

DEPOSITION OF THIN METAL, METAL OXIDE AND METAL ALLOY FILMS: KINETICS, ADHESION AND APPLICATIONS

Christos F. Karanikas¹ and James J. Watkins*

¹Department of Chemical Engineering, University of Massachusetts, Amherst 01003, USA

*Department of Polymer Science and Engineering, University of Massachusetts, Amherst 01003, USA

watkins@polysci.umass.edu

INTRODUCTION

Conformal deposition of metal, metal oxide and metal alloy films are of interest for a number of applications ranging from electrodes for dynamic random access memory (DRAM), gate oxides, and conducting diffusion barrier layers for copper interconnects in integrated circuits for the microelectronics industry to alternative materials for energy storage applications. Many processes either require or would benefit from a highly conformal and controllable deposition method in complex geometries with high aspect ratios. Supercritical fluid deposition (SFD)¹ has enabled the rapid, efficient and conformal deposition of device quality conformal metal, metal oxide and metal alloy films in high aspect ratio features, which is due in part to high fluid phase precursor concentrations that are enabled by the use of a supercritical fluid (SCF) as the process medium. These precursor concentrations can be orders of magnitude higher than precursor concentrations typical of chemical vapor deposition. Here we report the kinetics of conformal ruthenium film deposition via the hydrogen assisted reduction of bis (2,2,6,6-tetramethyl heptane-3,5-dionato) (1,5-cyclooctadiene) ruthenium, (Ru(tmhd)₂cod). This study was performed in order to determine reaction orders and develop a reaction mechanism. Additionally, four point bend fracture mechanics was used to quantify the adhesion energy of deposited films at interfaces of interest. Finally, co-deposition of Ce/Pt in supercritical CO₂ is shown to form a mixed metal system at reduced deposition temperatures.

MATERIALS AND METHODS

Organometallic precursors were obtained from Strem Chemicals, Inc. (Newburyport, MA) and were used as received without any further purification. Carbon dioxide, 99.99% (coleman grade) and hydrogen, 99.999% (ultra high purity grade) was obtained from Merriam Graves Corp. (Charlestown, NH) and was used as received.

The kinetics study was performed in a batch reactor comprised of two opposed stainless steel flanges sealed with a 2-236 Buna-N o-ring (Marco Rubber and Plastic Products, Inc., North Andover, MA). A cylindrical (D = 1 inch) aluminum stage heated by three high wattage density cartridge heaters (Omega Engineering, Inc., Stamford, CT) was used to quickly attain the desired substrate temperatures. The wall of the stainless steel reactor was heated using four similar high wattage density heaters and was maintained at a lower temperature than the reaction stage. The reaction was performed in a batch process and precursor conversion never exceeded 15% conversion, which allows use of the differential method of rate analysis for the kinetics study.

A 12 mm by 12 mm silicon wafer <100>, with a 500 nm thermally grown oxide layer, was mounted to the aluminum heated stage and secured with clips. A known amount of precursor was loaded into the vessel. The vessel was then sealed and placed behind 1" thick polycarbonate protective housing. The reaction vessel volume was purged continuously over a 15 minute period with a constant flow

nitrogen source. The reactor was then sealed and heated to the desired temperature and allowed to equilibrate. Carbon dioxide was introduced to the system using a computer-controlled syringe pump (Teledyne Isco, Inc., Lincoln, NE), which enabled precise volume measurement of the added CO₂. A suitable amount of time was allowed for complete dissolution of precursor. The aluminum stage was then heated to the desired reaction temperature and the reaction was allowed to proceed. The heated stage was then allowed to cool down while fresh CO₂ was used to flush multiple reactor volumes through the system to remove reaction byproducts. The effluent passed through an activated carbon bed and silicon oil bubbler before being vented to the atmosphere. During the reaction, small gas phase samples of known volume were collected using HPLC sample loops. Samples were decompressed and the precursor was recovered in a known volume of organic solvent and the resulting solutions were analyzed using UV-Vis spectroscopy in order to determine precursor concentrations in the fluid phase and confirm conversions of less than 15%. A differential method of rate analysis was used to develop a rate expression for the growth rate. The method of excess was used to account for multiple reactants.

