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AUTHOR(S): J. C. DeSantis, J. R. Laia, A. P. Sattelberger, and D. C. Smith

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Los Alamos National Laboratory
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LOW TEMPERATURE OMCVD OF THIN RHODIUM FILMS

J. C. DeSantis[†], J. R. Laia[#], A. P. Sattelberger[‡], and D. C. Smith^{§,*}

[†] Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, [#] Los Alamos National Laboratory, MST-7, MS E549, Los Alamos, NM 87545, [‡] Los Alamos National Laboratory, INC-DO, MS J515, [§] Los Alamos National Laboratory, INC-4, MS C346, Los Alamos, NM 87545

Abstract

Thin, highly reflective rhodium films with metal compositions greater than 98% (elemental weight percentage) have been deposited by chemical vapor deposition using Rh(allyl)₃ (allyl = η^3 -C₃H₅) in the presence of a hydrogen plasma. Uniform, crystalline films that adhere well to several types of substrates result from depositions at temperatures as low as 150°C. Depositions using H₂ (no plasma), or an argon plasma yields material that is amorphous, contains a significant amount (>14%) of residual carbon, and has a dramatically slower growth rate. The composition of these materials does not vary significantly from that of the materials obtained from the *in vacuo* thermal deposition with Rh(allyl)₃.

* To whom correspondence should be addressed

Introduction and Background

In recent years, chemical vapor deposition (CVD) has become an essential technology, finding widespread applications in a number of areas. Since CVD is not a "line of sight" process, it is ideal for coating geometrically complex shapes such as tools, cylinders, and parts with holes and recesses.

Most conventional metal-halide based CVD processes take place at temperatures in excess of 800°C and produce corrosive gases (e.g., HCl, HF) [1]. The high process temperatures come about because the metal halide bonds are strong and transition metal halides are quite thermally robust. In many CVD processes the presence of a halogen is detrimental. It can promote corrosion of the film either during deposition or, if halogen atoms become incorporated into the film, after deposition by exposure of the finished product to air, water, or extreme temperature. In some cases, conventional CVD processes do not yield high-quality materials or consistently reproducible materials.

Organometallic complexes as CVD precursors are a simple and powerful method for producing coatings at low temperatures, eliminating deleterious byproducts, and removing the halide from the process completely. Many organometallic compounds have attractive decomposition temperatures, in the range of 100-200°C. The reduced deposition temperatures opens up the possibility of coating thermally sensitive materials such as polymers and conducting glasses. Also, low-temperature depositions can yield materials not stable at higher temperatures as well as metastable materials and phases. These new materials and phases can exhibit properties such as corrosion and wear resistance, oxidation resistance not presently available with current materials. Lowering the temperature that solid materials can be synthesized at not only increases the energy efficiency but also makes it possible to use the material in applications where higher temperatures lead to undesirable consequences such as interlayer atomic diffusion, decohesion of overlayers due to mismatches in thermal expansion coefficients, or temperature-induced changes in the shape or the crystallinity of the substrate or nearby structures. With an organometallic complex it is possible to assemble the desired components of a composite material into a single precursor, ($Zr(CH_2CMe_3)_4$ for ZrC [2], $Nb(C_6H_5CH_3)_2$ for NbC [3, 4]) enhancing process control thereby providing a low-temperature route to complex composite materials. While organometallics do decompose at temperatures lower than many conventional metal-halide precursors, the use of robust organometallics in high-temperature processes could lead to higher quality high-temperature materials.

Despite these advantages, organometallic precursors have not gained wide acceptance in CVD applications. There are several reasons for this. Many organometallic compounds that are attractive for CVD application are either not available from commercial sources, or are only available in small research quantities (1-10 grams). Many of the complexes are air sensitive, and, most important, the thermal decomposition of most organometallics leads to undesirable amounts of residual carbon in the product materials.

