Materials Chemistry and Physics 205 (2018) 253–260

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Ni-V(or Cr) Co-addition Cu alloy films with high stability and low resistivity

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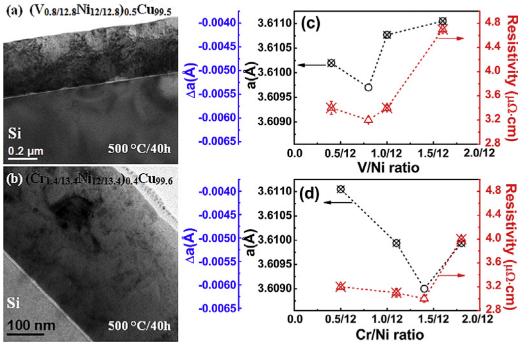
HIGHLIGHTS

- Co-doping of Ni-V or Ni-Cr with smaller content could improve the thermal stability of barrierless Cu alloy film.
- The relationship between the cluster ratio and the effective distortion of Cu lattices was established.
- The stable solid solution cluster-plus-glue-atom model was used to design the composition of Cu seed layers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 May 2017
Received in revised form
5 September 2017
Accepted 29 October 2017
Available online 31 October 2017

Keywords:
Film
Copper alloy
Stability
Magnetron sputtering
Resistivity

ABSTRACT

In order to inhibit Cu, interconnecting in ultra-large-scale integration, from diffusing with surrounding dielectric materials and enhance its chemical inertness and maintain its excellent electrical performance as well. In this paper, the stable solid solution cluster-plus-glue-atom model was used to design the composition of Cu seed layers. In this model, insoluble element V (or Cr) was dissolved in Cu via Ni which is soluble both with Cu and V(or Cr), causing a certain degree of lattice distortion to improve the stability of Cu film. Cu-Ni-V(or Cr) alloy films were deposited directly on single crystal Si(100) substrates, without a designated barrier layer, subsequently annealed in vacuum. For the $(V_{0.8/12.8}Ni_{12/12.8})_{0.5}Cu_{99.5}$ (at.%) film with the addition of large atomic radius element V, it showed the minimum electrical resistivity of 3.2 μΩ·cm after 500 °C/1 h annealing; after 500 °C/40 h annealing, no diffusion between Cu and Si was observed and the resistivity remained stable. Likewise, the $(Cr_{1.4/13.4}Ni_{12/13.4})_{0.4}Cu_{99.6}$ film also remained a minimum resistivity of 3.0 μΩ·cm after annealing at 500 °C for 40 h. The greater the relative lattice distortion is in a single system, the higher the stability and the lower the resistivity achieved. Obviously, the stability of Cu alloy film which satisfy the requirements of the microelectronics industry can be improved dramatically by the additive of Ni and V (or Cr) conform to the proportion of clusters.

1. Introduction

The electronic devices with Cu interconnection have been widely employed because they can satisfy the requirements of high speed, high integration, large capacity, and long service life, etc.

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https://doi.org/10.1016/j.matchemphys.2017.10.071
0254-0584/

However, Cu is easy to react with the surrounding dielectric materials (such as Si-containing dielectrics), resulting in circuit failure [1–4]. In order to obtain excellent interconnects, the early approach was to introduce diffusion barriers. In recent years, the “barrierless structure” has been favored due to the diminishing feature size of interconnects [5–7]. This structure maintains the inherent high electromigration resistance of copper [8], reduces the overall resistance of Cu wire with less impact on the resistivity of Cu seed layer and improves the stability of Cu film as well.

The “barrierless structure” refers to the addition of a diffusion barrier element directly to the Cu seed layer (a conductive layer that must be prepared before plating the Cu wire) to remove a specific diffusion barrier. Thus, some insoluble elements such as Nb, Mo and W [2,9] were added directly into the Cu seed layer, as these elements precipitated at the grain boundaries and defects in the film, the interdiffusion channels between Cu and the surrounding dielectric was blocked and the film stability was improved. However, the precipitation elements with high content also inhibit the combined growth of Cu grains, and a large number of grain boundaries are retained in the film, increasing the electron scattering at grain boundaries, which has negative efficiency on the resistivity improvement and can not be effectively restored despite annealing. For example, the resistivity of the Cu(7.6 at.%V) film [10] remained at a high value of 8.1 μΩ·cm after annealing at 300–400 °C for 1 h. For the 500 °C-annealed Cu(1 at.% Cr) film [11], the resistivity was still as high as 4.5 μΩ·cm.

The research indicated that the addition of a small amount of solid solution element to Cu resulted in a pinning effect within the Cu lattice, and also reduced the chemical reactivity activity of Cu. For instance, Cu(0.5 at.%Ti) film [12] was still stable after annealing at 400 °C for 5 h, and the resistivity was 3.1 μΩ·cm; the resistivity of Cu(0.6 at.%Sn) film [13] was as low as 3.2 μΩ·cm after annealing at 600 °C and there was still no film-substrate interface reaction after annealing at 700 °C for 1 h. More significantly, Cu grains in the 700 °C-annealed film grew to hundreds of nanometers. That is, a small amount of solid solution element would not hinder the combined growth of Cu grains, but contribute to the lower resistivity after annealing. However, the addition of a single element to solid solution in the Cu film resulted in slight lattice distortion, and the effect of enhancing the film stability was limited.

