H-assisted plasma CVD of Cu films for interconnects in ultra-large-scale integration

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Abstract

H-assisted plasma CVD (HAPCVD), in which Cu(hfac)$_2$ is supplied as the source material, realizes control of qualities of Cu films, since H irradiation is effective in purifying the Cu films, increasing the grain size, and reducing the surface roughness. Conformal deposition in fine trenches can be realized by decreasing dissociation degree of Cu(hfac)$_2$ using the HAPCVD. Cu(hfac) is identified as the radical mainly contributing to the deposition. Based on the results, we proposed a model in which Cu(hfac) and H react on surfaces to deposit Cu films. We also demonstrated conformal deposition of smooth Cu films of 30 nm thickness and 1.9 $\mu$Ω cm resistivity and almost complete Cu filling in trenches 0.35 $\mu$m wide and 1.6 $\mu$m deep using the HAPCVD. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since Kilby proposed the concept of the integrated circuit (IC) in 1958 [1], manufacturing technologies of microelectronics have evolved towards higher integration density with smaller design rules. As the push towards ultra-large-scale integration (ULSI), i.e. beyond one million transistors on a chip, is pursued, device feature size continues to shrink into the sub-half-micron range in order to optimize the reliability and to improve performance. The resulting demands on interconnects require multilevel metallization, which reduces interconnection lengths and signal transmission delays. Although aluminum-based interconnection has been commonly used for many years, it is becoming a primary limiting factor in chip performance, because of RC delay due to the relatively high resistivity of aluminum (2.65 $\mu$Ω cm at 20°C), and also open circuit failure induced due to electromigration and stress-voiding as device feature size is scaled down.

Copper is a promising material as a multilevel interconnect metal for ULSI applications than aluminum, because it has low bulk resistivity of 1.72 $\mu$Ω cm at 20°C and excellent resistance against electromigration and stress migration. The electroplating method, which is currently employed for formation of Cu interconnects for ULSI in industry, needs thin Cu seed layers deposited by other means [2,3]. At present, it is difficult to obtain such thin layers in small via- and contact-holes of a diameter below 0.13 $\mu$m and a depth above 0.8 $\mu$m. For thermal and plasma CVD’s, more conformal films tend to be deposited when reducing surface reaction probability $\beta$ of Cu-precursors [4]. Table 1 shows requirements for Cu films to be applied on interconnects [5] and possible solutions for them when using plasma CVD. For the thermal CVD, the $\beta$ value is controlled by varying the substrate temperature $T_s$ and/or the flow rate of material gas, changing of such parameters also influence the deposition rate and film qualities such as purity and resistivity. The plasma CVD has a significant advantage over the thermal CVD in control of $\beta$, because its value can be changed by varying the dissociation degree of material gas under a constant $T_s$ [6,7].

Regarding Cu film deposition from Cu(hfac)$_2$ using a conventional plasma CVD reactor, several studies have been reported [8–11]. These studies show that (1) pure Cu films can be grown at a deposition rate of above 100 nm/min with H$_2$ dilution [8], (2) apparent activation energy of the deposition is 9 kcal/mole [10], and (3) plasma CVD realizes a high deposition rate at a low substrate temperature compared to that of thermal CVD [10]. Although these previous studies suggest the importance of H$_2$ dilution to obtain pure Cu films, roles of H and H$_2$ as well as...
the mechanism of pure Cu deposition has not been clarified yet.

Previously, we showed the useful effects of H atoms on removing the impurities in Cu thin films deposited using the plasma CVD, in which Cu(hfac)$_2$ is supplied as a source material [11]. Based on this result, we have developed a plasma CVD reactor equipped with an H atom source (hereafter referred to as HAPCVD reactor, standing for H-assisted plasma CVD reactor) [11–14]. Using HAPCVD reactor, we have studied effects of H atom irradiation on qualities of Cu films such as purity, surface roughness as well as grain size and crystal orientation.

