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Filling Subquarter-Micron Trench Structure with High-Purity Copper Using Plasma Reactor with H Atom Source

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Abstract : A plasma chemical vapor deposition reactor with an additional source of H atoms, in which concentrations of both H atoms and Cu-containing radicals are controllable independently, is developed to fill fine patterns for interconnects with high-purity Cu. Cu-filling property in trench structure with the reactor is evaluated under deposition conditions of high-purity (≈100%) Cu films. The surface reaction probability β of Cu-containing radicals is deduced from the coverage shape of Cu deposition in the trench structure and its Monte Carlo simulation. With decreasing the main discharge power P_m, the β value decreases from 0.2 for P_m=35W to 0.01 for P_m=3W. Using this reactor, we have realized filling of high purity Cu in a trench 0.3μm wide and 0.9μm deep.

Keywords : Cu thin films, Plasma CVD, Interconnection, LSI, Trench, Monte Carlo simulation

1. Introduction

Because of its lower resistivity and better electromigration properties, copper metallurgy is a desirable alternative to aluminum for interconnects of ultra large scale integration (ULSI). Void-free filling of high-purity copper in subquarter-micron trench structure is a key requirement in formation of metal interconnects in ULSI. While high-purity Cu films can be deposited using various methods such as electroless-, electrolytic-, physical-vapor-deposition and chemical vapor deposition (CVD) including plasma CVD, it is difficult to fill small via and contact holes, of a diameter below 0.2 μm and a depth above 0.8 μm, at a high deposition rate above 200nm/min[1-8]. For the CVD, almost complete filling of such holes can be achieved when the surface reaction probability β of precursors is a low value below 0.02[9]. For the thermal CVD, its processes are essentially characterized by heterogeneous decomposition of a reactant on an activated surface and hence the β value is controlled by varying substrate temperature (T_s) and/or flow rate of material gas. However, such control also influences the deposition rate and film properties such as purity and resistivity. The plasma CVD has a significant advantage over thermal CVD in β control ; its value can be changed by varying the dissociation degree of material gas under a constant T_s. Previously, we studied the effects of H atoms on removing impurities in Cu thin films deposited from Cu (hfac)$_2$ by the plasma CVD[10-12]. *In situ* FT-IR measurements have shown that H atoms are effective in removing impurities within the film for T_s> 70°C[11,12]. While H atoms are important to obtain high-purity Cu films, the deposition rate and film conformality presumably depend on the kind of Cu-containing radicals and their concentration, which are closely related to the dissociation degree of Cu (hfac)$_2$. Therefore, a plasma CVD reactor with an additional H atom source has been developed to control the concentration of H atoms and the dissociation degree of Cu (hfac)$_2$ independently[11,12]. Using this reactor, high-purity Cu films (≈100%) with a low resistivity of 2$\mu\Omega$cm has been successfully deposited even for a low H_2 gas volume fraction of 50-67%, while high-purity films are obtained only for a high H_2 gas volume fraction above 90% with no additional H atom source[10].

In this paper, we present results of experiments and simulation concerning Cu-filling in trench structure and then report that filling in the trench of 0.3μm in width and 0.9μm in depth is realized by controlling independently the concentrations of H atoms and Cu-containing radicals using the plasma CVD reactor with the H atom source.

2. Experimental

Experiments were performed using a capacitively coupled parallel plate reactor with an H atom source[11,12]. **Fig. 1** shows a schematic diagram of reactor. Electrodes for the main discharge and the H atom source were installed in a stainless steel vessel

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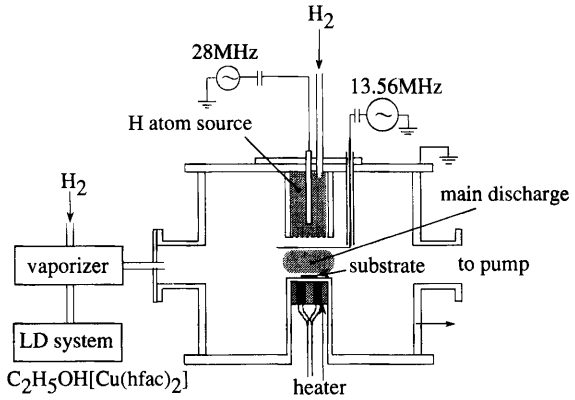


Fig. 1 Plasma CVD reactor with additional H atom source.

