Metallization Using Supercritical Fluids

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Biography

Professor E. Kondoh obtained his BE and ME degrees from Waseda University, and Ph.D. from Kyoto University all in materials science. He has experience in R&D for thin films processing at Kawasaki Steel, Max-Plank Institute, and IMEC. Since 1998 he holds professorship and is now with Graduate School of University of Yamanashi, Japan. He can be reached at kondoh@yamanashi.ac.jp.

Abstract:

Supercritical CO_2 behaves like both a gas and a liquid, and possesses unique features such as nanopenetration capability, high diffusivity, and solvent ability. The technique described in this paper uses the supercritical CO_2 as a reaction medium for thin film growth and realizes filling or coating of nanofeatures with conducting metals. In this paper, we demonstrate the possibilities of this technique in Cu and Ru thin film deposition. A basic approach to achieving Cu metallization of deca-nanometer trenches or vias were studied. Ru, a new candidate for the next-generation Cu barrier, was successfully deposited and the formation of Cu/Ru stack was demonstrated. The chemistry to deposit the barrier layer directly on dielectric/nonconductive layers was further studied.

Introduction:

CO_2 transforms into a supercritical fluid above its critical point (P_C = 7.4 MPa and T_C = 31 ºC, see Fig. 1) (1). Supercritical CO_2 ($scCO_2$) is a compressive fluid and behaves like both a gas and a liquid. $ScCO_2$ has so far been successfully utilized in chemical processing, such as for the extraction of fragrant materials, and is now of considerable interest for application to microprocessing. Advantageous characteristics of the supercritical CO_2 ($scCO_2$) fluid in view of microprocessing are, for instance, 1) a wide controllability of molecular number density, reaching as high as that of liquids, as functions of operating temperature and pressure, 2) high diffusivity and low viscosity, allowing deep penetration into small features, 3) zero surface tension and complete evaporation, which results in perfect wetting and drying without capillary force, 4) good solvating capability, allowing its use as an alternative to organic solvents, and) ease of design of an environmentally friendly closed-loop system. In addition, CO_2 is affordable and nonhazardous, and its critical point is low. The reported applications of $scCO_2$ for microelectronic processing include photoresist drying (2)(3), precision cleaning (4)(5)(6), and the fabrication of porous low-dielectric-constant thin films (7)(8).

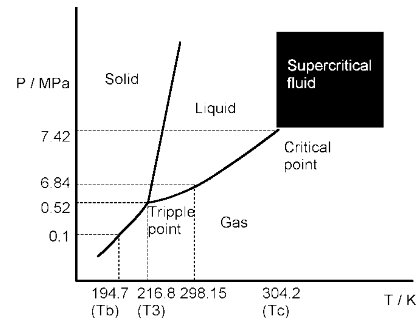

Fig. 1 Phase diagram of CO_2

The author's research group has conducted pioneering and intensive research using $scCO_2$ for ULSI metallization, proving remarkable *nano gap filing* capability In this technique, metalorganic compounds (chelates), the recursors, are dissolved in $scCO_2$ and are transformed into thin films through an appropriate reaction chemistry (Fig. 2). Nano-penetration capability and wide density controllability are expected to afford the fabrication of high-aspect-ratio metal components from intrachip interconnects to interchip interconnects and to MEMS. Our final goal is to realize metallization all in supercritical fluids, *supercritical integration*, so as to say. In this article, Cu nano gap filling and Ru deposition possibility are described.

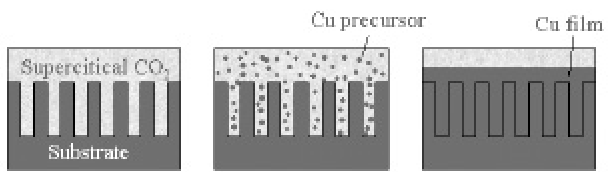

Fig. 2 Process concept of $scCO_2$ nano filling.

