Vacuum 84 (2010) 130–133

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

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Keywords:
Diffusion barrier
Tantalum
Tantalum-oxide

A B S T R A C T

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

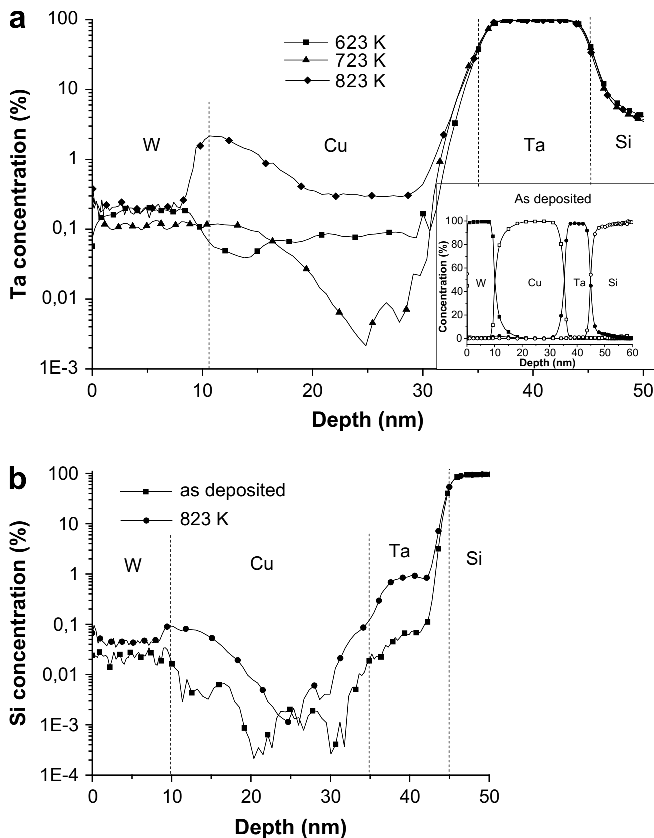

Fig. 1. (a) Evolution of Ta depth profile in the Si/Ta/Cu/W system; Ta fills up Cu grain boundaries and segregates at the W/Cu interface. (The changes of the Tantalum concentration cannot be seen on a logarithmic scale). Dotted lines represent the position of interfaces. (b) Evolution of Si depth profile 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.

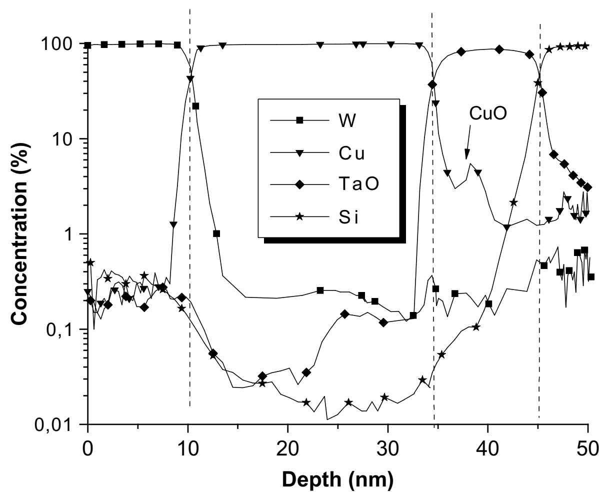

Fig. 3. SNMS depth profile of as-deposited Si/TaO_x/Cu/W film. The shape of the Cu profile can be interpreted by the formation of a thin copper-oxide layer (thickness of around 2 nm) at the Cu/TaO_x interface. Dotted lines represent the position of interfaces.

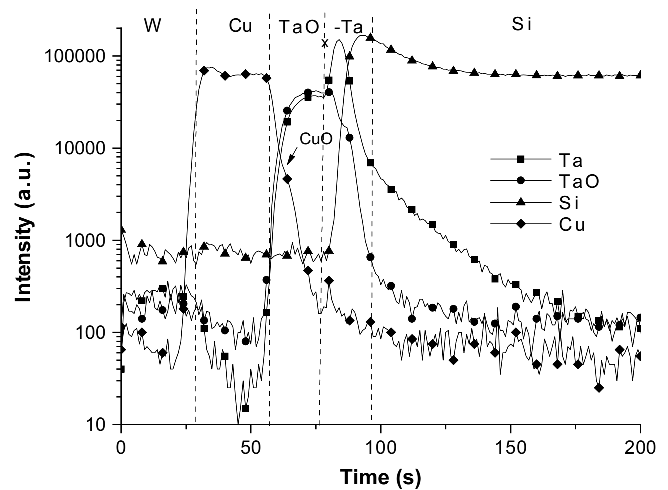

Fig. 5. SNMS depth profile of as-deposited Si/TaO_x–Ta/Cu/W system. The higher Ta signal represents the pure Ta layer, the lower one the TaO_x film. The form of the Cu profile at the Cu/TaO interface indicates the presence of some reaction product. Dotted lines represent the position of interfaces.

ratio of the stoichiometric tantalum pentoxide (2.4). These measurements were carried out on separate TaO films.

The depth profile of an as-deposited sample is presented in Fig. 3. This profile indicates that the interface between the Cu and TaO_x (TaO_x was detected using the ^{181}Ta ^{16}O molecular ion) is not sharp and it shows a graded shape. The shape of the profile can be interpreted by the formation of a thin copper-oxide layer (thickness of around 2 nm) at the Cu/TaO_x interface. The TEM measurement (Fig. 2) confirms this picture. Such an interfacial Cu_2O layer was also observed by other authors [18,19]. The evaluation of depth profiles during the annealing is also shown in Fig. 4. No changes occur during heat treatments up to 773 K. However, at 823 K, Si atoms diffuse through the TaO_x barrier into the Cu layer and segregate at the W/Cu interface (Fig. 4). Weak segregation was also found at the Cu/TaO_x interface, probably due to the presence of an interfacial CuO_x layer. The deterioration of sample at temperature $T \geq 823$ K takes place very fast. This enhancement of degradation can be attributed to the crystallization of an amorphous TaO_x film [20]. Very low diffusion of Cu into the TaO can also be detected. Interestingly, a TaO_x concentration peak appears in the Cu layer (Fig. 4).