In this paper, first we show the advantages of the HAPCVD of Cu films for interconnect application by describing experimental results regarding effects of H irradiation on the qualities of Cu films, second we propose a simplified reaction model for the deposition based on those results, and finally we demonstrate the conformal deposition of smooth thin Cu films and filling of Cu in trenches by using the HAPCVD reactor. After a description about the experimental setups and methods in the next section, we describe effects of H irradiation on impurities, surface roughness, grain size and crystal orientation, and adhesion strength in Sections 3.1–3.4, respectively. Then in Section 3.5 a description is given concerning the control of surface reaction probability of Cu-containing radicals under conditions of 100% Cu film deposition using the HAPCVD. Identification of the main deposition species is given in Section 3.6, and based on the results in Sections 3.1–3.6 a simplified reaction model for the deposition is proposed in Section 3.7. Finally we show conformal deposition and filling of Cu in trenches in Section 3.8.

2. Experimental

The source material for Cu deposition used in this study was Cu(hfac)$_2$, bis(hexafluoroacetylacetone) copper (II), dissolved in ethanol (C$_2$H$_5$OH) at a concentration of 0.1 mol/l. The mixture was vaporized at 198°C and then transported to a reactor with H$_2$ carrier gas of 10 sccm. The flow rates of C$_2$H$_5$OH[Cu(hfac)$_2$] and H$_2$ were supplied at 36–50 and 36–250 sccm, respectively. The total pressure was 23–220 Pa. Typical deposition rate was in a range of 1–100 nm/min. A Si substrate was set on the lower grounded electrode and the substrate temperature $T_s$ was set in a range from room temperature to 250°C.

Experiments were performed using two capacitively coupled parallel plate reactors (HAPCVD reactors), A and B, each has an additional H atom source [11–14].

The reactor A was employed mainly to study the effects of H irradiation on qualities of deposited Cu films. All electrodes for the main discharge and the H atom source were installed in a stainless steel vessel of 160 mm in inner diameter and 240 mm in height. The H atom source was composed of coaxial stainless steel tubes. The outer tube, of 130 mm inner diameter and 38 mm length, was used as a grounded electrode. The inner one, of outer diameter 16 mm and length 22 mm, was used as a powered electrode. The main discharge side (lower end) of the tube for the H atom source, operated as its grounded electrode was covered with a grounded mesh (50 mesh/inch) to prevent charged species in the H atom source from being transported into the main discharge. For the main discharge, powered and grounded electrodes, which were made of stainless steel mesh and plate of 50 mm in diameter respectively, were placed at a distance of 40 mm. The excitation frequency and power $P_m$ for the main discharge were 13.56 MHz and below 75 W, respectively, while the excitation frequency and power $P_a$ for the H atom source discharge were 13.56 MHz and below 75 W, respectively. Relative concentrations of impurities in the films were measured by in situ Fourier-transform Infrared (FT-IR) spectroscopy. The measurement system is shown together with the reactor A in Fig. 1(a). The Cu

| Requirements | Required values | Possible solutions when using plasma CVD | Values realized using plasma CVD$^b$ |
|--------------|----------------|------------------------------------------|-------------------------------------|
| High purity  | 100% Cu        | H irradiation                            | 100% Cu                             |
| Low resistivity | < 1.8 μΩ cm | H irradiation                            | 1.9 μΩ cm                           |
| Large grain size | > 1 μm | H irradiation                            | 0.44 μm                             |
| (111) crystal orientation | > 90% | Ion irradiation?                         | Random orientation                  |
| Good adhesion to diffusion barrier films (TaN, WN, TiN) | > 800 N/cm$^2$ | H irradiation                           | > 800 N/cm$^2$                       |
| Smooth thin continuous films | 5 nm with 0.2 nm roughness | H irradiation                           | 30 nm with 1 nm roughness            |
| Miniaturization | β < 0.01$^a$ | Independent control of fluxes of Cu-containing radicals and H atoms on depositing film surface | β < 0.01$^a$ |
| High deposition rate | > 200 nm/min; fill >10 nm/min: seed | Plasma decomposition with H irradiation, higher partial pressure and higher flow rate of Cu complex | > 10 nm/min |

$^b$ Cu(hfac)$_2$ is used as a Cu precursor.

