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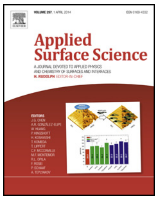

Thermal stability of barrierless Cu–Ni–Sn films

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ABSTRACT

To increase the thermal stability against interface reaction, barrierless Cu–Ni–Sn seed layers, with compositions formulated according to the cluster-plus-glue-atom model for stable solid solutions, was investigated in this paper. In this model, Sn is dissolved in Cu via Ni which is soluble both with Cu and with Sn, and the stable solid solution is formulated as $[Sn–Ni_{12}]Cu_x$, where the Sn-centered $[Sn–Ni_{12}]$ octahedral clusters are embedded in an FCC Cu matrix of x atoms. Cu–Ni–Sn films with various Ni/Sn ratios were deposited onto the Si(1 0 0) substrate by magnetron sputtering and were characterized for microstructure and for electrical resistivity. The $(Sn_{1.1/13.1}Ni_{12/13.1})_{0.3}Cu_{99.7}$ (at.%) film, with its Ni/Sn composition ratio being close to the ideal 12/1 value of the model, showed the minimum electrical resistivity of 2.7 μΩ cm on 500 °C/1 h annealing among all the samples. The resistivity maintained as low as 2.8 μΩ cm even after 400 °C/40 h annealing. No Cu silicide was observed by XRD and TEM in this sample, though a minute amount of fine Cu–Sn compound precipitates was present. The superior diffusion inhibiting effect was attributed to Sn in solid solution via intermediate of Ni.

1. Introduction

With the development of the ultra-large-scale integrated circuit, as an emerging interconnection material, Cu is replacing Al because of its high electrical conductivity and great resistance to electromigration. However, at a relatively low temperature of 200 °C, Cu readily reacts with Si and SiO_2, resulting in device failures [1–4]. Hence, a diffusion barrier layer between Cu film and substrate have to be introduced to avoid their direct contact [5–8]. As interconnect feature sizes shrink, preparing a thin barrier layer of about several nanometers in thickness turns out to be a real challenge. A barrierless scheme, adopting a Cu seed layer doped with diffusion barrier elements such as Ru, W, Nb, Mo, have been proposed as the alternative [9–11]. All these elements inhibit the diffusion, but since they have very limited solid solubilities in Cu, they usually exist in the precipitates that restrain recrystallization and grain growth [10]. Consequently, the improvement in chemical stability is always accompanied by decreased electrical conductivity. The full dissolution of an appropriate amount of diffusion-inhibiting elements in Cu lattice would produce high thermal stability [12,13]. At the same time, in single-phase solid solution, defects would easily be annihilated and stresses would also be released upon annealing, which counterbalance the increase in electrical resistivity due to alloying. The latter factor is particularly important for as-deposited thin films that generally contain extensive structural defects and large stresses.

To dissolve the insoluble diffusion-inhibiting elements in Cu, a third element, which is soluble both with the diffusion-inhibiting elements and with Cu, could be introduced. According to the cluster-plus-glue-atom model [14] for stable solid solution established by Dong et al., if an element M has a negative enthalpy of mixing with Ni and positive enthalpy of mixing with Cu, the M atoms would tend to be neighbored with Ni atoms, in separation from the Cu matrix. So an idealized nearest-neighbor atomic configuration would be that the M atoms are all neighbored with the Ni atoms so that the M atoms are completely separated from Cu. The nearest-neighbor coordination polyhedron, or cluster for short, consisting of one central atom M surrounded by 12 Ni shell atoms, are distributed in the Cu lattice in a homogeneous manner (Fig. 1). The cluster-plus-glue-atom model has been presented in detail in the reference [15], and this model has been successfully used in obtaining highly stable and electrical conductive Cu–Ni–Mo [12] and Cu–Ni–Nb [15] films.

