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ScienceDirect
Thin Solid Films 516 (2008) 5527–5530
www.elsevier.com/locate/tsf

Diffusion barrier properties of AlMoNbSiTaTiVZr high-entropy alloy layer between copper and silicon

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Available online 14 July 2007

Abstract

The application of an AlMoNbSiTaTiVZr high-entropy alloy film as diffusion barrier for copper metallization has been investigated. The AlMoNbSiTaTiVZr and copper layers are deposited sequentially, without breaking vacuum, onto silicon substrates by DC magnetron sputtering. The AlMoNbSiTaTiVZr films are found to possess a stable amorphous structure due to their high-entropy and limited diffusion kinetics. The AlMoNbSiTaTiVZr high entropy alloy film is determined to prevent copper–silicide formation up to 700 °C for 30 min. Thus, HEAs appear to have potential use as effective diffusion barriers for copper metallization.

Keywords: High-entropy alloy; Diffusion barriers; Amorphous structure; Thermal stability

1. Introduction

With the ever-increasing demand for higher circuit density and reduced RC time delay in microelectronics, there has been a drive towards the replacement of aluminum by copper for the interconnection material, due to the improved resistance to electromigration and lower resistivity of the latter. Unfortunately, the high diffusivity of Cu into Si or SiO_2 at elevated temperatures is a serious issue for device reliability. This facilitates the use of a diffusion barrier layer between copper and Si or SiO_2, which, due to the continual scaling down of the interconnections, must be as thin as possible. These diffusion barrier layers are therefore required to have excellent high-temperature chemical and structural stability. Furthermore, due to grain boundaries of crystalline materials offering fast diffusion paths for copper, the barrier layer is required to have an amorphous structure [1].

In recent efforts to produce efficient diffusion barrier layers for Cu metallization, a variety of methods have been explored. Some research has focused on modifying conventionally used systems, such as the addition of a thin Al interlayer to improve the performance of TiN diffusion barrier layers [2]. Another approach is to alloy copper with a strong oxide former, such as Al, Mg or Mn [3,4]. The use of alternative process techniques, such as atomic layer deposition (ALD) [5], has also been examined. The most recently explored diffusion barrier layers appears to be the ultrathin organic layers produced by the self-assembled monolayer (SAM) technique [6,7], however the low working temperature is a drawback of these barrier layers. An alternative candidate material, known as "high-entropy alloy" (HEA), is considered in the present work for its potential use in diffusion barrier applications.

HEAs are defined as alloys that are composed of at least five principal metal elements, with the concentration of each principal element ranging from 5 to 35 at.% [8]. It has been found that HEAs exhibit a wide range of novel properties, such as the tendency to form multiprincipal element solid solutions instead of numerous complex compounds [9], the development of nanoscale or even amorphous structures without the need for special process treatments [8,10], have wide ranging mechanical properties [8], exhibit good corrosion properties [11,12], show limited diffusion kinetics [8,13] and have high thermal stability [8]. The high thermal stability, amorphous forming capability and limited diffusion kinetics suggest HEAs to have great potential to be used as diffusion barrier materials. In the present work, the diffusion barrier capabilities of an equimolar AlMoNbSiTaTiVZr HEA shall be examined.

A standard Cu/HEA/Si test structure, with the barrier thickness set at 100 nm, shall therefore be produced in order to test the

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doi:10.1016/j.tsf.2007.07.109

applicability of the present HEA as a diffusion barrier for copper metallization. The test structure is to be fabricated by sequentially depositing the barrier and copper layers onto Si substrates in a dual-target magnetron sputtering system. The structure, composition and resistivity of the device after annealing at various temperatures will be examined in order to determine the performance of the HEA diffusion barrier layer. The reasons for HEA films providing good diffusion barrier capabilities are also discussed.