$^a$ β is surface reaction probability of Cu-containing radicals.
films for the FT-IR experiments were deposited on a Si(100) wafer with an Al-coated back surface at room temperature.

The reactor B was employed for Cu deposition by controlling the concentration of H atoms and the degree of dissociation of Cu(hfac)$_2$ independently. Fig. 1(b) shows a schematic diagram of the reactor B. All electrodes for the main discharge and the H atom source were installed in a stainless steel vessel of 250 mm in inner diameter and 315 mm in height. The H atom source was composed of coaxial stainless steel tubes. The outer tube, 48 mm in inner diameter and 145 mm in length, was used as a grounded electrode. The inner one, 8 mm in outer diameter and 110 mm in length, was used as a powered electrode. The main discharge side (lower end) of the grounded electrode tube of the H atom source was covered with a grounded mesh (50 mesh/inch) to prevent charged species in the H atom source from being transported into the main discharge. The excitation frequency used for the atom source was 28 MHz and the power $P_m$ was below 90 W. For the main discharge, a stainless steel mesh (50 mesh/inch) powered electrode of 55 mm in diameter and a plane grounded electrode of 85 mm in diameter were placed at a distance of 42 mm in the vessel. The excitation frequency used for the main discharge was 13.56 MHz and the power $P_m$ was below 45 W. A quadrupole mass spectrometer (Hiden EQP300) was installed to the side port of vessel to identify main ionic species in the main discharge and to measure partial electron impact ionization cross-sections of Cu(hfac)$_2$.

Intensity measurements of the optical emission from the discharge space were performed using an optical detection system, which consists of a lens and a 20 cm monochromator with a photomultiplier. The electron temperature and ion concentration were measured with a tungsten double probe of 0.5 mm in diameter and 3 mm in length. The ion concentration was deduced based on the experimental finding that the most dominant ions are H$^+$, as revealed by the mass spectra of ions sampled from the discharges.

3. Results and discussion

3.1. Effects of H irradiation on impurity removal

First, we have studied the effects of H irradiation on purifying Cu films. For this purpose, Cu films containing impurities of C, O, and F were deposited at $T_i$ = room temperature and then time evolution of impurity concentration of the Cu films during a period irradiating H$_2$ molecules, He plasmas, H$_2$ plasma, or H atoms was studied by in situ FT-IR spectroscopy. In this study, He and H$_2$ plasmas were irradiated using only the main discharge, while H atoms were irradiated using only the discharge of H atom source. Since absorption intensities at wave numbers due to the impurities have quite similar time evolution [12], we use the absorbance at 1200 cm$^{-1}$ (C−CF$_3$ stretching [15]), which is the strongest among them, as a measure of impurity concentration in the Cu films. These results are shown in Fig. 2. While the impurity concentration for the H$_2$ molecule irradiation decreases slightly with irradiation time $t$, most impurities still remain even at $t = 30$ min. The impurity concentration for the He plasma irradiation decreases rapidly from 1.0 to about 0.66 during 3 min after the discharge initiation and then continues to decrease slightly. The first rapid decrease in the concentration for the He plasma irradiation is due to their removal on the surface. The impurity concentration for the H$_2$ plasma irradiation decreases rapidly from 1.0 to 0.64 during 2 min after the discharge initiation, does slightly during the subsequent 3 min, and then begins to decrease rapidly again at $t = 5$ min to become almost zero at $t = 8$ min. While the first rapid decrease corresponds to the removal of impurities on the surface, the second rapid decrease relates to the removal of impurities in the film, since the impurity concentration for the first decrease is independent of the Cu film thickness and that for the second decrease is proportional to the thickness (not shown here). The impurity concentration for the H
irradiation steadily decreases with $t$ and becomes almost zero at $t = 7$ min. These results indicate that H atoms are the major contributor to removing impurities both on the surface of the Cu film and inside it, while the positive ions are also effective in removing impurities on the surface.

