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Morphology and microstructure control of sputter-deposited copper films by addition of Cr

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Abstract. Pure Cu and Cu with 1 at.% and 2.6 at.% Cr films were sputtered on (100) single crystal Si wafers in the presence of native suboxide (SiO\textsubscript{1-x}). Samples were vacuum-annealed to investigate effects of Cr on the microstructural characteristics of Cu films. Cr refines the columnar structure and decreases the surface roughness of Cu films. Upon annealing, most films undergo the process of crystallite growth and coalescence. Cross-sectional images show that Cr stabilizes the columnar structure and inhibits the agglomeration of annealed Cu(Cr) films at high temperatures. The fine grains of Cu(Cr) films suggest that the extensive Cu crystallite/grain growth at 400 °C is effectively impeded by the presence of Cr. The noticeable grain growth occurs around 450 °C with Cr precipitates in Cu(Cr) films. After annealing, the final resistivity of the annealed Cu(Cr) film is approached to that of the Cu film. Adding Cr to films has obtained significant changes in morphology and microstructure of Cu films before and after annealing.

1. Introduction

For the 250 nm technology node and beyond, Cu interconnections have replaced Al alloy ones in the advanced metallization because of their reduced $RC$ delay [1]. The shift from Al alloy to Cu has made a significant difference in interconnect fabrication methods.

The method being developed for Cu metallization was referred to as the damascene method [2]. In multilevel metallization schemes, preserving a smooth planar morphology of the copper layers is needed to build upper levels. Nevertheless, copper undergoes significant grain growth at 400 °C, an interesting annealing temperature in Si-LSIs, and this can lead to roughening of copper films [3]. Alloying has been suggested to address this problem. This alloying scheme is intended to dissociate the dopant out of the alloy film upon annealing to change the microstructure of films [4]. Cu films containing alloy elements such as Ti, Ag, Mo, Zr et al., respectively, have been investigated to have enhanced thermal stability than pure Cu films [5-8].

However, for a potential application, resistivities of Cu alloy films after annealing around 400 °C must be lower than those of Al alloy films (< 3 μΩ·cm). Solute satisfying the requirement are Zr, Cr, Ag [9-11]. Among these, Cu-Cr alloy films have been studied to have the low electrical resistivity, high corrosion resistance and improved adhesion to SiO\textsubscript{2} owing to the segregation of Cr at the surface and interface [12-15]. Carl et al. have reported the effect of microstructural changes in Cu-1 at.%Cr films on the final resistivity after annealing [12]. Yet, the morphology and microstructure of low-
alloyed Cu(Cr) films, as an important characteristic of thermal stability, have not been received enough recognition and research, although they play a significant role in affecting the properties of Cu(Cr) films.

The present work is directed toward Cu(Cr) films in order to investigate effects of Cr dopant on the morphology and microstructure of the Cu/SiO$_x$/Si(100) system before and after annealing, which will provide an experimental reference for the application of Cu(Cr) in the microelectronic field as a new interconnect material or a seed layer.

2. Experimental

Cu(Cr) films were deposited on Si(100) substrates by magnetron sputtering a pure Cu (99.98%, purity) target inlaid with Cr sticks(99.99%, purity). Different numbers of Cr sticks were inlaid to control the Cr content. Before loading in the sputtering system, the silicon wafers were successively cleaned in acetone and alcohol, followed each time by deionized water rinsing, in an ultrasonic tank. Because the substrates were not etched with hydrofluoric acid, there was a native suboxide (SiO$_x$) layer about 15 Å thick on the surface [16].

