

loss from Ru(hfb)(CO)₃ (eq 3) will become increasingly competitive leading to metallic films of ruthenium. Trapping the volatile CVD byproducts was accomplished using a liquid nitrogen cooled U-tube filled with glass beads. The products were distilled into a NMR tube which was sealed under vacuum. After obtaining a ¹⁹F NMR spectrum, the contents of the tube were further analyzed using GC-MS-FTIR. These methods established that the majority of the material was hexafluoro-2-butyne. The gas chromatogram showed the elution of two smaller, less well-resolved peaks immediately following the elution of hfb. The highest mass values for these two peaks were *m/e* = 362 and 324, respectively. These values and the associated fragmentation patterns correspond to the formulas C₈F₁₄ and C₈F₁₂. Although it is tempting to attribute the formation of these fluorocarbons to deposition originating from Ru₂[μ-η¹:η¹:η⁴-C₄(CF₃)₄](CO)₆, additional studies are required to verify or refute this supposition.

In summary, Ru(hfb)(CO)₄ has sufficient volatility to be used in standard CVD equipment. It was found to give smooth, adherent films of metallic ruthenium on Si(100) at 500 °C. At lower temperatures, a new dinuclear ruthenium complex, Ru₂[μ-η¹:η¹:η⁴-C₄(CF₃)₄](CO)₆, was isolated during the chemical vapor deposition. Comparison of the gas-phase and solution synthesis of this dimer has yielded some clues regarding the mechanism of the CVD itself.

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Supplementary Material Available: Complete list of crystallographic data, atom positions and thermal parameters, and bond distances and angles (9 pages); list of structure factors (20 pages). Ordering information is listed on any current masthead page.

Supercritical Fluid Transport-Chemical Deposition of Films

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There are many chemical vapor deposition (CVD) techniques available that can be used for the formation of thin films on a substrate surface. One of the major limitations of CVD methods, however, is that volatile precursor compounds are required. Furthermore, the deposition of mixed-metal compositions by CVD usually requires more than one precursor chamber, and the delivery rates of each of the reagents must be simultaneously controlled to maintain the correct stoichiometric ratio. The preparation of YBa₂Cu₃O_{7-x} films by metal-organic

chemical vapor deposition (MOCVD), for example, has been shown to require separate, individually temperature- and carrier-flow-rate-controlled reservoirs for the Y, Ba, and Cu precursor compounds.¹⁻⁴ Supercritical fluid transport-chemical deposition (SFT-CD) is a new film deposition technique which can utilize nonvolatile precursors.⁵⁻⁸ In the SFT-CD process, precursor reagent(s) are dissolved in a supercritical fluid in a single reservoir, and then this solution, under high pressure, passes through a restrictor into a deposition chamber where the rapid expansion of the supercritical fluid causes vaporization of the solute(s). The vaporized precursor compounds are then induced to react at or near a substrate surface to form a thin film.^{5,6} This new process has some important advantages over CVD. Unlike CVD processes, it is not necessary for the precursors to be volatile. When the high-pressure supercritical fluid solution is allowed to expand rapidly into a region of much lower pressure, the solute compounds form very small molecular clusters, ion pairs, or dispersed individual molecules.⁹⁻¹¹ If aerosols rather than vapors are formed, the aerosol particles are much smaller than those formed by the nebulization of ordinary liquid solutions followed by desolvation,⁹ such as in spray pyrolysis.