3.3. Thermal stability of Si/TaO_x (5 nm)–Ta (5 nm)/Cu (25 nm)/W (10 nm)

The Fig. 5 represents the SNMS depth profiles of the Cu/TaO_x–Ta/Si system. In the as-deposited state, the higher Ta signal represents the pure Ta layer, and the lower one the TaO_x film. The form of the Cu profile at the Cu/TaO interface indicates the presence of some reaction product. This product was identified as CuO_x using TEM, as we have seen in the case of the Si/TaO_x (10 nm)/Cu (25 nm)/W (10 nm) samples. No changes occur during heat treatment up to 773 K. Detectable changes in the depth profiles can be observed at temperatures $T \geq 823$ K. Two important characteristic features can be detected (Fig. 6): (i), there is smearing at the TaO_x–Ta interface; (ii), Si atoms migrate through the barrier and there is Si accumulation at the Cu/TaO_x, and W/Cu interface. At the same time Cu starts to diffuse into the TaO_x–Ta barrier. The smearing of the TaO_x–Ta interface can be explained by oxidation of pure Ta in the barrier layer due to the released oxygen from the TaO_x film during the heat treatment. The quantification of Fig. 5 and Fig. 6 cannot be carried out because the sputtering rate of TaO_x-metastable TaO–Ta system is not known.

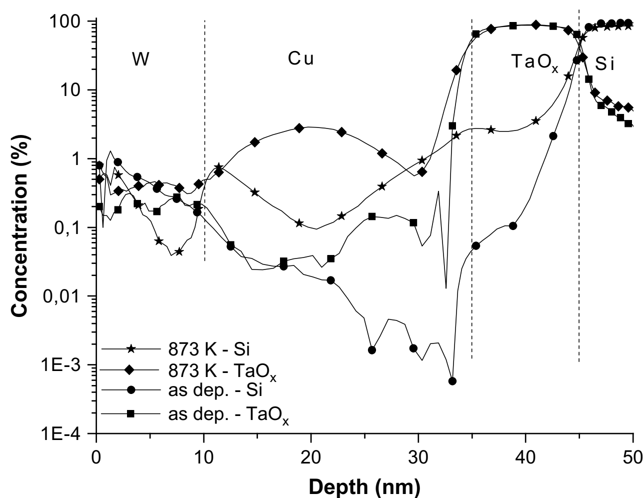

Fig. 4. SNMS depth profile of Si and TaO_x at 823 K. At 823 K, Si atoms diffuse through the TaO_x barrier into the Cu layer and segregate at the W/Cu interface. Dotted lines represent the position of interfaces.

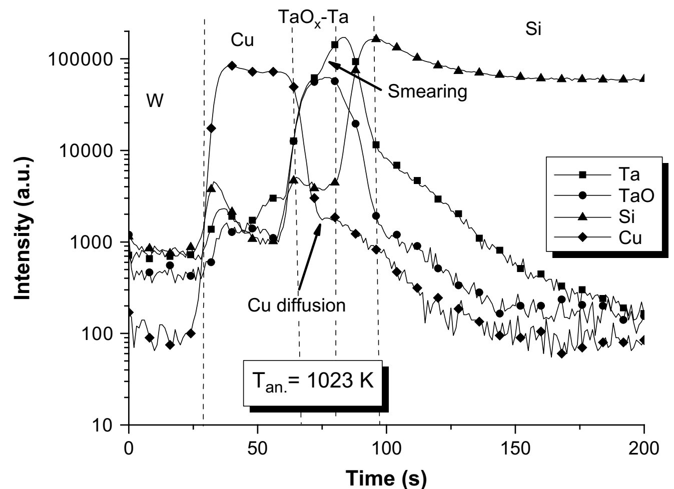

Fig. 6. SNMS depth profile of Si/TaO_x–Ta/Cu/W sample at 1023 K. There is smearing at the TaO_x–Ta interface. Si atoms migrate through the barrier and there are Si accumulation at the Cu/TaO_x, and W/Cu interface. Cu starts to diffuse into the TaO_x–Ta barrier. Dotted lines represent the position of interfaces.

4. Conclusion

Our investigations, based on depth profile analysis, show, that early degradation of a Ta barrier takes place by the diffusion of Ta through the Cu layer and simultaneously the diffusion of Si into the Ta layer. Around 773 K, Ta-silicide formation was observed. Furthermore, deterioration of the barrier layer is strongly affected by the coarsening of the Ta film.

The failure mechanism in the TaO_x barrier seems to be a crystallization controlled process (823 K). At higher temperature (873 K) the decomposition of the TaO_x film also influences the degradation.

The combined TaO_x–Ta barrier proved to be much more effective than that of individual Ta or TaO_x films. The observed outstanding performance of the combined film can be explained by the continuous oxidation of the Ta film in the TaO_x–Ta bilayer. The reaction product of the oxidation process, the freshly formed TaO_x film between the as-deposited TaO_x and Ta, is probably amorphous (metastable TaO). This oxide layer in an amorphous state is less permeable to Si and Cu than the layer in crystalline form, therefore, it successfully prevents the degradation of samples up to 1023 K.

Acknowledgements

The authors gratefully acknowledge the support of the Hungarian Scientific Research Fund (OTKA) through Grants K 67873, K 61253 and K67969, RET-06/2004.

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