Rhodium thin films are of interest for several of reasons. Rhodium films grown by physical vapor deposition (PVD) techniques have been found to offer excellent resistance to oxidation and other types of corrosion. These films are also highly reflective in the visible, infrared, and ultraviolet regions of the spectrum, leading to their use as mirrors in optics [5]. In addition, rhodium may find uses in the microelectronics industry [6].

To date, rhodium has been deposited by sputtering [7], vacuum deposition [8], electrochemical deposition [9], and thermal decomposition of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [10]. While processes involving metal-halides and molecular hydrogen have been used to deposited thin metal films, (e.g., Ir from IrF_6 and H_2 at 775°C [11]), no such process exists for rhodium. This is a result of the unfortunate lack of a stable, gaseous rhodium halide complex [12].

Rhodium films have been deposited from organometallic precursors. Thin films have been prepared with greater than 95% metal composition from $\text{Rh}(\text{CO})_2(\text{acetylacetonate})$ in a plasma enhanced CVD (PECVD) process [13]. However, there was insufficient characterization of the final material. $\text{Rh}(\text{allyl})_3$ in an atmospheric pressure CVD (APCVD) process with molecular hydrogen has been used to deposit thin rhodium films [14]. No detailed characterization of the thin film materials was presented.

We wish to report the deposition of high purity Rh films from $\text{Rh}(\text{allyl})_3$ in a remote plasma enhanced CVD process. Detailed characterization of the final materials reveals a metal content of greater than 98% (elemental weight percentage) with a nanocrystalline microstructure. The deposition mechanism is presumed to be a gas phase plasma process analogous to the PECVD process.

Experimental

Manipulation of air-sensitive solids and solutions were performed within the confines of a helium-filled Vacuum Atmosphere glovebox, equipped with a high-capacity (MO-40-2H) Dri-Train purification system. Deuterated solvents were degassed with several freeze-pump-thaw cycles and stored over sodium amalgam. Proton NMR spectra were obtained on an IBM AF-250 instrument.

Literature methods exist for the synthesis of Rh(allyl)₃ [15]. To eliminate some of the steps in the multiple step synthesis of Rh(allyl)₃ from RhCl₃·xH₂O and improve the overall yield, a new synthetic route to Rh(allyl)₃ was developed. An ether solution of Li(allyl) [16] at -40°C was slowly added to an ether solution of RhCl₃(THT)₃ [17], also at -40°C. The solution was allowed to warm to room temperature with stirring. The ether was removed under vacuum, and the resulting brown residue extracted with hexane. The hexane solution was filtered through a medium porosity sintered glass frit to remove the precipitated LiCl. The clear brown filtrate was then gravity filtered through a short alumina packed frit. The resulting filtrate was a clear, bright yellow. The hexane was removed under vacuum to yield a bright yellow solid that could be further purified by sublimation (76% yield). ¹H NMR (benzene-d₆, 25°C): δ 1.57 (d, 4H), 2.55 (d, 2H), 2.66 (d, 4H), 2.86 (d, 2H), 3.72 (m, 2H), 5.13 (m, 1H).

In vacuo depositions of Rh(allyl)₃ were conducted using a horizontal hot-wall reactor. The operating pressure of this system was 3-10 microns. A cold-wall CVD reactor was used for depositions with hydrogen gas (H₂), a hydrogen plasma (H•), or an argon plasma (Ar•). Plasmas were generated with an Evenson cavity operating at 2.45 GHz. Rh(allyl)₃, in an argon carrier stream flowing at a rate of 15 sccm, was impinged onto a heated substrate; simultaneously, through a separate inlet, H₂, H•, or Ar• at a flow rate of 25 sccm, was directed at the substrate. The base pressure of the cold-wall reactor was 10-15 microns with a working pressure of 195-200 microns for depositions using H₂ or H•, and 160-170 microns for Ar•. The working pressure in the precursor sublimation zone was approximately 13 mm Hg. The substrate temperature was varied from 100 to 350°C. The precursor was maintained at room temperature.