Since not only H atoms but also positive ions remove impurities on the surface for the H$_2$ plasma irradiation, the decrease in impurity concentration on the surface is fast compared that in the Cu film. The impurity removal rate tends to increase with increasing $P_m$ for the H irradiation and $P_m$ for the H$_2$ plasma irradiation, and also with decreasing the distance between the film surface and the H atom source for the H irradiation. These tendencies show that the faster impurity removal is realized when the higher H atom flux irradiates on the Cu surface. The removal rates for irradiation of H atoms and H$_2$ plasma were also found to increase with increasing $T_s$. Further results concerning the effects of H irradiation on impurity removal have been reported elsewhere [6,12,13].

3.2. Effects of H irradiation on surface roughness

Before studying effects of H irradiation on the surface roughness, we define a roughness parameter which represents well surface roughness for Cu films obtained in this study. For this purpose, we examined the cumulative distribution of film thickness variation, namely difference between film thickness and its average value [16], by the atomic force microscopy, the cross-section scanning electron microscopy (SEM), and the cross-section transmission electron microscopy (TEM). Fig. 3 shows the cumulative distribution versus the film thickness variation normalized by its standard deviation for typical experimental results together with the Gaussian cumulative probability function. Since the experimental cumulative distribution is quite close to the Gaussian one as shown in Fig. 3, the standard deviation of film thickness variation, which is identical to the root mean square roughness [16], represents well surface roughness of Cu films obtained in this study. Therefore, hereafter ‘surface roughness’ is used to denote the standard deviation of film thickness variation. Moreover, films are continuous when the average film thickness is more than three times larger than the surface roughness, as the normalized thickness variation less than $-3$ corresponds to almost 0% in the cumulative distribution.

Effects of H irradiation on surface roughness were evaluated using Cu films, of 100 nm in thickness, deposited on Si substrate without trenches. Time evolution of surface roughness deduced from H irradiation is shown in Fig. 4. The roughness decreases considerably from 18 nm at $t = 0$ min to 6 nm at $t = 40$ min, indicating that the H irradiation contributes significantly to reducing the surface roughness. This feature is important to obtain smooth thin Cu seed layers for the Cu electroplating.

The decrease in surface roughness using the H irradiation is probably brought by (1) impurity removal on surfaces by H atoms and (2) reduction in the diffusion barrier for Cu due to H atoms adsorbed on surfaces [17]. The H irradiation is highly effective in reducing impurities both on Cu film.
surfaces and in Cu films for \( T_s > 70^\circ\text{C} \) [6]. Since contamination at \( 10^{-4} \) monolayer level on Cu surfaces can drastically reduce the surface diffusion rate of Cu [17], impurity removal on the surfaces by H atoms restrains such reduction of the surface diffusion rate of Cu. Moreover, H atoms adsorbed on Cu surfaces enhance the Cu self-diffusion on surfaces, since those on surfaces are considered to reduce the binding force between Cu atoms of the top layer and ones under the layer [17].

Next, we evaluated the roughness of the top-, side- and bottom-surfaces of the trenches using three samples of different film thicknesses prepared on Si substrate with trenches 0.35 \( \mu \text{m} \) wide and 1.6 \( \mu \text{m} \) deep. The results are shown in Fig. 5. The surface roughness at the top, side and bottom does not significantly depend on the film thickness, while that at the bottom tends to be slightly higher than those at the side and top. The latter tendency is probably attributed to the low H atom flux on the bottom compared to those on side and top.

Dependence of surface roughness of Cu films on \( T_s \) was examined using a Si substrate without trenches. The results are shown in Fig. 6. The surface roughness decreases considerably from 11.5 nm for \( T_s = 170^\circ\text{C} \) to an almost constant value of 3.5 nm for \( T_s = 90 - 130^\circ\text{C} \). Thus decreasing \( T_s \) below about 130°C is effective in reducing roughness. This indicates a significant advantage of plasma CVD over thermal CVD, because pure Cu deposition from Cu(hfac)$_2$ by thermal CVD becomes appreciable at \( T_s > 300^\circ\text{C} \).