Supercritical fluid solutions have previously been used in purely physical processes for the formation of thin films and fine powders.¹⁰⁻¹⁴ However, this physical deposition method has the disadvantage that the film to be formed must be soluble in the supercritical fluid, because the deposit is chemically identical to the starting material. Many desirable materials, e.g., semiconductors, metals, metal oxides, and mixed-metal oxides, are insoluble in common supercritical fluids such as CO₂ and N₂O. SiO₂ and GeO₂ have been shown to be soluble in supercritical water, but the experimental conditions were rather extreme (445 °C, 8400 psi).¹³ The SFT-CD process is distinctly different from the previously described physical process

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Table I. Representative Metal and Oxide Films Deposited

film	precursor	substrate	supercritical fluid	substrate temp, °C
aluminum	Al(hfa) ₃	Si or SiO ₂	pentane	680
chromium	Cr(acac) ₃	Si or SiO ₂	acetone	800
indium	In(acac) ₃	Si or SiO ₂	CO ₂	600
nickel	Ni(thd) ₂	Si or SiO ₂	pentane	600
copper	Cu(oleate) ₂	Si or SiO ₂	pentane	740
copper	Cu(thd) ₂	Si	N ₂ O	700
palladium	Pd(tod) ₂	Si or SiO ₂	pentane	600
silver	Ag triflate	Si or SiO ₂	diethyl ether	600
silver	AgI	Si or SiO ₂	acetone	600
yttrium	Y(thd) ₃	Si	N ₂ O	687
zirconium	Zr(tfa) ₄	Si or SiO ₂	diethyl ether	600
YBa ₂ Cu ₃ O _{7-x}	Y(thd) ₃ + Ba ₅ (thd) ₉ (H ₂ O) ₃ OH + Cu(thd) ₂	Si or SiO ₂	pentane	800
CuO	Cu(thd) ₂	Si or SiO ₂	N ₂ O	100
Al ₂ O ₃	Al(hfa) ₃	Si or SiO ₂	N ₂ O	100
Cr ₂ O ₃	Cr(hfa) ₃	Si or SiO ₂	N ₂ O	100
SiO ₂	Si(OC ₂ H ₅) ₄	Si or Al	N ₂ O	100
SiO ₂	Si(OC ₂ H ₅) ₄	cast acrylic	N ₂ O	100
BPSG	Si(OC ₂ H ₅) ₄ + P(OC ₂ H ₅) ₃ + B(OC ₂ H ₅) ₃	Si or Al	N ₂ O	100

because the film deposited is chemically different from the precursor compounds. Almost any precursor reagent which is soluble in a supercritical fluid can be used in SFT-CD. Virtually all of the volatile CVD and MOCVD reagents and many semivolatile or nonvolatile reagents, which are often less toxic, less expensive, and easier to transport and handle, can be used. After the reagents are decompressed and discharged into the deposition chamber, they can become involved in many of the same chemical reactions that are used in CVD. As shown in Table I, most of the films in this study were deposited from volatile metal β -diketonate complexes, e.g., bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) [Cu(thd)₂] and analogs Ni(thd)₂ and Y(thd)₃, tris(2,4-pentanedionato)indium(III) [In(acac)₃] and Cr(acac)₃, tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum(III) [Al(hfa)₃], tetrakis(1,1,1-trifluoro-2,4-heptanedionato)zirconium(IV) [Zr(tfa)₄], and bis(2,2,7-trimethyl-3,5-octanedionato)palladium(II) [Pd(tod)₂].¹⁵ However, we also demonstrated that nonvolatile precursors such as silver iodide, silver triflate (silver trifluoromethanesulfonate), or the oleic acid salt of copper(II) can be used to form films of elemental silver or copper. The metal films were formed on substrates heated between 500 and 800 °C, while most of the metal oxides were deposited from plasmas, with the substrates not significantly above 100 °C.

Films that require more than one reagent in the CVD process can be deposited with SFT-CD using a single supercritical fluid solution containing all of the precursor reagents. The solutions can be made by weighing the precursor reagents and then dissolving them in a solvent near or above the temperature required to form a supercritical fluid solution. This allows precise control of the stoichiometry and homogeneity of the reagents at the substrate surface because they are from a *single source* which is well mixed before it enters the deposition chamber, unlike in traditional MOCVD processes. Also, thermally unstable precursors can be more readily used in SFT-CD than in MOCVD, because it is not necessary to heat them to high temperatures. Usually the solutions in CO₂ or N₂O were maintained between 40 and 70 °C. When *n*-pentane was used, the solution was kept at 25 °C until it was injected through a heated capillary flow restrictor at 210 °C, in which the transit time was approximately 1

