

Effects of Cr dopant on microstructure and properties of Cu films on Si(100)

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Abstract: The thin films of pure Cu and Cu-2.18%Cr (mole fraction, %) were deposited on Si(100) substrates. Then the samples were vacuum-annealed at 573–773 K to investigate the effect of Cr on the microstructural and electrical characteristics of Cu/Si systems. The XRD results reveal that the annealed Cu(Cr) film has a strong (111) texture. The results of AFM and FESEM indicate that the Cu(Cr) films with insoluble Cr have compact surface morphology and fine columnar microstructure. Upon annealing, most Cr segregates at the surface and interface. The residual insoluble Cr is enriched in amorphous structure between Cu grains and retards the crystallization of annealed Cu(Cr) films. As a result, the minimal annealing resistivity of the Cu-2.18%Cr film is $2.76 \mu\Omega\cdot\text{cm}$ at 773 K, which approaches to $2.55 \mu\Omega\cdot\text{cm}$ of the Cu film at 673 K. Significant changes in the microstructure and properties are obtained by adding Cr to Cu films after annealing.

Key words: Cu(Cr) films; annealing; texture; thermal stability; segregation

1 Introduction

Copper has received considerable attention as an interconnect material in advanced metallization technology since it possesses intrinsically better electromigration resistance and lower resistivity compared with aluminum[1]. However, Cu metallization has several important technical problems, such as passivation of the exposed Cu surface, adhesion to SiO_2 or Si substrate and surface roughness of Cu films[2–3]. Hence, alloying addition has been suggested as a potential alternative to address these problems[4–6]. Recently, elements (Mo, Nb, W, Ta, etc) that don't form any compounds or are immiscible with Cu have attracted much attention because they can be expected to improve performance of Cu films upon annealing[7–11]. However, the annealing resistivity of Cu films doped with elements mentioned above is too high ($>3.0 \mu\Omega\cdot\text{cm}$) to be suitable interconnect materials[8]. In contrast, Cu(Cr) films, as a potential alternative for interconnect materials, have not received enough recognitions, although they have high surface hardness, resistance to corrosion and very low

annealed electrical resistivity relatively (with 1% Cr dopant)[12–13].

In this work, Cu and Cu(Cr) films were prepared by sputtering on Si(100) in order to investigate the effect of Cr on the surface morphology, microstructure and resistivity of Cu films before and after annealing around 673 K (the typical processing temperature in device fabrication), and to provide a reference for application of Cu(Cr) films in the microelectronic field.

2 Experimental

Cu(Cr) films were deposited on Si(100) substrates by radio-frequency magnetron sputtering a high-purity Cu target(99.96%). To prepare the Cu(Cr) films, small pieces of Cr sticks(99.9%, purity) were inlaid in the Cu target. The base pressure was about 0.5 mPa and the substrate temperature was ambient temperature. All films were sputtered in pure Ar at a working pressure of 0.67 Pa with a power of 100 W. The composition determined by EDX was Cu-2.18%Cr. The film thickness were about 300 nm for Cu films and 250 nm for Cu-2.18%Cr films, measured by a surface profile-meter and field emission

scanning electron microscope(FESEM). After deposition, all samples were vacuum-annealed in temperature range of 573–773 K for 30 min. The annealing resistivity was measured by the four-point probe method. An X-ray diffractometer(XRD) was employed to obtain the crystallographic texture information. The surface morphology was observed by AFM. The microstructural and compositional depth profile analysis were carried out by TEM and AES.

3 Results and discussion

3.1 Surface Morphology observation

Fig.1 shows the typical three-dimensional representations of Cu and Cu-2.18%Cr films before and

after annealing. The as-deposited Cu film presents a rather rough surface with many particles and small columnar structure, as a result of the grain nucleation and growth during the deposition process. After annealing at 673 K, these particles and columnar structure have grown independently or agglomerated and the undulation of the surface increases. As the annealing temperature increases to 773 K, these neighboring particles grow and joint together, building up mountains and deep valleys on the surface. With increasing Cr content, more small-sized islets grow and increase the surface evenness and compactness of the as-deposited Cu(Cr) films, which is resulted from the refine microstructure. Correspondingly, the columnar structure and particles on the surface become smaller in size after annealing.