Prior to the deposition process, the base pressure in the chamber was lower than 0.5×10$^{-3}$ Pa. All films were sputtered in pure Ar at a working pressure of 0.67 Pa with a power of 100 W. The substrates were unheated, resulting in a deposition temperature of ~ 80 °C. The Cr content in Cu-Cr films was determined with energy dispersive X-ray spectrum (EDX) to be 1 at.% (referred to as Cu-1%Cr) and 2.6 at.% (referred to as Cu-2.6%Cr), respectively. After deposition, all samples were vacuum-annealed in the 300 °C-600 °C temperature range for 1 h. Film morphology was observed by Sirion 200 field emission scanning electron microscopy (FESEM) and the surface roughness was obtained by Nanoscope III atomic force microscopy (AFM). Microstructural analysis was carried out in a JEM-2100 transmission electron microscopy (TEM) operating at 200 kV. The resistivity as a function of annealing temperature was measured by the four-point probe method.

3. Results and discussion

3.1. The feature of film morphology

Figure 1 shows the cross-sectional FESEM images of Cu/SiO$_x$/Si and Cu(Cr)/SiO$_x$/Si samples before and annealing. A columnar structure could be observed in the as-deposited Cu films, which was textured in (111) orientation [7,17]. However, the poorly textured Cu film had a significant fraction of films ((a), (d), (g) as-deposited, (b), (e), (h) annealed at 400 °C and (c), (f), (i) annealed at 500 °C). regions with equiaxed grains near the surface of film. Distinctly, the typical columnar structure of Cu(Cr) films was much finer than that of copper films. The formation of equiaxed grains was attributed to the in-situ annealing on the growing film during the sputtering process [18]. In such an in-situ annealing process, the impurity effect of Cr atoms is prominent. The film thickness decreased noticeably with the increasing Cr content as a result of decreases in the deposition rate.

After annealing at 400 °C, with continuous, extensive growth and coalescence of crystallites taking place, the columnar structure became invisible and the film became coarse for pure Cu and Cu-1%Cr films. At 500 °C, the Cu film agglomerated and cavities formed in the film and the substrate. The coalescence of Cu films, perpendicular to sample surface, resulted in the great roughness of Cu/SiO$_x$/Si samples. At even higher temperatures (> 650 °C), the formation of Cu-Si compound crystallites would aggravate the surface roughness [19].

In contrast, although the aggregated crystallites grew, the annealed Cu-2.6%Cr film was much more continuous and compact than the annealed Cu and Cu-1%Cr films. Because the wettability of film on the substrate can be defined by the agglomeration of films [20], the investigation of alloying effect on Cu agglomeration suggested that the addition of Cr increased the Cu film wettability on substrate and enhanced the thermal stability of Cu films. Therefore, the Cu-Cr alloy film is rather stable and keeps a smooth surface at the processing temperature of Si-LSIs.
AFM has been employed to obtain the corresponding surface roughness RMS (root mean square) of samples, which is shown in Figure 2. The measurement was performed in tapping mode with 256×256 data collected over an area of 5×5 μm and a scan speed of 2 Hz. The RMS value is determined by the following formula:

\[
RMS = \frac{1}{(256)^2} \sum_{i,j}^{256} \left| z(i, j) - \bar{z} \right|
\]

where \(z(i, j)\) represents the height measured at position \((i, j)\) and \(\bar{z}\) is the height averaged over the entire area. It was clear that the as deposited Cu(Cr) films had smaller RMS values than Cu films. The RMS values decreased from 14.128 nm of Cu films to 3.837 nm of Cu-1%Cr films. This suggested that Cr atoms mixed with Cu atoms and prevented from the growth of Cu grains on the growing film surface by reducing the diffusion rate of Cu atoms during the deposition process. However, the RMS value did not change much as the Cr content was increased to 2.6%. After annealing, RMS values of Cu films increased owing to the grain growth and agglomeration at above 500 °C. Exactly, annealed Cu(Cr) films had much smaller surface roughness, indicating the high thermal stability upon annealing. In fact, the Cu-2.6%Cr film was heated to a maximum temperature of 700 °C in this research and no agglomeration had taken place, whereas the pure Cu film was ruptured at all so that the RMS value could not be measured accurately.

