Thin Solid Films 517 (2009) 4961–4965

Contents lists available at ScienceDirect

Thin Solid Films

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

High thermal stability of AlCrTaTiZr nitride film as diffusion barrier for copper metallization

Shou-Yi Chang *, Ming-Ku Chen

Department of Materials Science and Engineering, National Chung Hsing University, Taichung 402, Taiwan

ARTICLE INFO

Available online 20 March 2009

Keywords:
Interconnect
Nitride
Diffusion barrier
Thermal stability

ABSTRACT

To inhibit rapid Cu diffusion in interconnect structures, an effective diffusion barrier layer with high thermal stability, low electrical resistivity and good interface adhesion is strongly demanded. Thus in this study, an amorphous nitride film of equimolar AlCrTaTiZr alloy with an N content of about 41 at.% was deposited by reactive radio-frequency magnetron sputtering. Thermal stability of the AlCrTaTiZr nitride film and its barrier property to Cu diffusion were investigated under thermal annealing at 700–900 °C. The AlCrTaTiZr nitride film remained an amorphous structure after thermal annealing at 700 °C and then crystallized at 800 °C. However, no interdiffusion between Si substrate and Cu metallization through the AlCrTaTiZr nitride film occurred. The electrical resistivity of the film remained at the low level of as-deposited value, indicating its good thermal stability as an effective diffusion barrier layer. With temperature further increasing to 900 °C, severe interdiffusion occurred, along with the formation of silicides and large pores. The electrical resistivity then significantly increased, implying the failure of the AlCrTaTiZr nitride film.

1. Introduction

As the packing density of integrated circuits drastically increases in the last decade, Cu has been practically adopted as interconnect metallization to reduce the problem of serious resistance–capacitance delay [1,2]. However due to the high diffusivity of Cu and the easy formation of Cu silicides, early failure of microelectronic devices occurs [3–5]. To inhibit rapid Cu diffusion, an effective diffusion barrier layer with high thermal stability, low electrical resistivity and good interface adhesion is thus strongly demanded for Cu interconnects [6]. The nitride films of transition metals, such as TiN and TaN, have been widely used as diffusion barrier materials [7]. However due to the strict requirements for Cu interconnects in the generations below 65 nm, the nitride systems of ternary and even quaternary elements with better barrier performances have been continually developed to replace conventional TiN and TaN [8–11].

Recently, a high-entropy alloy (HEA) system with the incorporation of multiple principal elements has been developed [12–17]. The HEAs easily yield the formation of simple solid solutions attributed to the effect of high mixing entropy. Importantly, these HEAs exhibit many extraordinary properties, including very good mechanical properties, thermal stability, and even corrosion and wear resistance [12–16]. Some of the HEAs even yield an amorphous structure which will effectively inhibit rapid diffusion of atoms [12]. Furthermore, thin films of the HEAs and HEA nitrides (denoted as HEANs) can be easily deposited by a simple sputtering process [12,16,17]. Especially, the HEAN films are of great interest as appropriate candidates for the diffusion barrier layers in Cu interconnects because of the expected high diffusion resistance provided by the mixed incorporation of multiple principal elements and the stuffing effect of N [17,18].

The thermal stability of diffusion barriers and the interface reactions or interdiffusion behaviors between the barrier layers and Cu wires significantly dominate the lifetime of interconnect structures and need to be clarified. Thus in this study, equimolar AlCrTaTiZr HEAN films with the incorporation of five principal metallic elements are deposited by a reactive radio-frequency (RF) magnetron sputtering process. The microstructures, crystal structures and electrical resistivity of the HEAN and Cu layers before and after thermal annealing at very high temperatures are characterized to evaluate the thermal stability and interfacial diffusion behaviors of the films.

2. Experimental details

AlCrTaTiZr five-element HEAN films were deposited on Si substrates by reactive RF magnetron sputtering. The sputtering target was prepared with equimolar Al, Cr, Ta, Ti, and Zr elements by vacuum arc-melting repeatedly for at least 5 times, and then cut and polished into a disc of 50 mm in diameter. The HEAN films of about 50 nm thick were then deposited at a plasma power of 150 W in an $Ar+N_2$ mixed atmosphere under a working pressure of 6×10^{-3} Torr at room temperature. The distance between the target and substrates was set as 75 mm, and a substrate bias of −100 V was applied. The $Ar+N_2$ flow

* Corresponding author.
E-mail address: shouyi@dragon.nchu.edu.tw (S.-Y. Chang).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.03.078

rate was controlled at a constant value of 30 sccm, and the N_2 flow ratio ($N_2/(Ar+N_2)$) was adjusted as 10%. On the top of the HEAN films, a Cu film of about 50 or 500 nm thick was subsequently deposited under a plasma power of 50 W and a working pressure of 10^{-3} Torr. To examine the thermal stability and interfacial diffusion behaviors of the HEAN and Cu films, thermal annealing at 700 to 900 °C for 30 min was applied to the films in a vacuum of 10^{-6} Torr.

A scanning electron microscope (SEM, JEOL JSM-6700F) was applied to observe the surface morphologies and cross-sectional microstructures of HEAN and Cu films, and an atomic force microscope (AFM, SPA-400) was used to characterize surface morphologies and film roughness. Film compositions were measured by field-emission electron probe micro-analyses (FE–EPMA, JEOL JXA-8500F). A glancing incident angle (0.5°) X-ray diffractometer (GIA-XRD, Rigaku Dmax 2000) with Cu K_α radiation was used to analyze crystal structures under a scanning speed of 4°/min. High-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G^2 20 S-Twin) was used to examine microstructures and lattice structures. The electrical resistivity of the HEAN films and HEAN/Cu bi-layers was measured by a four-point probe method (Keithely 2400).