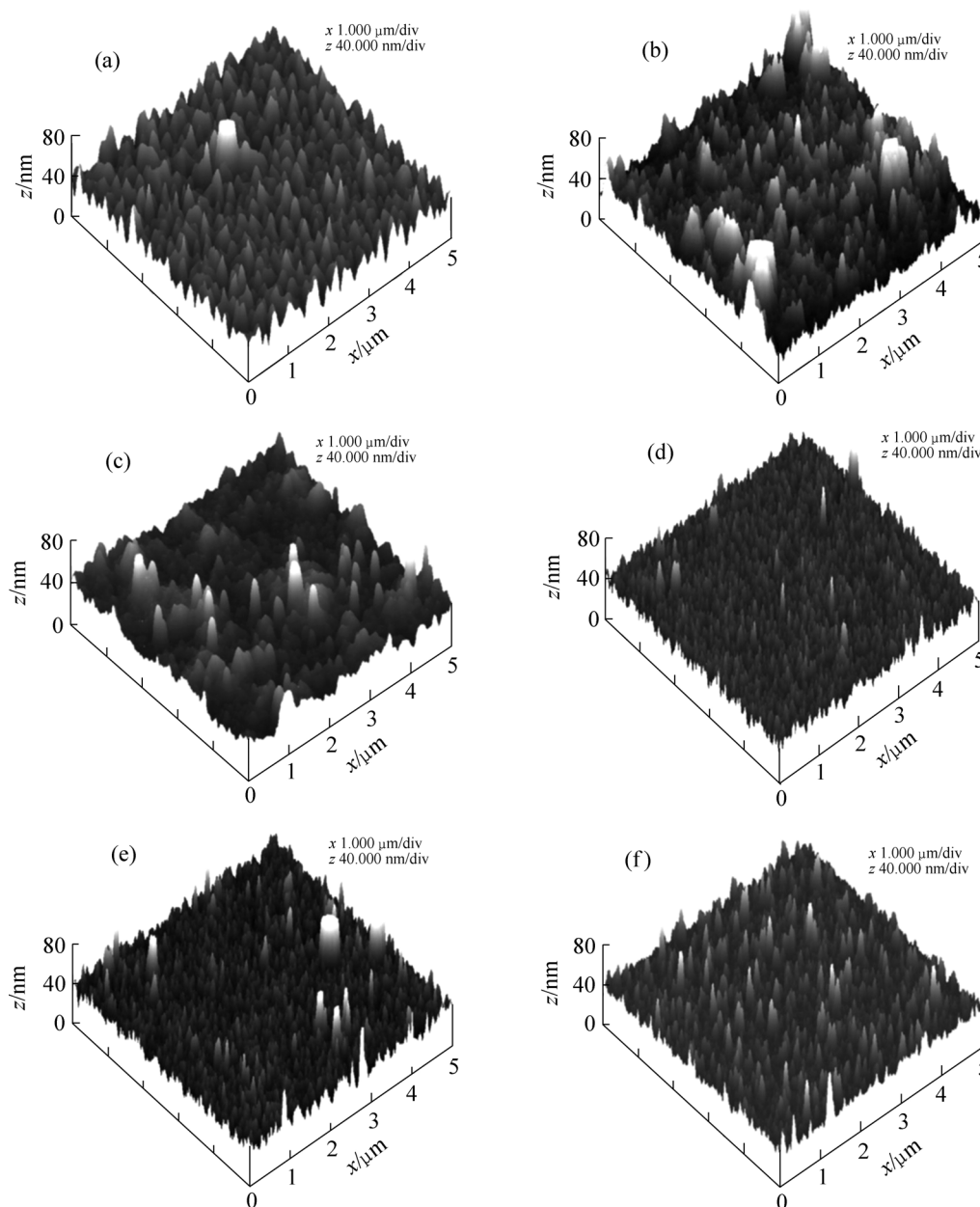


Fig.1 AFM images of Cu(a, b, c) and Cu-2.18%Cr(d, e, f) films: ((a), (d) As-deposited; (b), (e) Annealed at 673 K; (c), (f) Annealed at 773 K

3.2 Crystallography and cross-sectional morphology

The crystallographic texture of films was assessed by XRD. All films only exhibit Cu diffraction peaks. The integrated intensities of the Cu(111) and Cu(200) reflections were measured and the ratio of $I_{(111)}/I_{(200)}$ was used to characterize the degree of texture, as shown in Fig.2. The ratio changes little for the pure Cu films before and after annealing. However, compared with the pure Cu films, a strong (111) crystallographic texture is observed in the annealed Cu(Cr) films, which has been shown to be important in determining the performance and reliability of Cu interconnects[7].

