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Investigations of failure mechanisms at Ta and TaO diffusion barriers by secondary neutral mass spectrometry

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One of the most important processes in Cu metallization for highly integrated circuits is to fabricate reliable diffusion barriers. Recently, thin films made of refractory metals and their compounds have been widely used in solid-state electronics as barriers because of their good electric properties, favourable thermal properties and chemical stability. Thermal stability of Tantalum (Ta) and Tantalum-oxide (TaO_x) layers as a diffusion barrier in Si/Ta/Cu, Si/TaO_x/Cu and Si/Ta-TaO_x/Cu systems have been investigated. Si/Ta (10 nm)/Cu (25 nm)/W (10 nm), Si/TaO_x (10 nm)/Cu (25 nm)/W (10 nm) and Si/Ta (5 nm)TaO_x (5 nm)/Cu (25 nm)/W (10 nm) thin layers were prepared by DC magnetron sputtering. A tungsten cap layer was applied to prevent the oxidation of the samples during the annealing process. The samples were annealed at various temperatures (473 K–973 K) in vacuum. Transmission Electron Microscopy, X-ray diffraction, X-Ray Photoelectron Spectroscopy and Secondary Neutral Mass Spectrometry were used to characterize the microstructure and diffusion properties of the thin films. Our results show that at the beginning phase of the degradation of the Si/Ta/Cu system Ta atoms migrate through the copper film to the W/Cu interface. In the Si/TaO_x/Cu system the crystallization of TaO and the diffusion of Si through the barrier determine the thermal stability. The Ta–TaO bilayer proved to be an excellent barrier layer between the Si and Cu films up to 1023 K. The observed outstanding performance of the combined film is explained by the continuous oxidation of Ta film in the TaO_x–Ta bilayer.

1. Introduction

Copper is a widely used interconnect material as a replacement for aluminium in semiconductor devices because of its high electrical conductivity and electromigration resistance. [1,2] The most important life-time limiting process in devices is diffusion between semiconductor and interconnect layers. It was an early observation that Cu can easily migrate to silicon, forming silicides even at temperatures as low as 473 K. [3–5]. In order to prevent mixing and silicide formation, reliable diffusion barriers are needed. As for barrier materials for copper metallization, Ta and its alloys are expected to be the best candidates due to their high melting points, lack of reactivity with Cu, as well as relatively good adhesion to SiO_2. Detailed discussion of barrier properties and failure mechanisms for Ta and its compounds can be found in Refs. [6–10]. Experimental investigations demonstrated that Ta alloys with an amorphous structure are promising barrier materials.

In this paper we report on the thermal stability and barrier performance of Ta, TaO_x films and a TaO_xTa system containing an amorphous, metastable TaO film between the TaO_x and Ta layer. Our research is focused on the very early stage of the degradation of these systems. Structural and compositional changes in the thin films were investigated by an X-ray diffractometer (XRD, equipped with a Siemens made Cu-anode X-ray tube), an X-ray photoelectron spectroscope (XPS, home-built equipment [11], 6×10^{-4} relative energy resolution in fixed retardation ratio mode, with non-monochromatic AlK_α excitation [12]) and a transmission electron microscope (TEM, type: JEOL 2000 FX+EDS). A secondary neutral mass spectrometer (SNMS, type: INA-X, SPECS GmbH, Berlin) was used to map the depth profiles.

2. Experimental

The Ta/Cu/W, TaO_x/Cu/W and Ta-TaO_x/Cu/W films were deposited onto (111)-oriented p-type silicon substrates by DC magnetron sputtering at room temperature. The base pressure of the sputtering chamber was lower than 2×10^{-5} Pa. Circular Ta, Cu, W targets, 2″ in diameter, were used as sputtering sources. During Tantalum, copper and tungsten layer deposition, the Ar (99.999%) pressure (under dynamic flow) and the sputtering power were 5×10^{-1} Pa and 40 W, respectively. The TaO layer was deposited in pure oxygen

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at 150 W sputtering power [13,14]. The sputtering rates were calculated from the layer thickness measured by an AMBIOS XP-1 profilometer. The layer depositions were performed without interrupting the vacuum; only the working gas was changed. The nominal thickness of each Ta, TaO_x and W film was 10 nm, and the thickness of each copper layer was 25 nm. The tungsten cap layer was applied in order to avoid the sample oxidation during the heat treatments. All samples were annealed under vacuum (3×10^{-5} Pa) at various temperatures ranging from 473 K to 1023 K for 60 min. In each annealing process, a new, individual sample was used.

Microstructure of samples was analyzed by TEM, XRD and XPS. The depth profiles and time evolution of interfaces were detected by SNMS. This instrument works with noble gas plasma and the bombarding ion current has an extremely high lateral homogeneity. The low bombarding energies (in order of 10^2 eV) and the homogeneous plasma profile result in an outstanding depth resolution (<2 nm) [16]. In this case the detection limit of the SNMS is about 10 ppm. Details of quantification procedure of SNMS spectra is described in Ref. [15].

