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Diluting and annealing effects on electromigration and morphology of chemical vapor-deposited copper films

S. Wu, X.-F. Li, X. Liu, Q. Wang*

Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, PR China

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Abstract

The crystallization and orientation of chemical vapor-deposited copper films were investigated by means of X-ray diffraction. The ratios of Cu (1 1 1) peak intensity to Cu (2 0 0) [$I(1\,1\,1)/I(2\,0\,0)$] of the film deposited at different temperatures were plotted as a function of temperature. Then it can be found that the ratio of $I(1\,1\,1)/I(2\,0\,0)$ increased with the deposition temperature, and 400 °C is the best one for electromigration when the films are grown in diluting N_2, and/or annealing by N_2 or by H_2. In addition, the morphology of copper films was characterized by atomic force microscopy, and it was found that the smoothness of the films grown in diluting N_2 and/or annealing by N_2 are improved, while the films annealing by H_2 have no significant changes.

Keywords: Copper film; MOCVD; Silicon substrate; Annealing; Diluting; Electromigration; Morphology

1. Introduction

The chemical vapor deposition (CVD) technique for the growth of thin solid films has become increasingly important for deposition of thin metal films and for filling of high-aspect ratio vias in ultra-large scale integrated circuit (ULSI) multi-level interconnects. Copper is expected to become the interconnect material for chip technology at feature dimensions below 0.25 μm, owing to its low resistivity and high electromigration (EM) resistance. In addition, compared to the physical vapor deposition (PVD), copper films by CVD have a better step coverage [1].

At the present time, EM resistance is an important factor on ULSI reliability concerned with its multi-level metallic interconnects [2] because of the increasing current density in miniaturized devices. Currently, improvement of Cu EM resistance performance attracts the most attention from industry and academia [3]. Thus, it is of great interest how to improve Cu EM resistance performance. Vaidya [4] reported that the microstructure of a metal line used as an interconnect in VLSI affects the EM reliability in such a way as the following equation:

$$\mathrm{MTTF} \propto G = (S/\sigma^2)\ln\left[I(1\,1\,1)/I(2\,0\,0)\right]^3,$$

where MTTF—mean time failure, G—geometrical factor, S—average grain size, σ—standard deviation of grain size and I—X-ray diffraction peak intensity. That is to say, Cu $I(1\,1\,1)/I(2\,0\,0)$ is a key feature to the EM resistance of copper films. Moreover, Mane [5] found that the (1 1 1) surface of Cu also provides a higher oxidation resistance. Since the (1 1 1)-oriented copper film is desirable for good EM resistance, the ratios of Cu (1 1 1) peak intensity to Cu (2 0 0) [$I(1\,1\,1)/I(2\,0\,0)$] are investigated by X-ray diffraction (XRD) in this work. Furthermore, the morphology of the thin Cu films, another important factor in the metallization which is a significant procedure in ULSI fabrication, is also studied.

Annealing is beneficial to some properties of films, such as EM [6], morphology [7,8], yield strength [9], dielectric property [10], resistance [11], microstructure [12], optical [13] and so forth. Especially, Chen [14] reported that annealing by N_2 combines both a moderate resistivity increase and a very good adhesion of films. Besides, introducing diluting gas would affect the morphology [15] of thin films and growth kinetics of the CVD reaction [16].

*Corresponding author. Tel.: +8657187952424; fax: +8657187951895.
E-mail address: qiwang@zju.edu.cn (Q. Wang).

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Furthermore, APCVD with the diluting gas N_2 and H_2 can produce films with high dielectric constant [17]. Therefore, in this work, studies on EM resistance performance and surface morphology were conducted by means of diluting and annealing processes.

2. Experimental

The MOCVD apparatus used in this work is made up of three sub-systems: precursor supplying system, reaction system and high-vacuum system. The precursor supplying system consists of a carrier gas mass flow controller (MFC) and precursor evaporator. The CVD reaction system is mainly a reactor which contains a high-vacuum obturated chamber, a knockdown sample holder and four well-controlled heaters. The high-vacuum system is composed of a mechanical pump, a turbo pump and a cold trap, which is designed for preventing the pump from polluting.