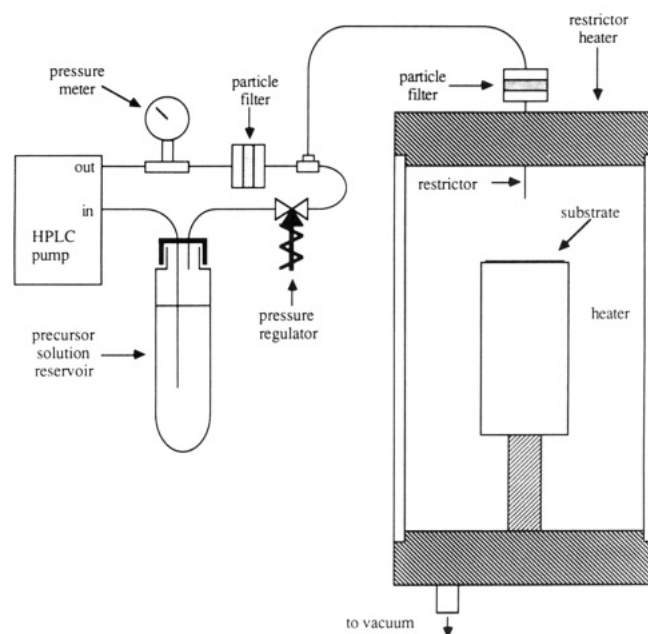


Figure 1. Liquid solution-supercritical fluid deposition apparatus.

ms. This short residence minimizes thermal degradation of the precursors in the capillary restrictor.

As is shown in Table I, most of the metallic films were deposited on single-crystal silicon with [100] lattice orientation or on fused amorphous silica with the apparatus shown in Figure 1. The solution reservoir contained the metal precursors dissolved in a liquid solvent, such as *n*-pentane. With this system, the precursor solutions are easy to prepare because the reservoir is at atmospheric pressure and room temperature. A high-pressure liquid chromatography (HPLC) pump was used to force the solution through two 2- μ m filters to eliminate any particles that could block the restrictor and to pressurize the solvent to its supercritical fluid state. Typically a 4.5-cm-long, 25- μ m-i.d. piece of fused silica tubing was used as the flow restrictor into the deposition chamber. The pressure regulator valve was set at 1300 psi to maintain the solution above the critical pressure and to allow any excess solution that did not flow through the restrictor to return to the reservoir. As the solution was pumped through the restrictor, it was heated from room temperature to above the

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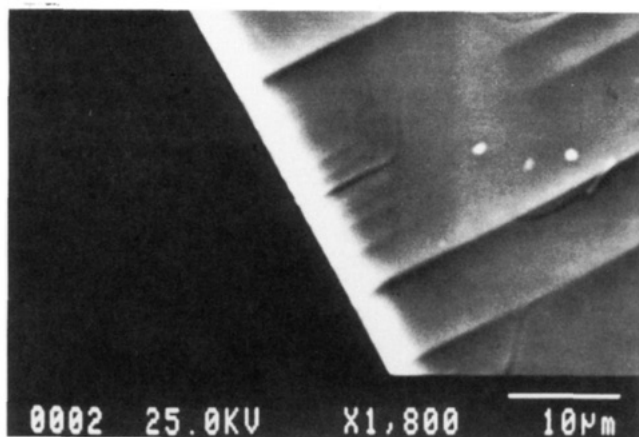


Figure 2. Zirconium film on fused silica as viewed on edge by SEM. The white region is the Zr film on the SiO₂, which appears gray.

