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Electrical properties of Ag/Ta and Ag/TaN thin-films

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ABSTRACT

Although wide band gap devices (WBG, e.g. GaN and SiC) are eminently suitable for high temperatures and harsh environments, these properties cannot be fully taken advantage of without an appropriate interconnect metallization. In this context, silver shows promise for interconnections at high temperatures. In this work, the thermal stability of Ag with two barrier metals – Ta and TaN – was therefore investigated. Metal stacks, consisting of 100 nm of silver on 45 nm of either Ta or TaN were sputter-deposited on the substrate. Each metal system was annealed in vacuum for one hour at temperatures up to 800 °C. Both systems showed stable performance up to 600 °C. The system with Ta as a barrier metal was found to be more stable than the TaN system. Above 700 °C, silver agglomeration led to degradation of electrical performance.

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1. Introduction

Wide band gap (WBG) materials and devices have been the subject of several research projects world-wide. The work so far has mainly concentrated on those material properties that give WBG devices a far better performance than Si devices under similar operating conditions. It is now time to investigate how the specific process steps and material combinations can be developed and optimized so as to widen the field of WBG applications towards reliable operation at very high temperatures and harsh environmental conditions.

The durability and reliability of metal–semiconductor contacts and interconnects are factors that presently limit the high-temperature operation of the otherwise singularly suited WBG-devices [1,2]. In view of this, Ag is found to have many interesting properties, such as low resistivity, excellent high-frequency properties (terahertz) [3], a relatively high melting point, high electromigration resistance and a low diffusion coefficient in SiO₂ in comparison with Cu [4–6].

Earlier research work on Ag contacts has focused on TiN and TaN as barriers below electron-beam deposited Ag films [4]. These results show that TaN diffusion barriers are stable up to 650 °C for 30 min during vacuum annealing. Barrier failure and de-wetting of Ag was observed beyond 700 °C [4]. Moreover, Ag and Ta do not form any intermediate phases or compounds upon heat treatment up to 900 °C, according to published phase diagrams [7].

In view of the foregoing, we have investigated the thermal stability of two metallization systems consisting of Ag on SiO₂ with an interposed layer of Ta or TaN as a diffusion barrier [8]. Contrary to previous work, all metal layers were sputter deposited sequentially in a multi-target system without breaking vacuum so as to minimize oxidation of the layers. This was judged essential in order to avoid possible negative influences on the barrier properties from oxides at the interfaces.

2. Materials and methods

The substrates used in the experiments were (100)-oriented p-type silicon wafers with a resistivity of 16–24 Ω-cm and a diameter of 100 mm. After subjecting the wafers to a cleaning procedure in SC-1 and SC-2 [9], approximately 550 nm of SiO₂ was thermally grown at 950 °C in a pyrolytic steam ambient using a vertical furnace manufactured by Koyo.

The oxidized wafers were transferred into the sputtering chamber of a Lesker magnetron system using a semi-automatic load-lock. The base pressure prior to deposition was 1×10^{-6} Torr. For deposition of Ta and TaN a 100 mm diameter target of 99.99% purity was used. Ag was deposited from a smaller sized target, 50 mm in diameter, with a purity of 99.99%.

Two different metal stacks consisting of 100 nm of Ag on 45 nm of either Ta or TaN were deposited on the substrates. Respective layer thicknesses were selected so as to avoid an extensive overlap between the Ag and Ta signals in the RBS spectra. Both bi-layer structures were deposited. Consecutively without breaking the vacuum. No external heating was applied to the substrate during

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deposition. The magnetron was operated in a pulsed DC mode at a power level of 800 W and a pulse frequency of 250 kHz for the Ta and TaN depositions. A pulse frequency of 100 kHz at a power level of 80 W was used for the Ag deposition due to the smaller target size.

During deposition the wafer is mounted horizontally in a face-up configuration on a substrate holder centred 18 cm below the targets that are mounted at an angle of 45 degrees with respect to the substrate normal.

Pure Ta was deposited at a pressure of 4 mTorr, whereas the two differently deposited TaN layers were obtained at 3.9 and 4.48 mTorr.

Two different N_2 -to-Ar flow ratios of 0.28 and 0.16 were used for the reactive sputter-deposition of the TaN layers (see Table 1). All layers were deposited with an Ar flow of 50 sccm and constant pumping speed.

After deposition the wafers were cut into square samples with an area of approximately 1 cm^2 .

The samples were subsequently annealed in a vacuum furnace, at pressures below 1×10^{-6} Torr, for one hour at different temperatures up to 800 °C.

The composition of as-deposited and subsequently annealed films was characterized by Rutherford Backscattering Spectrometry (RBS) and Time-Of-Flight Elastic Recoil Detection Analysis (TOF-ERDA).

