# Deposition of Ru Thin Films from Supercritical Carbon Dioxide Fluids

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Ruthenium has been of interest for application in ULSI capacitor electrodes and more recently as a barrier metal against Cu diffusion. Thin-film deposition from supercritical $CO_2$ has gained particular attention as a new deposition technique that provides nano-penetration capability and a possibility of developing new deposition chemistries. However, few papers have been published on this technique. In this article, first, the deposition characteristics of Ru thin films using $H_2$ reduction chemistry were described. It was found that Ru films grow only on conductive surfaces when $H_2$ reduction chemistry was employed. These films can be beneficial for some specific applications; however they are not very much favored for general deposition technology. Second, we report that Ru films, oxygen-containing Ru films in fact, grew on dielectric/non-conductive surfaces when oxidative chemistry was used. $O_3$ was used as an oxidant for thin film deposition from supercritical fluids for the first time. The use of $O_3$ promotes heterogenous nucleation and increases the amount of oxygen in the films. Oxygen-containing Ru was reduced by another reduction run using supercritical $CO_2$. [DOI: 10.1143/JJAP.44.5799]

KEYWORDS: supercritical fluids, thin-film deposition, ruthenium

## 1. Introduction

Supercritical $CO_2$ (sc$CO_2$) is a compressive fluid that behaves as both a gas and a liquid. sc$CO_2$ possesses unique properties such as high diffusivity, a high molecular number density, zero surface tension, and solvent capability. Considerable attention is now paid to using sc$CO_2$ for semiconductor processing from wafer cleaning to drying. Thin-film growth from sc$CO_2$ fluids has recently been of crucial interest because of the superb gap filling capability, conformable deposition possibility, good film quality, high growth rate, and precursor/$CO_2$ recyclability of sc$CO_2$. The basic concept of this technique is the decomposition of a metal chelate dissolved in sc$CO_2$. The nanopenetration capability of sc$CO_2$ enables the delivery of metal chelate molecules deep into small structures and thus narrow and high-aspect-ratio gap filling. The metal chelate is converted to a metal deposit through proper reaction chemistry, usually assisted by an additional reaction reagent such as $H_2$. The solvent capability of sc$CO_2$ affords reaction byproducts, either gas or organic compounds, to be well dissolved in sc$CO_2$ ambient. This effect promotes not only the deposition temperature to be lowered but also film impurities to be less incorporated.

We have thus far demonstrated the above-mentioned advantages of the thin-film deposition technology from sc$CO_2$ in Cu thin film growth, aiming at its application to ULSI interconnect fabrication.[1–6] In our past Cu deposition studies,[1–6] $\beta$-diketonate copper compounds were dissolved in sc$CO_2$ and reduced by $H_2$. The use of this chemistry resulted in a narrow gap filling as low as 50 nm, and a decrease in deposition temperature by about 100°C compared to typical chemical vapor deposition (CVD) temperatures.

Ru has received much attention as a promising capacitor material because of its low resistivity, good etching capability, and good electric conductivity even in its oxidized state. Recently, Ru has been proposed as a next-generation barrier material against Cu diffusion,[7] because of

its insolubility in Cu and high melting point of more than 2300°C as well as the properties already mentioned.

This paper covers two topics on Ru thin-film growth from sc$CO_2$ fluids. First, Ru deposition using $H_2$ reduction chemistry is studied, following our first report using cyclopentadienyl Ru (RuCp$_2$) as a precursor.[6] RuCp$_2$ is used as a Ru source material in many CVD studies; however, oxidative chemistry is mainly used.[8–10] The original objective of the present study is to research more on the deposition characteristics of Ru.

Through this work, we discovered that Ru grows only on conductive surfaces, so-called selective deposition. Such surface sensitivity may be beneficial to certain applications. However, in view of applying Ru as a Cu barrier, this surface sensitivity is not very much favored. Conductive barrier layers are usually formed on a dielectric underlayer. That is, as long as there is surface sensitivity, an additional conductive layer must be formed first, thus, a different deposition method should be employed. Our challenge is to establish a novel and continuous process that permits the deposition of a barrier metal and Cu in sc$CO_2$. In such a vehicle, the underlayer must be a dielectric or an insulator, i.e., Ru should be grown directly on dielectrics without the surface sensitivity. In the second part, we report a means of obliterating surface sensitivity.

