R.F.-Sputtered Tantalum-based diffusion barriers between copper and silicon

J.M.T. Molarius, I.Suni,
VTT Microelectronics, P.O.Box 1101, FIN-02044 VTT, Finland.

T.Laurila, K.Zeng, and J.K.Kivilahti
Lab. of Electronics Production Technology, P.O.Box 3000, FIN-02150 HUT Finland.

There is clear need to apply copper for metallisation in integrated circuits and micropackaging, but its usage has been hindered by chemical incompatibility of copper with silicon. However, tantalum-based diffusion barriers, like tantalum nitrides (Ta_2N and TaN), seem to provide a feasible solution. In this study the effects of the reactive r.f-sputtering process parameters on the formation of tantalum based diffusion barriers has been studied. Moreover, the evolution of various reaction products and their relation to the barrier properties are discussed.

1. Introduction

Copper is the interconnection material of choice for ultra large scale integrated (ULSI) microelectronics, because of its lower bulk resistivity (1.72 $\mu\Omega$cm as compared to 2.83 $\mu\Omega$cm for aluminium) and higher resistance to electromigration [1]. But there are several other reasons why copper was introduced only recently into integrated circuit fabrication. Copper diffuses rapidly into silicon and can form recombination-generation centres at active regions of devices. Additionally it reacts with silicon at very low temperatures, even below 150 ^{o}C, forming Cu_3Si. When on top of silicide, copper can react either with silicide or the underlying silicon forming Cu_3Si or intermetallic compounds. Cu reacts at low temperatures with metals, like Al, Au and Pd, which are commonly used in microelectronics. Oxidation of copper and formation of CuO and Cu_2O phases also degrade electrical and mechanical properties of copper thin films. When copper is in contact with silicon oxide under biased thermal stress (BTS), copper moves to SiO_2/Si interface. On polymers, such as polyimide, Cu forms agglomerates at room temperature. Copper also has poor adhesion to both polymers and silicon dioxide. The aforementioned problems with thermal stability are summarised in figure 1. [2]

To avoid these problems copper has to be encapsulated with a diffusion barrier. Diffusion barrier should be chemically inert with copper (or react only at high temperature) and it should provide protection for bulk and grain boundary diffusion of Cu. Refractory metals are natural candidates and among them tantalum has many good properties for a diffusion barrier for copper. In this paper we focus on rf-sputter deposition of tantalum and how it affects thin film diffusion barrier properties of Ta.

2. Experimental

All tantalum films were deposited with Von Ardenne CS 730 S cluster tool sputtering system, which was mounted in VTT Microelectronics Centre cleanroom recently. This system consists of three sputtering chambers, load lock and dealer.

The load lock is capable of handling 13 wafers, with diameters up to 150 mm, in a special loading cassette. Left chamber (see Fig. 2) is used for rf-sputtering and sputter cleaning with hollow cathode sputter etcher. Right chamber has four dc-magnetron sputter sources. Third chamber, behind the dealer is called chamber one and it has only one target. This chamber is dedicated for deposition of oxides.

Tantalum was sputtered in the left chamber, not because metals would need radiofrequency sputtering, but subsequent tantalum nitride depositions are better carried out with rf than dc. This would also minimise the system down time and contamination, arising from Ta-target
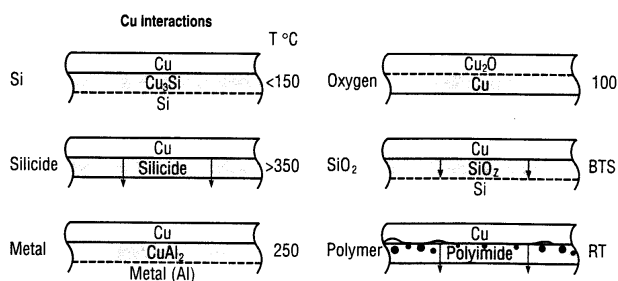
Figure 1. Schematic diagram shows the interfacial reactions between copper and its contact materials at different temperatures. Arrows show atom transportation.
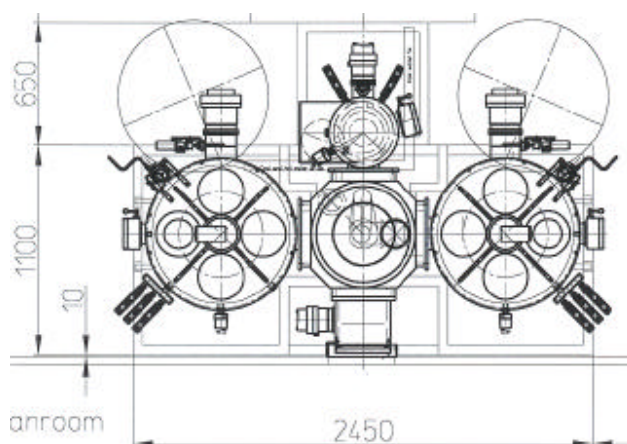
Figure 2. Schematical top view of the VA 730 S sputtering system used to deposit tantalum films.