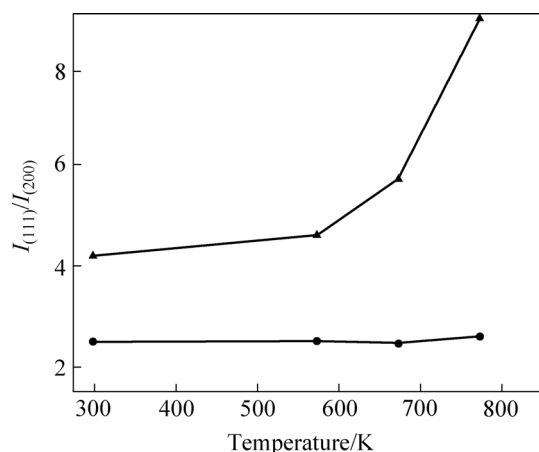


Fig.2 Texture intensity ratio versus annealing temperature for Cu and Cu-2.18%Cr films

Fig.3 shows the cross-sectional FESEM images of Cu and Cu-2.18%Cr films before and after annealed at 673 and 773 K. Columnar and compact structure can be observed in as-deposited pure Cu films. However, the poorly textured as-deposited Cu film has a significant fraction of regions with equiaxed grains. After annealed at 673 K, with continuous, extensive growth and coalescence of crystallites, the columnar structure becomes indistinct in the Cu film, and there are some voids in the pure Cu film near the Cu/Si interface when annealed at even higher temperatures(773 K), which is considered to be a result of the inter-diffusion of Cu and Si and agglomeration of grains during the annealing period. In contrast, a typical finer and more compact columnar structure is observed in the as-deposited and annealed Cu(Cr)/Si systems. The film thickness decrease noticeably for Cu(Cr) films as a result of decreases in the deposition rate. The thermal stability of Cu film is enhanced markedly by adding Cr to films. In the case of thin films heated at high temperatures, the thermal instability is caused by two ways[14] as follows: 1) The local energy equilibrium in an as-deposited thin film has not been reached at the GB triple joints on both sides of the copper films. When the thin film is annealed at an elevated temperature, adjacent grains with similar energies will groove at the GB triple joints in order to reach an equilibrium state by boundary diffusion and surface diffusion. 2) The as-deposited thin film has a