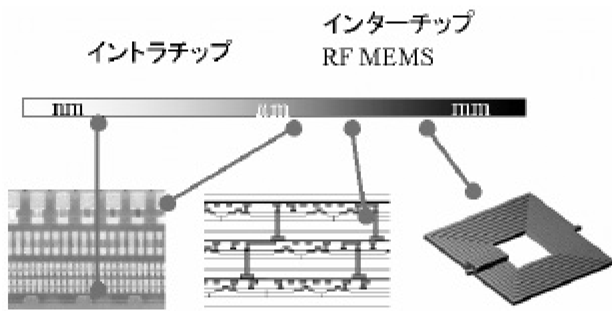

Fig. 3 Metallization applications that the $scCO_2$ deposition targets.

$ScCO_2$ Nano filling Processor:

The $scCO_2$ deposition tool consists of a stainless-steel made high pressure reactor, liquid CO_2 supply unit, high pressure pump, gaseous additive supply unit, and back pressure regulation unit. The precursor can be placed inside the reactor before deposition, or can be supplied with $scCO_2$ being premixed in another reservoir. Besides this *batch* arrangement, the flow-type arrangement like CVD apparatus is also used. For this purpose, a gas mixing unit that admits a low pressure ($<$ 1 MPa) gaseous additive to high pressure ($>$7.4 MPa) $scCO_2$ was developed in the research group.

A 200 mm compatible deposition tool is now under development based on these technologies (Fig. 4). However, most of the results stated in this article were obtained with small reactors.

Fig. 4 200mm-wafer $ScCO_2$ nano filling processor.

Deposition of Cu and Nanofilling:

Cu Deposition Characteristics

Cu films were deposited in the reactor through H_2 reduction chemistry from a mixture of CO_2, Cu precursor (chelate) and H_2. The pressure and temperatures were 10–15 Ma and 180–400ºC all under supercritical conditions. The precursor used were hexafulloacetylacetnatecopper ($Cu(hfac)_2$) and diisobutyrylmethanatecopper ($Cu(dibm)_2$). The substrates used were blanket or hole/trench-patterned SiO_2/Si wafers coated with atomic-layer-deposition (ALD) TiN, unless otherwise stated. The substrates were coated with Au using a conventional sputtering tool for electron micrography prior to the supercritical fluid deposition. The nominal thickness of the Au layer was about 50 Å.

A preferential growth on conductive substances, e.g. on Fe, Au, Cu, WN, TiN, TaN, and HF-treated p-Si was observed. Shiny and continuous films were formed on the metals, whereas on the p-Si that received a laboratory-level HF-treatment the film exhibited a less shiny and continuous feature. Such effects of the H_2 addition are similar to the ones reported for chemical vapor deposition (9). This similarity suggests that the surface dissociation of H_2 is involved in the deposition mechanism presumably as the rate-determining step.

The deposition rates obtained were 30–50 nm/min. These values are practically sufficient at sub-100mm technology nodes. A further increase would be achieved by increasing the precursor concentration. The yield of Cu was excellently high, reaching almost 100% when the batch reactor was used. This high yield makes $scCO_2$ deposition very attractive against Cu CVD; in the latter most of the Cu source is exhausted and wasted.

Figure 5 shows XPS depth profiling of a deposited Cu film. Practically no carbon, oxygen, and fluorine impurities are found in the film. In the XRD spectrum shown in Fig. 6 the (111) peak at 43º is predominant, which indicates the preferential growth of (111) faces parallel to the substrate.

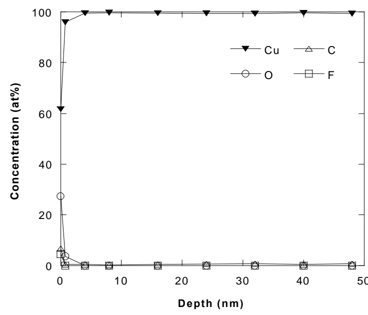

Fig. 5 XPS depth profiling of a deposited film.