Cu thin films were grown in a vertical, cold wall (80 °C) reactor. The precursor, Cu(II)(hfac)$_2$ was evaporated at 80 °C. The substrate was Si (1 0 0) wafers. The background pressure was 10^{-4} Pa. Depositions were conducted with carrier gas H_2 at 20 sccm (standard cubic centimeter per minute). The reaction pressure was kept at 5 Torr (1 Torr = 133.3 Pa), and the reaction time was 15 min. The samples were divided into three groups: the first group used N_2 as diluting gas; the second one were annealed in H_2 at 175 °C for 1 h; the third one were annealed in N_2 at 175 °C for 1 h.

The EM resistance performance and surface morphology of CVD copper film samples were analyzed by XRD and by atomic force microscopy (AFM).

3. Results and discussion

3.1. Effect on EM resistance of copper films

Fig. 1 shows the XRD patterns and the peak intensity ratio of Cu (1 1 1) to Cu (2 0 0), $I(1\,1\,1)/I(2\,0\,0)$, of copper films deposited at various reaction temperatures by 1 h annealing in H_2 at 175 °C. As Choi [18] and Kang [19] reported before, the ratio of $I(1\,1\,1)/I(2\,0\,0)$ tends to increase with increasing deposition temperature. Figs. 2 and 3 show the $I(1\,1\,1)/I(2\,0\,0)$ of copper films deposited at various temperatures by annealing in N_2 and diluting with N_2, respectively. At lower temperature, such as 360 °C, the peak intensity of copper films is too weak. When temperature is higher than 435 °C, only little copper is deposited on the silicon substrate [20], which is the reason that we used a temperature from 380 to 420 °C. It can be found that 400 °C is the best temperature for EM resistance of the deposited copper in this work. Furthermore, the deposited copper films at 400 °C without further processes were also investigated, and the $I(1\,1\,1)/I(2\,0\,0)$ values are presented by "□" in Figs. 1(b), 2 and 3 and in Table 1 for comparison. It can be observed that both diluting and annealing processes benefit the EM resistance of the

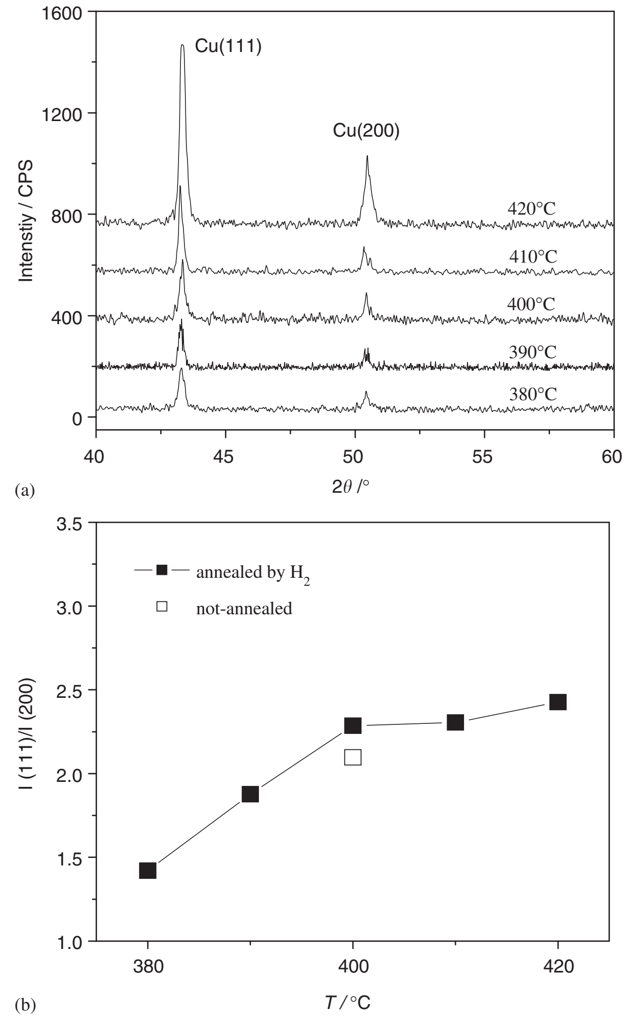

Fig. 1. CVD Cu films by 1 h annealing in H_2 at 175 °C. (a) XRD patterns at different temperatures; (b) $I(1\,1\,1)/I(2\,0\,0)$ of Cu films as a function of temperature.