Dependence of the surface roughness of Cu films on total filling pressure was examined using a Si substrate without trench. The results are shown in Fig. 7. The surface roughness decreases slightly from 8.5 nm for 220 Pa to 6.3 nm for 73 Pa, and then decreases considerably to 2.0 nm for 23 Pa. The minimum roughness suggests a possibility of depositing an extremely thin Cu seed layer of less than 10 nm in thickness by using the HAPCVD. Since the surface roughness is almost the same as that (=1.4 nm) of WN diffusion barrier layer just below the Cu film, the decrease in surface roughness of WN is necessary for improving further smoothness of Cu films.

### 3.3. Effects of H irradiation on grain size and crystal orientation

In order to study the effects of the H irradiation on grain size and crystal orientation, high purity Cu films (\( \approx 100\% \) Cu), which were prepared onto Si (100) substrates, were irradiated by H atoms supplied from the H atom source without using the main discharge, and then their crystal orientation and grain size were observed by X-ray diffraction and TEM analyses as a parameter of the irradiation.
time. The methods for these analyses are similar to those in Ref. [18].

Fig. 8 shows typical examples of X-ray diffraction intensity of Cu films on TaN diffusion barrier without and with the H irradiation for 5 min. The orientations of both films are random. We also carried out similar measurements of Cu films on WN, TiN, SiO$_2$, and Si. All the crystal orientations were random, indicating that the irradiation had no effect on aligning the orientation.

Results concerning the effects of H irradiation on grain size are shown in Fig. 9. For the film of 500 nm in thickness, the grain size increases rapidly from 230 nm at $t = 0$ min to 435 nm, close to the film thickness, at $t = 5$ min and then decreases to 200 nm at $t = 20$ min. Therefore, there is an optimum H irradiation time to obtain the maximum size, while the mechanism for grain-size variation due to the irradiation is unclear at present. It should be noted that both the growth rate and the maximum grain size for the H irradiation at $T_0 = 250^\circ$C are considerably large compared to that due to one hour annealing in H$_2$ gas at $T_0 = 400^\circ$C [8]. For the deposited film of 250 nm in thickness, the grains of which have almost the same size as the film thickness, the H irradiation does not change their size. For the film of 100 nm in thickness, the grain size increases gradually from 80 nm at $t = 0$ min to 150 nm at $t = 20$ min. The largest size for this specimen can surpass the films thickness, probably because the volume, which is not filled with Cu, in valleys on the surface becomes appreciable compared to that of the as-deposited film as observed in the SEM photograph (not shown here). Thus, the grain size for the dense Cu films seems to increase up to the film thickness by the H irradiation. This limitation is similar to that for room
temperature annealing of Cu films deposited by the electroplating method [19].

3.4. Effects of H irradiation on adhesion strength

The adhesion strength of Cu film to the diffusion barrier layer was examined by the scotch tape test. There was no failure in the tests for Cu films on TaN, TiN, and WN diffusion barriers prepared for $P_{as} \geq 40$ W with the reactor A. This result suggests that the adhesion strength is larger than 500 N/cm$^2$. Taking into account the effects of H irradiation on impurity removal in Section 3.1, the stronger adhesion for films deposited under higher H irradiation may be attributed to lower impurities around the interface between the Cu film and diffusion barrier layer.

3.5. Control of surface reaction probability of Cu-containing radicals

While the H irradiation contributes significantly to the purification and the reduction of the surface roughness of depositing Cu films as described in Sections 3.1 and 3.2, their deposition rate and the conformity depends on species and flux of Cu-containing radicals, which are closely related to dissociation of the material gas. Therefore, it is important to control the concentration of H atoms and the degree of dissociation of Cu(hfac)$_2$, independently, in order to fill completely of high-purity films in fine trench structures at a high deposition rate. For this purpose, we have developed the HAPCVD reactor.

