DEPOSITION AND TREATMENT OF TITANIUM BASED BARRIER LAYERS BY MOCVD

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Three different approaches for producing binary or ternary TiN/Ti-Si-N films by MOCVD were developed and investigated:

(1) plasma treated TiN using thermal precursor decomposition for barrier against Cu diffusion
(2) ternary Ti-Si-N films using thermal or plasma post-treatments of the TiN with silane
(3) Ti-rich TiN using PECVD as adhesion promoter between TiN barrier and CVD Cu.

The barrier efficiency of the different treated TiN barriers was tested using a pn-diode structure and measuring the leakage current. The barrier performance of the standard TiN was not impaired by the adhesion layer. The additional N_2 plasma treated TiN showed the best stability to Cu diffusion.

The TiN barrier layers were produced by a multistep process consisting of alternating pyrolysis steps and plasma treatment steps. The process parameters for the deposition step are 350°C substrate temperature and 133 Pa chamber pressure. In order to get a higher barrier performance, an additional N_2 plasma step was introduced after each cycle. For the second approach the TiN layer was exposed to a silane flow or a silane plasma after 4 of 8 cycles. The adhesion layer between the TiN barrier and CVD Copper was produced by a plasma enhanced deposition process. The deposition temperature was at 270°C substrate temperature. The used plasma with a RF power of 100 W additionally contained H_2. The copper CVD was immediately carried out after a short cooling down in the loadlock chamber. The copper precursor CupraSelect™ is thermally decomposed at 170°C substrate temperature at a chamber pressure of 2.66 kPa. After the copper deposition the wafer was post-treated at 390°C in Ar atmosphere. The adhesion was tested with the X-cut tape test before and after the heat treatment. The function of the adhesion layer was tested by CMP also.

The barriers were investigated by RBS to characterise the composition and the N/Ti ratio. The standard TiN was also analysed by ERD to determine the H content. The AES analysis was used for investigation of the interaction of Cu and Ti from the adhesion layer.

The barrier property of different TiN and copper stacks was assessed using a pn-diode as electrical test device. The wafers run through cycles of measurement and thermal stress was conducted in hydrogen (1 at) for 30 min at 350°C and 60 min at higher temperatures increased by 50°C steps.

An additional N_2 plasma after the standard plasma treatment introduces more N in the layer. The electrical resistivity is increased at 260 µΩcm, also the thickness by 20 %. With RBS there was a higher N/Ti ratio of 1.4 determined compared to the standard TiN with the ratio of 1.1.

For the adhesion layer the analysis by RBS shows a shifted N/Ti - ratio to Ti-rich compared with the standard TiN. The amounts of impurities for C and O are higher. Fig. 1 shows a standard TiN layer (5 nm) with a thick TiN adhesion layer (10 nm) and CVD-Cu. The reason for the more light appearance of the adhesion layer is its lower density. In the high resolution TEM picture any crystallographic planes are visible. The structure consists probably of TiN nanocrystallites in an amorphous-like Ti-N-O-C matrix. There is no interlayer visible between Cu and the adhesion layer.

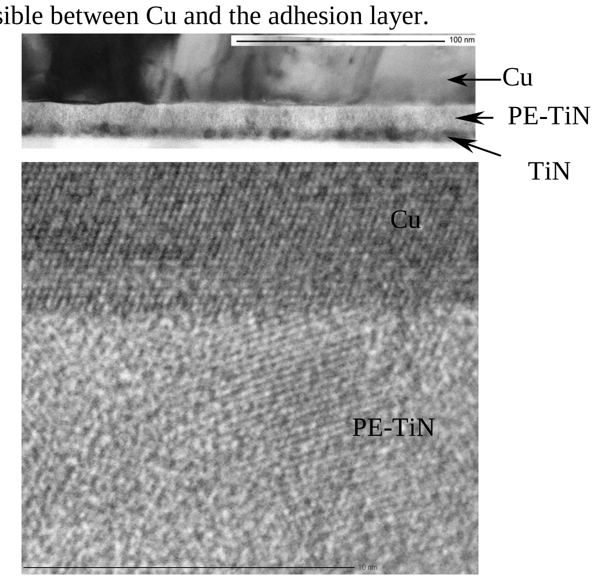

Fig.: 1 XTEM of 5 nm TiN/10 nm PE-TiN/ Cu (upper)
HRTEM of the interface PE-TiN/Cu (lower)

The electrical measurements do not show an improvement with respect to the failure temperature for the additional treatments. For all variants the diodes were stable up to 450°C. Only the number of the failed diodes after 500°C and 600°C was different. These diodes are randomly distributed over the wafer surface. The number of the destroyed diodes increases with higher thermal load.

The distribution of the leakage currents is divided in classes (1 magnitude per class) for the failure temperature (500°C) and 600°C. Class 1 includes all diodes which have leakage current densities S_s 0.1 nA/cm^2 ≤ Ss ≥ 1 nA/cm^2. Standard TiN without and with adhesion promoter show the same behaviour. If a diode is failed their leakage current rises by several orders of magnitude. With higher temperatures the number of diodes is redistributed to classes with higher leakage current densities.

The redistribution of the diodes in higher classes is also recognizable for the barrier with the silane treatment, but 60 % of the intact diodes at 500°C remain intact. The TiN with an additional N_2 plasma treatment shows different behaviour. The split in the distribution is not so evident, the leakage current increases only by one order of magnitude for the diode failure. At 600°C the number of the intact diodes does not change compared to 500°C.

CONCLUSION

Both treatments of the standard TiN with an additional N_2 plasma and a silane soak/plasma are possible ways to improve the barrier performance. The failure temperature of the pn-diodes was at 500°C, but the number of the intact diodes after 600°C was significantly increased. The Ti-rich adhesion layer does not impact the barrier properties of the TiN. The Copper layer shows excellent adhesion to this double-layer after a heat treatment. This could be proven by applying CMP without adhesion failure.