Vacuum 126 (2016) 51–54

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

The properties of self-formed diffusion barrier layer in Cu(Cr) alloy

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ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form
24 January 2016
Accepted 25 January 2016
Available online 28 January 2016

Keywords:
Cu(Cr) alloy film
Diffusion barrier
Thermal stability
Self-forming
Annealing

ABSTRACT

The properties of Cu(Cr) alloy films were measured to evaluate its potential application as self-formed diffusion barrier in copper interconnect. Pure Cu and Cu(4.5 at%Cr) alloy films were deposited on SiO_2/Si substrates using magnetron sputtering and subsequently annealed in vacuum (2×10^{-4} Pa) at the temperature of 350°C–550 °C. After annealing, the film properties were examined using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and four-point probe (FPP) method. The results indicate that there was no intermetallic compound (copper–silicide) detected at the interface after annealing. A 7 nm Cr rich layer was self-formed at the interface between Cu(Cr) and SiO_2/Si after annealing which acted as a thermally stable barrier against the diffusion of Cu into SiO_2. The resistivity of the films decreased with increasing the annealing temperature. After annealing at 550 °C for 1 h, the resistivity of the studied alloy films was 6.9 μΩ cm, which is comparable to that of Cu films (5.17 μΩ cm). These evidences suggest that Cu(Cr) films with excellent thermal stability and low sheet resistance would become a promising material for future advanced barrierless Cu interconnects.

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1. Introduction

With continuously decreasing the feature size of integrated circuits (ICs), resistance-capacitance (RC) delay appears to be a main bottleneck in restricting the IC development [1]. In order to reduce the RC delay and improve the speed of the device, Al has been replaced by Cu as a preferable interconnect material for ultra-large scale integration (ULSI), because of its excellent electric conductivity (1.67 μΩ cm) and electromigration resistance [2]. However, Cu also has many shortcomings as interconnector materials. For instance, Cu can easily diffuse into silicon and silicon-oxides at low temperature, which may lead to the device breakdown [3]. In addition, Cu has poor adhesion to dielectric, which reduces the reliability of the circuit [4]. Consequently, Ta and Ta/TaN barrier layers with good adhesion performance have widely been used to prevent inter-diffusion [5–7]. However, it is a huge challenge for semiconductor industries to obtain an ultra-thin barrier layer with step coverage on the sidewalls and bottom corners of trenches and vias due to decreasing line width of interconnector [8]. Moreover, the diffusion barrier layer reduces the cross-sectional area of Cu resulting in an increase in electrical resistivity of Cu interconnects. Therefore, it is essential to remove barrier layers which will reduce the manufacturing cost.

Recently, a promising method called self-forming diffusion barriers process is invented to satisfy the requirement of advanced technological nodes [9,10]. In those studies, Cu in addition to an appropriate element is directly deposited on the dielectric. Subsequently, alloying element is segregated to the interface as a diffusion barrier layer during annealing. The self-formed barrier layer, an alternative to conventional barrier layer, offers low electrical resistivity, resistance to Cu diffusion, resistance to electromigration, and compatibility with conformal deposition techniques. Various alloying elements, such as V [11], Mn [12], Ti [13], Ru [14], Zr [15], C [16], Mo [17], Ag [18] and W [19] and their nitrides or carbides [20,21] have widely been studied. It is concluded that a thin layer was formed at the interface which works as an adhesion and diffusion barrier layer.

In this study, Cr was used as the solute since the effective average residual resistivity per at.% Cr is lower than 1 μΩ cm. Barmak et al. [22] reported that the resistivity of Cu(0.6 at% Cr) alloy film was 2.1 μΩ cm after annealing at 400 °C for 4 h, which is very close to pure Cu films. Besides, Wang [23] reported that a small amount of Cr solute is sufficient for the precipitation of the Cu matrix and refine Cu grains after annealing, which decreases

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http://dx.doi.org/10.1016/j.vacuum.2016.01.019
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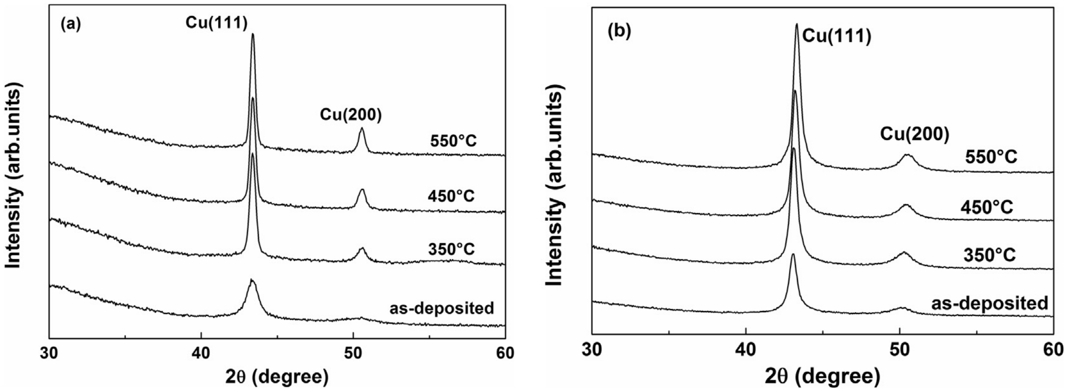

Fig. 1. The XRD diffraction patterns of (a) Cu/SiO_2/Si and (b) Cu(4.5 at%Cr)/SiO_2/Si samples before and after annealing at various temperatures in the range of 350–550 °C for 1 h.