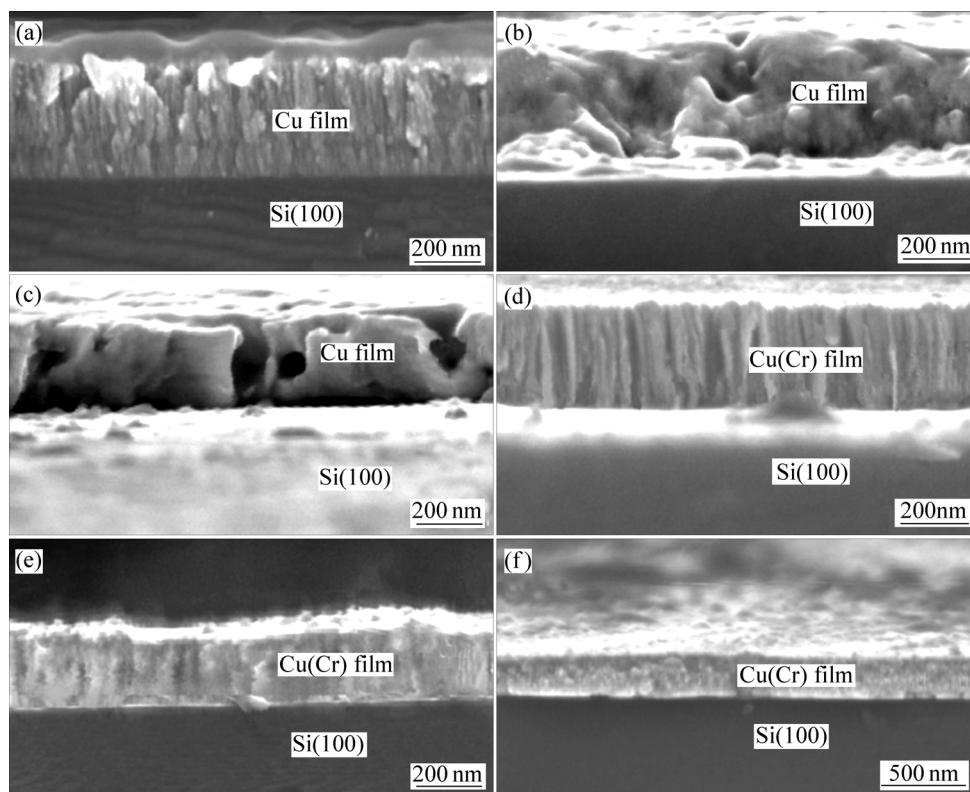


Fig.3 Cross-sectional FESEM images of Cu(a, b, c) and Cu-2.18%Cr(d, e, f) films: (a), (d) As-deposited; (b), (e) Annealed at 673 K; (c), (f) Annealed at 773 K

high density of grain boundaries. The grains with different energies will grow to cause agglomeration when the thin film is annealed at high temperature.

Therefore, the columnar structure would definitely contribute to the thermal stability of films, with no triple-point grain boundaries that are energetically stable in bulk materials. As discussed above, Cr plays an important role in developing significant changes in the texture and microstructural evolution of Cu films after annealed at above 573 K.

3.3 TEM analysis

Transmission electron microscopy was performed on sputtered Cu and Cu(Cr) films after annealed at 673 K. The TEM images are shown in Figs.4 and 5. After annealed at 673 K, the Cu film has been fully crystallized with a grain size of about 100 nm(Fig.4) and the grains become more continuous and larger in size significantly compared with the as-deposited films. In contrast, large numbers of Cu crystallites form and grow in the annealed Cu(Cr) film(Fig.5). The smallest Cu grains are about 30 nm in size and the largest grains with typical twins formed in the film are 80~100 nm in size. However, residual amorphous structure with enriched chromium could be observed in some regions of the film. Fig.5 also indicates the results of EDX measurements for regions *A* and *B*. Although the compositional analysis by EDX in TEM is probably limited by some of the X-ray signal that is almost certainly associated with the amorphous matrix. The microanalysis of EDX reflects that the Cr content in the crystal marked with *A* in Fig.5 is much smaller than that in the amorphous matrix marked with *B*. As a result, chromium is enriched at the amorphous phase between Cu grains will close down the fast diffusion path at the boundaries and slow down the grain growth known as crystallization.