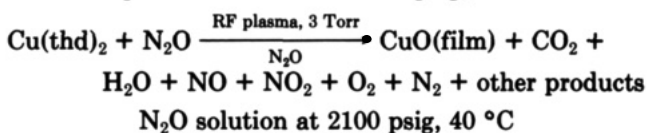
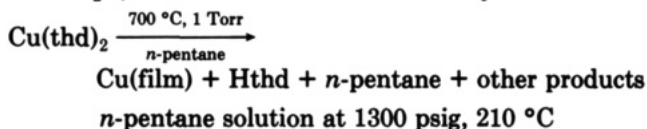
critical temperature (e.g., 210 °C was used in the case of *n*-pentane). The restrictor was heated by contact with the heated top of the deposition chamber; acceptable thermal contact was maintained using silicone grease. After the solution was discharged through the restrictor, it rapidly expanded into the deposition chamber maintained at 0.2–2.0 Torr and formed an aerosol or a vapor of the film precursors. The vaporized precursor mixture reacted at or near the heated substrate surface to form a metallic film. The substrate was heated with infrared radiation projected through a quartz window from a 600-W quartz halogen lamp mounted in a parabolic reflector coated with gold. The temperature of the substrate was controlled between 500 and 800 °C using a variable transformer.

The metallic films were usually very smooth and uniform, and highly reflective. In Figure 2 the bright and relatively uniform layer is the edge of a 3- μ m Zr film on fused silica viewed with a scanning electron microscope (SEM) at 1800 \times magnification. This cross-sectional view of the film was created by breaking the film-coated substrate in half. Figure 3 is an X-ray dot map of the film viewed at the same location and magnification as Figure 2. The white dots represent Zr X-ray emission from the sample scanned by the electron beam. This Zr film was deposited at a rate of 120 nm/min from tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium(IV) [Zr(tfa)₄] dissolved in supercritical diethyl ether. In another experiment, a silica fiber was coated with Pd on all sides using a single flow-restrictor nozzle from which a supercritical fluid solution of bis(2,2,7-trimethyl-3,5-octanedionato)-palladium(II) [Pd(tod)₂] in *n*-pentane was expanded at 205 °C and allowed to contact the fiber maintained at 600 °C. This demonstrated that the SFT-CD process is not limited to line-of-sight deposition, unlike sputtering or evaporation deposition methods. Mixed-metal alloy films of Y, Ba, and Cu were deposited from a *n*-pentane solution containing Y(thd)₃, Cu(thd)₂, and Ba₅(thd)₉(H₂O)₃OH¹⁶ in the stoichiometry needed to form a superconductor. The metal alloy was subsequently oxidized and annealed in oxygen at 500 °C to form a YBa₂Cu₃O_{7-x} superconducting film; resistivity measurements at 77 K showed that it was superconducting. The atomic ratios of Y, Ba, and Cu were shown by electron probe microanalysis (EPMA) to be in the expected range.

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Most of the metal oxide films were formed by in situ oxidation and/or pyrolysis reactions using the apparatus shown in Figure 4. The high-pressure solution cell and gas-tight syringe pump in this system allows the use of supercritical fluids which are gaseous at room temperature and atmospheric pressure, such as CO₂. The precursor compounds were placed into a thermostated solution reservoir, which also served as the cover to the deposition chamber. The precursors were dissolved to form a supercritical fluid solution when the solution was pressurized with N₂O (2100–2800 psi) and heated (40–70 °C). The supercritical fluid solution was allowed to expand into the evacuated deposition chamber (1–5 Torr), vaporizing the film precursor compounds. For safety reasons, a different solvent will be used in future work, and a small volume of N₂O gas will be admitted to the evacuated deposition chamber to act as the oxidizing agent. An external, helical resonator was driven at 13.6 MHz to induce a plasma inside the deposition chamber, typically with 50–300 W of power. The N₂O acts as a strong oxidant because it decomposes into oxygen-containing ions and radicals in the high-energy plasma.¹⁷ The plasma also causes dissociation of the precursor compounds and induces deposition of oxidized films in situ. The substrate was unheated, except by the plasma, and rarely exceeded ca. 100 °C. Deposition with a low substrate temperature is advantageous because it minimizes the possibility of causing damage to the underlying structures and reduces diffusion of contaminants into the film. It is interesting to note that when a plasma was not used, a metallic Cu film was deposited on a 700 °C silicon substrate from Cu(thd)₂ dissolved in supercritical N₂O at 60 °C, expanded into a deposition chamber evacuated to \sim 1 Torr. When the same reagents were discharged into a 13.6-MHz rf plasma at 3 Torr, a CuO film was formed on an unheated silicon substrate.