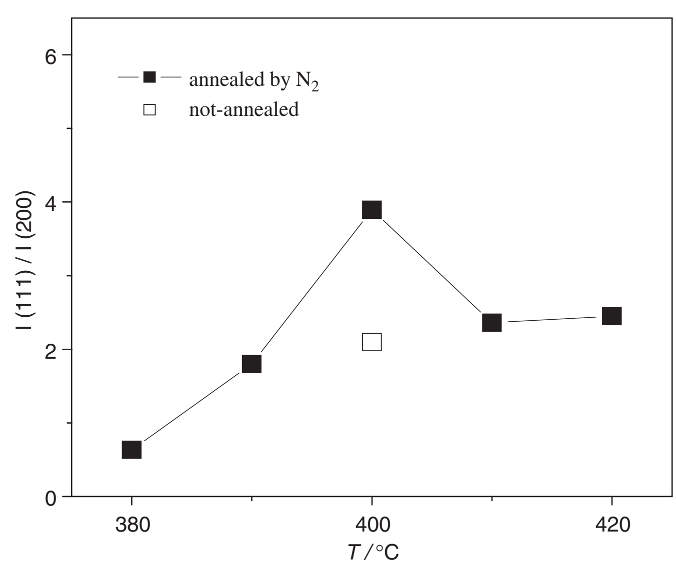

Fig. 2. $I(1\,1\,1)/I(2\,0\,0)$ of Cu films as a function of temperature by 1 h annealing in N_2 at 175 °C.

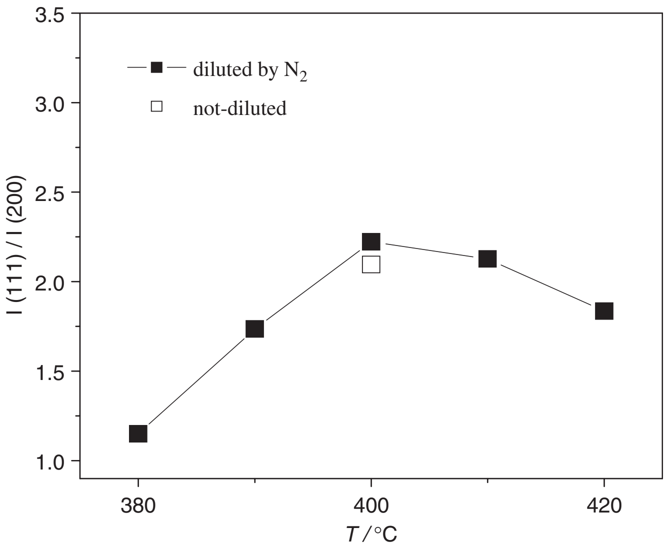

Fig. 3. $I(1\,1\,1)/I(2\,0\,0)$ of Cu films as a function of temperature by diluting with N_2.

Table 1
Comparison of the ratio $I(1\,1\,1)/I(2\,0\,0)$ for Cu films by annealing and diluting at 400 °C

Process	$I(1\,1\,1)/I(2\,0\,0)$
None	2.10
Diluting with N_2	2.22
Annealing by N_2	3.90
Annealing by H_2	2.29

deposited copper films, and annealing in N_2 at 175 °C for 1 h is the best process.

In the reaction of $Cu(II)(hfac)_2(g) + H_2(g) \rightarrow Cu(s) + 2\,H(hfac)(g)$, the reaction rate constant increases with increasing temperature. The copper nucleation and film deposition are easier, and the intensity of XRD peaks becomes stronger at higher temperatures. On the other hand, all the Cu, Ag, Ni and Pd are face-center-cubic (FCC) lattices. It is found that the surface energy increases with crystal index (1 1 1), (1 0 0) and (1 1 0) [21,22], the preferred orientation (texture) of FCC thin films should be the (1 1 1) face on the basis of the minimization of surface energy. When diluting with N_2 Cu (1 1 1) is advantageous. It is because there are no effects of film-substrate boundary energy and thermal strain energy, or the thermal strain energy is negligibly low here. Hence, the growth of crystal grain and the final texture are controlled by the minimization criterion of surface energy, which lead to Cu (1 1 1) being the strongest peak in the XRD pattern. The (1 1 1) texture tends to be a more stable state as the partial pressure of the precursor is reduced, which leads to the increased ratio $I(1\,1\,1)/I(2\,0\,0)$. When annealing, Cu(1 1 1) increased, especially increased clearly when annealing by N_2. Due to the low temperature, the thermal strain energy could be ignored in annealing, and only the surface energy was taken into consideration. But when annealing in H_2, the remnant precursors on the deposited Cu surface, which do not react completely, and the possibly produced Cu_2O would react with H_2. It affects the texture of the deposited copper films. But N_2 only plays the role of inert gas, which means it would not react with the Cu films.