3.4 Composition analysis

Fig.6 shows the AES compositional depth profiles

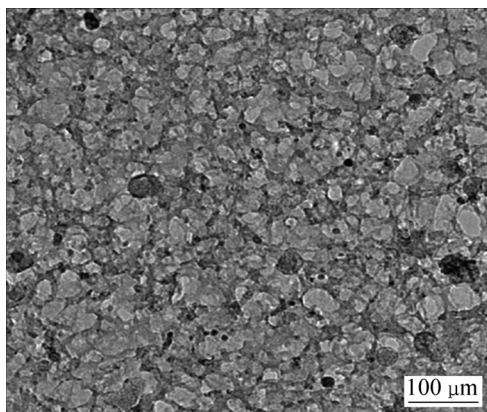


Fig.4 TEM micrograph of Cu films annealed at 673 K in vacuum

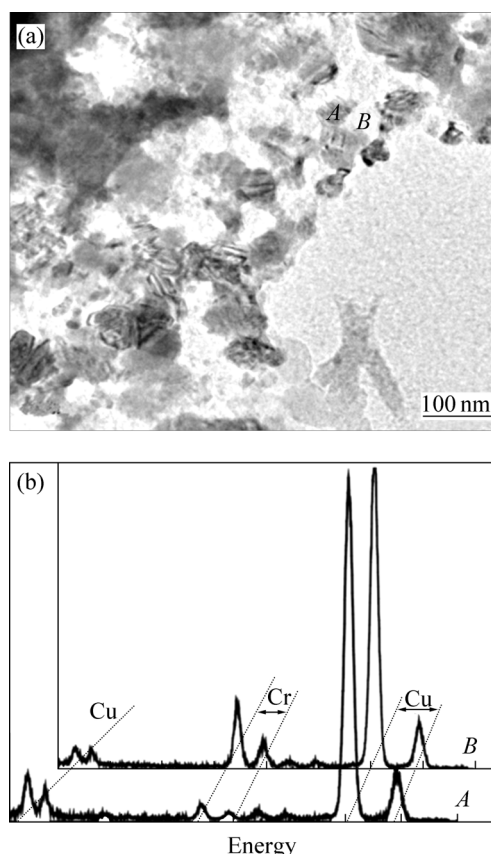


Fig.5 TEM micrographs(a) of Cu(Cr) films annealed at 673 K in vacuum and results of EDX measurements for regions *A* and *B* (b)

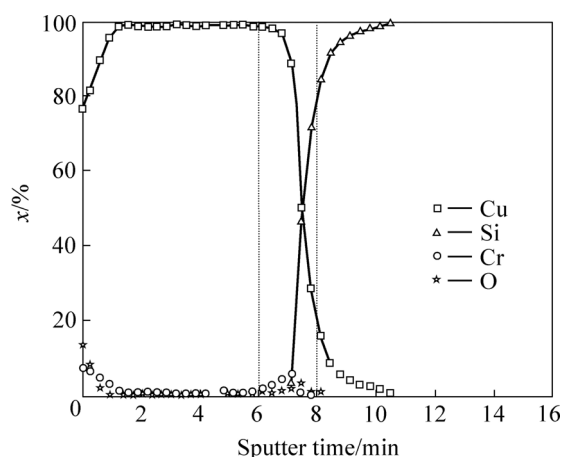


Fig.6 AES depth profiles of Cu(2.18%Cr)/Si samples after annealing at 673 K for 30 min

for Cu(2.18%Cr)/Si samples after annealed at 673 K for 30 min. Upon annealing, for the Cu-2.18%Cr film, most Cr segregates at the surface of the film and the interface between the film and the substrate. A high oxygen concentration about 13% was also measured at the out surface of the film and this suggests that Cr at the surface has been oxidized. Cr or its oxide segregating at the surface can also increase the thermal stability of copper

thin films.

The Auger survey spectra at different sputtering times of the interior surface of the Cu-2.18%Cr film annealed at 673 K for 30 min after peeling from the Si substrate are shown in Fig.7. Obvious Cr peaks are found at the interface, and ultimately disappeared after sputtered for 2 min, which indicates the distribution of Cr in the zone of the film near the interface, just as marked in Fig.6. Meanwhile, no Si peaks are found. In contrast, Si substrate was investigated after peeling off the film by AES and no Cr peaks were observed. This indicates that Cr doesn't diffuse into the Si substrate. Combined with our previous research[15], it is suggested that the segregation of Cr in the film near the interface depends on the content of Cr in the film. Since Cr does not react to an appreciable extent with Si at 673 K, the segregation of Cr at the interface may be due to a slight degree of chemical interaction between Cr with the Si substrate[16].