In order to confirm the supply of H atoms from the H atom source to the main discharge region, the spatial intensity profile of H$_a$ emission intensity (656.3 nm) between the electrodes in the main discharge (reactor B) was measured for $P_{as} = 45$ W as a parameter of $P_{as}$. Fig. 10 shows the result at 35 nm above the grounded electrode. The emission intensity for $P_{as} = 50$ W increases up to a value three times higher than that for $P_{as} = 0$ W. Similar dependence of the intensity on $P_{as}$ was obtained in the whole main discharge region. The electron temperature and positive ion concentration in the main discharge were 3 eV and $4 \times 10^8$ cm$^{-3}$, respectively, and these values were independent of $P_{as}$. Therefore, H atoms can be supplied into the main discharge region without appreciably affecting plasma parameters. This supply of H atoms is also expected from the facts that both the rate of three-body recombination reaction of H atoms in gas phase ($2H + H_2 \rightarrow 2H_2$) and their loss probability on the wall surface of reactor made of stainless steel are low values of $8 \times 10^{-33}$ cm$^3$/s [20] and 5% [21,22], respectively. Moreover, the deposition rate of Cu increases only slightly with $P_{as}$, indicating that the production of the Cu-containing radicals by gas phase reactions between H atoms and Cu(hfac)$_2$ is insignificant compared to that by electron impact dissociation of Cu(hfac)$_2$.

Next, in order to confirm an expectation that the concentration of Cu-containing radicals can be controlled by changing $P_{as}$, dependence of the degree of dissociation of Cu(hfac)$_2$ on $P_{as}$ was studied by the FT-IR spectroscopy using the reactor A. The IR-beam was passed 2 cm above the grounded electrode surface, being parallel to it. The degree of dissociation was deduced evaluating the deference of absorption intensity at 1260 cm$^{-1}$ (CF$_3$ stretching [15]) between with and without the discharge, assuming homogenous gas composition over the IR-beam path in the reactor. The results are shown in Fig. 11. The degree of dissociation increases with $P_{as}$ and attains 32% for $P_{as} = 75$ W. This
means that the concentration of Cu-containing radicals, which presumably increases with the degree of dissociation, can be controlled by changing $P_m$.

Filling property of Cu in trenches essentially depends on $\beta$ of Cu-containing radicals, which is the sum of probabilities for the radicals to contribute to film and to form volatile molecules, $s$ and $\gamma$ respectively. Coverage shape of Cu film in a trench of 0.3 $\mu$m in width and 0.9 $\mu$m in depth was examined under deposition conditions of high-purity ($\approx 100\%$) Cu films using the reactor B. To deduce $\beta$ from the trench coverage profile of deposited film, the cross-section profile of film in the trench was simulated by the Monte–Carlo method as a parameter of $\beta$ [7]. Then the $\beta$ value was deduced comparing the simulated profile with the experimental one obtained by cross-section SEM. In order to obtain information about relation between the film conformity and the flux of Cu-containing radicals to film surfaces, the $\beta$ value was examined as a parameter of $P_m$ to which the flux or concentration of Cu-radicals is proportional as shown in Fig. 11. The circles in Fig. 12 show the results deduced experimentally from film deposition profiles. The $\beta$ value decreases significantly with decreasing $P_m$, that is, the dissociation degree of material gas, resulting in a low value of $\beta = 0.01$ for $P_m = 3$ W. Such a low $\beta$ value is necessary for realizing conformal deposition of thin Cu seed-layer and complete Cu filling in trench structures of extremely small width and high aspect ratio.

3.6. Main species for Cu deposition

In order to obtain information about the Cu-containing radicals produced in plasmas, partial electron impact ionization cross-sections of Cu(hfac)$_2$ were measured using the quadrupole mass spectrometer installed to the reactor B. For this purpose, pure Cu(hfac)$_2$ was sublimated at 198°C, and then introduced in the reactor without any carrier gas at a pressure of 1.3 Pa. Fig. 13 shows the results of major fragment ions in a range of electron energy up to 70 eV. The cross-section for the most dominant product Cu(hfac)$^+$ has a threshold energy of 10 eV and is maximum around 24 eV.