change from one chamber to another. In all of the chambers targets are placed horizontally in chamber floors facing up. Substrates are placed horizontally facing down and they are kept in place by gravity. In large chambers there are four substrate positions on round table. Sputtering can be done in stationary, swing (+/- 6°) or rotation mode. In rotation all four substrates are rotated over a target and a specially shaped shutter is used to get uniform thickness over the whole 150mm diameter wafer.

Tantalum target is 99.9% pure with main impurity being neighbouring transition metal, niobium. Active target diameter is 200mm, which at 500W power, (forward net power is kept constant) gives 1,6W/cm^2. Argon gas purity is 99.9999%. Chamber pressure was regulated by argon flow (15 to 30 sccm in these runs) through the mass flow controller (Tylan 2901) and butterfly type throttle valve in close position. There is no feedback from pressure meter to either the throttle valve or the mass flow controller, but once set, pressure was very steady at the set pressure varied from 0.4 to 0.75 Pa.

Vacuum system consists of Pfeiffer turbodragpumps as high vacuum pumps and four chamber diaphragmpumps for fore vacuum. This guarantees oil free operation, which is necessary to avoid contamination in semiconductor industry. Turbopumps are placed horizontally on back side of the sputtering chambers as seen in fig. 2. Chambers and vacuum accessories are mainly made of stainless steel, but system is build using O-rings. Baking is not possible, but hot water is used on chamber walls to prevent water vapour condensation, when chamber is open for maintenance. Resulting base vacuum is limited to low 10^{-5} Pa range. When substrates (100mm, (100) silicon wafers) are loaded into the loadlock, it is pumped and vented three times with dry nitrogen, to get rid off atmospheric contamination.

Samples were annealed in a vacuum of 10^{-6} Pa at tempera-tures from 600 to 800 °C for 30 min. Samples were then characterised by x-ray diffraction (XRD) and Rutherford backscattering (RBS). Surfaces of as sputtered samples were viewed with optical microscope and atomic force microscope (AFM). Scanning electron microscopy (SEM) was also used on both planar and correctional samples.

3. Results and discussion

Figure 3 shows a typical x-ray diffraction pattern of a rf-sputtered tantalum film on Si. Narrow peaks as well as the very strong peak at 69.2° (Si (004)) originate from silicon single crystal substrate. As can be seen there are difficulties to recognise the phases formed during deposition, due to small grain size, thin film and substrate peaks overlapping. The possibility of incorporating nitrogen into the target during manufacturing was suspected, because peak at 33.8° (see fig. 3) looked like originating from the Ta$_2$N-phase (100). But it could also be (002)-peak from the β−Ta, the tetragonal tantalum phase. It has been reported earlier that sputtering yields both α- and β-tantalum phases, depending
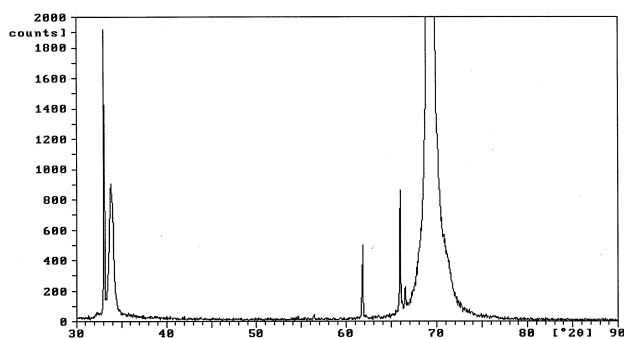