## 2. Experimental

A mixture of $CO_2$, metal precursor and gaseous reagent was processed in a high-pressure reactor with a substrate. The pressure and temperature range was 13 MPa and 180–350°C, respectively. The precursor used was *bis*-cyclopentadienylruthenium [ruthenocene, RuCp$_2$ (Cp = C$_5$H$_5$)]. RuCp$_2$ is yellow solid that dissolves well in sc$CO_2$.[6] The schematic diagram of the experimental setup was described elsewhere.[6] The substrates used were Si wafer pieces, approx. 1 cm sq., coated with a thin film. The types of coating were described along with the experimental data. Prior to deposition RuCp$_2$ was weighed and placed in a reactor. The volumetric concentration was varied from $1 \times 10^{-5}$ mol/m$\ell$ to $5 \times 10^{-5}$ mol/m$\ell$. The reactor was then filled with $H_2$, $O_2$ or $O_3$, following reactor evacuation with a

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rotary vane pump. $O_3$ gas was supplied from a gas cylinder with a balancing $CO_2$ gas. The inner surface of the cylinder was lined with a special passivation layer (WinZone[11]). The nominal concentration of $O_3$ in the supplied gas was 4.5%, and the gas pressure was 0.56 MPa (so the partial pressure of $O_3$ was 25 kPa). Reactor wall temperature was measured with a thermocouple inserted to a drilled hole. The temperature difference between the wall and the reactor center was less than 3°C. The reactor was then heated with a cylindrical mantle heater at a ramp rate of $\approx 10$°C. The temperature was held at a target temperature, for 5 min unless otherwise stated, which is hereafter defined as the deposition temperature. Film thickness was determined by cross-sectional secondary electron microscopy (SEM). The depth distribution of the elements in the films was characterized by Auger electron spectroscopy (AES) using 1 keV Ar ion sputtering gun.

## 3. Results and Discussion

### 3.1 Ru deposition characteristics

Figure 1(a) shows deposits obtained at 250°C with addition of 1 MPa $H_2$. The substrates were Si wafers lined with a TiN film. Prior to the deposition, the substrates were coated with a Au film having a nominal thickness of approximately 50 Å. The purpose of this coating was to initialize the surface to a conductive and unoxidized state, where a sputtering gold coater for SEM observation was used. Thick and uniform Ru films were obtained when $H_2$ was added; however, practically no deposits were observed when a gaseous reagent was not used [Fig. 1(b)]. The $O_2$ addition resulted in heavy-particle formation. A SEM photo in Fig. 1(c) shows one of the bulky and particulate agglomerates isolated from the reactor after the deposition run.

Figure 2 shows a graph of film thickness plotted against deposition temperature. Film thickness increases with temperature and takes a maximum at 250°C. This trend is the same for Cu deposition.[6] The activation energy for the growth can be roughly estimated from the first two data points in the lower temperature regime. The obtained activation energies were 1.1, 0.75, and 0.27 eV for 0.1,

Fig. 1.   SEM photographs of Ru films deposited with addition of (a) $H_2$ and (b) $O_2$, and (c) without gaseous reagent addition.

Fig. 2.   Temperature and $H_2$ pressure dependences of Ru film thickness.

0.5, and 1.0 MPa added $H_2$ pressures, respectively, where the first two values are closer than the rest. The reported values of Ru CVD from $RuCp_2$ or its homologue are in the range of $0.4 - 3$ eV,[10,12,13] which fairly agrees with our data. The decrease in activation energy observed when a large amount of $H_2$ (1.0 MPa) was added may suggest a change in the deposition mechanism. Note that a similar observation was reported for Ru CVD using $O_2$ at a high concentration as a process gas, the activation energy of which decreases to 0.4 eV.[10]

Cyclopentadiene is an organic acid, so that a possible reduction formula of $RuCp_2$ to Ru is written as

$$Ru^{II}Cp_2 + H_2 \rightarrow Ru^0 + 2HCp. \tag{1}$$
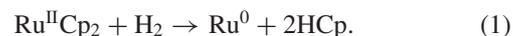
However, it has been reported that Ru films can be obtained under oxidative chemistry, or at least not under reducing chemistry at low deposition temperatures. Green *et al.* reported, in their pioneering Ru metalorganic CVD experiments, that no film growth is observed when $H_2$ is conducted with vaporized $RuCp_2$.[8] It has also been reported that Ru thin films are rarely grown from $RuCp_2$ or its homologues either in inert gas or in vacuum ambient.[8–10] In another report on Ru CVD, $H_2$ reduction chemistry was employed but $\beta$-diketonate compounds were used.[14] From these results, we conclude that reaction (1) is not a generally acceptable scheme, at least in the present work.