![Fig. 11. Main discharge power $P_m$ dependence of degree of dissociation of Cu(hfac)$_2$. Experimental conditions are material gases H$_2$(50%) and C$_2$H$_5$OH[Cu(hfac)$_2$], total flow rate 72 sccm, and pressure 73 Pa. Experiments were carried out using reactor A.](image1)

![Fig. 12. $P_m$ dependence of $\beta$ obtained using model (solid line) and deduced comparing cross-section SEM photographs of deposited films in trench with results of Monte Carlo simulation (circles). Solid line was obtained using $\alpha_s/\alpha_t = 1.3$, $\theta_s = 0.2$, and $\theta_{\text{subl}} = 0.6$. Experiments were carried out using reactor B under following conditions: material gases H$_2$ (83%) and C$_2$H$_5$OH[Cu(hfac)$_2$], total flow rate 300 sccm, pressure 73 Pa, $P_m = 60$ W, and $T_i = 170$°C.](image2)

![Fig. 13. Partial electron impact ionization cross-sections of Cu(hfac)$_2$. Experiments were carried out using reactor B.](image3)
Cu(hfac) is adsorbed on the surface, then (b-1) H removes hfac in the Cu(hfac) and the resultant Cu is deposited on the surface, or (b-2) two Cu(hfac) radicals react each other on the surface and the produced Cu(hfac)₂ and Cu are desorbed and deposited on the surface respectively. The reaction (b-1) is effective for $T_s > 70°C$ [6], while the reaction (b-2) becomes appreciable for $T_s > 150°C$ [10]. Using this model, the deposition rate $D$ may be given by

$$D = a_1[H][Cu(hfac)] + a_2^2[Cu(hfac)]^2,$$

where $a_1$ and $a_2$ are proportional constants, [H] and [Cu(hfac)] denote densities of H and Cu(hfac) near the surface, respectively. As [H] and [Cu(hfac)] are nearly proportional to $P_{in}$ and $P_{in}$ respectively, average deposition rates on the top and inner-wall surfaces of trench, denoted by $D_o$ and $D_i$ respectively, may be given by

$$D_o = \alpha_1 P_{in} + \alpha_2 P_{in}^2,$$

where $\alpha_1$ and $\alpha_2$ are constants.

3.7. A simplified reaction model

Taking into account the results in Sections 3.1–3.6, we propose the following simplified deposition model of Cu films. In the model, (a) Cu(hfac)₂ is dissociated into Cu(hfac) and hfac by electron impact in the plasma and

Other major fragment ions are hfac⁺, CuO₂C₃⁺ and Cu⁺¹, but their contribution to the total ionization cross-section remains marginal below 20 eV. According to the ion-core model, the fragmentation pattern into neutral radicals such as Cu(hfac), hfac, and so on should be identical to that into ions such as Cu(hfac)⁺, hfac⁺, and so on [23]. Therefore, taking into account, an electron temperature of 7 eV for the main discharge employed [11]. Cu(hfac) is considered to be the Cu-containing radical produced dominantly in our present case.

Next, in order to identify the Cu-containing radical mainly contributing to Cu films, their deposition was carried out at room temperature for which H atoms hardly remove the impurities. Fig. 14 shows relative concentration of composition in the Cu film measured by Auger electron spectroscopy. Concentration ratios of O and C to Cu at the surface are about 2 and 5 respectively, which are identical to ratios of them belonging to a Cu(hfac) radical. This suggests that the main deposition species is Cu(hfac), since the radical should be adsorbed on the film surface. Moreover, this suggestion is partly supported by the results of in situ FT-IR measurement regarding material gas showing that C≡C bond is hardly broken in the plasmas (not shown here).

![Fig. 14. Depth profiles of atomic composition in film deposited on Si(100). Cu film was deposited under following conditions: material gases H₂ (50%) and C₃H₆OH [Cu(hfac)₂], total flow rate 72 sccm, pressure 133 Pa, $P_{in} = 45 W$, $P_{in} = 0 W$, and $T_s$ = room temperature. Experiments were carried out using reactor B.](image)