3. Results and discussion

3.1. Thermal stability of Si/Ta (10 nm)/Cu (25 nm)/W (10 nm) samples

The structure of the as-deposited Ta layer was identified as nanocrystalline beta phase. No texture or preferred orientation of Ta grains can be observed. The Cu film was polycrystalline with grain size of about 20 nm. Our XRD measurement confirmed that the Ta layer after 773 K/60 min annealing remained beta phase, in accordance with other observations published in the literature [17].

The SNMS depth profile of an as-deposited sample verifies the nominal thicknesses of the films (Fig. 1a) and indicates that the interfaces are sharp, and no intermixing takes place between the neighbouring layers. No changes were detected after heat treatments up to 623 K (Fig. 1a). At this temperature Ta and Si atoms start to diffuse. According to the profiles (Fig. 1a) Ta fills up Cu grain boundaries and segregates at the W/Cu interface. (The changes of the Tantalum concentration cannot be seen on a logarithmic scale.) The depth profile measured after heat treatment at 823 K, shows an increased Si concentration in the Ta layer and segregation of Si at the W/Cu interface (Fig. 1b). The higher Si concentration in Ta layer can probably be explained by Ta-silicide formation [17,18]. On the other hand, the SNMS profiles do not show any evidence of Cu-silicide formation. The interfaces of the Ta and Cu layers remain sharp and there is no sign of Ta diffusion into the Si substrate.

3.2. Thermal stability of Si/TaO_x (10 nm)/Cu (25 nm)/W (10 nm) samples

The TaO_x film between the Cu layer and Si substrate (covered with native oxide) was prepared by reactive sputtering in 100% oxygen. The as-deposited TaO_x is amorphous. This observation correlates with the result of diffraction experiments and it is verified by TEM investigations (Fig. 2). The chemical composition and binding states of the deposited TaO_x film were studied by XPS using an Al anode (Al K_α). We detected the Ta 4*f* and O 1*s* spectra. The O/Ta ratio was found to be about $2.35 \pm 10\%$, which is very close to the

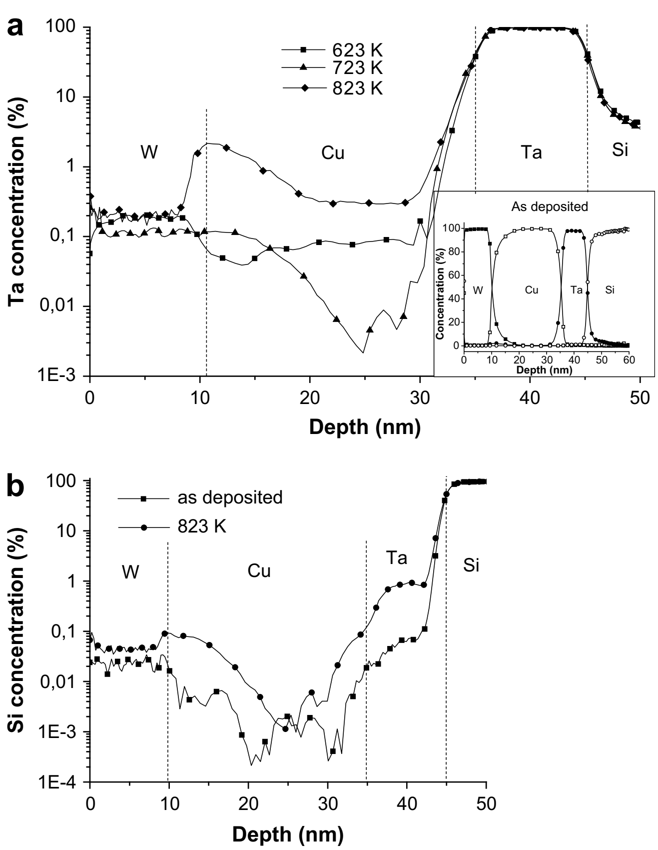

Fig. 1. (a) Evolution of Ta depth profile in the Si/Ta/Cu/W system; Ta fills up Cu grain boundaries and segregates at the W/Cu interface. (The changes of the Tantalum concentration cannot be seen on a logarithmic scale). Dotted lines represent the position of interfaces. (b) Evolution of Si depth profile in the Si/Ta/Cu/W system. At 823 K the increasing of Si concentration in Ta layer and segregation of Si at the W/Cu interface can be seen. The higher Si concentration in Ta layer can be explained by Ta-silicide formation. Dotted lines represent the position of interfaces.

Fig. 2. TEM picture of as-deposited Si/TaO_x/Cu/W system.