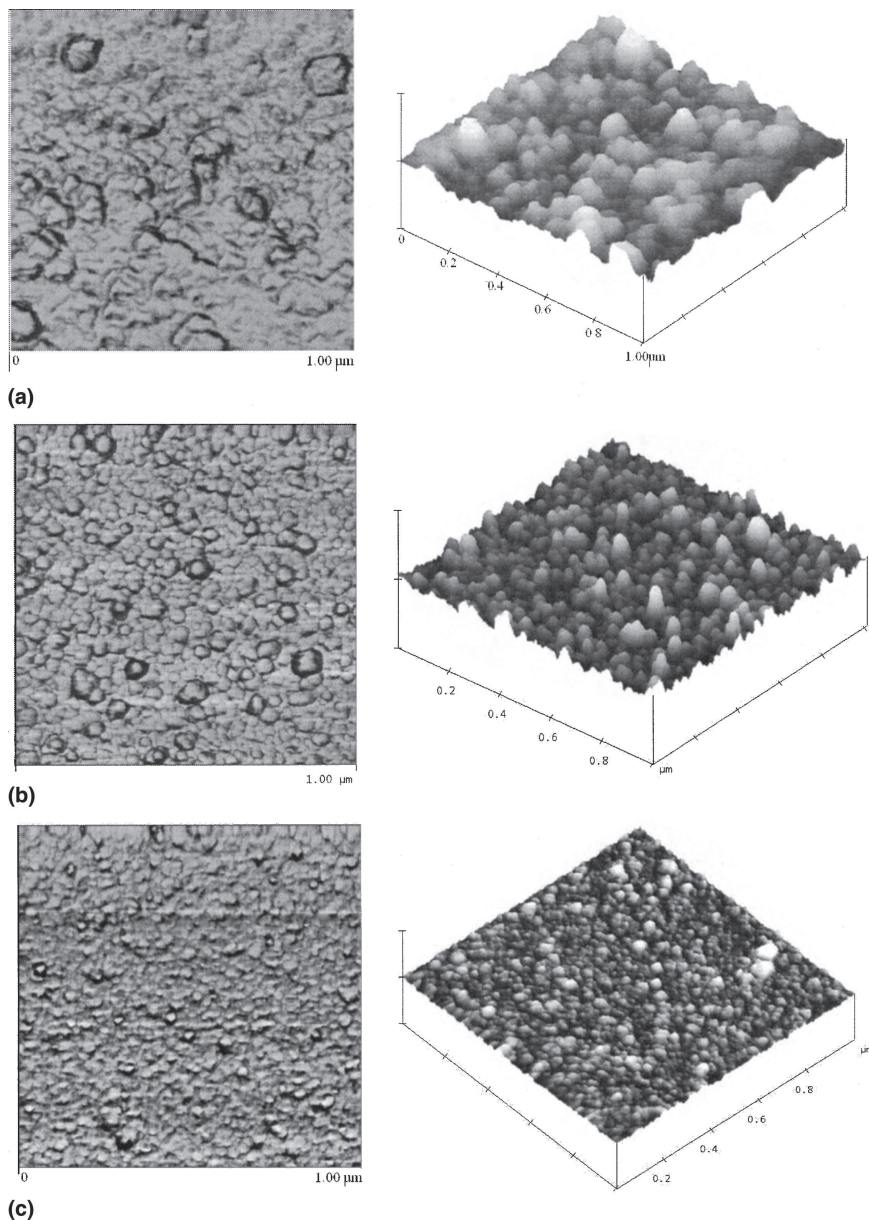


FIG: 5. In-plane and three-dimensional AFM images of Fe₂O₃ coatings deposited by spray pyrolysis. (a) Without and (b) with laser heating for a precursor concentration of 0.1 M. (c) With laser heating for a precursor concentration of 0.05 M.