We propose the possibility of a different reaction mechanism where $CO_2$ is involved. $H_2$ reacts with $CO_2$ catalytically at metal surfaces, and rather easily in $scCO_2$ through

$$CO_2 + H_2 \xrightarrow{Ru} HCOOH.$$
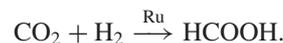
Here Ru refers to metallic Ru or Ru compounds. For this reaction, other metal surfaces also function. The nucleophilic HCOO group or related intermediates can attack the Ru-Cp bond so as to ease the reduction by hydrogen atoms. This mechanism can explain both an important role of $H_2$ and the incorporation of oxidative chemistry observed in CVD.

The decrease in thickness at higher temperatures is not a general phenomenon observed in CVD. According to CVD reaction chemistry, deposition rate levels off at higher temperatures when the rate-determining step of growth is changed from reaction-limited to transport-limited of reaction species. Indeed, the leveling off of deposition rate has
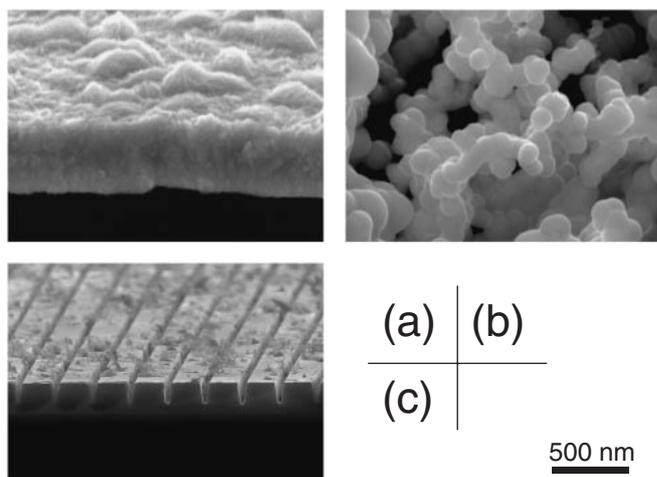
been observed.[9,12,13,15] The transition temperature range reported in the literature is $250-300°C$, which fairly agrees with our observation.

The deposition rate lowering at elevated temperatures is usually attributed to the presence of a reverse reaction or etching reactions. Matsui *et al.* reported that a decrease in deposition rate occurs above $280°C$ when a high concentration of oxygen is added.[10] The reason for this was discussed in view of the decrease in oxygen concentration in the ambient. When the oxygen concentration is high, the growing Ru is oxidized or Ru oxide grows. Ambient oxygen easily dissolves in the deposited Ru oxide and much more at higher temperatures. This leads to a deficiency of oxygen in ambient or at the growing surface. Since ambient $O_2$ removes Ru and its ligand, a deficiency in oxygen causes a decrease in growth rate.

This discussion may hold true in our case, but for $H_2$. It is known hydrogen dissolves well in Ru, especially at high temperatures.[16] As we have seen in our data, $H_2$ is a species necessary for Ru deposition, therefore a mechanism similar to that in the case of hydrogen deficiency may work. Indeed, the more $H_2$ was added the higher the deposition rate was obtained (see Fig. 2).

Another possible reason for the peaking of the deposition rate is based on the nature of $scCO_2$. $ScCO_2$ is a compressive fluid whose density varies with temperature, for instance, from $3.18\,mol/\ell$ ($250°C$) to $2.54\,mol/\ell$ ($350°C$). Even if the pressure of $scCO_2$ and the molar ratio of $RuCp_2$ are the same, the molecular number density decreases by 20% when the temperature is increased.