Metal, metal oxide and co-depositions were carried out in a similar cold wall reactor. A custom built cylindrical aluminium stage (D = 2 inches) was heated with a resistive coiled heater (Belilove Company Engineers, Hayward, CA). Various sizes of TaN, TiN and Ta wafers were used as the deposition substrates. The reaction procedure was similar.

The deposited films were analyzed for thickness using a surface profiler. Five or more measurements were used to obtain the average film thickness which was then used to calculate the growth rate. Growth rates were calculated by dividing average film thickness by the reaction time. Elemental analysis via sputter depth profiles to determine film purity was attained via x-ray photoelectron spectroscopy (XPS). Resistivity was calculated via sheet resistance measurements obtained with a four point probe.

RESULTS

Kinetic Study

Using the Arrhenius equation, the activation energy was determined for the SFD of ruthenium films by the hydrogen assisted reduction of Ru(tmhd)₂cod. The temperature dependence was studied over the range of 240 °C to 280 °C at a constant 172 bar reaction pressure, 0.07 wt. % precursor concentration and 0.3 wt. % hydrogen concentration. The data are shown in Figure 1. The apparent activation energy is 45.3 kJ/mol.

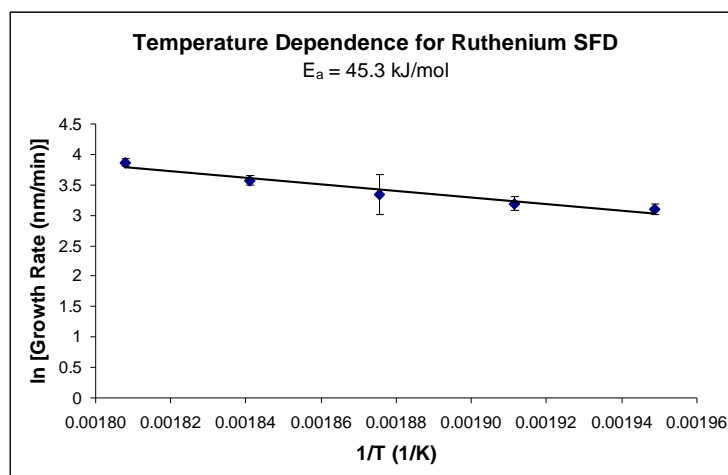


Figure 1. Temperature dependence of Ru(tmhd)₂cod by the Arrhenius law for the supercritical fluid deposition of ruthenium thin films from carbon dioxide

The growth rate dependence on precursor concentration was studied at a constant temperature of 260 °C. The initial reaction pressure was 172 bar for all reactions and hydrogen concentration was constant at 0.3 wt. % for all reactions. A plot of the data is shown in Figure 2. At low precursor concentrations, less than 0.06 wt. %, the growth rate dependence on concentration is first order. Above precursor concentrations of 0.06 wt. %, there is no increase in the growth rate with concentration, indicating a zero order dependence.