Films were deposited on polished glass, polished sapphire, or polyetheretherketone polymer substrates. Glass and sapphire substrates were cleaned with methanol, trichloroethane, and finally with methanol, and blown dry under a stream of nitrogen. Thermal contact with the hot-stage was ensured by mounting the substrates with silver mounting paste. The coated substrate was allowed to cool to room temperature *in vacuo* before being removed from the reactor. Each film was analyzed for composition and thickness using Rutherford backscattering spectroscopy (RBS), nuclear resonance analysis (NRA), and electron microprobe analysis (EMPA). Film crystallinity was determined by x-ray powder diffraction and electron diffraction, while morphology was examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission microscopy (STM), and atomic force microscopy (AFM).

Nuclear Resonance Analysis

Conventional RBS uses helium ions with an energy in the range of 1 to 3 MeV. Analysis in this energy range suffers from poor sensitivity to low Z elements such as carbons [18]. The practical lower limit for carbon analysis is 2% (elemental weight percentage). The sensitivity to carbon can be increased by taking advantage of the broad elastic-scattering resonance for helium bombardment from 6.0 to 6.8 MeV (Figure 1). At a helium ion energy of 6.4 MeV, low carbon concentrations are easily detected. The lower limit for detection of carbon is approximately 0.5%.