![Fig. 15. Cross-section SEM photograph of Cu film deposited in trench of 0.35 μm in width and 1.6 μm in depth. Cu film was deposited under following conditions: material gases H₂ (83%) and C₃H₆OH[Cu(hfac)₂], total flow rate 300 sccm, pressure 73 Pa, $P_{in} = 3 W$, $P_{in} = 60 W$, and $T_s$ = 110°C. Experiments were carried out using reactor B.](image)
\[ D_o = \alpha_1 \theta_H P_{as} \theta_{Cu(hfac)} P_m + \alpha_2 \theta_{Cu(hfac)}^2 P_m^2, \]

where \( \alpha_1 \) and \( \alpha_2 \) are proportional constants, \( \theta_H \) and \( \theta_{Cu(hfac)} \) are ratios of [H] and [Cu(hfac)] near the inner-wall surface of trench to those near its top surface, respectively. Moreover, using the blackbody approximation [24], the surface reaction probability \( \beta \) of Cu-containing radicals can be written in the form

\[ \beta = \frac{D_o A_o / D_a A_1 - A_o / A_1}{1 - A_o / A_1}, \]

where \( A_o \) and \( A_1 \) are opening and inner-wall areas of trench, respectively, and \( A_T = A_o + A_1 \). Using Eqs. (2)–(4), one can obtain \( P_m \) dependence of \( \beta \) for a constant value of \( P_{as} \). The result is shown by the solid line in Fig. 12. One can see that the experimental \( \beta \)'s are well expressed by the theoretical curve. From the model mentioned above, independent control of [H] and [Cu(hfac)] is important for the control of \( \beta \) with keeping \( T_i \) constant. Thus, the developed HAPCVD reactor is useful for realizing such control.

3.8. Conformal deposition and filling in trenches

By controlling \( \beta \), we demonstrated conformal deposition of smooth Cu film in a trench of 0.35 \( \mu \)m in width and 1.6 \( \mu \)m in depth (aspect ratio is 4.6), which has a WN diffusion barrier layer of 40 nm in thickness, using the HAPCVD reactor. A typical cross-section SEM photograph of the film is shown in Fig. 15. As shown in this figure, conformal deposition of smooth Cu film of 30 nm in thickness is realized by controlling \( \beta \). The auger electron spectroscopy shows that the film is pure Cu (=100%), and the resistivity of 30 nm film is 1.9 \( \mu \)\( \Omega \)cm, being close to the bulk value of 1.72 \( \mu \)\( \Omega \)cm. Hence the film is considered to be suitable for a Cu seed layer for the Cu electroplating.

Next, we tried to fill Cu in a trench of 0.3 \( \mu \)m in width and 0.9 \( \mu \)m in depth (aspect ratio is 3) by controlling \( \beta \). Fig. 16(a) and (b) show cross-section SEM photographs for \( P_m = 5 \) W and 1 W, respectively. The filling with quite small voids is obtained for 1 W, while a large hole is observed for 5 W. In order to realize void-free filling, studies regarding formation mechanism of voids are required.

4. Conclusions

The H assisted plasma CVD (HAPCVD) reactor has been proposed for the formation of Cu interconnect for ULSI. The studies of Cu deposition using the reactor indicate its
advantages. The following conclusions are obtained in these studies.

1. The H irradiation is effective in removing impurities in the Cu film at a substrate temperature above 70°C.
2. The H irradiation can reduce surface roughness down to a few nm.
3. The grain size increases rapidly up to film thickness by the H irradiation, while the crystal orientation is not affected by the irradiation.
4. The HAPCVD reactor can control the density of H atoms in the main discharge as a parameter of the discharge power of the H atom source.
5. The Cu-containing radical contributing mainly to the Cu film deposition is Cu(hfac).
6. The HAPCVD reactor can control the surface reaction probability of Cu(hfac) as a parameter of the main discharge power, that is, dissociation degree of Cu(hfac)_2.
7. The proposed simplified reaction model, in which Cu(hfac) and H react on the surfaces to deposit Cu films, explains well the dependence of surface reaction probability obtained in our experiments.
8. Excellent conformal deposition of smooth Cu films of 30 nm in thickness and 1.9 μΩcm in resistivity and filling of Cu in trenches have been demonstrated by using the HAPCVD reactor.

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