The chemical processes by which the films are formed can be approximated as follows, and hydrolysis probably also occurs. Traces of water are often present because some chelates are hydrated and water is formed by oxidation of ligands, as well as being carried as impurities in solvents and gases. Under reducing conditions in the presence of excess *n*-pentane at elevated temperatures, elemental copper films and the protonated form of the ligand are products. The hydrogen that protonates the β -diketonate ligand, thd, may come either from *n*-pentane at 700 °C or from other decomposition or reaction products or from moisture impurities. Under oxidizing conditions with N₂O in an rf plasma, the chelating agent is destroyed, and copper oxide films are formed, together with various oxides of nitrogen, as well as O₂ and N₂ that are formed from N₂O, as has been observed earlier by others:¹⁷



Gas chromatographic-mass spectrometric analysis of the cold-trapped effluent from the deposition of copper metal from Cu(thd)₂ in supercritical *n*-pentane showed that the

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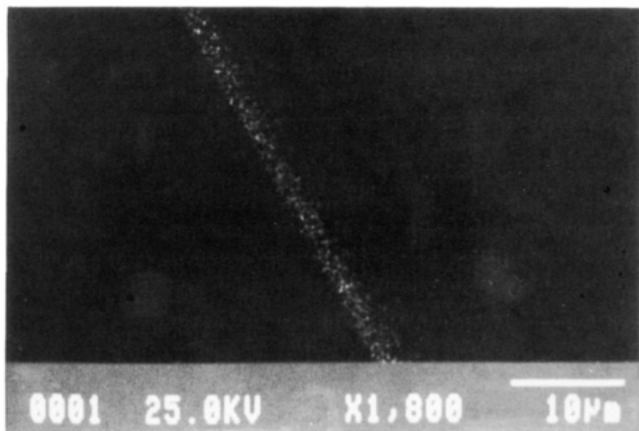


Figure 3. X-ray dot map of the zirconium film shown in Figure 2.

free ligand, H(thd), was a major product. This indicates the possibility of recovering and recycling the organic ligand through many synthesis and deposition cycles. In addition, much smaller amounts of propene, 2-methylpropene, 2-methyl-2-butene, and 3,3-dimethyl-2-butanone were identified in the effluent.

In the instances in which fluorine is present in the ligands, e.g., in aluminum(III) hexafluoroacetylacetonate, it is important to recognize that under certain experimental conditions, fluorine may be incorporated in films or particles formed from these precursors. In the present experiments fluorine was not detected by X-ray emission in the alumina films formed in an rf plasma in the presence of N_2O . By contrast, in independent studies of the oxidation of $Al(hfa)_3$ by O_2 at 820 °C production of fine particles of aluminum fluoride was observed.⁷

In some early experiments we used N_2O as the supercritical fluid and mixed this with a few percent of polarity modifiers such as alcohols as has been done by others^{18,19} in supercritical fluid chromatography. However, we discontinued this practice following a serious explosion of a small volume ($\sim 1\text{ cm}^3$) of a solution containing $\sim 9\%$ ethanol plus 90% N_2O with small amounts of other solutes (0.9% of tetraethylorthosilicate, and 0.07% each of triethyl borate and triethyl phosphite) when pressurized to 2000 psi at 40 °C. Because the cause of the explosion which ruptured a stainless steel tee is unknown, we urge that chromatographers discontinue the practice of adding alcohols to modify nitrous oxide in both supercritical fluid chromatography and in supercritical fluid extractions. While supercritical N_2O in contact with potential fuels has been used by others without incident at temperatures near ambient ($\sim 40\text{--}60\text{ °C}$), this practice may be extremely hazardous. Consequently, other ways of adding N_2O gas to the evacuated deposition chamber should be used when depositing oxidized films, rather than using it to form supercritical fluid solutions.

