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Chemical stability of Ta diffusion barrier between Cu and Si

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Abstract

The reactions in the Si/Ta/Cu metallization system produced by the sputtering process were investigated by means of sheet resistance measurements, X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), scanning electron microscopy (SEM) and optical microscopy. In particular, the reaction sequence was emphasized. The reaction mechanisms and their relation to the microstructure and defect density of the thin films are discussed on the basis of the experimental results and the assessed ternary Si–Ta–Cu phase diagram at 700°C. It was found out that the effectiveness of the Ta barrier is mainly governed by the defect density and their distribution in the Ta film. The failure was induced by the Cu diffusion through the Ta film and almost simultaneous formation of Cu_3Si and $TaSi_2$.

Keywords: Phase diagrams; Diffusion barriers; Copper metallization; Tantalum

1. Introduction

There has been considerable interest recently in the use of Cu as on-chip metallization in microelectronic devices due to its lower electrical resistivity and higher electromigration resistance compared with aluminium. However, the interaction between Si and Cu is very strong and detrimental to electrical performance of Si even at temperatures as low as 200°C [1–4]. Thus, it is necessary to implement a barrier layer between Cu and Si. Tantalum has many good properties from the diffusion barrier point of view. It has a high melting point (3020°C) and, therefore, high activation energy for both lattice and grain boundary self-diffusion. It does not form intermetallic compounds with copper, providing a relatively stable interface between copper and tantalum [5]. However, in a recent publication the formation of a thin amorphous layer between Cu and Ta was reported [6]. The reaction between silicon and tantalum is known to require quite high temperatures (650°C) [7], enabling a reasonable stable Si/Ta interface. Hence, it is not suprizing that tantalum and its compounds have been suggested by number of authors as feasible diffusion barriers in copper-based metallization schemes [8–14]. Despite the amount of publications on the Ta as a diffusion barrier, information about the interfacial reactions in the Si/Ta/Cu system is still inadequate. To obtain a better understanding of the system one should combine experimental results with the available thermodynamic and kinetic information to produce a reliable description of the system.

2. Materials and methods

The copper and tantalum films were sputtered onto cleaned and oxide-stripped Si(100) substrates in a Von Ardenne CS730 S sputtering machine. The thickness of the tantalum layer was approximately 100 nm. The copper layer with thickness of 400 nm was subsequently sputtered onto this film without breaking the vacuum. The base pressure for the deposition runs was 3×10^{-5} Pa. The samples were annealed in the vacuum of 10^{-6} Pa at temperatures ranging from 600 to 800°C for 30 min.

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An initial study of the interfacial reactions was taken by using four-point sheet resistance measurements. The interfacial reactions at the Si/Ta/Cu metallization scheme were characterized by X-ray diffraction (XRD), and Rutherford backscattering spectroscopy (RBS). Surfaces of the samples were also monitored with optical microscopy and scanning electron microscopy (SEM).

Even though the complete thermodynamic equilibria are never met in thin film systems — because the materials at contact regions are under continuous microstructural evolution — the local equilibrium is, however, generally attained at interfaces. Therefore, the phase diagrams provide us an efficient method for designing diffusion barrier layer between various metallizations, especially when they can be combined with the kinetic information. Hence, a ternary Ta–Si–Cu phase diagram was calculated from the assessed binary thermodynamic data and compared with the experimental results obtained.

3. Results

The sheet resistance vs. temperature curve is shown in Fig. 1. After the initial stage the resistance increases in a nearly linear manner consistent with that of metallic copper overlayer. At 625°C there is a slight increase in the sheet resistance. However, the change is so small that it can be attributed to experimental error. At 685°C there is an abrupt rise in resistivity, indicating that a reaction has occurred in the film. Beyond 700°C the sheet resistance starts to decrease, and the structure behaves as an intrinsic semiconductor. The underlying silicon is now carrying almost all the probe current.