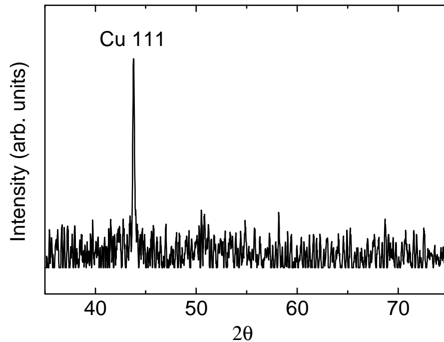

Fig. 6 XRD pattern of Cu film

Deposition kinetics

The most fundamental experiment necessary to understand film deposition chemistry is the determination of the temperature dependence of growth. Film topography in narrow features is generally a trade-off between mass transport and the reaction proceeding inside. Therefore, better understanding of deposition chemistry is crucial for the improvement of film topography

Cu started to be deposited at around 180ºC when $Cu(hfac)_2$ was used as a precursor (Fig. 7). This is much lower than typical CVD temperatures observed under $Cu(hfac)_2$ + H_2 chemistry (11). As stated above the preferential growth on conductive substances observed without the Au coating of the substrate. When the Au coating was applied, no deposition selectivity was observed. Without the Au coating, the deposition starting temperature increased by several tens of ºC. The logarithmic deposition rate plotted against the reciprocal temperature is shown in Fig. 8. The deposition time was fixed at 15 min for all experiments. The film thickness shows a maximum at around 220ºC and then decreased with increasing temperature. The activation energy for deposition was evaluated to be 0.42 eV. This value is almost one-half of the values reported for CVD and is approximately the same as that for plasma-assisted CVD (Table 1) (17)(18)(19).

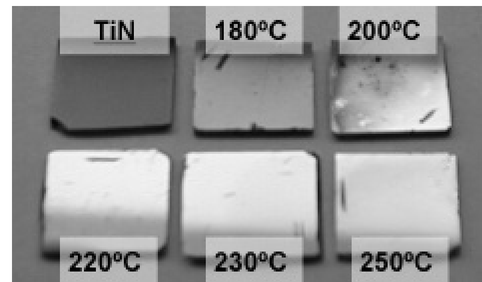

Fig.7 Appearance of Cu films deposited on ALD-TiN at various temperatures

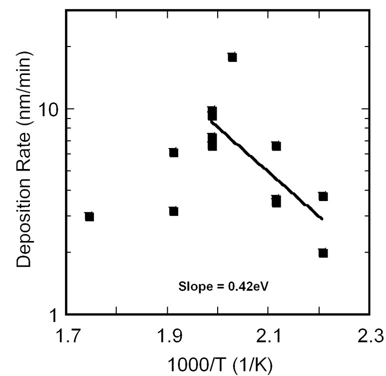

Fig. 8 Arrhenius plot of Cu film growth rate.

Table 1 Application energies for Cu growth using $Cu(hfac)_2$-H_2 chemistry (eV).

This Worl	Thermal CVD	Plasma CVD
0.42	0.65	0.39

Nano gap filling capability

Such differences in deposition chemistry are thought to greatly effect the deposition topography. Figure 9 shows cross-sectional SEM images of Cu films deposited in narrow trenches using $Cu(hfac)_2$. The films formed in larger trenches show smooth and conformal topography. The size of the smallest trenches seen in Fig. 8 is about 50 nm at the opening. Cu plugged in these trenches at 230ºC as continuous and showed no clear seams.

An interesting feature to stress here is that lowering the temperature from 230ºC to 180ºC was ineffective in improving the film conformability. For instance, Cu did not reach inside the trenches where the trench sealing occurred. A better Cu penetration is seen for the larger trenches; however, a discontinuity is still

seen at the sidewall. This tendency is contrary to the general belief in CVD to occur where the conformability improves as the deposition temperature decreases.