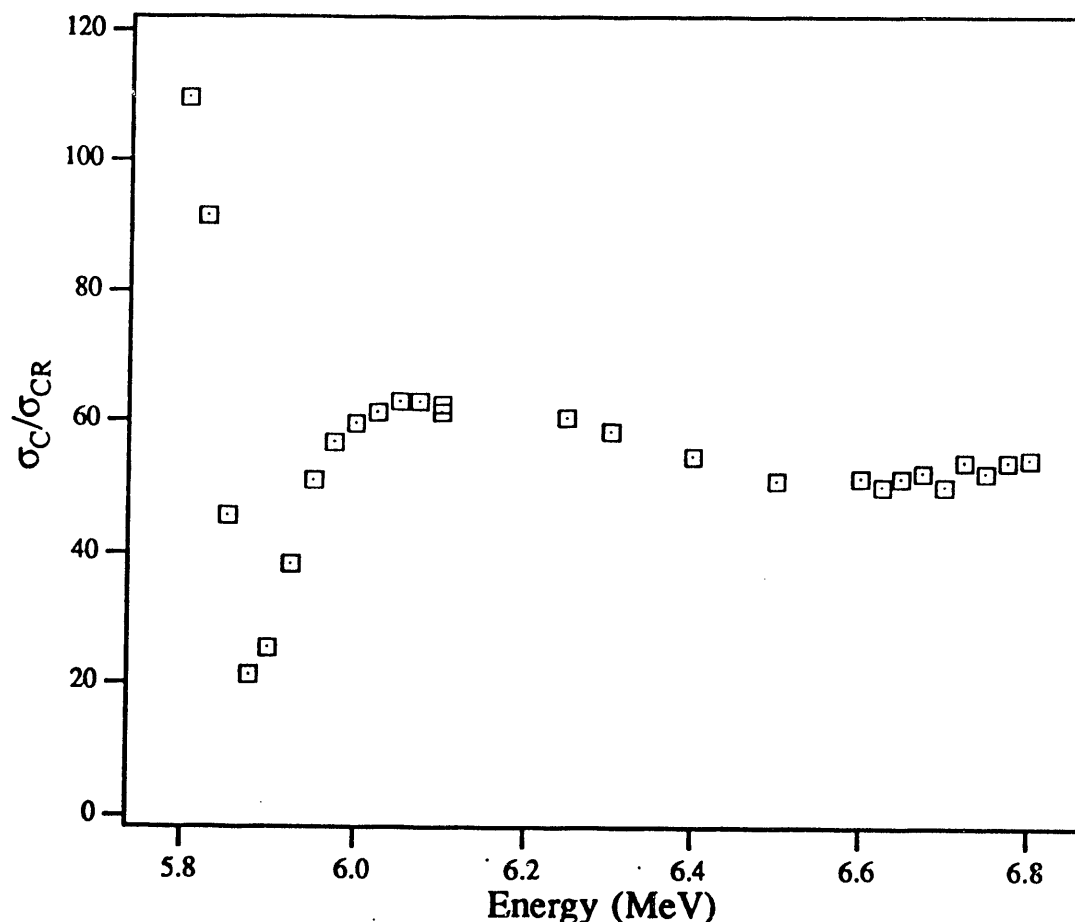


Figure 1. Differential scattering cross section for $C(\alpha, \alpha)C$ measured at $\vartheta_{lab} = 166^\circ$ for the energy range 5.8 to 6.8 MeV. σ_{CR} denotes the Rutherford cross section at energy E.

At the higher beam energy, backscattering yields are measured directly and analyzed as described elsewhere [19, 20]. This analysis is a direct measure of the number of carbon atoms to rhodium atoms in the material. With the fixed ratio, the 2.2 MeV spectra can be reanalyzed. Deviation of the observed

spectra from the modeled spectra with the fixed carbon to rhodium ratio is inferred to be due to the hydrogen content of the material.

Results and Discussion

Highly reflective, silvery films are rapidly formed at 250°C in the *in vacuo* deposition with Rh(allyl)₃. EMPA of the material revealed a significant amount of residual carbon (Table I). This result is in line with earlier work that found that, in the absence of H₂, thermally deposited metal films contain a large amount of residual carbon [13, 14, 21, 22, 23]. A slight (<5%) increase in metal content was found when the substrate temperature was increased to 450°C. The films were amorphous by x-ray powder diffraction.

Films grown at 250°C in the cold-wall reactor with molecular hydrogen contain slightly less carbon than those obtained from the thermal *in vacuo* decomposition of Rh(allyl)₃ (Table I). The growth rate for these materials was substantially reduced from those of the *in vacuo* depositions. The slower growth rate is due to the decrease in the organometallic sublimation rate resulting from the increased operating pressure in the sublimation zone of the deposition system.

Scanning electron micrographs of these films show them to be extremely smooth, with no discernible features (Figure 2). Transmission electron microscopy, at 77K, reveals a very fine grain structure with grain sizes about 6 nm. Weak diffraction rings are observed at this temperature that correspond to the expected diffraction pattern for crystalline rhodium, indicating that these materials are nanocrystalline in nature.

In the hopes of improving the purity of the deposited rhodium material, the molecular hydrogen was replaced with a hydrogen plasma. Films deposited with the plasma, appear to be identical to those obtained with molecular hydrogen. Transmission electron microscopy (Figure 3), STM, and AFM all reveal a very fine grain structure of about 40 nm. The materials are crystalline by x-ray powder diffraction in contrast to the amorphous materials obtained from the depositions with H₂.

The significant increase in the growth rate for the plasma process (Table I) is believed to be due to a reaction pathway that involves the gas phase plasma reaction of Rh(allyl)₃. In a few of the films, the presence of deposits (nodules) beneath the plasma inlet that appear to have resulted from gas phase nucleation or a sputter process supports this theory. The carbon content of the material in these areas was greater than 14%. No rhodium or carbon species were observed in the plasma induced emission spectrum of the discharge region.

Table I. Deposition Conditions and Characterization of Rhodium Films

Type of Deposition	Substrate Temperature (°C)	Plasma Power (W)	%M ^a	Growth Rate (nm/hr)	Crystallinity ^b
<i>in vacuo</i>	250		83	150	amorphous
H ₂	250		89	3-12	amorphous ^c
H ₂ plasma	250	20	97	35-50	crystalline
H ₂ plasma	250	40	98	35-120	crystalline
H ₂ plasma	100	20	85	d	d
Ar plasma	250	20	86	4-6	d

a. Elemental weight percentage as measured by ion beam analysis ($\pm 1\%$).

b. As determined by x-ray powder diffraction.

c. This material appeared to be amorphous by x-ray powder diffraction; however, with electron diffraction this material did show weak diffraction rings which correspond to the expected pattern for crystalline rhodium

d. Not determined.