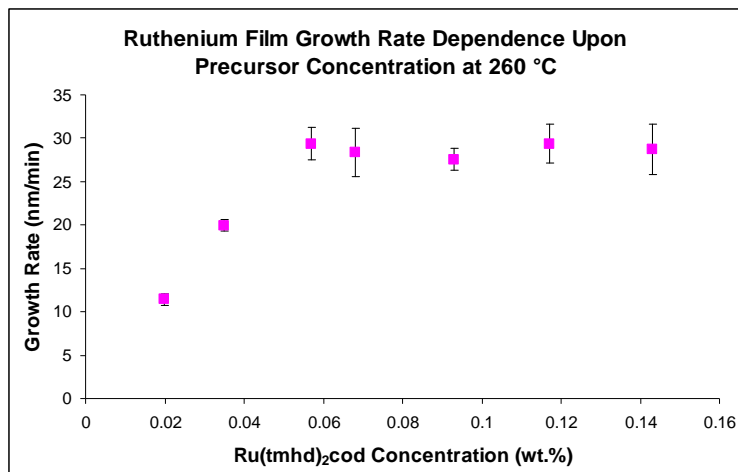


Figure 2. Growth rate dependence upon Ru(tmhd)₂cod concentration

The dependence of growth rate upon reaction pressure is shown in Figure 3. The temperature was held constant at 260 °C and the hydrogen concentration was held constant at 0.3 wt. % while the pressure was varied between 159 bar and 200 bar. For the entire range of pressure studied, it was found that the reaction pressure has no effect on the growth rate of the system. Growth rates remain constant at approximately 27 nm/min.

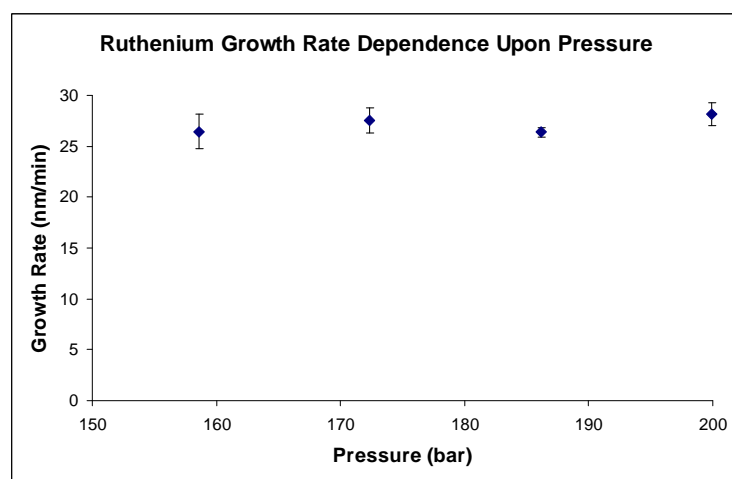


Figure 3. Growth rate dependence upon reaction pressure

Hydrogen's effect on the growth rate of ruthenium films was studied. The data are shown in Figure 4. The study was performed at a constant reaction temperature of 260 °C for 3 minutes, 172 bar and Ru(tmhd)₂cod at a loading of 0.09 wt. %. Hydrogen concentration at 0.26 wt. % and higher had no effect on the growth rate of the ruthenium film. It was noted that at hydrogen concentrations of 0.4 wt. %

and above, the films foiled due to increased stress in the film. At concentrations below 0.26 wt. %, the film growth rate increased with increasing hydrogen concentration. The effect of hydrogen was 2nd order with respect to ruthenium film growth rate. At concentrations of 0.1 wt. % and below, there was no deposition which was attributed to parasitic deposition on the stage during the time that the substrate was reaching reactive conditions for film deposition.