2. Experimental details

The high-entropy alloy sputtering target was prepared using vacuum arc-melting technique, in which the elemental raw materials, with purities better than 99.9%, were arc-melted and solidified in a water-cooled copper crucible. The chamber was Ti-gettered and had a vacuum better than 10^{-2} Torr. The melting procedure was repeated five times for improved homogeneity of the target material. The ingot was machined to produce a target of 5 cm in diameter. The HEA barrier films were deposited on (100) Si substrates by DC magnetron sputtering. The base pressure of the system was better than 8×10^{-6} Torr. An argon working pressure of 5 mTorr and DC target power of 150 W were employed during deposition. The HEA diffusion barrier and Cu layers, with respective thicknesses of 100 and 300 nm, were deposited sequentially in the same deposition system without breaking vacuum. The target power and working pressure during copper deposition were 80 W and 5 mTorr, respectively. The targets were pre-sputtered to remove surface contamination prior to film deposition. The as-deposited test structures were subjected to rapid thermal annealing (RTA) at 700, 750, and 800 °C for 30 min in vacuum. Glancing-angle X-ray diffraction (GAXRD, MAC Science MXP18 diffractometer) was performed with Cu Kα radiation operated at 40 kV and 150 mA, giving an X-ray wavelength of 1.5405 Å. The incidence angle was 1° and the scanning speed was 4°/min. Sheet resistance was measured by four-point probe method. Cross-sectional concentration profiles were performed by Auger electron spectroscopy (AES; Physical Electronics Auger 670 PHI Xi). To determine the composition of the HEA barrier layer, HEA film with thickness around 1 μm was deposited on (100) Si wafer and examined via an electron probe X-ray microanalyzer (EPMA, JOEL JXA-8800M) so as to avoid substrate signals. Table 1 shows the chemical composition of the film. It can be seen that Al, Si and V show a larger deviation from equimolar ratio.

3. Results and discussion

Fig. 1 shows the XRD spectra of the as-deposited Cu/AlMoNbSiTaTiVZr/Si sandwich structures before and after annealing for 30 min at various temperatures. Only diffraction peaks corresponding to copper can be observed for the as-deposited and film annealed at 700 °C, indicating that the HEA film is XRD amorphous. Grain growth in the copper layer is considered to be the reason for the sharper diffraction peaks and lower sheet resistance, as noted from Fig. 2, after annealing at 700 °C. After annealing at 750 °C and 800 °C, it can be seen that peaks of copper silicide emerge in the diffraction pattern. This is accompanied by a significant increase in the sheet resistance at 750 °C, thus indicating the formation of high resistance copper silicide at the surface. This demonstrates that the protection offered by the AlMoNbSiTaTiVZr HEA film fails at about 750 °C.

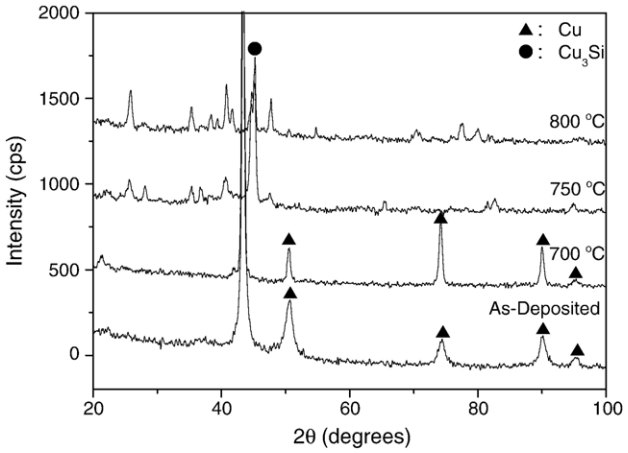

Fig. 1. XRD spectra from the Cu/HEA/Si structure before and after annealing at 700, 750 and 800 °C, respectively.

The AES compositional depth profiles of the as-deposited and annealed samples are shown in Fig. 3. The interfaces are well-defined for the as-deposited sample. After annealing at 700 °C, however, the signals of Cu and HEA are found to overlap. This indicates that there is Cu penetration into the barrier layer but that Cu has not reached the Si substrate yet.

Table 1
Composition of the high-entropy alloy film (at.%)

Element	Al	Mo	Nb	Si	Ta	Ti	V	Zr
Nominal composition	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Composition by EPMA	5.09	14.52	12.68	15.15	11.91	12.96	17.08	10.60

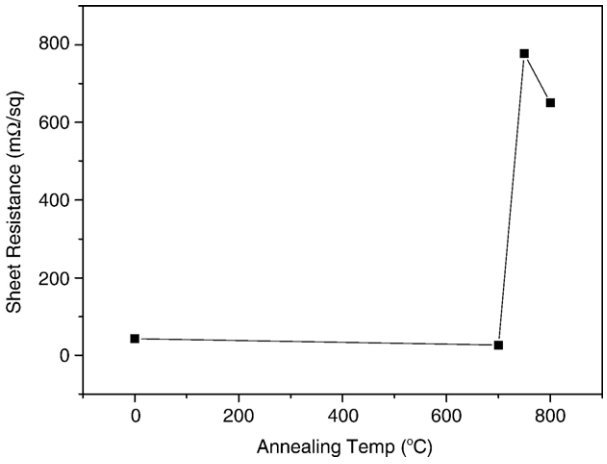

Fig. 2. Sheet resistance of the Cu/HEA/Si sandwich structure as a function of annealing temperature.