3. Results and discussion

Fig. 1 shows the SEM cross-sectional microstructures of Si/AlCrTaTiZr HEAN/Cu film stacks before and after thermal annealing at 700 °C to 900 °C for 30 min. From Fig. 1 (a), it was clearly observed that a continuous and smooth AlCrTaTiZr HEAN layer with a thickness of about 50 nm was deposited, and a Cu film of 500 nm thick well adhered to the HEAN film. The surface roughness of the HEAN layer was measured as small as only 0.22 nm by AFM analyses. In some regions of the HEAN film, the growth morphology in form of columnar structure was observed. From EPMA analyses, it was known that the as-deposited HEAN film was constituted of Al–6.4 at.%, Cr–14.2 at.%, Ta–13.7 at.%, Ti–10.6 at.%, Zr–12.3 at.% and N–41.2 at.%. The lower content of Al was due to a resputtering effect of light element. After thermal annealing at 700 °C as shown in Fig. 1(b), continuous and smooth HEAN and Cu films with clear Si/HEAN and HEAN/Cu interfaces were still observed without particular difference from the as-deposited films. After annealing at 800 °C as shown in Fig. 1(c), some of the Cu film began to agglomerate due to its surface tension at the high temperature. Though the boundary between the HEAN and Cu films became slightly undulated, however the Si/HEAN/Cu layered structure was still clearly identified. A much different morphology from the as-deposited one was observed with further increasing temperature to 900 °C as seen in Fig. 1(d), in which the layered structure became difficult to identify. Compounds or crystalline phases seemed to form at the interfaces, along with the appearance of large pores, implying the occurrence of severe interdiffusion between the Si, HEAN and Cu layers.

Fig. 2 shows the XRD patterns of AlCrTaTiZr HEAN films and HEAN/Cu bi-layers (Cu: 50 nm thick) before and after thermal annealing. For the as-deposited HEAN film shown in Fig. 2(a), only a broaden peak was observed, indicating an amorphous structure; while in Fig. 2(b), the Cu film was characterized as a typical face-centered cubic (fcc) crystal structure with diffraction peaks at about 43° and 51° corresponding to (111) and (200) lattice planes. After thermal annealing at 700 °C, the broaden peak of the as-deposited amorphous HEAN film tended to very small diffraction peaks, indicating the beginning of few crystallization in the mostly remained amorphous matrix. After annealing at 800 and 900 °C, the diffraction peaks became more obvious. According to JCPDS cards, the average diffraction angles of the (111), (200) and (220) lattice planes of fcc AlN (JCPDS No. 871053), CrN (No. 762494), TaN (No. 491283), TiN (No. 741214) and ZrN (No. 350753) were rather close to the measured values of three main peaks at about 35°, 41° and 60°, respectively, implying that the HEAN films formed a mixed solid solution also with a simple fcc crystal structure from these five constituted nitrides. However, despite the occurrence of crystallization, the HEAN films remained thermally stable without reactions to Si substrate at the high temperatures. As for the HEAN/Cu bi-layer, grain growth of the Cu film during annealing at 700 °C induced the sharpening of the Cu diffraction peaks. However, only diffraction peaks of the crystalline

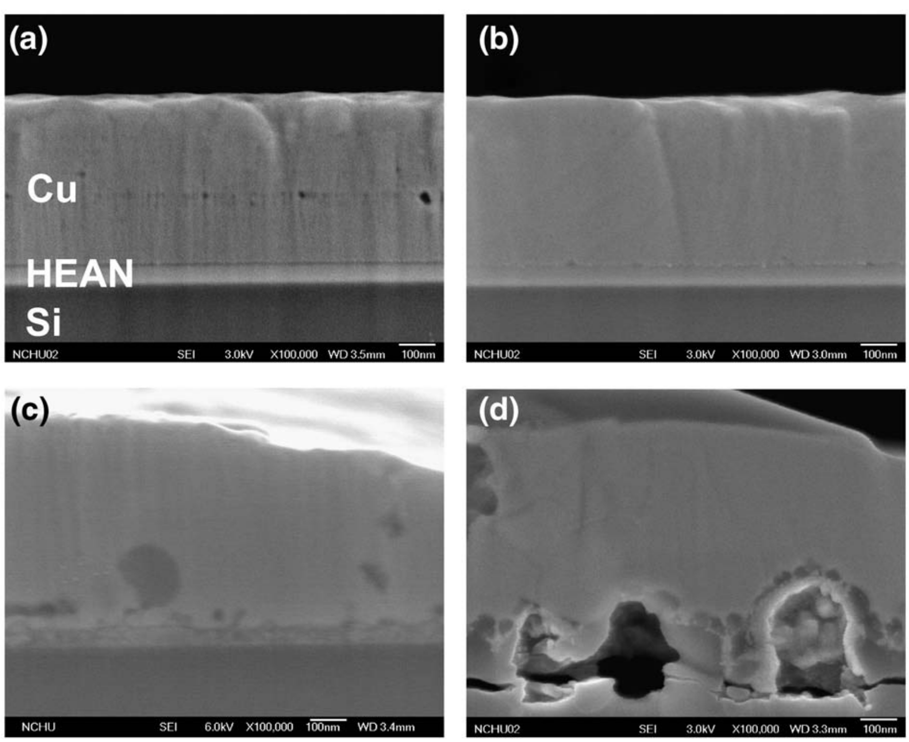

Fig. 1. SEM cross-sectional microstructures of Si/AlCrTaTiZr HEAN/Cu film stacks, (a) as-deposited, and after thermal annealing at (b) 700 °C, (c) 800 °C, and (d) 900 °C for 30 min.