The TOF-ERDA was used to determine the nitrogen content of the TaN films since the technique provides simultaneous and quantitative elemental depth distributions for light-mass elements in heavy matrices.

RBS and TOF-ERDA were performed at the Tandem-laboratory at Uppsala University employing 2 MeV He^+ (backscattering angle 170 degrees) and 36 MeV I^{8+} ions (recoil detection angle 45°) respectively.

The evaluation of RBS and TOF-ERDA data was supported by the software packages SIMNRA [10] and CONTES [11] respectively.

The crystal structures were analyzed by X-ray Diffraction (XRD) using a Philips Xpert MRD instrument, operating in the theta-2-theta mode and equipped with a Cu $K\alpha_1$ radiation source.

The layer thicknesses were estimated from RBS, cross-sectional SEM (LEO FEG 1550) and surface profilometry (Dektak 150) data. In combination with the thickness data, four-point probe measurements were used to determine the resistivity as a function of the annealing temperature.

3. Results

As-deposited layers of Ta on SiO_2 were analyzed by XRD. Only the high resistivity β -Ta phase was observed. TOF-ERDA and XRD analysis of as-deposited TaN layers revealed that these layers were polycrystalline stoichiometric mono-nitrides. The TaN layers exhibited resistivity values in the range of 300–400 $\mu\Omega\text{ cm}$, consistent with reported data for fine-grained stoichiometric fcc-TaN [12]. Annealing of TaN layers up to 800 °C marginally affected the resistivity.

All samples were characterized before and after annealing. TaN samples deposited with different nitrogen flow rates all showed the same behavior.

Fig. 1. Sheet resistance as function of temperature for Ag/TaN and Ag/Ta structures.

The measured sheet resistance of as-deposited and subsequently annealed Ag films on Ta or TaN barrier layers is shown in Fig. 1. The calculated resistivity of the as-deposited Ag-films is around $2.6\text{ }\mu\Omega\text{ cm}$, which is within the expected range considering the layer thicknesses and the small grain size as shown in Fig. 2a and b.

The sheet resistance decreases slightly after annealing up to 600 °C and 700 °C for Ag/TaN and Ag/Ta, respectively, Fig. 1. At 700 °C, a slight increase in resistance is observed for the films deposited on TaN. However, after annealing at 750 °C the sheet resistance increases dramatically for these films. On the contrary, the sheet resistance of the Ag/Ta films only marginally increases after annealing at 750 °C. An abrupt increase is, however, observed after annealing at 800 °C. After the 800 °C anneal, the sheet resistance increased to more than $40\text{ }\Omega/\text{sq}$ for all films, thus indicating that conduction now occurs mainly in the barrier metal layer.

SEM micrographs show an increase of the grain size after annealing up to 600 °C and 700 °C for Ag on Ta and TaN, respectively, Figs. 2 and 3a. After annealing at 700 °C of the Ag/TaN films, SEM micrographs indicate the presence of small holes in the Ag layer, which indicates the onset of agglomeration, Fig. 3b. After heat treatment at 750 °C, SEM micrographs indicate the presence of larger holes in the Ag layer, thus revealing more of the underlying TaN barrier layer compared to the case at 700 °C.

The RBS analysis of the Ag/TaN films indicates no diffusion or change after annealing up to 600 °C. After heat treatment at 700 °C, however, a signal originating from Ta at the surface is visible, Fig. 4a. For the Ag/Ta films, RBS analysis shows no diffusion or change up to 700 °C. A signal indicating the presence of Ta at the surface shows up for the sample annealed at 750 °C, Fig. 4b. After an 800 °C anneal almost all Ag is lost on all samples, see Fig. 4a.

Fig. 5a presents θ -2 θ XRD diffractograms of the Ag/TaN samples, as deposited and after annealing at 600 °C and 800 °C, respectively. The substrate Si peak has been suppressed by an off-set of 1.5° . The as-deposited and 600 °C annealed samples show the same diffraction silver peaks: Ag(111), Ag(200), Ag(220), Ag(311) and

Table 1
Fabrication parameters.

Material stack	N_2 flow [sccm]	N_2/Ar flow ratio	Pressure [mTorr]	Power [8] Ag/barrier
Ag/TaN	8	0.16	3.9	80/800
Ag/TaN	14	0.28	4.48	
Ag/Ta	0	–	4

Fig. 2. SEM micrographs of: (a) Ag/TaN structure as deposited, (b) Ag/Ta structure as deposited, (c) Ag/TaN structure annealed at 600 °C and (d) Ag/Ta structure annealed at 600 °C.