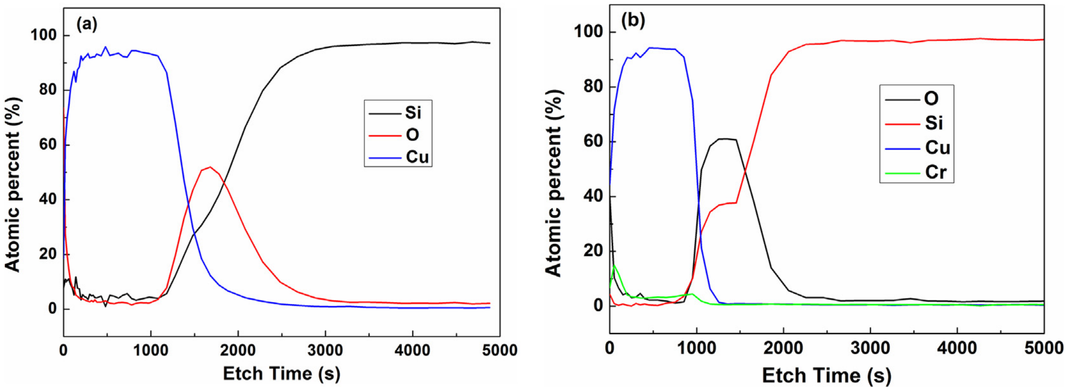

Fig. 2. The XPS atomic depth profiles of the (a) Cu/SiO_2/Si and (b) Cu(4.5 at%Cr)/SiO_2/Si annealed at 450 °C for 1 h.

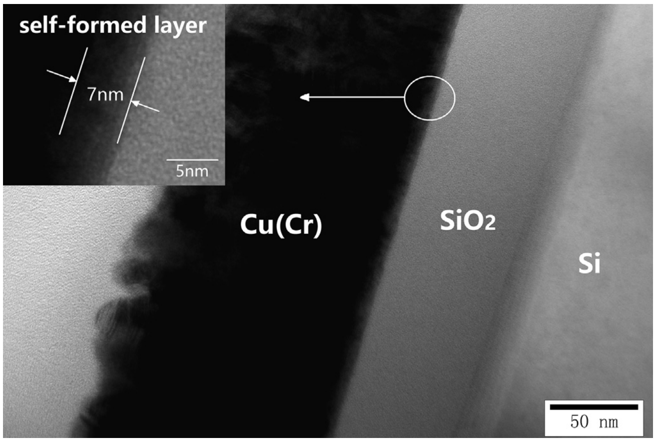

Fig. 3. The cross-section TEM image of Cu(4.5 at%Cr)/SiO_2/Si annealed at 450 °C for 1 h.

resistivity and enhances chemical stability. The problem of interest is to investigate the formation and properties of the Cu(Cr) film.

2. Experiment

Cu(Cr) thin films were deposited on the substrates using direct-current (DC) magnetron sputtering from a pure Cu target(99.99% purity, diameter of 60 mm × thickness of 3.8 mm) and pure Cr chips (99.99% purity, length of 1 mm × width of 1 mm). Cu(4.5 at%Cr) alloy films were obtained by controlling the number of Cr chips placed on the Cu target. The substrates were boron-doped p-type (100) oriented silicon wafers with a thermally grown SiO_2 surface layer. Following, sputtering conditions were used: base pressure of the sputter chamber was 2×10^{-4} Pa, Ar flow rate was 20 SCCM, sputtering power and working pressure were 90 W and 0.5 Pa, respectively, and the distance between the targets and the substrate was 200 mm. Negative DC bias of the substrate holder was 100 V. Ambient temperature was used as substrate temperature. Before deposition, pre-sputtering was performed by the targets for 10 mins to remove the impurities. In addition, pure Cu films were prepared under the same condition for comparison. The thicknesses of pure Cu and Cu(Cr) films were determined using an Alpha Step 200 profilometer, and are 110 nm and 100 nm, respectively.

After deposition, a part of the samples were annealed in vacuum with the pressure of 2×10^{-4} Pa at the temperature range from 350 °C to 550 °C for 1 h. Four-point probe (FPP) method was used to measure the sheet resistance of the films after annealing. The crystal structure of sample was evaluated using X-ray diffraction (XRD). X-ray diffractometer was operated at a voltage of 40 kV and a current of 40 mA with Cu Kα radiation for scanning from 20° to 80°. The compositional depth profile was obtained using X-ray Photoelectron Spectroscopy (XPS: K-Alpha, Thermofisher Scientific Company) with Al Kα radiation generated at 12 kV and 150 W. Depth profiling of each structure with 4×4 mm^2 area was obtained via sputtering where Ar ions were used in XPS chamber at an accelerating voltage of 2 kV. The interfacial reaction was also analyzed using XPS with Al Kα radiation at 1.5 KeV. A Cu reverse-plating process was used to remove the top Cu film to expose the self-formed layer which will ensure the intactness of the self-formed layer for analysis. A photoelectron take-off angle of 45°an

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