In another experiment, amorphous silicon dioxide, the most widely used insulating material in integrated circuit processing, was deposited in an rf plasma maintained at 1 Torr at a rate of 20 nm/min from tetraethylorthosilicate (TEOS) dissolved in supercritical N_2O (*caution!*). As shown in Table I, boron and phosphorus-doped silicon glass (BPSG), a material that is desirable for integrated

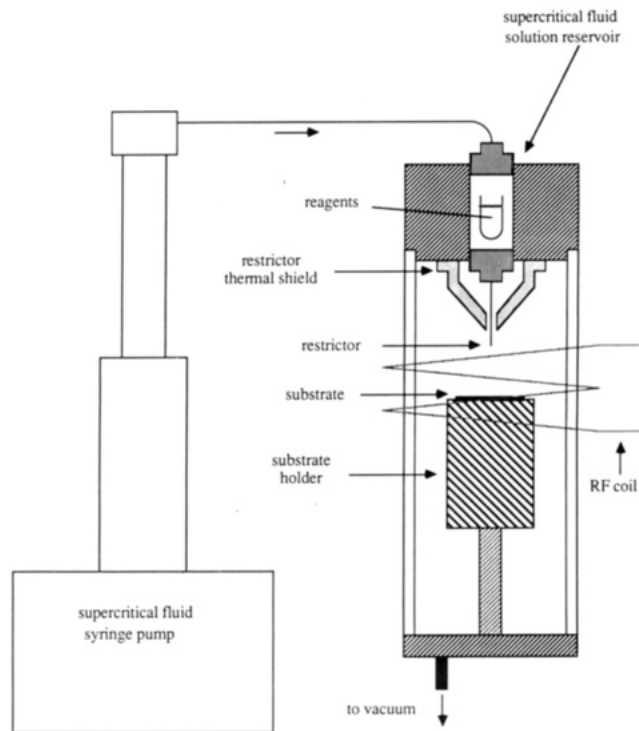


Figure 4. Supercritical fluid deposition apparatus.

circuit applications,²⁰ was deposited in an rf plasma from a single precursor solution in supercritical N_2O . A BPSG film was deposited at a higher deposition rate (240 nm/min) by using a modified version of the system shown in Figure 4 which allowed an ethanolic solution of the precursor compounds to be fed along with N_2O into the supercritical fluid solution cell (*explosion hazard!*). This modified system was also used to deposit a SiO_2 film on a Du Pont Lucite cast acrylic (poly(methyl methacrylate)) substrate without causing any visible melting or distortion, which indicated that the heating by the plasma did not result in a substrate temperature of more than about 100 °C. Insulating films of Al_2O_3 and Cr_2O_3 , materials that can be used as hard, protective coatings, were deposited. X-ray diffraction analysis of these films indicated that they were amorphous. Mixed-metal oxide films of Y, Ba, and Cu were also deposited from a plasma without deliberate auxiliary heating of the substrate.

In summary, a new chemical deposition process has been discovered and developed for depositing films on substrates using supercritical fluids to dissolve and vaporize or aerosolize precursors. SFT-CD has important advantages over other traditional methods of film deposition. The process is simple, rapid, and inexpensive and permits precise control of the stoichiometric ratios of precursors for multielement coatings. The precursors need not be inherently volatile. Complex shaped objects can be coated, and the process is not limited to line-of-sight deposition. Deposition reaction processes include oxidation, reduction, hydrolysis, photolysis, and pyrolysis. Deposition can also be facilitated by the generation of plasmas.

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