Ag(222). After the 600 °C annealing, the Ag(111) and Ag(222) peak were larger and narrower. After annealing at 800 °C the underlying numerous Ta and TaN peaks appeared at the expense of the Ag peaks. Fig. 5b shows the XRD results for Ag/Ta samples before and after annealing. The as-deposited and the 600 °C annealed samples show the same peaks: Ta(001), Ag(111), Ag(200), Ag(220), Ta(400), Ag(311) and Ag(222). The Ag(111) and Ag(222) peaks were larger and narrower after the 600 °C anneal. Numerous Ta peaks appeared after the 800 °C anneal whereas the silver peaks decreased or vanished.

Moreover, it was also observed in the RBS analysis that after annealing at 750 °C some Ag had diffused into the SiO₂ in the case of the Ag/TaN samples, while no diffusion was observed for the Ag/Ta samples.

4. Discussion

The observed decrease in resistivity between 100 °C and 600 °C can be linked to the increased grain size in the Ag film. From the SEM micrographs in Fig. 2c and d it is evident that grain growth has occurred in films that were annealed at 600 °C. As-deposited films exhibit a pebbles-like surface with a fairly uniform grain size that appears to be independent of the composition of the barrier layer. An average grain size for as-deposited films at the order of 50 nm was estimated from the SEM micrographs, Fig. 2a and b. After annealing at 600 °C a large variation in grain size is observed, Fig. 2c and d. Several grains have a dimension of several hundreds of nm. An estimate of the average value indicates a grain size of around 200 nm for Ag films on Ta or TaN barriers. No significant impact on the grain growth process could be attributed to the composition of the barrier layer.

A significant grain growth of Ag films upon annealing was also evident from Atomic Force Microscopy (AFM) measurements and XRD characterization. AFM topography measurements after annealing at 600 °C indicated that the originally smooth surface,

being characteristic of as-deposited films, had become much more uneven with some signs of hillocks.

XRD measurements of Ag-films annealed at 600 °C, Figs. 5a and 5b, clearly show that the Ag(111) and Ag(222) peaks are larger, which implies that grain growth occurred in the silver films.

Absence of a TaN (111) peak for the as deposited and 600 °C annealed Ag/TaN layers, Fig. 5a, is due to a low signal intensity arising from the fine-grained TaN-structure and the fact that the peak, located at $2\theta \sim 35^\circ$, is overlapped by the large Ag (111) signal. XRD analyses of the Ag/Ta system, Fig. 5b, however clearly show presence of crystalline β -Ta. No significant impact of the barrier layer on the surface morphology and crystalline structure (texture) of the Ag-films could be observed.

Above 600 °C, the Ag/TaN and Ag/Ta samples show different behaviors. Upon further annealing, the Ag/Ta samples follow the decreasing trend of the measured sheet resistance up to around 700 °C, while the resistivity starts to increase for the Ag/TaN films.

After annealing at 700 °C of the Ag/TaN films, RBS analysis shows a signal originating from Ta at the surface, which could also be interpreted as the consequence of diffusion. However, SEM micrographs reveal that agglomeration and void formation has started. It is therefore most likely that the Ag film is not homogeneous anymore and that minor parts of the TaN barrier layer are revealed, Figs. 3b and 4a.

The void formation after anneal at 700 °C appears to follow the grain boundaries of the Ag film. Since heterogeneous void nucleation in thin films is reported to occur through grain boundary and triple junction grooving [13] it is likely that this mechanism is responsible for the development of voids.

After annealing at 700 °C of the Ag/Ta films, RBS analysis shows the same spectra as for the as-deposited samples, indicating almost no agglomeration and absence of void formation. Furthermore, SEM micrograph, Fig. 3a, confirms that the Ag-layer is composed of grains of an increased grain size and without any signs of void formation.

Fig. 3. SEM micrographs of: (a) Ag/Ta and (b) Ag/TaN, both annealed at 700 °C. The observation of small holes indicates the onset of agglomeration.

Fig. 4a. Experimental RBS spectra obtained for 2 MeV He⁺ for Ag/TaN at room temperature (RT), 600 °C, 700 °C and 800 °C (open symbols). The full lines represent Monte Carlo simulations by SIMNRA [10]. The spectra clearly reveal beginning sample degradation (Ta at the surface) starting from 700 °C and absence of Ag at the surface at 800 °C degrees.

Fig. 4b. Experimental RBS spectra obtained for 2 MeV He⁺ for Ag/Ta at RT, 600 °C and 750 °C. The full lines represent Monte Carlo simulations by SIMNRA [10]. The spectra clearly reveal beginning sample degradation (Ta at the surface) starting from 750 °C.

Following a 750 °C anneal the sheet resistance increases dramatically for the Ag/Ta films. SEM analyses reveal severe agglomeration and void growth that results in Ag island formation and a non-continuous film. In parallel, RBS analysis shows a clear surface signal of Ta.