In the present paper, the introduction of a third element Sn as the diffusion-inhibiting element is addressed. Unlike Mo and Nb, Sn has a low melting point as well as a large atomic radius, and it reacts with Cu. Sn is also a widely-used element in integrated circuit, so that the Sn doping can easily adapt to the present industrial

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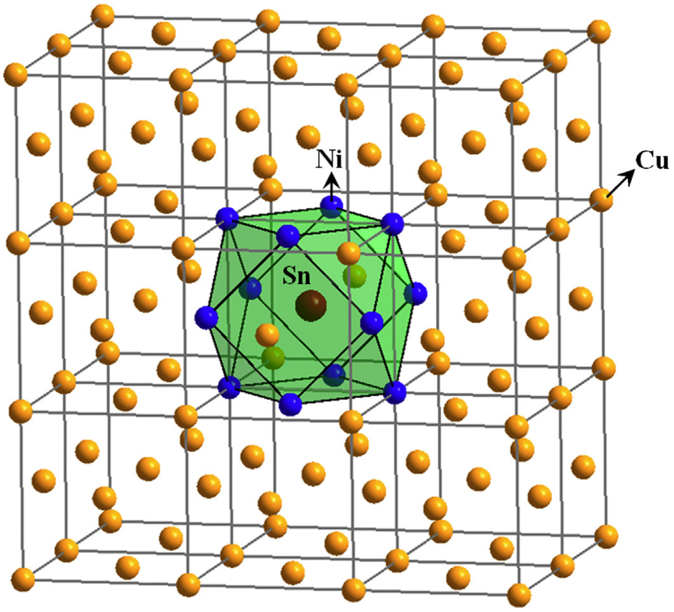

Fig. 1. Cluster-plus-glue-atom model of a $[Sn_1Ni_{12}]Cu_x$ stable solid solution, where the square-bracketed part stands for the Sn-centered and Ni-shelled cluster.

processes. Again the cluster-plus-glue-atom model will be used in the composition design of the Cu–Ni–Sn alloy film compositions. In this model, Sn is dissolved in Cu via Ni which is soluble both with Cu and with Sn, and the stable solid solution is formulated as $[Sn–Ni_{12}]Cu_x$, where the Sn-centered $[Sn–Ni_{12}]$ octahedral clusters are embedded in an FCC Cu matrix of x atoms.

2. Experimental procedures

Six Ni–Sn alloys with different Ni/Sn atomic ratios, including $Ni_{12}Sn_1$, $Ni_{12}Sn_{1.5}$, $Ni_{12}Sn_2$, $Ni_{12}Sn_{2.5}$, $Ni_{12}Sn_3$ and $Ni_{12}Sn_{3.5}$, were prepared by arc melting and suction casting in an argon atmosphere. The Ni–Sn alloys were cut into slices, 3 mm in diameter and 1 mm in thickness, which were pasted onto a pure Cu magnetron sputtering target with conductive adhesive. By co-sputtering the Cu target and the Ni–Sn slices, Cu–Ni–Sn films with different Ni/Sn ratios were deposited onto Si(1 0 0) wafers, without intentional heating of the substrates. The substrate wafers prior to the deposition experiments were first ultrasonically cleaned in acetone, ethanol, and de-ionized water, then followed by an immersion in a 5% HF solution for 3 min, and finally dried with nitrogen gas.

Isothermal annealings were performed in vacuum of 10^{-5} Pa for 1 h, at temperatures ranging from 400 °C to 700 °C. For the evaluation of long-term thermal stability, 8-cycle annealings at 400 °C (5 h per cycle) were also carried out, thereby reaching a total annealing time of 40 h. The film composition was determined by electron probe micro-analyzer (EPMA). The distribution of the elements in the film was observed through secondary ion mass spectrometry (SIMS) and EPMA elemental area-scanning. Sheet resistances were measured using the four-point probe method as already stated in the reference [16]. The base resistivity for Si(1 0 0) wafers was 6–9 Ω cm. Crystallographic and microstructural studies of the films were carried out using grazing-angle incidence X-ray diffraction (XRD) with a grazing angle of 1° (Cu Kα, out of plane mode) and transmission electron microscopy (TEM).