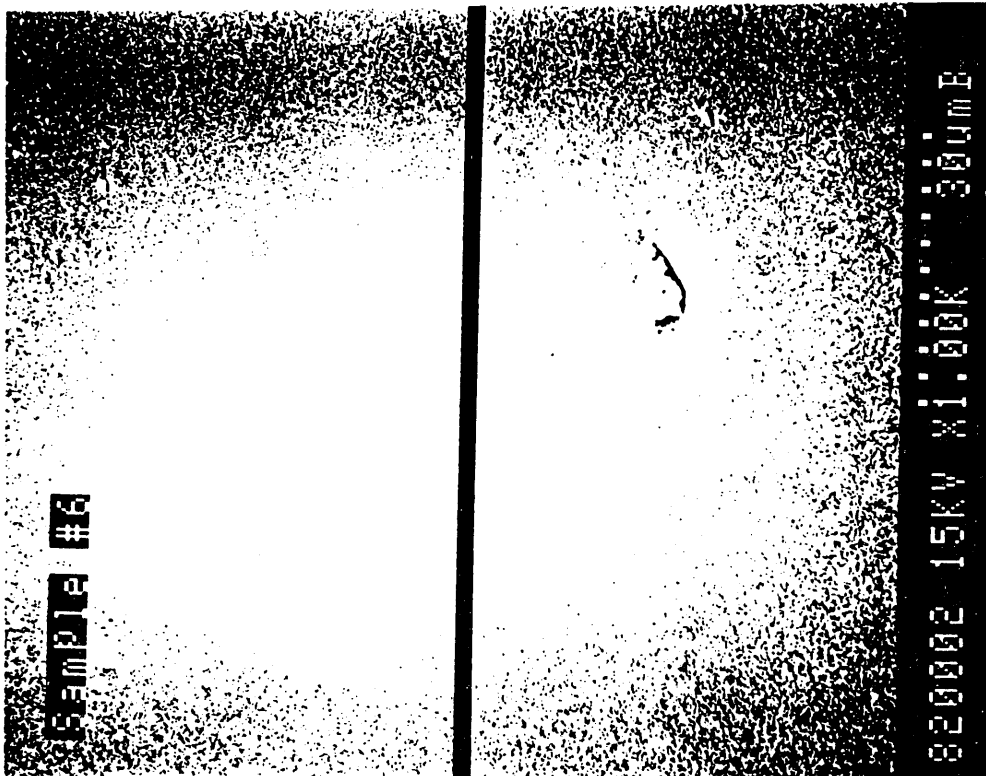


Figure 2. Scanning electron micrograph of a rhodium film deposited at 250°C from Rh(allyl)₃/H₂. The dotted line in the bottom black margin indicates the length scale of the upper photo. The area of magnification shown in the lower photo (5000X) is boxed in the upper photo.