3.2. Effect on morphology of copper films

In order to investigate the effects of the reaction conditions and the thin film deposition process on the morphology of the deposited copper films, incorporating the fact that EM resistance of Cu films at 400 °C was the highest one from Section 3.1, AFM was used to study the film structure and surface morphology of the copper films that were grown in diluting N_2, and/or annealing by N_2 or by H_2 at 400 °C reaction temperature.

Fig. 4 shows the AFM images of CVD Cu films, and Table 2 presents the effects of diluting and annealing on the particles of Cu film. On the basis of the AFM images and the surface roughness parameter (Sq, the root-mean-squared roughness) listed above, it can be found that the Sq values of the films change only a little after annealing by N_2 at 175 °C, but in contrast, the Sq value changes to 7.32 nm after annealing by H_2. Meanwhile, diluting with N_2 has an obvious influence on the thickness of films (decrease the thickness), while the surface roughness has no obvious changes. From the analysis of particles, there are no great changes on the number of particles, averaged area, averaged height and averaged diameter after annealing at 175 °C; however, all of them change in diluting N_2, which indicates that the surface roughness gets better in this case.

When annealing by N_2, the N_2 gas would not react with the films but only plays the role of an annealing gas. Therefore the Sq value changes only a little. But, when annealing by H_2, the H_2 gas would react with the precursor which has not reacted completely, and probably by-produced Cu_2O, which led to a rougher surface and bigger Sq values. There is no remarkable influence on Sq values of Cu films when diluting with N_2 due to the fact that N_2 does not react with Cu on the surface. On the basis of Hanaoka's [23] growth mechanism of copper grains on a silicon substrate, the growth type is the Stranski–Krastanov (layer-by-layer plus island) type at the latter reaction period. Owing to the reaction time and partial pressure of the precursor being identical as in N_2 and H_2 annealing processes, the number and size of particles had no obvious changes after annealing. While diluting with N_2, the number of particles increased, and the averaged area, averaged height and averaged diameter became smaller, which means that the silicon substrate is covered with copper grain islands at this time. It is on account of the different partial pressure (the partial pressure is lower when diluting than when annealing) of the precursor for the same reaction time (15 min) in these cases. In addition, based on the growth mechanism of copper grains on a silicon substrate, copper grains are islands when diluting, while