### 3.2 Deposition surface sensitivity

Figure 3 shows secondary electron micrographs of the deposits on (a) pre-sputtered Ru, (b) Si with native oxide, (c) Au-coated TiN, and (d) Au-coated Si. Continuous or quasi-continuous films were observed in Figs. 3(a), 3(c), and 3(d), however, practically no deposits were observed in Fig. 3(b). This demonstrates that Ru films grow only on conductive or
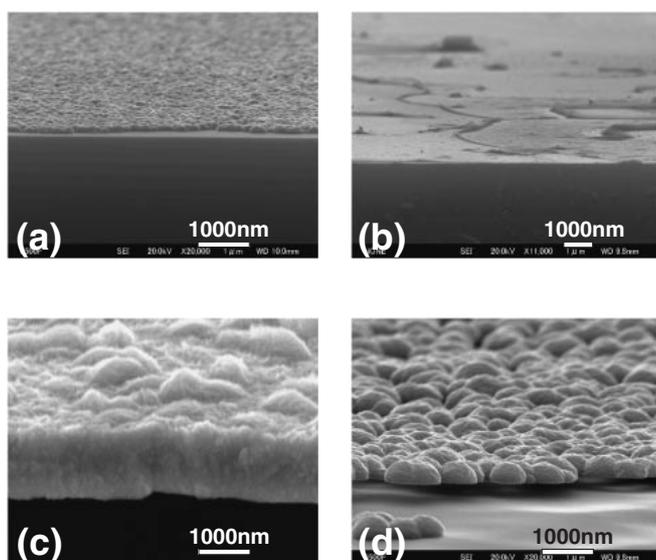


Fig. 3. Secondary electron micrographs after deposition runs using various substrates, (a) presputtered Ru, (b) Si with native oxide, (c) Au-coated TiN, and (d) Au-coated Si. The deposition times were not the same.

Table I.  Summary of Ru and Cu film growth chemistry.

|      | Metallic Surface | Dielectric Surface |
|------|------------------|--------------------|
| Ru   | Reductive Chemistry | Oxidative Chemistry |
|      | Oxidative Chemistry |                    |
| Cu   | Reductive Chemistry | n.a. |

metallized surfaces. This is in good agreement with our observation in Cu deposition from $scCO_2$.[1,2,6]

Such surface sensitivity in reduction chemistry has been explained by the ability of the metal surface to donate electrons to attractively adsorbed chemical species.[17,18] This is of course part of our model, as mentioned earlier.

From a practical deposition point of view, the elimination of this surface sensitivity is generally preferred. Oxidation chemistry was investigated instead, because surface sensitivity is thought to be a peculiar phenomenon as long as reduction chemistry is used. Table I summarizes the results of deposition experiments. Reductive chemistry refers to the reduction of the metal precursors by $H_2$, and oxidative chemistry refers to the use of $O_2$ or $O_3$ as a gaseous reagent. The partial pressure of the gases introduced in the reactor before deposition was fixed at $25\,kPa$ for both $O_2$ and $O_3$. Figure 4 shows Ru films deposited on Si with $O_2$ (left) and $O_3$ (right). The film obtained with $O_3$ shows a smoother surface topography.

$O_3$ dissociates preferentially at surfaces via

$$O_3 \rightarrow O_2 + O_{ads}, \qquad (2)$$

where $O_{ads}$ refers to a free oxygen radical adsorbed onto a surface. The released oxygen radicals enhance Ru-Cp bond cleavage proceeding at the surface via[10]

$$RuCp_2 + O_{ads} \rightarrow Ru(O) + CO_2 + H_2O, \qquad (3)$$
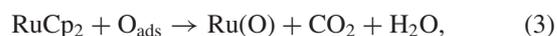
where the coefficients are ignored. $Ru(O)$ is an oxygen-containing Ru but can also be pure Ru. As a result, inhomogeneous nucleation is promoted and homogeneous nucleation in the $scCO_2$ ambient is suppressed. Figure 5 shows the result of AES depth analyses of a Ru film deposited using $O_3$ (above) or $O_2$ (below). The plot above shows a higher oxygen content than that below. This suggests that more oxygen is involved in reaction (3) according to oxygen-releasing reaction (1).

Finally, the obtained Ru films, oxygen-containing Ru films in fact, were reduced to Ru. The reduction was carried out with a $H_2$-added $scCO_2$ fluid. This treatment was carried
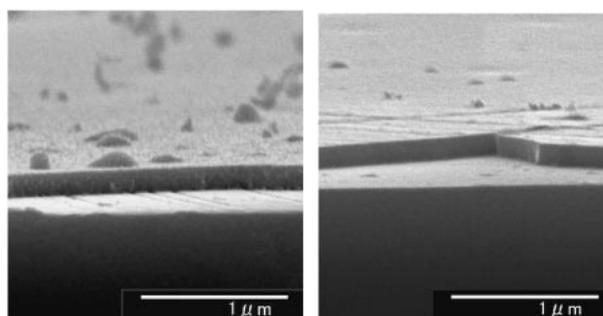