amount of laser energy into the gas, a gas flow rate of 3 L/min was used in film growth. The morphology of the coatings studied by AFM for depositions with and without laser heating of the gas for TiO₂ is shown in Fig. 3. The concentration of the Ti compound was 0.1 M. Without laser heating of the gas, the droplets ~1.5 μm in size that are striking the heated substrate tend to flatten themselves during the impact. This leads to the larger grain sizes observed in TiO₂ coatings. However, with laser heating of the gas closer to 100 °C, most of the solvent (toluene) gets evaporated before striking the substrate. As a result, the drops condense into a smaller particle with a high concentration of the organometallic

compound. Because the laser-gas interaction is limited to the focal volume of the laser, heating of the flowing gas takes place in a length that is closer to the waist of the laser beam (~1 mm). Under these conditions, complete conversion of the liquid droplets into solid particles does not take place. This is evident by the wet coating deposited when the substrate is not heated. The average particle size of TiO₂ without laser heating is about 250 nm. Irregular particle shapes and sizes produced because of flattening of the drops on the substrate are visible in the three-dimensional image. In comparison, coatings deposited with CO₂ laser heating of the carrier gas show a distribution of well-defined particles [Fig. 3(b)] with

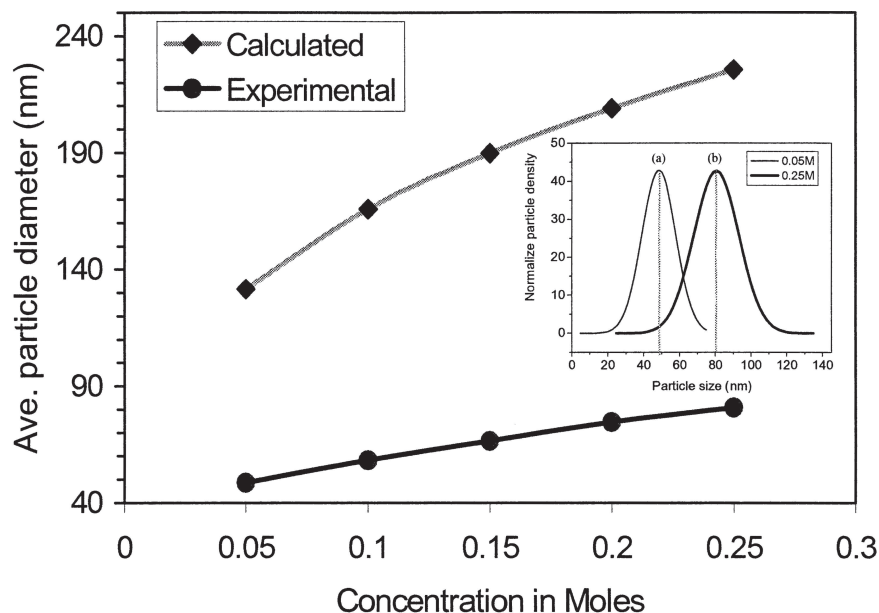


FIG. 6. Calculated and experimentally observed variation of average particle size for Fe₂O₃ coatings with molar concentration of Fe(CO)₅ in the precursor solution. The inset shows the particle size distribution derived from AFM images for the two concentrations 0.05 and 0.25 M.

average particle sizes of 100 nm. TiO₂ nanoparticles grown by other techniques, including vapor hydrolysis,¹⁶ were shown to be amorphous at 260 °C, and become predominantly anatase form above 600 °C. An x-ray diffraction (XRD) pattern of the TiO₂ nanoparticle coatings grown by our technique showed the formation of the anatase phase of TiO₂ at 350 °C (Fig. 4).