of 250mm in inner diameter and 315mm in height. The H atom source was composed of coaxial stainless steel tubes. The outer tube, 48mm in inner diameter and 145mm in length, was used as a grounded electrode, the lower-end of which was covered with a stainless steel mesh (50mesh/inch) to prevent transport of charged species from the discharge of H atom source in the main discharge. The inner tube, 8mm in outer diameter and 110mm in length, was used as a powered electrode. For the atom source, the frequency used was 28MHz and the RF power P_{as} was 60W. For the main discharge, a powered electrode of 55mm in diameter (stainless steel mesh, 50mesh/inch) and a grounded plane electrode of 85mm in diameter were placed at a distance of 42mm. The frequency used was 13.56MHz and an RF power P_m was below 35W. The source material was Cu $(hfac)_2$ dissolved in ethanol (C_2H_5OH) at a concentration of 0.1mol/l, where $(hfac)_2$ stands for bis (hexafluoroacetylacetonato). The source material used was vaporized at 155°C and then transported to the reactor at a flow rate of 50sccm mixing with H_2 carrier gas of a flow rate of 10sccm. Hydrogen gas was also supplied to the H atom source at 240sccm. Their total pressure was 73Pa. A Si substrate with trench structure 0.3μm wide and 0.9μm deep was set on the lower grounded electrode and heated to T_s=170°C.

Filling property of Cu films essentially depends on the β of Cu-containing radicals, which is the sum of the probabilities for the radicals to be incorporated into film and to form a volatile molecule, s and γ respectively. An upper limit of β can be deduced from a two-dimensional profile of film in trench structure, assuming that values of s and γ on the trench wall are equal to those on the top surface of substrate[13]. The total volume of film deposited on the top surface area equivalent to the opening area of trench (its width times length) during a period τ is

$$V_0 = sFA_0\tau, \tag{1}$$

where F is the incoming radical flux and A_0 the opening area of trench. The total volume V_i of film deposited inside the trench (total wall area A_i) is approximately given as follows, assuming that the radicals incoming into the trench undergo multiple reflections; at each encounter with the wall, they react with a probability β or exit through the opening with a probability A_0/A_t, where $A_t = A_0 + A_i$.

$$Vi = sFA_0\tau\sum_{n=0}^{\infty}\left[(1-\beta)\left(1-\frac{A_0}{A_t}\right)\right] = \frac{sFA_0\tau}{1-(1-\beta)\left(1-\frac{A_0}{A_t}\right)}. \tag{2}$$

Using eqs. (1) and (2), the β can be written as

$$\beta = \frac{V_0/V_i - A_0/A_t}{1-A_0/A_t}. \tag{3}$$

Thus, the β value can be deduced from V_0/V_i determined from the spatial profile of film in the trench structure. The probability for radicals to be lost from the trench becomes larger than an A_0/A_t as the trench width becomes narrower, because with decreasing the trench width radicals experiencing their first collision around the opening of trench increases, leading to the loss probability large compared to the A_0/A_t. Therefore, the value obtained using eq. (3) is considered to be an upper limit of β.

3. Method of Trench Coverage Profile Simulation

In order to obtain the β value of Cu-containing radicals, Monte Carlo simulation[9,13,14] was carried out regarding their motion and surface reactions. The outline of the simulation model is shown in **Fig. 2**. Only one kind of Cu-containing reactive species is assumed to be involved in film growth, beacuse Cu (hfac) radicals are considered to be a predominant reactive species for Cu deposition from Cu $(hfac)_2$ by plasma CVD[15]. They are emitted with an equal probability from a line source positioned at 1μm above the top surface of substrate. The emission of radicals at the line source and their reemission from the surfaces are assumed to follow a cosine law. In the model, the surface diffusion of radicals is neglected because of its negligible effect on the deposition profile[9], and also collisions in gas phase are neglected because of the mean free path of radicals quite large

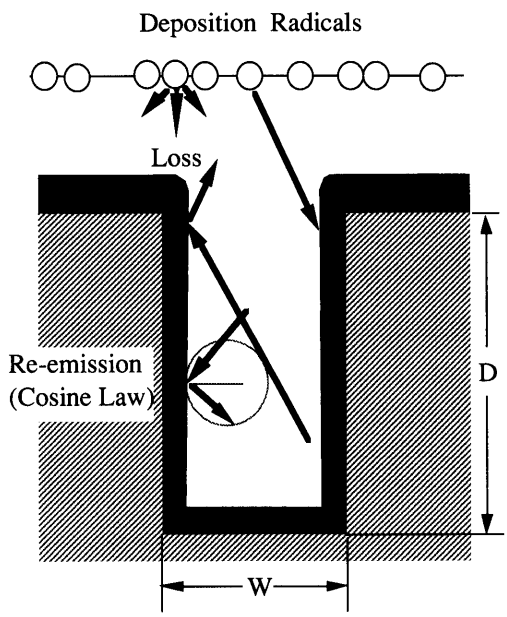


Fig. 2 Monte Carlo simulation model regarding film deposition in a trench structure of width W and depth D.