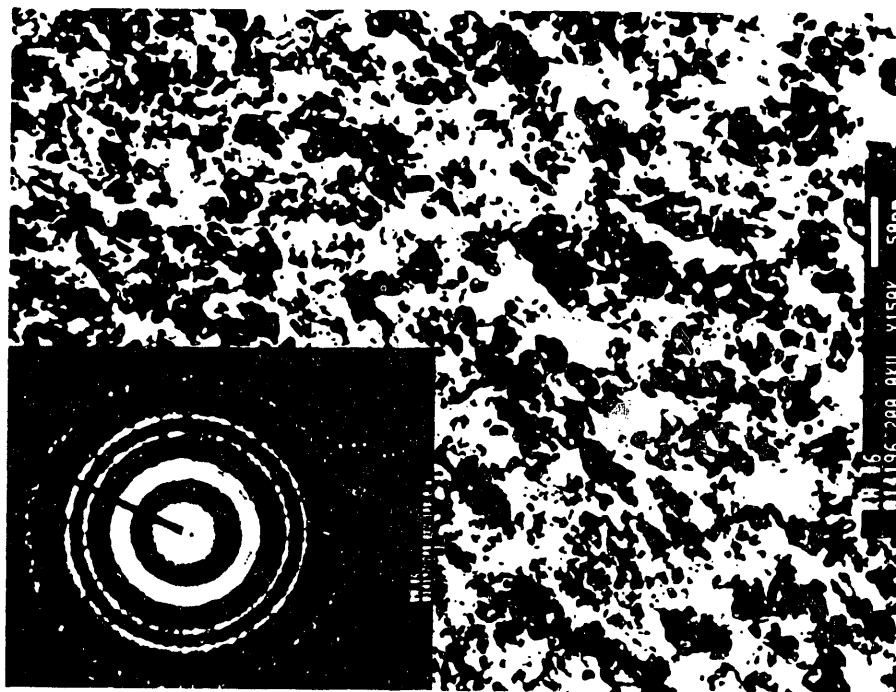


Figure 3. Transmission electron micrograph of a rhodium film deposited at 250°C from Rh(allyl)₃ in the presence of a hydrogen plasma

The amount of residual carbon in the films deposited with the hydrogen plasma is drastically reduced from that of the films deposited with molecular hydrogen (Table I). With a microwave power of approximately 20 W, films with up to 98% metal content were obtained. Doubling the plasma power to 40 W resulted in a further drop in the residual carbon content to less than 0.5%. However, with the increased plasma power come an increase in the amount of nodular deposits beneath the plasma inlet.

Surprisingly, variations in stage temperature from 150 to 350°C did not noticeably alter either the film composition or the growth rate of the process. Brownish films were deposited at substrate temperatures less than 150°C. The compositions of the thin films were less than 85% metal (Table I).

The composition and growth rates of the rhodium films were found to be sensitive to the geometry of the deposition system. Growth rates increased near the Rh(allyl)₃ inlet with the metal content greatest when substrates were positioned near (<1 cm) the hydrogen plasma inlet.

To learn more about this plasma-assisted deposition process, a rhodium film of high (19%) residual carbon content was placed on the hot stage and "etched" with the hydrogen plasma for approximately 4 hrs. The absence of Rh(allyl)₃ in the argon carrier stream was the only departure from standard deposition conditions. Roughly a third of the carbon in a 50 nm layer was etched from the surface of the film. This preferential etching of carbon along with the gas phase plasma reaction must result in the extremely low amounts of residual carbon found in the hydrogen plasma deposition process.

A final set of films was deposited with an argon plasma in place of the hydrogen plasma. Both metal content and growth rate dropped substantially (Table I). Again, these films appeared highly reflective with no discernible features by SEM. Nodular deposits were not observed.

Rhodium films were deposited on the polymer substrate using the remote hydrogen plasma process. The films were not continuous and appeared to have a nodular structure by SEM. This may be a result of the high surface roughness of the polymer substrate, and the nucleation and film growth mechanism on the polymer substrate.

One of the intriguing issues concerning these materials is their hydrogen content. An estimate of the hydrogen content can be made using NRA and conventional RBS. The composition of materials with 5 to 6% residual carbon has been determined to be Rh₁C_{0.43-0.51}H_{0.3±0.1}. As the amount of residual carbon in the thin film materials decreases, a drop in the hydrogen content is also observed. It becomes very difficult to estimate the hydrogen content of materials with carbon contents below about 3%. Also, the nature of the hydrogen in these materials remains to be determined. A direct measurement

of the hydrogen content can be obtained from forward recoil spectroscopy, and these measurements are currently underway.

Still under investigation is the nature of the hydrogen plasma deposition mechanism, the form of the residual carbon, and the effects of varying the sublimation rate of the organometallic on film composition and growth rate.

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