The effect of the laser heating and the starting concentration of Fe(CO)₅ on Fe₂O₃ coating morphology and the particle size is shown in Fig. 5. Similar to TiO₂, laser heating the gas helped to produce well-defined and much smaller particles of Fe₂O₃ [Figs. 5(a) and 5(b)]. For a starting concentration of 0.1 M, the average size of the particles produced was about 60 nm, which is about 40% smaller than the TiC particles produced with the same 0.1 M starting concentration. The boiling point of Fe(CO)₅ is 103 °C and it decomposes at 200 °C. For C₅H₅TiCl₃, the melting point is 170 °C and it decomposes at 210 °C. Clearly, along with toluene, a significant percentage of Fe(CO)₅ may also have been evaporated during laser heating, leading to smaller particle sizes. Deposition of evaporated Fe(CO)₅ and subsequent decomposition forms a brown coating on the walls of the glass chamber, which supports this assumption. Furthermore, reduction of the concentration of Fe(CO)₅ in the solution from 0.1–0.05 M changed the particle size from 60 nm to about 48 nm [Figs. 5(b) and 5(c)].

Particle coatings deposited with precursor concentrations of 0.05, 0.1, 0.2, and 0.25 M have been analyzed by AFM to study the concentration-particle size relation in the laser-assisted spray pyrolysis process. Figure 6 shows the particle size distribution obtained from AFM images

for the concentrations of 0.05 and 0.25 M. As indicated by the full width at half-maximum, the size distribution of the particles becomes narrower at low concentrations. A simple computation can be performed to derive a rough estimate of the expected particle size for a given precursor concentration. For example, the number of Fe(CO)₅ molecules in a 1.5- μ m drop of a 0.1 M solution can be computed to be 1.07×10^8 . Assuming that the solvent is completely evaporated and that all of the Fe(CO)₅ molecules in a droplet are converted into Fe₂O₃ that become a compact spherical solid particle of density 5.7×10^3 kg/m³, which is the true density of Fe₂O₃, the diameter of the particle can be calculated to be 164 nm. Because we assume the individual particles to be single crystal or polycrystalline, we have used the upper bound of density for this computation. However, the bulk density of the coating will be smaller, between the true density of 5.7×10^3 kg/m³ and the value of 1.2×10^3 – 2.4×10^3 kg/m³ for Fe₂O₃ powder because of voids in the coating.¹⁹ If the particle impinging on the substrate is in the liquid form, some degree of flattening can be expected, leading to a larger profile on the surface. Therefore, the computed value is even a lower estimate of the final particle size. Figure 6 shows the experimental and computed particle size variation with the precursor concentration. Experimental and calculated particle size variation with concentration follows a similar trend. However, the experimental value is about a factor of 3 smaller than the calculated values. This indicates that a large percentage of Fe(CO)₅ is evaporated along with the solvent during laser heating.

IV. CONCLUSIONS

We have incorporated a CO₂ laser into a chemical spray pyrolysis system to heat the droplets of an organo-metallic precursor dissolved in a volatile organic solvent. The droplets with an average diameter of 1.5 μm in a narrow size distribution were generated by an ultrasonic nebulizer. Our experiments have shown that when the droplets were directly incident on the substrate, they initially flatten on the surface, followed by evaporation of the solvent and decomposition, leading to large particle sizes. When the droplets are heated above the boiling point of the solvent before incidence on the heated substrate, most of the solvent is evaporated, leading to solid particles impinging on the substrate. Coatings with much smaller and well-defined grains have been grown by the laser heating the droplets. The experiments have also shown that by manipulating the concentration of the precursor, the grain size of the deposited coating can be controlled on the nanoscale. Because the laser radiation in this process is absorbed into the carrier gas, resonance absorption by the precursor is not important. Therefore, this technique can be extended to any organometallic compound that can be dissolved in a volatile solvent.

ACKNOWLEDGMENT

This work was partially supported by the National Science Foundation under Grant No. DMI-0217939.