Fig. 4. Secondary electron micrographs after deposition runs using $O_3$ (left) and $O_2$ (right).
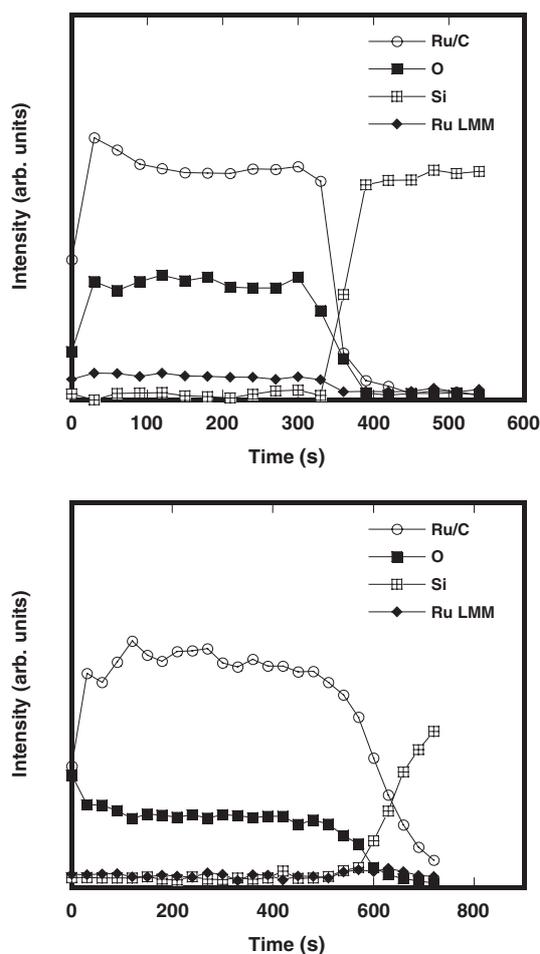
Fig. 5.   AES depth analyses of Ru films deposited on Si using $O_3$ (above) and $O_2$ (below). Note that Ru KLL signals overlap with C KLL signal.
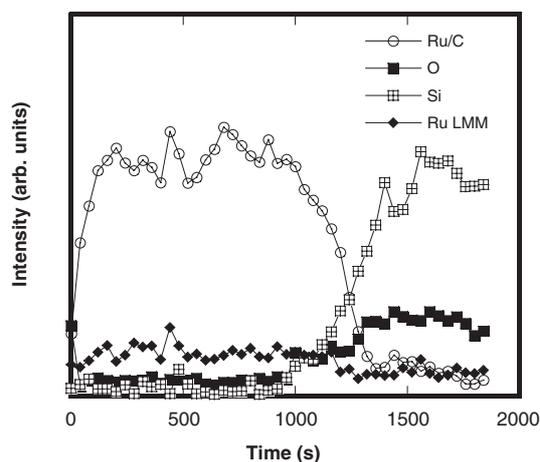


Fig. 6.   AES depth analysis of oxygen-containing Ru film on $SiO_2$ after processing in a supercritical $CO_2$-$H_2$ fluid.

out presuming that it is identical to conventional furnace annealing using a forming gas. The AES depth profiling of that film (Fig. 6) shows practically no oxygen in the film. Obviously the oxygen-containing Ru films were reduced to metallic Ru by $H_2$ dissolved in $scCO_2$.

## 4.   Conclusions

This article demonstrated the deposition characteristics of Ru thin films in $scCO_2$ fluid. $RuCp_2$ was dissolved in $scCO_2$ together with a gaseous reagent so as to obtain deposits at elevated temperatures. Pure Ru films were obtained when $H_2$ was added. Film thickness was a function of temperature and the amount of $H_2$ added. The positive temperature dependence of film thickness is said to be a reasonable observation, as also observed in the reported CVD results. The negative temperature dependence in the higher temperature regime was also discussed. An interesting feature observed in $H_2$ reduction chemistry was surface sensitivity or deposition selectivity. That is, Ru films grew only on conductive or metallized surfaces. Surface sensitivity did not appear when oxidative chemistry was used. $O_2$ or $O_3$ was used as an oxygen source, and oxygen-containing Ru films were obtained. $O_3$ was found to promote heterogeneous nucleation and increase oxygen amount. Oxygen-containing Ru films were reduced to Ru using $H_2$ dissolved in a supercritical fluid. That is, the formation of pure and continuous Ru films on nonconductive surfaces was succeeded.

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