Fig. 5a. X-ray diffraction spectra of Ag/TaN, as deposited and after annealing at 600 °C and 800 °C.

Fig. 5b. X-ray diffraction spectra of Ag/Ta, as deposited and after annealing at 600 °C and 800 °C.

A different behavior is observed for the Ag/Ta sample since only a minor increase in sheet resistance was observed after annealing at 750 °C. This indicates that onset of Ag void formation on Ta barrier layers occur at a higher temperature than on TaN barriers. RBS analysis reveals the presence of Ta at the surface, Fig. 4b, confirming the onset of void formation. The observed difference may be due to different surface properties of the diffusion barrier layers, as also has been reported for the Ag/TiN system [14] as well as for the Cu/Ta/TaN system [15].

After annealing at 800 °C, RBS and SEM analyses show that most of the Ag film has vanished presumably via evaporation, Fig. 4a. The recorded sheet resistance is consequently very high and mainly reflects the electrical properties of the barrier layer.

In a subsequent XRD analysis of both metal-stacks several additional Ta-peaks appeared. This confirms that parts of the underlying barrier layers were revealed as a result of Ag agglomeration, Figs. 5a and 5b.

Since Ag has been considered a likely replacement for Cu as interconnect for IC metallization by the ITRS community it is appropriate to compare our findings on the temperature stability of Ag with those reported in literature for Cu.

Agglomeration of Cu at elevated temperatures was recently investigated by Yang and Chen [15] using similar types of barrier layers and annealing conditions as described above.

An increased sheet resistance of thin (50 nm) Cu layers on TaN was detected already after annealing at 600 °C. The increase was attributed to formation of intergrain voids. In our experiments, Ag films on TaN barriers showed a similar behavior after annealing at 700 °C, see Fig. 3b. The Ag films were however twice as thick (100 nm) as the Cu films. That should explain the improved thermal stability of the Ag films, since thicker films are more resistant to void formation. Thicker Cu films (200 nm) on TaN barriers also remained unaffected despite being annealed at 800 °C.

If however the TaN barrier was replaced by a Ta barrier layer, thin (50 nm) Cu layers showed no degradation in resistivity after annealing up to 700 °C. A small increase was recorded after heat treatment at 800 °C. SEM micrographs of the Cu samples revealed crystallographic voids, characteristic of grain boundary grooving, that resembled those observed in our Ag films being annealed at 750 °C.

Consequently both Cu and Ag exhibit an improved thermal stability on Ta barriers compared to TaN barriers. The improved thermal stability of Cu compared to Ag at temperatures in the vicinity of 800 °C, is most likely a direct result of the higher melting point of Cu (Cu: 1083 °C, Ag: 961 °C). Yang and Chen [15] suggested three explanations for the improved thermal stability of Cu films on Ta barriers:

Out-diffusion of Ta to the surface and formation of a TaOx cap layer on top of Cu could restrict mass transport along the surface and movement of grain boundaries.

This explanation is probably not valid for our experiments with Ag/Ta metal-stacks since our RBS analysis detected no Ta at the surface after annealing at 700 °C. Recent experiments by us with Ag-films capped with TaN show improved thermal stability and that onset of Ag agglomeration now occurs at higher temperatures. Formation of a capping layer would therefore improve thermal stability.

Movement of Ta atoms could result in stuffing along the Cu grain boundaries. As a result, the grain growth rate of Cu on Ta is decreased, thus suppressing agglomeration. The average grain size of Cu on TaN was found to be two times larger than on Ta. On the contrary, similar grain sizes were observed for all Ag films irrespective of being deposited on Ta or on TaN barrier layers, Fig. 2c and d. No impact on the morphology from the barrier layer was detected. Within the detection limit, RBS analysis indicated no diffusion of Ta

towards the Ag surface. Grain boundary stuffing of Ag films by Ta is therefore not observed after vacuum annealing. This mechanism can therefore not be responsible for the improved thermal stability of Ag films on Ta barriers.

An additional factor preventing Cu-agglomeration on Ta could be due to a different interaction between Cu–Ta and Cu–Nitride since a similar behavior was reported for the Cu–W system [16].

Whether a similar interaction mechanism is responsible for the improved thermal stability of Ag on Ta needs to be further investigated.

5. Conclusion

Our experimental results for Ag on Ta and TaN indicate stable properties in terms of resistivity up to at least 600 °C. At 700 °C Ag/Ta is stable while Ag/TaN starts to show early void formation which occurs at 750 °C for Ag/Ta. This work shows that Ag on barrier metals like Ta or TaN can be used as a stable high-temperature metallization up to at least 600 °C. Future work targeting stacked barrier layers that encapsulate the Ag interconnect may provide a possibility to further increase the thermal stability and integrity of Ag interconnects.

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