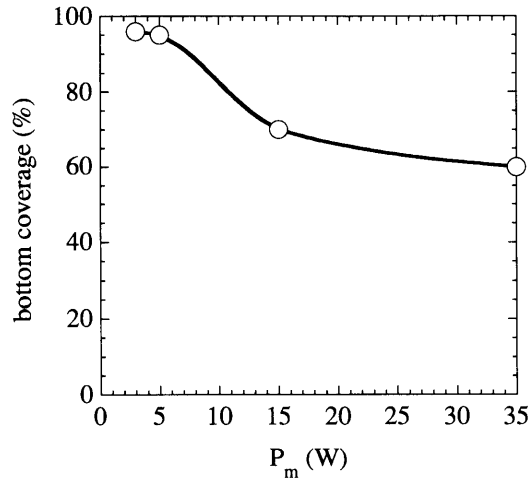


Fig. 3 P_m dependence of film bottom coverage in trench 0.3μm wide and 0.9μm deep. Experiments were carried out under conditions of material gases H_2 (83%) and C_2H_5OH [Cu (hfac)$_2$], total flow rate 300 sccm, pressure 73Pa, and P_{as}=60W. H_2 flow rates at vaporizer and H atom source were 10 and 240sccm, respectively.

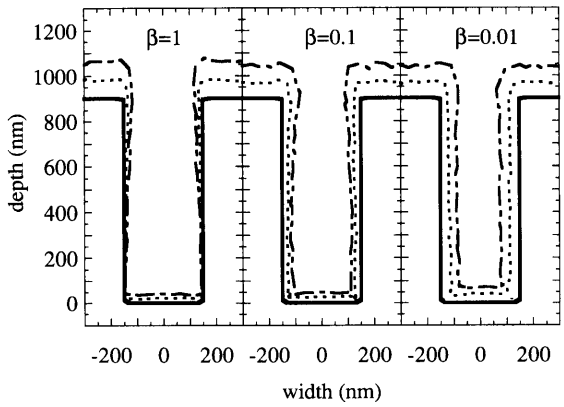


Fig. 4 Monte Carlo simulation results of film thickness profile in trench for β=1, 0.1, 0.01.

compared to the trench depth[14]. H atoms are not considered in the simulation, because trench coverage profile depends only on the β value of Cu-containing radicals.

4. Results and Discussion

In order to evaluate the Cu-filling property in the trench structure using the developed plasma CVD reactor, the coverage shape of Cu film in a trench of 0.3μm in width and 0.9μm in depth was examined under deposition conditions of high-purity ($\approx$100%) Cu films. **Fig. 3** shows P_m dependence of bottom film coverage, which is given by the thickness ratio of the film on the bottm of trench to that on the top surface of substrate. When decreasing P_m, the coverage increases from 60% for P_m=35W to 95% for P_m=3W. Moreover, films were not deposited without the main discharge, suggesting the sticking probability of Cu-containing species is zero for P_m=0W. These results indicate that the decrease in P_m leads to reduction in β, which is essential to fill completely the small trench structure of interest.

To deduce the β from the trench coverage profiles obtained experimentally, the cross-section profile of film in the trench was simulated by Monte-Carlo method as a parameter of β. The β was obtained comparing the profile obtained by the simulation with the experimental one. **Fig. 4** shows simulated thickness profiles for β=1, 0.1 and 0.01. The minimum fractional coverage occurs around the side wall near the bottom. The fractional coverage in the trench tends to increase with decreasing β. **Fig. 5** shows P_m dependence of β deduced using Monte Carlo simulation (circles) and P_m dependence of upper limit of β deduced using eq. (3) (triangles). In these deductions, we use real profile of film in trench obtained by cross-section scanning electron microscopic (SEM) photographs. While upper limit values of β obtained using eq. (3) are larger than β values obtained using Monte Carlo simulation and their difference increases with the decrease in β, both the methods give the same tendency that the β decreases significantly with decreasing P_m. A low β value of 0.01 is realized for P_m=3W.

Next, we have demonstrated filling of Cu in the trench structure by controlling the main discharge

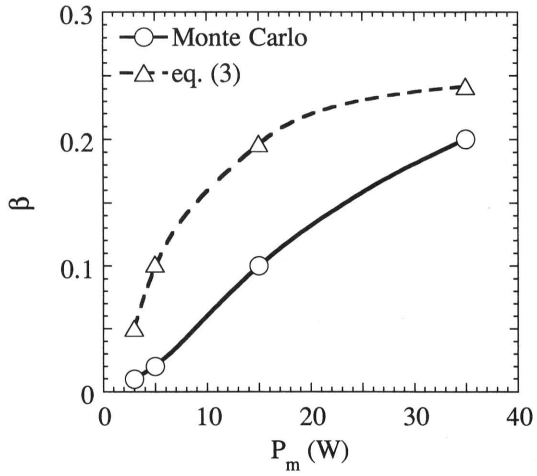


Fig. 5 P_m dependence of β deduced from cross-section SEM photographs of film deposition in trench structure using Monte Carlo simulation (circles), and P_m dependence of upper limit of β deduced from the photographs using eq. (3) (triangles). Experimental conditions are the same as in **Fig. 3**.

power. **Fig. 6** shows cross-section SEM photographs for P_m=5W (a) and 1W (b). As shown in this figure, the filling with quite small voids is realized for 1W, while a large void is observed for 5W. In order to realize void-free filling, studies regarding formation mechanism of void are required.