Surfaces of the samples maintained a shiny copper-like appearance up to 675°C. However, at this temperature and even at 625°C, there were a few small spot-like defects indicating the initiation of local reaction(s). Samples annealed at 685°C had already completely lost their metallic copper appearance and their colour appeared to be hazy and silver-like. The SEM picture from the surface structure of the sample annealed at

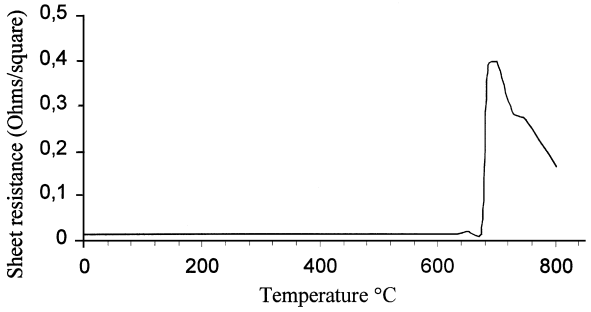

Fig. 1. Sheet resistance vs. temperature behaviour of the samples.

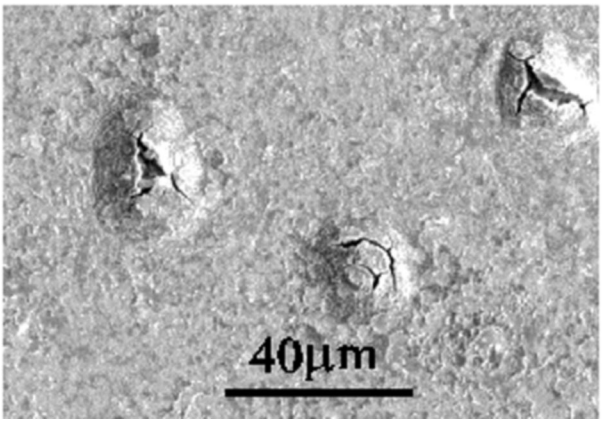

Fig. 2. Surface of the sample annealed at 685°C for 30 min.

685°C is shown in Fig. 2. To reveal the nature of the spot-like 'precipitates', a cross-sectional SEM sample was prepared (Fig. 3). The large volume of these 'precipitates' enabled the use of energy dispersive spectrometry (EDS) to quantify the composition of the precipitate. The defect turned out to be Cu_3Si.

The appearance of the Cu_3Si precipitates is explained as follows. Copper atoms come into contact with silicon only at specific sites at the Ta/Si interface due to the nature of the short-circuit diffusion, which is assumed to be the mechanism for the Cu penetration through the Ta layer as explained later. The nucleation of Cu_3Si takes place at these sites. Formation of Cu_3Si in silicon is associated with large volume expansion of 150% [15] leading into stress relaxation and production of intrinsic point defects. After the initial stage of nucleation the further growth of the Cu_3Si 'precipi-

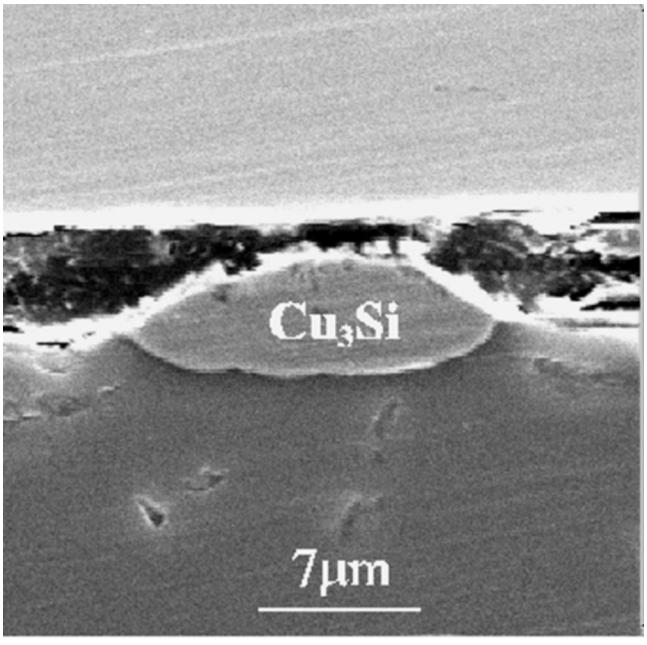

Fig. 3. Cross-sectional SEM image from the specimen.

tates' is continued by the conventional Ostwald ripening, which lead to the formation of the observed relatively large particle colonies.

The calculated ternary Si–Ta–Cu phase diagram is shown in Fig. 4 Possible ternary silicides have been excluded from the phase diagram due to the fact that there no known report in the literature suggesting such an equilibria exists. The presence of $TaSi_2$ in the reaction layer was predicted from the phase diagram, since it is in local equilibrium both with Cu_3Si and Si as shown in Fig. 4.