The trench/via filling capability was found to also depend on the kind of precursor. When fluorine-free Cu(dibm)$_2$ was used instead of Cu(hfac)$_2$, a significant improvement in deep via filling was achieved under the same deposition conditions (Fig. 10).

The reason for obtaining better filling in the Cu(dibm)$_2$ experiment is not clear at present. Thermal analyses of the precursors show much higher sublimation and decomposition temperatures of Cu(dibm)$_2$ than those of Cu(hfac)$_2$(20). The higher decomposition temperature suggests a lower deposition rate at the same deposition temperature and thus better filling, as long as the CVD theory is valid. However, as described above, lowering the temperature does not always lead to conformal topography or better filling.

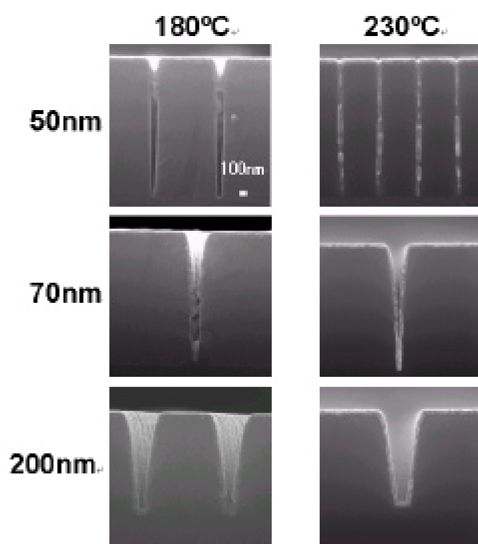

Fig. 9 Temperature dependence of gap filling.

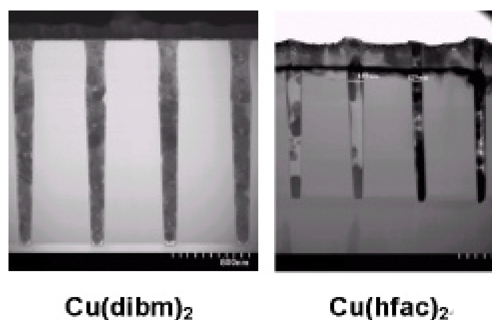

Fig. 10 Comparison of via filling capability using different precursors.

Ru deposition: a way to *supercritical integration*.

Ru deposition and Cu/Ru stack formation from supercritical fluids

One challenge in supercritical fluid metallization is barrier metal deposition. Recently, Ru has been proposed as a next-generation barrier metal against Cu diffusion (14). In addition to its low resistivity (6.67 µÙ cm, Ru is almost insoluble in Cu, has a high melting point of over 2300ºC, and may be formed by CVD or be plated by electroless deposition. Moreover, Ru has received much attention as a promising capacitor material, because it has a low resistivity and etching capability, and its oxides are conductive. In view of deposition topography, fundamental requirements for the above applications are the same; namely good step coverage and filling capability. In the following, the characteristics of Ru deposition from supercritical CO_2, the first success deposition to the author's knowledge, are described and the possibility of the application to the Cu barrier metal is demonstrated.

The precursor used was bis(cyclopentadienyl)-ruthenium(II), (ruthenocene, $RuCp_2$). $RuCp_2$ is a yellow solid with a vapor pressure of about 0.01 Torr at 85ºC (15). A preliminary experiment was carried out to study the solubility of $RuCp_2$ in $scCO_2$ using a high-pressure cell having view ports. $RuCp_2$ dissolved well in $scCO_2$ at 13 MPa and 30–80ºC and became more soluble with increasing temperature. Although the solubilities of $RuCp_2$ at higher temperatures have not been quantitatively documented, there is no doubt that the solubility considerably at much elevated temperatures, since the vapor pressure of $RuCp_2$ has a large positive temperature dependence.

Deposition was carried out at 250–350ºC and 13 MPa with the addition of H_2. The deposits obtained with the addition of O_2 were granular or porous bulk. When H_2 was used, the deposits became continuous metallic film and were assigned to metal Ru using XPS (Fig. 11) and XRD.