Finally, we have studied orientation and size of Cu grains in the film deposited on Si substrate without trench by X-ray diffraction and transmission electron microscopic (TEM) analysis, respectively. The methods are similar to those in reference 9). Their orientation was random. **Fig. 7** shows a typical area fraction of Cu grains. While their sizes distribute from 100 to 900nm, the median Cu grain size is 400-450nm, which is almost the same as that of Cu films deposited by thermal CVD[9]. Additional studies are necessary for increasing the size of the grains and to align their orientation.

5. Conclusions

We have evaluated the Cu-filling property in the trench structure using the plasma CVD reactor with

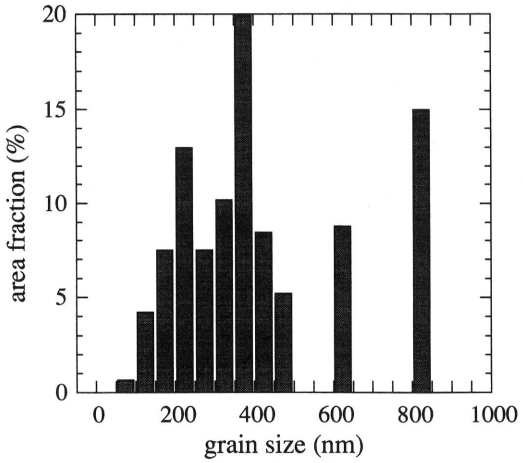
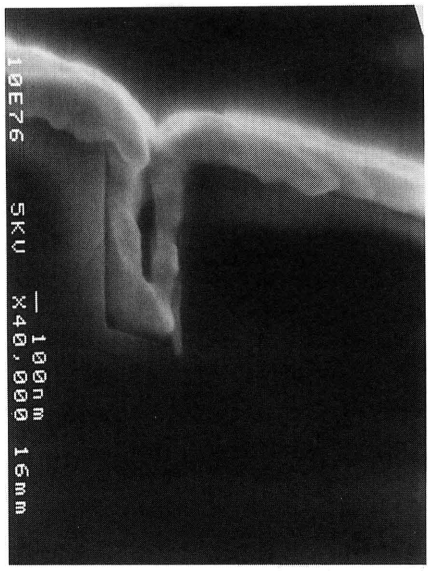
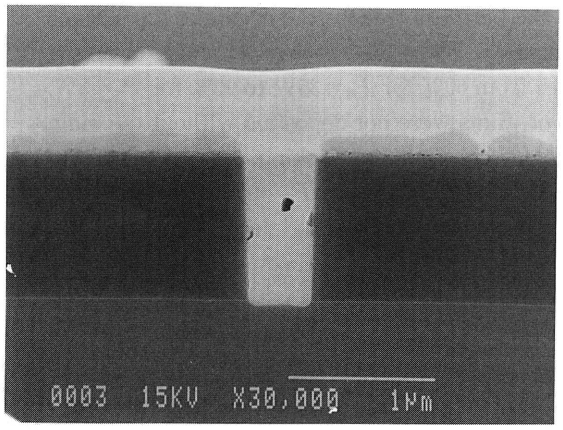


Fig. 7 Area fraction of Cu grain size obtained from TEM observation. Experimental conditions are the same as in **Fig. 3** except total flow rate 216sccm, pressure 133Pa, P_m=15W and P_{as}=0W.



(a) 5W



(b) 1W

Fig. 6 Cross-section SEM photographs of Cu deposition in trench of 0.3μm in width and 0.9μm in depth for P_m= 5 W (a) and 1W (b). Experimental conditions are the same as in **Fig. 3.**

the additional source of H atoms under deposition conditions of high-purity (≈100%) Cu films. Comparison of the profile of film in the trench structure with the Monte Carlo simulation reveals that the decrease in P_m leads to reduction in the β of Cu-containing radicals, which is essential for the complete filling of fine trench structure. The developed reactor is found to make it possible to control the β keeping the purity of Cu films high. Using this reactor, the trench 0.3μm wide and 0.9μm deep has been filled with quite small voids.

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