Figure 1. Cross-sectional FESEM images of Cu (a, b, c), Cu-1%Cr (d, e, f), and Cu-2.6%Cr (g, h, i)

Figure 2. RMS values of Cu, Cu-1%Cr and Cu-2.6% films at various annealing temperatures.
3.2. TEM analysis
Transmission electron microscopy was performed on the sputtered Cu and Cu-2.6%Cr films before and after annealing (Figure 3). After removal from the substrate, the films were glued onto 3 mm Cu double cirques and thinned to electron transparency in a Gatan 691 precision ion polishing system (PIPS). The as-deposited Cu film had a fine microstructure with the average grain size around 50 nm. After Cr was added, the crystallinity of films became incomplete, with some little crystallites agglomerated or dispersed in the film. After annealing at 400 °C, Cu and Cu(Cr) films showed evidence of grain growth. The selected area diffraction (SAD) showed that the film was mainly the face-centered-cubic (fcc) Cu phase. The increase in diffracted intensity of Cu was taken as an indicator of grain nucleation and growth. The grains had grown to a few hundred nanometers in diameter and were frequently twinned in the Cu film. However, the average grains didn’t grow much in size for the Cu(Cr) film. At 500 °C, the Cu(Cr) film was composed entirely of large grains. The smallest Cu grains were about 40 nm and the largest grains were 200-300 nm, indicating the abnormal grain growth. In contrast, the extensive grain growth resulted in Cu grains about 1 μm in the Cu film, which led to the agglomeration of copper films at high temperatures.

![Figure 3. Bright-field transmission electron micrograph and selected area diffraction patterns of Cu (a, b, c) and Cu(Cr) films (d, e, f) ((a, d) as-deposited, (b, e) annealed at 400 °C, (c, f) at 500 °C.](image-url)

To understand the microstructural evolution of Cu(Cr) films upon annealing more clearly, we examined the microstructure of Cu(Cr) films annealed at 450 °C for 1 h (Figure 4). The smallest Cu grains were about 40 nm in size and the largest grains with typical twins were about 150 nm, exhibiting a bimodal grain size distribution.

It was reported that the dissociation of insoluble alloy elements, such as Co, Ag, B, et al, out of Cu alloy films resulted in an evident grain growth and coalescence at 400 °C [21]. However, the large Cu grains with equiaxed shape in annealed Cu-2.6%Cr films formed at above 450 °C, although Cr had the most approximate atomic size with Cu. K. Barmak suggested that this might be due to the effect of oxygen impurity [12]. In addition, that the insolvability of Cr in Cu and the delocalization of Cr 3d electron owing to the transition character of Cr contributes to the higher transition temperature. The
delocalization resulting from the interaction between Cr 3d and Cu 4s electrons increases the Cr atomic radius in solution, leading to the unexpectedly large grain boundary (GB) solute binding energy in the Cu-Cr alloy system [22,23]. Cr precipitating in the film and between grains inhibited the extensive Cu grain growth below 500 °C [12,17,23]. We think that microstructural changes will bring about great effects on the mechanical property and electromigration resistance of Cu(Cr) films, which needs further work to be confirmed.

![Figure 4](image)

**Figure 4.** TEM results of Cu(Cr) films annealed at 450 °C. (a) bright-field micrograph, (b) SAD pattern. Rings corresponding to Cu$_2$O(111) and Cu$_2$O(220) could also be seen.

Evidently, the presence of insoluble Cr dopant has appeared to play significant roles in refining the microstructure, affecting the crystallinity and improving the thermal stability of Cu films. Firstly, the impurity effect of Cr atoms is prominent in inhibiting the crystallinity of as-deposited Cu films. Since Cr has essentially no solid solubility with Cu at room temperature, the addition of Cr atoms reduces the rapid diffusion rate of Cu adatoms, which in turn alters the growing structure of as-deposited Cu films [24].