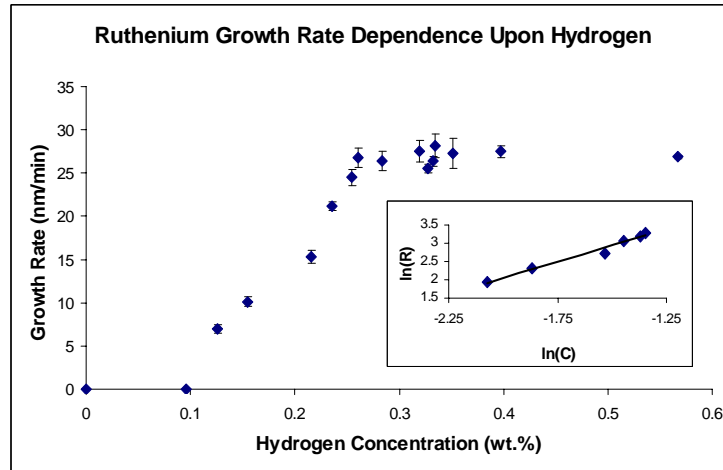


Figure 4. Growth rate dependence upon hydrogen concentration

Adhesion Study

The use of PAA as a pre-treatment at interfaces of interest was shown to increase the adhesion of films deposited via SFD². Using four point bend fracture mechanics, the adhesion of Cu/TaN interfaces was determined both with and without PAA adhesion enhancement pre-treatment.

It was found that the interfacial energy for the untreated TiN/Cu interface, Cu deposited by SFD, to be approximately 1 J/m². However, after PAA pre-treatment, the interfacial energy was found to be over 20 J/m², limited by the failure properties of the epoxy used.

Dauskardt³ found the adhesion energy for the TiN/SiO₂ interface, TiN deposited by plasma enhanced chemical vapor deposition (PECVD), to be 10.4 ± 1.3 J/m².

Co-deposition Study

Simultaneous batch deposition of multiple metals in supercritical fluids has yielded layered, mixed and alloyed systems. One such system is the simultaneous deposition of Ce/Pt to yield a mixed metal system, Figure 5.

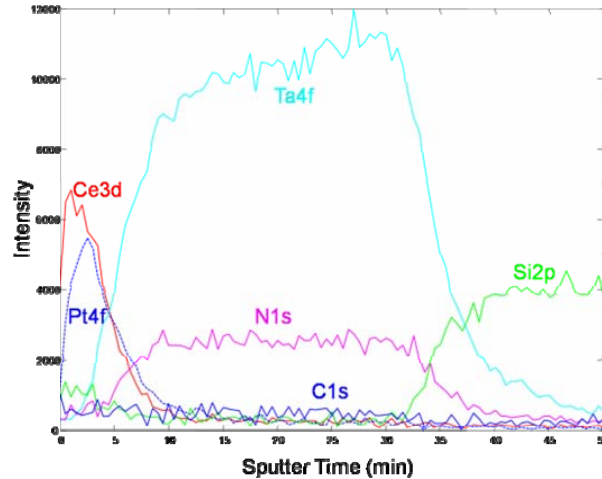


Figure 5. XPS sputter depth profile of a co-deposited Ce/Pt film

CONCLUSIONS

The kinetics of the deposition of ruthenium thin films from the hydrogen assisted reduction of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium(II) in supercritical carbon dioxide was studied in order to develop reaction orders for the growth rate as well as to determine a mechanism for the process. The deposition temperature was varied from 240 °C to 280 °C and the apparent activation energy was 45.3 kJ/mol. Deposition rates up to 30 nm/min were attained. The deposition rate dependence on precursor concentrations between 0 and 0.2 wt. % was studied at 260 °C with excess hydrogen and revealed first order deposition kinetics with respect to precursor at concentrations lower than 0.06 wt. % and zero order dependence at concentrations above 0.06 wt. %. The effect of reaction pressure on the growth rate was studied at a constant reaction temperature of 260 °C and pressures between 159 bar to 200 bar and found to have no measurable effect on the growth rate. Growth rate dependence upon hydrogen, the reducing agent, concentration was studied at 260 °C and 0.09 wt. % Ru(tmhd)₂cod. Hydrogen concentration was varied between 0 wt. % and 0.6 wt. %. At low hydrogen concentration, second order kinetics was observed while there was no dependence for hydrogen concentrations greater than 0.3 wt. %.

Four point bend fracture mechanics were used to quantitatively determine the interfacial adhesion energy of TiN/Cu interfaces, where Cu was deposited by SFD. Non PAA pretreated TiN/Cu interfaces had an interfacial adhesion of 1 J/m². PAA pretreated samples were found to have an interfacial adhesion energy of over 20 J/m², which is at least two times greater than TiN/SiO₂ deposited from PECVD.