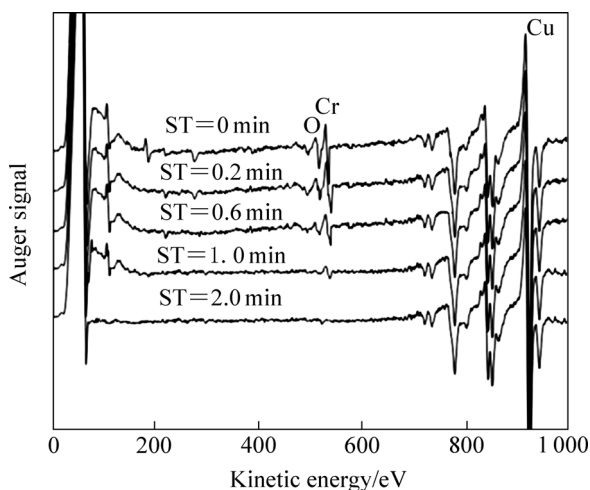


Fig.7 Auger survey spectra at different sputtering time of interior surface of annealed Cu-2.18 %Cr film peeled from Si substrate

3.5 Resistivity data

The resistivity variations of Cu and Cu-2.18%Cr films with temperatures are shown in Fig.7. Compared with the crystallized copper films (resistivity of $2 \mu\Omega\cdot\text{cm}$), the resistivities of as-deposited Cu and Cu-2.18%Cr films are $6.51 \mu\Omega\cdot\text{cm}$ and $20.43 \mu\Omega\cdot\text{cm}$, respectively. The high resistivity of pure Cu films is related with the deposition condition and the microstructure of films[15]. After annealing, the resistivity of Cu(Cr) films decreases sharply, with a minimum about $2.76 \mu\Omega\cdot\text{cm}$, which is approximated to that of the annealed Cu films at 673 K ($2.55 \mu\Omega\cdot\text{cm}$).

Cu(Cr) films have been studied as an example of thermodynamically metastable system. Such films deposited by sputtering provide collisional lattice mixing, fine grain size and have relatively high resistivities

compared with pure Cu films[17]. When the Cu(Cr) film is deposited from a gaseous state, the surface mobility of Cr on Cu is quite high and cannot be predicted by the low bulk diffusion coefficient, which may result in the segregation of Cr at the surface during the deposition process. After annealed at various temperatures, the resistivities of films decrease till a certain temperature range. The decrease of resistivities for annealed films can be attributed to the grain growth of Cu, just as shown in Figs.4 and 5. In contrast, the greater decline of resistivity for annealed Cu(Cr) films is related with the segregation of Cr at the surface and interface.

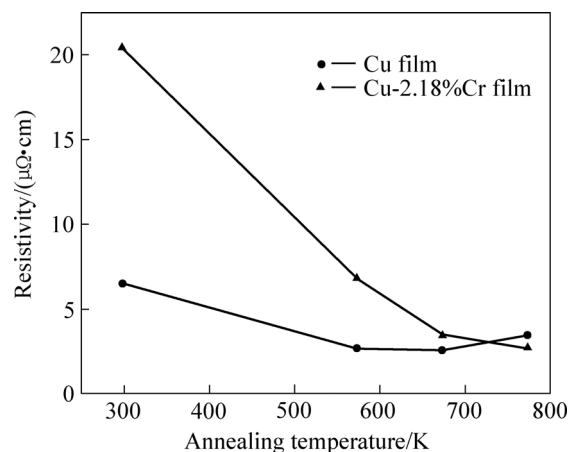


Fig.8 Resistivity variations of Cu and Cu-2.18%Cr films as function of annealing temperature

In a word, compared with the Cu film, the Cu(Cr) film has higher thermal stability and stronger (111) texture, which are preferable in Cu interconnects. Further studies should be carried out to find an optimal amount of Cr additive and annealing procedures so that the properties of Cu(Cr) films can be optimised. Thus Cu(Cr) films can be applied in microelectronic fields as a potential interconnect material or a seed layer.

4 Conclusions

1) Cu(Cr) films have a much smoother surface morphology and finer columnar microstructure than Cu films before and after annealing. A strong (111) texture is found in the annealed Cu(Cr) film and the thermal stability is enhanced markedly.

2) Upon annealing, most Cr segregates on the surface and at the interface between the film and substrate. The residual Cr precipitates in the amorphous matrix. Cr retards the crystallization of Cu films significantly.

3) The additive of Cr increases the resistivity of as-deposited Cu film, which decreases sharply upon annealing. The final resistivity of the Cu(Cr) film approaches to that of the Cu film. The relatively large

decrease of resistivity and increase of thermal stability of Cu(Cr) films are attributed to the grain growth and the precipitation of Cr.

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