Similarly, the beneficial effect of Cr atoms on the morphology and microstructure of Cu films upon annealing can be revealed. It is known that the grooving process occurs preferentially at the groove root (eg. the intersection of the GB and the film surface) upon annealing [25]. The local energy equilibrium in the as-deposited thin film has not been reached at GB triple joints on both sides of films. When the thin film is annealed at an elevated temperature, adjacent grains will groove at GB triple joints in order to reach an equilibrium state by the movement of boundaries, which results in the agglomeration finally. Based on a simplifying model for polycrystalline thin films with columnar grains, Nolan T P et.al suggested a maximum grain size $L_c$ for which agglomeration didn’t occur, and that addition of thin layer of high-melting materials or adding contaminants to the film could inhibit the agglomeration [26].

Upon annealing at low temperatures (~ 400 °C), Cr atoms inhibited the prevalent grain growth effectively and prohibited from the agglomeration of Cu(Cr) films. The substantial grain growth took place at 450 °C, where the Cr pinning effect on the Cu grain growth appeared to be overcome. The distribution of grain size became bimodal. Moreover, further annealing at a higher temperature resulted in the abnormal grain growth, which was often thought to arise from the growth of favorably oriented grains [21]. The AES result (not displayed here) has shown that most of Cr segregated at the surface after annealing, in the form of Cr oxide, and formed a protective cap layer on the film surface [12,17]. In any case, the segregation of Cr at grain boundaries, the film surface as well as the interface
between the film and the substrate, contributes to the thermal stability of the Cu film by inhibiting the diffusion of Cu atoms.

3.3. Resistivity Data

Resistivities of Cu/SiO$_x$/Si and Cu(Cr)/SiO$_x$/Si samples at various temperatures are shown in Figure 5. Cr increased the resistivity of as-deposited Cu films markedly. As the annealing temperature increased, the resistivity of all films decreased until a certain temperature range was reached. This was most likely due to the Cu grain growth and the annihilation of point defects. The dominant grain growth mechanism in this temperature range was the growth and coalescence of Cu grains. For the Cu-Cr alloy film, the grain growth was accompanied with the segregation of Cr [12,17]. An abrupt increase in resistivities of the pure Cu and Cu-1%Cr films occurred at 500 °C and 600 °C respectively, owing to the agglomeration of films. The observation of morphology after annealing was in agreement with the resistivity result. The minimum of resistivity was about 2.55 μΩ·cm and 2.76 μΩ·cm for Cu-1%Cr and Cu-2.6%Cr films respectively, which was approached to that of Cu films (2.1 μΩ·cm). Notably, a low resistivity (< 3 μΩ·cm) can be obtained for annealed Cu-2.6%Cr films till 600 °C. Therefore, Cu films doped with an optimal amount of Cr are suitable for the potential interconnect material resistant to high temperatures.

![Figure 5. Resistivity variation of Cu/SiO$_x$/Si, Cu(1% Cr)/SiO$_x$/Si and Cu(2.6% Cr)/SiO$_x$/Si samples upon annealing at various temperatures.](image-url)

4. Conclusions

As-deposited Cu and Cu(Cr) alloy films had a nanocrystalline microstructure. Cr dopant inhibited the crystallinity and refined the columnar structure, decreasing the surface roughness of as-deposited Cu films markedly. Upon annealing, the extensive Cu crystallite/grain growth was effectively impeded by the presence of Cr. For the annealed Cu-2.6%Cr film, noticeable grain growth occurred at 450 °C, resulting in a bimodal grain size distribution. The fine-grained microstructure inhibited the agglomeration of Cu(Cr) films at higher temperatures. A low resistivity (< 3 μΩ·cm) can be obtained for annealed Cu(Cr) films till 600 °C.

Low alloyed Cu(Cr) films with the improved surface morphology and refined microstructure have potential superiority to be used as the interconnecting material or the seed layer in the Damascence technology of Cu interconnection.

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