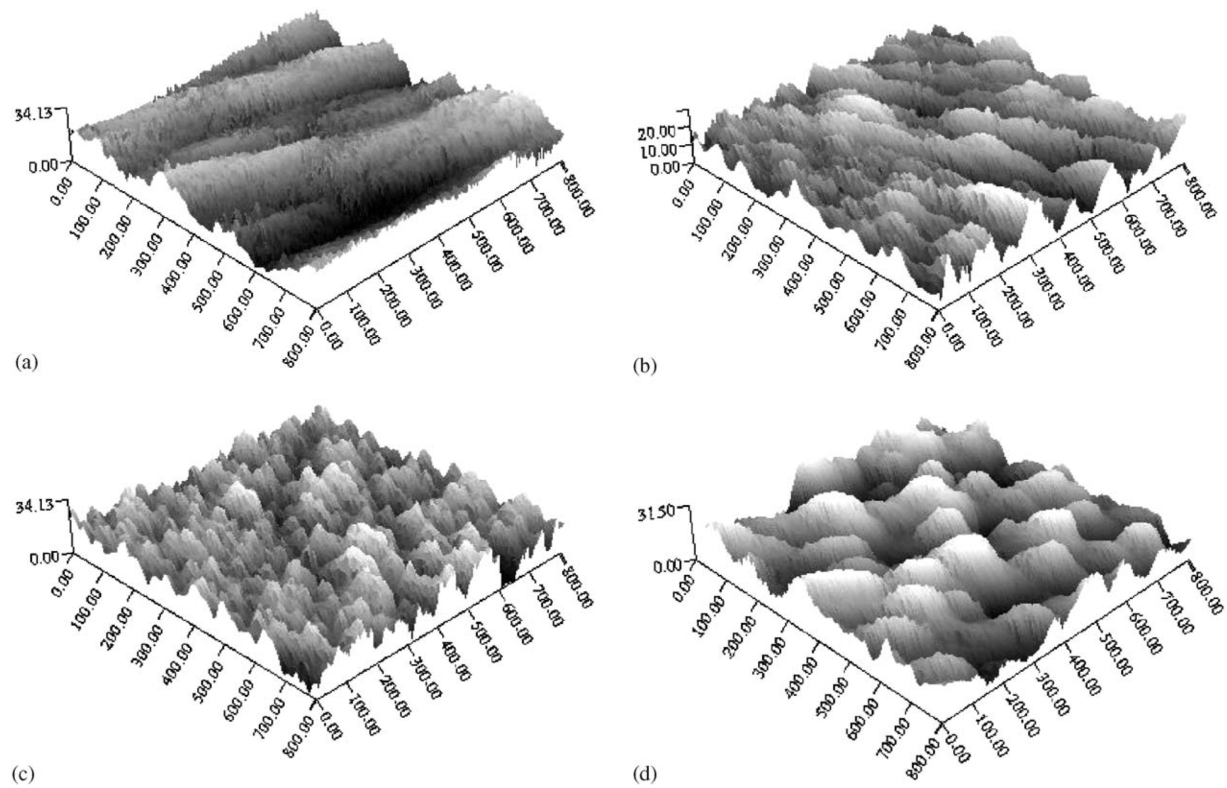

Fig. 4. AFM images of CVD Cu films: (a) without annealing and diluting (Sq = 6.08); (b) diluting with N_2 (Sq = 6.31); (c) annealing by N_2 at 175 °C (Sq = 6.18); (d) annealing by H_2 at 175 °C (Sq = 7.32).

Table 2
Effects of diluting and annealing on Cu film particles

	N^a	$H_a{}^b$ (nm)	$S_a{}^c$ (nm^2)	$D_a{}^d$ (nm)	$S_{max}{}^e$ (nm^2)	$S_{min}{}^f$ (nm^2)
None	1382	19.1	952	17.4	9670	42.7
Diluting with N_2	2957	14.4	432	11.7	2110	10.7
Annealing by N_2	941	22.5	1420	21.2	17,000	42.7
Annealing by H_2	1273	19.9	1030	18.1	19,300	16.0

[a]Number of particles.
[b]Averaged height.
[c]Averaged area.
[d]Averaged diameter.
[e]Maximum area.
[f]Minimum area.

grains become layer when annealing in this reaction time. As a result, the number of particles increases and the size of particles decreases in the diluting gas N_2, which means the Cu films obtained in the diluting gas N_2 are smoother than those annealed by H_2, and annealing by N_2 is the best process for the morphology of the films.

4. Conclusions

In our MOCVD film deposition system, using Cu(II)(h-fac)$_2$ as precursor, H_2 as carrier gas and reactant, N_2 as diluting and cleaning gas, Cu thin films were grown in a vertical, cold wall (80 °C) reactor. The precursor was evaporated at 80 °C. The background pressure was 10^{-4} Pa. The reaction pressure was 5 Torr. Depositions were made under flowing H_2 at 20 sccm. The other parameters were kept constant. The samples of deposited Cu films were analyzed by XRD and AFM. It was summarized as follows:

(1) Diluting with N_2, and/or annealing by N_2 or by H_2, Cu $I(1\,1\,1)/I(2\,0\,0)$ increases with the deposition temperature, and 400 °C is the best temperature when the films are grown in diluting N_2, and/or annealing by N_2 or by H_2. Furthermore, annealing is in favor of the EM resistance of the deposited Cu films.

(2) Diluting with N_2, the Sq value has no obvious changes. Meanwhile, the number of particles increases, but the averaged area, averaged height and averaged diameter decreases, which means diluting with N_2 is a profit to the morphology of Cu films. The Cu films deposited at 400 °C at first, then annealed in the other two processes. It can be found that the number and size of particles have no obvious changes. Annealing by N_2 is more beneficial to the surface roughness. In a word, annealing is the best process for the morphology of films.

Based on the results mentioned above, it can be concluded that annealing by N_2 is beneficial to the EM resistance and morphology of CVD copper films.

Acknowledgements

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