Figure 12 shows the result of AES depth analysis of a deposited Ru film. The signal from the Ru KLL band (◆) shows a typical depth profile of a single-element film. Signals of impurity elements are as low as the background signal. The signal from the Ru LMM band (not shown), of which the intensity is much weaker

than those of the others, showed the same behavior as that of the Ru KLL. The C KLL band overlapped the Ru KLL band, thus the C impurity was not easily detectable. An XPS surface spectrum obtained after Ar surface sputtering clearly indicates the presence of strong Ru peaks and no impurity C or O (Fig. 11).

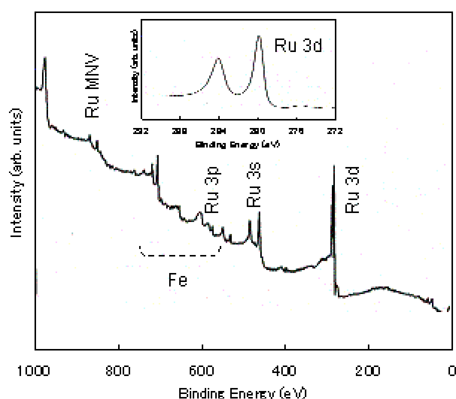

Fig. 11 XPS spectrum of deposited Ru film.

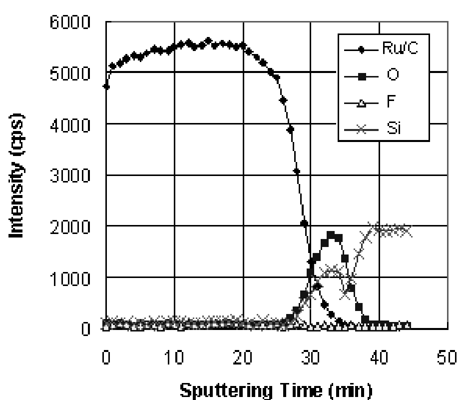

Fig. 12 AES depth profiling of deposited Ru film.

Figure 13 shows cross-sectional SEM images of an on-trial Cu/Ru stack (right) and a thin conformal Ru film (left). The Ru film in the right has a thickness of about 50 nm and shows very smooth and continuous topography. The Cu film in the left was also formed in $scCO_2$ using $Cu(hfac)_2$ following a different run for Ru deposition. The valley in Ru is filled with Cu to the bottom, and the Cu/Ru interface is very clear and sharp. These micrographs clearly indicate the vast potential of $scCO_2$ deposition for true metallization.

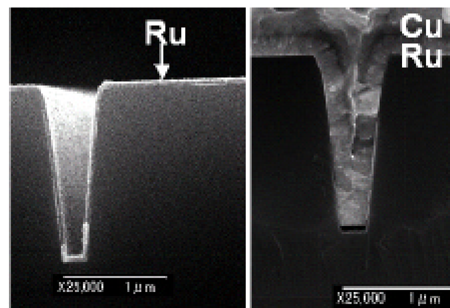

Fig. 13 Cross-sectional SEM images of a conformal 50-nm-thick Ru lm (left) and a Cu n Ru stack (right). Note that Cu and Ru were formed in supercritical uid.

Direct deposition of Ru on dielectric/nonconductive substrates

When reduction chemistry was used, the Ru deposition was observed only on metallic/conductive surfaces. The Ru films shown in Fig. 13 were indeed deposited on ALD-TiN. When oxidation chemistry was used instead, preferential growth on conductive surfaces was no more observed, and Ru grew directly on dielectric/nonconductive surfaces without an additional treatment or liner.

Oxidized Ru (Ru(O)) grew on Si, SiO_2, or metallized surfaces from a mixture of $scCO_2$, $RuCp_2$, and an oxidant. To promote thin film growth, or heterogeneous nucleation, ozone was used as a gaseous additive. Ozone was introduced to the reactor from an ozone-CO_2 (bal.) gas container. The ozone-CO_2 mixture gas is commercially-available (Iwatani International Corp.) and allows safe and easy ozone handling.