3. Results and discussion

The compositions of the Cu–Ni–Sn ternary films were measured by EPMA. The measured compositions in the sequence of increasing Sn contents (respectively corresponding to designed ratios of 12:1, 12:1.5, 12:2, 12:2.5, 12:3, 12:3.5) are $(Sn_{0.3/12.3}Ni_{12/12.3})_{0.3}Cu_{99.7}$, $(Sn_{0.7/12.7}Ni_{12/12.7})_{0.3}Cu_{99.7}$, $(Sn_{0.9/12.9}Ni_{12/12.9})_{0.3}Cu_{99.7}$, $(Sn_{1/13}Ni_{12/13})_{0.3}Cu_{99.7}$, $(Sn_{1.1/13.1}Ni_{12/13.1})_{0.3}Cu_{99.7}$ and $(Sn_{1.4/13.4}Ni_{12/13.4})_{0.3}Cu_{99.7}$. The Cu contents in all the films are substantially equal, about 99.7 at.%, and the total contents of Ni and Sn are about 0.3 at.%. However, the actual Ni/Sn ratios in the Cu–Ni–Sn ternary films are smaller than the designed Ni/Sn ratios of the alloy slices pasted on the Cu target, which is due to smaller sputtering rate of Sn as compared with Ni [17].

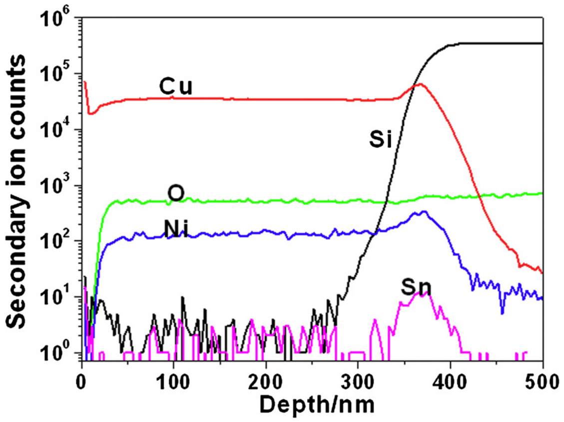

Fig. 2. SIMS depth profile of the as-deposited $(Sn_{0.3/12.3}Ni_{12/12.3})_{0.3}Cu_{99.7}$ film.

Fig. 2 shows an SIMS depth profile of the as-deposited $(Sn_{0.3/12.3}Ni_{12/12.3})_{0.3}Cu_{99.7}$ film. It can be observed that Ni and Sn are homogeneously distributed in the depth direction, and that Sn is enriched in the Cu/Si interface, which is still to be confirmed through further analysis of the interface. Additionally, the O element curve shows no fluctuations, which indicates that the oxygen content in the film is as low as that of the Si wafer; therefore, the Cu film was not oxidized during sputtering.

The EPMA elemental area-scanning of as-deposited and 400 °C/1 h annealed $(Sn_{0.3/12.3}Ni_{12/12.3})_{0.3}Cu_{99.7}$ films (Fig. 3) suggests that the elements are uniform, without segregation, in the film before and after annealing. The uniform distribution of Sn reflects the role of the element Ni that links both Sn and Cu.

The electrical resistivities obtained from this study, together with the electrical resistivities of Sn-doped Cu–Sn films from the literature [13,18] as the references, are shown in Table 1. The resistivities of all the films first decrease and then increase with increasing annealing temperature, which coincides with the results reported in the literature [10,19]. The decrease is due to the increase in crystallinity, the reduction in lattice distortion, the elimination of defects and the increase in solubility, and the increase with the increase of annealing temperature might be associated with the formation of high-impedance Cu–Si compounds. While for the $(Sn_{0.9/12.9}Ni_{12/12.9})_{0.3}Cu_{99.7}$, $(Sn_{1/13}Ni_{12/13})_{0.3}Cu_{99.7}$ and $(Sn_{1.1/13.1}Ni_{12/13.1})_{0.3}Cu_{99.7}$ films, the resistivities decrease again as the annealing temperature increases to 700 °C. The relevant mechanism requires further confirmation by XRD and TEM analysis. Apparently, in Table 1, the resistivities of the ternary films obtained in the present investigation are lower than those of the binary films reported in the literature.

Specifically, the resistivities of the $(Sn_{1.1/13.1}Ni_{12/13.1})_{0.3}Cu_{99.7}$ film with Ni/Sn = 12/1.1 always remain the lowest during the annealing from 500 °C to 700 °C, typically below 3 μΩ cm, which demonstrates that the stability of this Cu–Ni–Sn film is directly related to the Ni/Sn ratio being close to the ideal one of 12/1 required for a stable solid solution model. The resistivity reaches the minimum value of 2.7 μΩ cm at 500 °C/1 h. While as reported