In order to achieve large-sized solid solution, effectively improve the stability of Cu film and minimize the impact on its conductivity, stable solid solution cluster model [14] was used in this study [14] for composition design of barrierless Cu alloy film. Cu and Ni can be miscible due to the same crystal structure and little difference in atomic radius and element electronegativity. If the element which has positive enthalpy of mixing with Cu and has negative enthalpy of mixing with Ni is selected as the third element (M). It will tend to separate from the Cu atom and neighbour to the Ni atom, locally form cubic octahedral clusters $[M\text{-Ni}_{12}]$ with M as the center and 12 Ni as the first neighbor shell. The clusters are disordered dispersed into the Cu substrate to form $[M\text{-Ni}_{12}]\text{Cu}_x$ stable solid solution alloys (as shown in Fig. 1). Thus, the insoluble or undissolved solution element M is introduced into the Cu lattice by the addition of Ni, which can achieve the solid solution element for large-sized clusters. Based on this model, Cu-Ni-Sn [15], Cu-Ni-Mo [16], Cu-Ni-Nb [14], Cu-Ni-Ta and Cu-Ni-Ti [17] films with high thermal stability were prepared by using Sn, Mo, Nb, Ta or Ti as the third element M. The resistivity of these films was as low as 3 μΩ·cm after annealing at 400 °C for 40 h, which satisfied the follow-up processing requirements of microelectronics industry.

In the present paper, V and Cr were selected as the third element M. Their enthalpies of mixing with Cu and Ni and atomic radii are shown in Table 1. The Cr and Cu has the same atomic radii, the atomic radius of V is slightly larger than that of Cu, Cr and V both have a positive enthalpy of mixing with Cu and a negative enthalpy of mixing with Ni, that meets the requirements of solid solution cluster model. The comparison in melting point or boiling point between the elements shows that Cr and V meet the requirements of sample smelting, so they can be used for melting intermediate alloy together with Ni. In this study, Cu-Ni-V(or Cr) alloy film will be prepared by magnetron sputtering on single-crystal Si wafers, in order to investigate the relationship between the addition ratio of alloying elements and the stability and resistivity of the films as well as the influence of atomic radius on cluster model and film performance. The relationship between the cluster ratio and the effective distortion of Cu lattices was established for the first time, and the key to improve the stability was discussed in detail. Finally, the Cu alloy films with high stability and low resistivity which satisfied the requirements of the microelectronics industry were prepared.

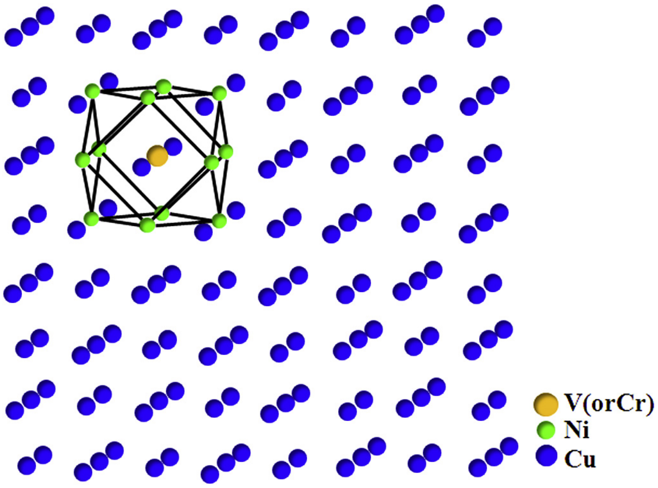

Fig. 1. Cluster-plus-glue-atom model of a $[M\text{-Ni}_{12}]\text{Cu}_x$ (M = V or Cr) stable solid solution, where the square-bracketed part stands for the M-centered and Ni-shelled cluster.

2. Experimental

Firstly, V(or Cr)-Ni intermediate alloy rods (3 mm diameter) with different V(or Cr)/Ni atomic ratios were prepared by arc melting and copper-mould suction-casting in argon atmosphere in identical conditions. Then the rods were cut into thin slices of about 1 mm thickness. These slices were adhered onto the sputtering areas of pure Cu target (purity: 99.999 at.%, diameter: 75 mm) to make a combined target. Finally, the Cu-Ni-V(or Cr) ternary thin films were deposited by radio frequency (RF) magnetron co-sputtering on p-Si(100) wafers, and the different film composition could be gained by changing the V (or Cr)/Ni ratios of intermediate alloy or adjusting the number of alloy slices on the Cu target. The working pressure was 4×10^{-1} Pa, using sputtering power of 100 W and substrate-target distance of 10 cm. Vacuum annealing was performed at different temperatures (300 °C, 400 °C, 500 °C, 600 °C) for 1 h and 400 °C for 40 h. The 40 h were separated into 4 cycles, each being 10 h.

The film composition was analyzed by Electron Probe Microanalyzer (EPMA-1600, SHIMADZU). Depth composition profiles were characterized by Auger Electron Spectroscopy (AES, PHI-700). Microstructure was examined by grazing-angle incidence X-ray Diffraction (GIXRD, Bruker D8 Discover, Cu Kα_1: $\lambda = 0.15406$ nm) with a grazing angle of 1° (out-of-plane mode) and Transmission Electron Microscopy (TEM, Philips Technal G^2). Profilometer