XRD-analysis with a small glancing angle was conducted in order to confirm this prediction. The layer thickness of the tantalum silicide(s) is so thin that it could not be reliably detected with the help of SEM. The results from the XRD-analysis shown in Fig. 5 confirm the prediction based on the ternary phase diagram. The RBS measurements were conducted to obtain more information on the reactions (Fig. 6). At 625°C there is slight shift in the Ta-peak towards the surface, but it can be attributed to the thickness variations in the Cu layer.

The occurrence of the small surface peak corresponding to that of Ta indicates that some diffusion has occurred between Ta and Cu. It seems that the tantalum has diffused to the surface of the sample. However, in this case it is expected that Cu has diffused into Ta layer as explained later. At 685°C the spectrum shows that the reaction(s) have lead to the catastrophic failure of the structure. The spectrum at this temperature is quite complicated and interpretation quite difficult. This can be explained with the help of Figs. 2 and 3, where the top and cross-sectional views from the reacted sample are shown. As the surface does not stay

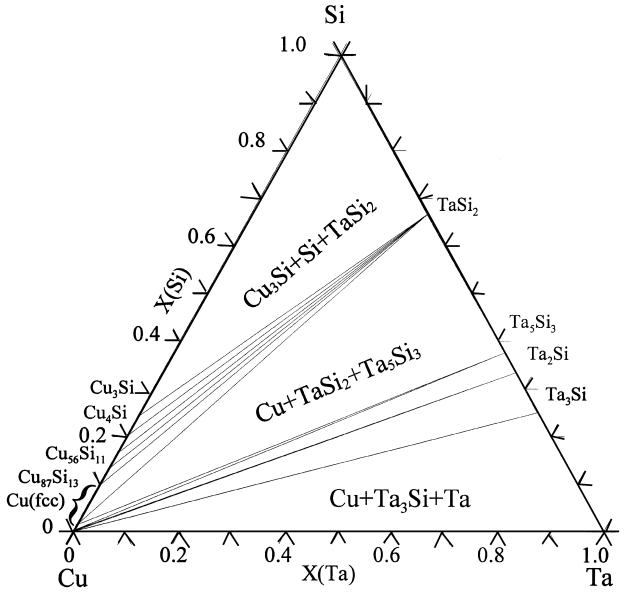

Fig. 4. Isothermal section of the Si–Ta–Cu phase diagram at 700°C.

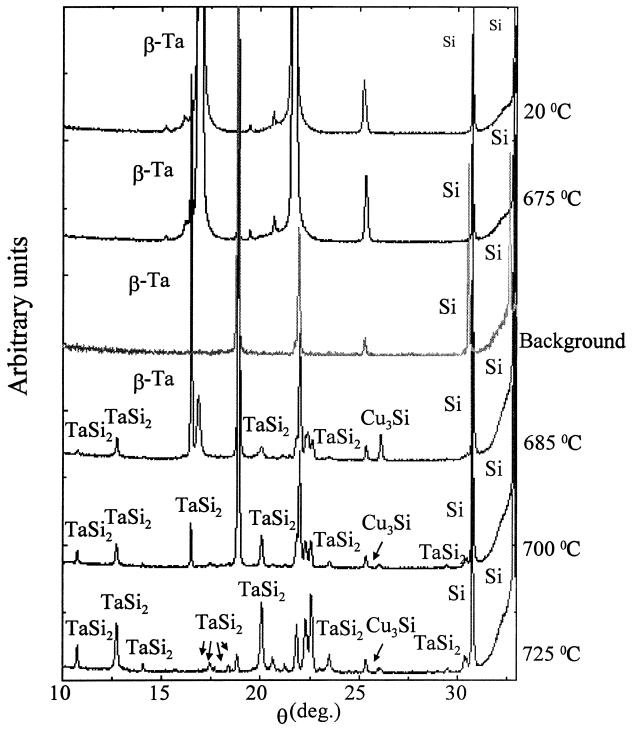

Fig. 5. XRD spectra from the Si/Ta (100 nm)/Cu (400 nm) samples annealed at different temperatures.

planar the interpretation of the RBS spectrum is not unambiguous.