The oxygen content, evaluated by the AES O/Ru peak intensity ratio, was dependent on the kind of oxidant used. The Ru(O) film formed using O_3 showed a higher oxygen content than O_2 or laboratory-made CVD Ru oxide ($\rho \sim 500\mu\Omega$.cm) (Fig. 14). The Ru(O) film surfaces generally showed good smoothness and using O_3 resulted in better surface topography; but there was still seen nodule-like irregular growth (Fig. 15).

Table I Summary of Cu and Ru film growth chemistry.

	Metallic Surfaces (barrier metals, transition metals, noble metals)	*Dielectric Surfaces (Si, t-SiO_2, inorganic porous low-k)*
Ru	Reductive Chemistry Oxidative Chemistry	Oxidative Chemistry
Cu	Reductive Chemistry	n.a.

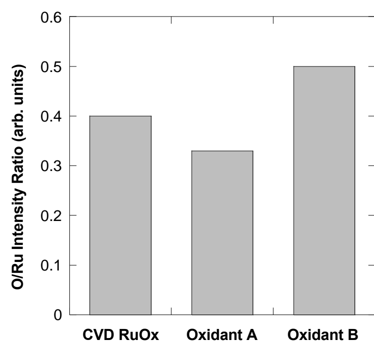

Fig. 14 Relative oxygen content of Ru(O) films. Oxidant A = O_2, Oxidant B = O_3

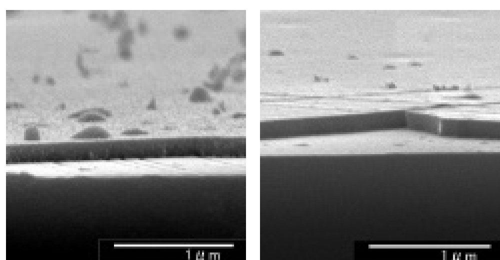

Fig. 15 SEM images of Ru(O) films grown using O_2 (left) and O_3 (right).

Cu was grown directly on the Ru(O) films using the $Cu(hfac)_2$-H_2 chemistry. This chemistry requires a conductive underlayer to nucleate Cu as stated in introduction. The use of conducting Ru(O) as Cu seed is therefore a key not only to realizing direct deposition on dielectric layers but also to laying Cu (Fig. 16).

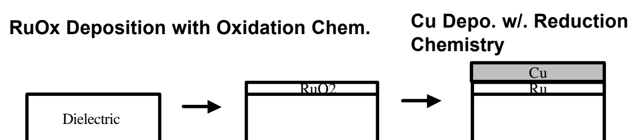

Fig. 16 Process flow of Cu/Ru/Dielectric formation.

Summary and Conclusion:

This article demonstrated the capability of a thin film deposition technique from supercritical CO_2 fluids to fill/coat nanofeatures. In this technique, a metal precursor was dissolved in $scCO_2$ and converted to a thin film through an appropriate reaction chemistry.

A Cu deposition process has been developed, and filling/coating properties of Cu were found to depend on the deposition temperature and the kind of precursor. Lowering the deposition temperature, which, in CVD, has been believed as an effective way of improving the conformability, did not result in better film coverage. The choice of precursor was also crucial, and using a low-vapor-pressure precursor led to a better performance for sub-100 nm trenches and holes.

The deposition of Ru—a strong candidate material for capacitor electrodes and also for future-generation Cu barriers—from $scCO_2$ using $RuCp_2$ was reported. Excellent filling and coverage performances were observed. Cu/Ru stacks were directly formed onto dielectric or non-conductive layers. This newly developed process does not require an underlayer or 'activation' treatment that has been regarded essential to promote nucleation in the past re-searches. Ru was used as a supposed barrier layer.

In conclusion, supercritical fluid chemical deposition has vast possibilities in LSI metallization from Cu nano-filling to barrier metal deposition.

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