Figure 3. XRD-pattern of stationary rf-sputtered thin tantalum film on silicon, power 300W, pressure 0.75Pa.

of process conditions [3]. Also sputtered superlattice tantalum structures have been reported [4].

As x-ray structure determination was unambiguous, we deposited thicker films of tantalum (> 1μm)on silicon (both with and without HF-dip for removing native oxide) and on thermally oxidised silicon wafers. All diffraction patterns with different power (300, 500 or 800W) and on different substrates looked like in fig.4. Three strong peaks marked with X dominate the pattern. They fit closely to Ta$_2$N; (100)-, (200)- and (300)-peaks, but there is no nitrogen in the films. On sample sputtered with 800W there is clear α-Ta (100) peak, which is not seen on other samples. But also on this sample there are the three dominating peaks and several small peaks for β-Ta.

We measured resistivity by four point probe on oxide samples. When sputtering power was 500W resistivity was ~169 μΩcm and at 800W ~165 μΩcm. The little higher resistivity at 500W is most probably due to impurity corporation of lower growth rate (28 nm/min vs 53 nm/min). This resistivity value points strongly to β-tantalum as Schauer and Roschy [3] also measured ~165 μΩcm resistivity for β-Ta compared to 25 μΩcm for α-Ta. Since turbopumps don't pump water vapour very well and there was no substrate preheating, this would explain the existence of β-Ta [3]. There is work going on to determine phases in films unambiguously.
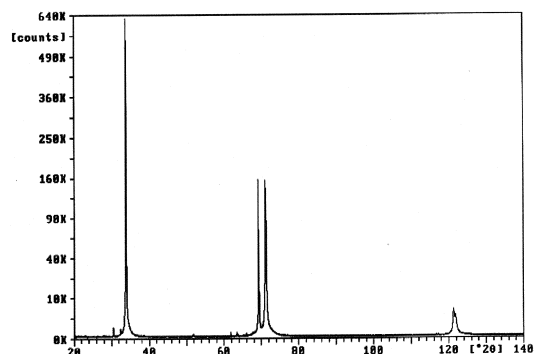

Figure 4. XRD-pattern of stationary rf-sputtered thick tantalum film on silicon, power 500W, pressure 0.5Pa. (Counts in root scale, in thousands.)

Film morphology changes, when different modes of deposition, namely stationary, swing and rotation, were used. In figure 5 there is an AFM-image of the tantalum thin film surface 100 nm thick sputtered in stationary mode. Columnar topography is clearly seen, although grain size is very small (also seen by x-ray) and uniform. This columnar microstructure is already evident on the 10 nm thick samples. There is also no detectable difference on the film morphology, if Ta-films were deposited either on single crystal silicon or on amorphous SiO_2.

However when tantalum films were deposited on rotation or swing-mode, appearance of the films was quite fuzzy as evidenced in fig. 6. Please note that vertical scale in fig. 6 is only 1/3 of that in fig. 5. Films are very flat, the R_a-values are below 0.1 nm and R_{max} are below 1.5 nm. Though these roughness values can only be considered as guidance due to small measurement areas, they are 1/3 of the stationary-mode values.

The difference between the swing and rotation modes is that in swing mode the growing tantalum film is all the time in the sputtered atom flux, but the film in rotation is most of the time away from the atom flux. Therefore it is interesting to note that settling time of atoms on growing film does not have any effect on microstructual evolution of the Ta-films. Overriding factor is the substrate movement itself.