SFD has enabled the deposition of a wide range of metals, metal oxides and alloys. Metals deposited to date include: Cu, Ru, Pt, Pd, Ag, Au, Ni, Co, Rh and Ir⁴⁻¹². Metal oxides deposited to date include: Hf, Zr, Ti, Ce, Ta, Nb and Bi. Simultaneous deposition of Ce/Pt has yielded a mixed metal system.

ACKNOWLEDGMENTS

Funding from NSF GOALI CTS – 0245002 and NSF Center for Hierarchical Manufacturing NSEC (DMI – 0531171) is gratefully acknowledged. Additional funding was provided by an NSF IGERT fellowship awarded to Christos F. Karanikas. Facilities supported by the NSF Materials Research Science and Engineering Center on Polymers and the NSF Center for Hierarchical Manufacturing (DMI – 0531171) at the University of Massachusetts Amherst were used in this study.

REFERENCES

- [1] D. P. Long, J. M. Blackburn, and J. J. Watkins, "Chemical fluid deposition: A hybrid technique for low-temperature metallization," *Advanced Materials*, vol. 12, pp. 913-915, 2000.
- [2] Zong, Y.; Shan, X.; Watkins, J., Sacrificial adhesion promotion layers for copper metallization of device structures. *Langmuir* **2004**, 20, (21), 9210-9216.
- [3] Dauskardt, R. H.; Lane, M.; Ma, Q.; Krishna, N., Adhesion and debonding of multi-layer thin film structures. *Engineering Fracture Mechanics* **1998**, 61, 141-162.
- [4] A. O'Neil and J. J. Watkins, "Reactive deposition of conformal ruthenium films from supercritical carbon dioxide," *Chemistry of Materials*, vol. 18, pp. 5652-5658, 2006.
- [5] Y. Zong and J. J. Watkins, "Deposition of copper by the H₂-Assisted reduction of Cu(tmhd)(2) in supercritical carbon dioxide: Kinetics and reaction mechanism," *Chemistry of Materials*, vol. 17, pp. 560-565, 2005.
- [6] J. M. Blackburn, D. P. Long, A. Cabanas, and J. J. Watkins, "Deposition of conformal copper and nickel films from supercritical carbon dioxide," *Science*, vol. 294, pp. 141-145, 2001.
- [7] J. M. Blackburn, D. P. Long, and J. J. Watkins, "Reactive deposition of conformal palladium films from supercritical carbon dioxide solution," *Chemistry of Materials*, vol. 12, pp. 2625-2631, 2000.
- [8] A. Cabanas, J. M. Blackburn, and J. J. Watkins, "Deposition of Cu films from supercritical fluids using Cu(I) beta-diketonate precursors," *Microelectronic Engineering*, vol. 64, pp. 53-61, Oct 2002.
- [9] A. Cabanas, D. P. Long, and J. J. Watkins, "Deposition of gold films and nanostructures from supercritical carbon dioxide," *Chemistry of Materials*, vol. 16, pp. 2028-2033, 2004.
- [10] N. E. Fernandes, S. M. Fisher, J. C. Poshusta, D. G. Vlachos, M. Tsapatsis, and J. J. Watkins, "Reactive Deposition of Metal Thin Films within Porous Supports from Supercritical Fluids," *Chemistry of Materials*, vol. 13, pp. 2023-2031, 2001.
- [11] E. T. Hunde and J. J. Watkins, "Reactive deposition of cobalt and nickel films from their metallocenes in supercritical carbon dioxide solution," *Chemistry of Materials*, vol. 16, pp. 498-503, 2004.
- [12] J. J. Watkins, J. M. Blackburn, and T. J. McCarthy, "Chemical fluid deposition: Reactive deposition of platinum metal from carbon dioxide solution," *Chemistry of Materials*, vol. 11, pp. 213-215, 1999.