REFERENCES

1. S.M. Rossnagel: Thin film deposition with physical vapor deposition and related technologies. *J. Vac. Sci. Technol. A* **21**, S74 (2003).
2. T. Hara and H. Toida: Properties of copper layers deposited by electroplating on an agglomerated copper seed layer. *Electrochem. Solid-State Lett.* **5**, C102 (2002).
3. K.K. Hyun, P.R. Taylor, and H.L. Lee: Characterization of La_{0.8}Sr_{0.2}MnO₃ produced by a reactive dc thermal plasma spray system. *Plasma Chem. Plasma Proc.* **23**, 223, (2003).
4. O. Gomez-Daza, V.M. Garcia, M.T.S. Nair, and P.K. Nair: Highly photosensitive CdSe coatings by screen printing and sintering technique. *Appl. Phys. Lett.* **68**, 1987 (1996).
5. W. Kern and B. Tracy: Titanium dioxide antireflection coating for silicon solar cells by spray deposition. *RCA Rev.* **41**, 113 (1980).
6. R. Krishnakumar, V. Subramanian, Y. Ramprakash, and A.S. Luxmanan: Thin film preparation by spray pyrolysis for solar cells. *Mater. Chem. Phys.* **16**, 385 (1987).
7. P.S. Patil and P.R. Patil: Electrochromic properties of tungsten oxide thin films deposited by solution thermolysis. *Tr. J. Phys.* **18**, 1330 (1994).
8. E. Rios, G. Poillerat, J.F. Koenig, J.L. Gautier, and P. Chartier: Preparation and characterization of thin Co₃O₄ and MnCo₂O₄ films prepared on glass/SnO₂:F by spray pyrolysis at 150 °C for the oxygen electrode. *Thin Solid Films* **264**, 18 (1995).
9. K. Okuyama, L. Wuled, N. Tagami, S. Tamaki, and N. Tohge: Preparation of ZnS and CdS fine particles with different particle sizes by a spray-pyrolysis method. *J. Mater. Sci.* **32**, 1229 (1997).
10. K. Omura, P. Valuchamy, M. Tsuji, T. Nishio, and M. Murozono: A pyrosol process to deposit large-area SnO₂:F thin films and its use as a transparent conducting substrate for CdTe solar cells. *J. Electrochem. Soc.* **146**, 2113 (1999).
11. P.S. Patil: Versatility of chemical spray pyrolysis technique. *Mater. Chem. Phys.* **59**, 185 (1999).
12. R.R. Chamberlin and J.S. Skarman: Fabrication of dye-sensitized solar cells by spray pyrolysis deposition (SPD) technique. *J. Photochem. Photobiol. A Chem.* **164**, 167 (2004).
13. M. Liu, M.L. Zhou, L.H. Zhai, D.M. Liu, X. Gao, and W. Liu: A newly designed ultrasonic spray pyrolysis device to fabricate YBCO tapes. *Physica C* **386**, 366 (2003).
14. N. Herlin, X. Armand, E. Musset, H. Martinengo, M. Luce, and M. Cauchetier: Nanometric Si-based oxide powders: Synthesis by laser spray pyrolysis and characterization. *J. Eur. Ceram. Soc.* **16**, 1063 (1996).
15. A. Muller, N. Herlin-Boime, F. Tenegal, X. Armand, F. Berger, A.M. Flank, R. Dez, K. Muller, J. Bill, and F. Aldinger: Comparison of Si/C/N pre-ceramics obtained by laser pyrolysis or furnace thermolysis. *J. Eur. Ceram. Soc.* **23**, 37 (2003).
16. B.L. Lee, X. Wang, R. Bhave, and M. Hu: Synthesis of brookite TiO₂ nanoparticles by ambient conduction sol process. *Mater. Lett.* **60**, 1179 (2006).
17. S. Veintemilles-Verdaguer, M.P. Morales, and C.J. Serna: Effect of oxidation conditions on the maghemites produced by laser pyrolysis. *Appl. Organometal. Chem.* **15**, 365 (2001).
18. C. Janzen, H. Wiggers, J. Knipping, and P. Roth: Formation and in situ sizing of γ-Fe₂O₃ nanoparticles in a microwave flow reactor. *J. Nanosci. Nanotechnol.* **1**, 221 (2001).
19. Reade Advanced Materials. Available at <http://www.reade.com/products/oxides/hematite.html>.