The tantalum films were tested between copper and silicon in various temperatures for 30 min. The RBS-spectra of the as deposited and heat treated samples are shown in figure 7. Thickness of the copper layer on the sample annealed at 625 ^{o}C is thinner, therefore Ta-peak shifts towards surface. Reaction appears as tantalum movement to the surface, but most probably is the opposite, i.e. copper movement through tantalum to the silicon interface. Copper is remarkably fast diffuser and diffuses through the defects and grain boundaries, which are mostly vertical in the columnar microstructure of stationary sputtered Ta-film (see fig. 5).
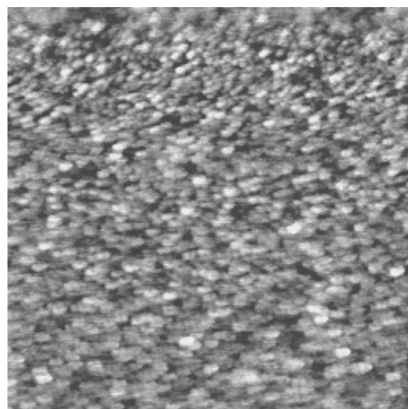

Figure 5. AFM-picture of stationary rf-sputtered tantalum film 100nm thick at 0,5Pa, 500W. Note side of the picture is 1µm, vertical scale is 5 nm and high areas are shown light, low ones dark.
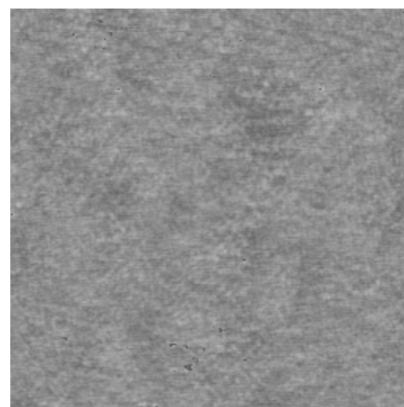

Figure 6. AFM-picture of swing-mode rf-sputtered tantalum film 100nm thick at 0,5Pa, 500W. Note side of the picture is 1µm, vertical scale is 1.5 nm and high areas are shown light, low ones dark.
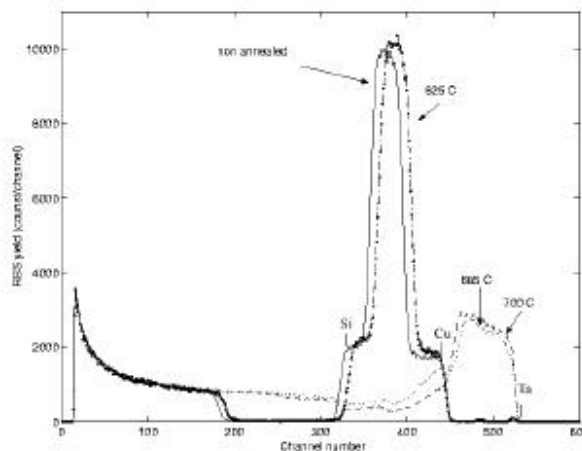

Figure 7. RBS-spectra of the Si/Ta/Cu-samples, as deposited, heat treated at 625 ^{o}C, at 685 ^{o}C and at 700 ^{o}C for 30 min. Surface positions of the elements are marked in the graph.

After the annealing at 685 °C and at 700 °C the thin film structure was completely intermixed. As surface does not stay planar (see ref. 5, fig 2 and 3) interpretation of the RBS-spectra is not unambiguous [6].

For diffusion barrier between copper and silicon these tantalum films are good to 650 ^{o}C for 30 min. anneals in vacuum. The morphology of swing and rotation mode sputter deposition gives promise for better diffusion barrier performance underlining the importance of deposition process for thin film growth and resulting film properties.

4. Summary and Conclusions

In this paper rf-sputter deposition of tantalum films was investigated. Grain size is small and columnar on as deposited films both on silicon and on SiO_2. Work is going on phase determination. The morphology of films deposited in the stationary mode was columnar and rougher than in

the swing or rotation mode deposited films. The settling time of atoms on growing tantalum films does not have effect on film morphology. As diffusion barriers stationary sputtered 100nm thick Ta-films between copper and silicon are good at 650 ^{o}C for 30 min anneals.

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