4. Discussion

The reaction mechanism leading to the failure is of great interest from the theoretical and practical point of view. Based on the results obtained the first phase to form is Cu_3Si, although the formation of $TaSi_2$ takes place almost simultaneously. The proposed mechanism is as follows. At the lower temperatures below the temperature of formation of $TaSi_2$, there is already significant Cu diffusion. This is supported by the RBS results. Cu atoms migrate along the interface to find a suitable penetration point (e.g. defect in the Ta film or grain boundary) and diffuse into Ta layer. The short-circuit diffusion of Cu in Ta layer is expected to be very fast (A. Kodentsov, personal communication). There exists indirect evidence of this assumption in the previously mentioned amorphous phase formation between Ta and Cu. One of the requirements for the solid state amorphization is the anomalously fast diffusion of one of the components [16]. The structure of the Ta film was also observed to be columnar, thus further enhancing the grain boundary diffusion of Cu [17]. Hence, evidence is that the Cu_3Si nucleation takes place at the vicinity of the Ta/Si interface due to the fast short-circuit diffusion of Cu in the Ta thin film. The nucleation takes place initially only at the specific sites along the

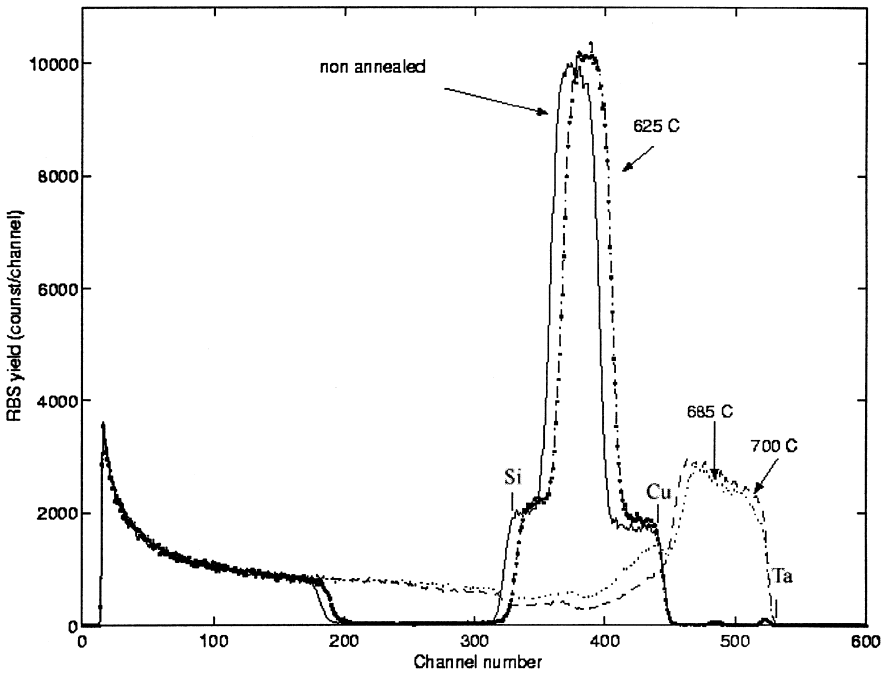

Fig. 6. RBS spectra from the samples.

interface between Ta and Si due to the nature of the short-circuit diffusion. The nucleation and growth of Cu_3Si probably enables the formation of $TaSi_2$ at the Ta/Si interface. It is suggested in the literature that the formation rate of $TaSi_2$ is mainly governed by the release rate of Si atoms from the Si lattice [18]. Therefore, it is likely that the penetration of copper through the tantalum layer and the formation of Cu_3Si help to release the Si atoms and facilitate the formation of $TaSi_2$.

5. Conclusions

Interfacial reactions in the Si–Ta–Cu metallization system were investigated. It was concluded that Cu_3Si is the first phase to form at the original Ta/Si interface mainly via the fast short circuit diffusion of Cu. However, the formation of $TaSi_2$ takes place almost simultaneously. It was concluded that the formation of $TaSi_2$ is likely to be enhanced by the formation of Cu_3Si. The reaction products, $TaSi_2$ and Cu_3Si, are in local equilibrium according to the ternary phase diagram. Therefore, further reactions are not expected to take place in the system. This corresponded to the experimental results, since no other phases were detected in any of the samples. It can be concluded that the stability of the Ta thin film as a diffusion barrier layer is mainly governed by the microstructure of the fabricated layer.

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