Requirements and challenges on an alternative indirect integration regime of low-k materials

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Abstract

An alternative indirect integration regime of porous low-k materials was investigated. Based on a single Damascene structure the intra level dielectric SiO_2 or damaged ULK was removed by using $HF:H_2O$ solutions to create free standing metal lines. The free spaces between the metal lines were refilled with a spin-on process of a low-k material. The persistence of barrier materials and copper against HF solutions, the gap fill behavior of the used spin on glass on different structure sizes and the main challenges which have to solve in the future are shown in this study.

1. Introduction

The direct integration of porous low-k materials (ULK) is one of the most critical challenges in the semiconductor industries. Porosity and organic species lead to a high sensitivity of the dielectrics. So it is necessary to deal with problems like absorption of process media, mechanical degradation or carbon extraction caused by plasma etching processes. Excellent techniques like pore sealing, low stress mask materials or plasma enhanced in situ repair of damaged material were developed to solve these problems. But to overcome all of these problems is currently not possible. For this reason a new approach of ULK integration was investigated in this study. The so called alternative indirect low-k integration is based on a sacrificial approach. In studies showing air gap technologies the possibility of successfully removal of sacrificial materials was already demonstrated [1]. Gap fill processes were developed and investigated, too [2]. Consequently a combination of both seems to be a solution for an indirect integration of ULK materials. As it is seen in figure 1, a Damascene structure with an inter metal sacrificial dielectric is the start point of the concept. The sacrificial material is removed by a wet etch process with HF/H_2O solution. After removing the sacrificial material the gaps between the free standing metal lines were filled with MSQ via spin on deposition, followed by a chemical-mechanical planarization (CMP). Consequently the concept requires different conditions of the included materials. So the persistence against HF must be given for all metals, barrier material and copper, and should be not destroyed during the HF attack to remove the sacrificial material. The wetting behavior of the MSQ during the spin on process is of great interest, too. Usually an interface of ULK and Cu should by prevent, by barrier materials. However, the concept closes with a CMP. Material formations at the top of the metal line should be removed by the planarization process.

2. Experimental

Investigations were executed to qualify the persistence against $HF:H_2O$ solutions of Cu, TaN and TiN. These blanket wafers were fabricated and underwent an etch attack in $HF:H_2O$ solution by using different HF-H_2O-proportions and etching time. The comparison of film properties, here roughness and sheet resistance before and after the etch attack leads to a qualitatively value about the HF-persistence of the metals. The MSQ used for the gap fill process was a commercial spin on material (k = 2.2) of SBA Materials. The feasibility study of the integration concept was done on different sample layouts. First, structures with 800 nm line space, SiO_2-sacrificial and SiC etch stop as it is seen in figure 1 were produced. Second, patterned samples with damaged ULK sacrificial, TEOS etch stop and line spaces down to 30 nm were provided by GLOBALFOUNDRIES.

3. Results and Discussion

3.1 Preliminary Investigations

One of the main questions of the integration concept was the persistence of Cu and barrier materials against HF solutions. So deposited materials Cu, TiN and TaN were underwent a HF attack by different time, one, two and three minutes which should be enough, because the etch rate of SiO_2 in BHF or 12% HF solution was determined to approximately 300 nm/min and 500 nm/min, respectively. The effect on the metal surfaces caused by the etch attack were investigated for buffered HF (BHF) and 12% HF in water ($HF:H_2O$, 3:25). A significant increase of sheet resistance (Fig. 2) is only visible for TiN and TaN by using 12% HF. In the case of BHF no influence on barrier materials was measured. The small increase for Cu (~ 3%) could affect by the oxidation of the surface during the handling of the samples. The roughness investigations are shown no effect on the metal surfaces, too.

Therefore, BHF was used for removal of the sacrificial dielectric in patterned samples.

The material MSQ was spun by a dynamic dispensation. So the spin on parameter angle acceleration, angle velocity and time were determined to 1500 rpms^{-1}, 1000-1500 rpm and 5-15 s. By using the proposed curing parameter of the material supplier (450°C, 90 min, in N_2 atmosphere) a refractive index of the material leads to values of 1.27. Indicated to reduce the thermal stress to the metal lines during the porogen removal curing tests with temperatures of 250°C and 350°C were investigated, too. As it is seen in the FTIR spectra (Fig. 3) of the samples created after the curing process, the temperature at 450°C are absolutely necessary. Compared to the low temperature the cross linking is much more better pronounced at 450°C since 250°C and 350°C, respectively. This is clearly recognizable by the missing OH-peak in the range of 3000-3750 1/cm at 450°C. Also incomplete porogen removals could be recognized at the lower temperatures in the wave number range of CH_x-absorption.

Additional wetting test with the spin on material showing contact angles lower than 10 degree, implying therefore a very good wetting of the liquid MSQ on the surfaces TiN, TaN, Cu and SiC. So problems during the gap fill process are not expected at this time.

3.2 Follow-up the Concept

After fabrication of a Damascene structure the first step of the concept is the removal of the sacrificial material. For this samples with 800 nm line width were produced and etched in BHF for different time. It was noticed that 5 min treatment in BHF is necessary to remove the SiO_2 completely between the metal lines. Moreover, the FIB cut images did not reveal any attack on Cu or the barrier (see Fig. 4b)). For the samples with more than one magnitude lower line distance, here 50 nm and 30 nm, the sacrificial material was damaged ULK and TEOS as etch stop layer. Therefore the described wet etch process with BHF was not applicable. Since, TEOS is etched with very high etch rates by BHF, it was necessary to dilute the etch solution further. However, stronger dilution led to destruction of Cu lines due to oxidation of Cu. To prevent the assumed oxidation of Cu an oxidation inhibitor, citric acid, was added to the solution. Only with high amount of the inhibitor (50%) in the solution it was possible to remove the sacrificial material without any particles or destructions on the patterned sample surface (see Fig. 5).

The free spaces between the metal lines were filled with spin on glass – MSQ. Independent of the used spin on parameters, good filling behavior was observed. In Figure 4c) the results for 800 nm gaps are shown. For each sample big line space as well as 30 nm line widths were filled without any defects (see Fig. 6). As the wetting tests suggested the spin on material is well suited for filling small and larger structures in a wide range of spin on parameters without holes or defects.

After the deposition process the MSQ has to be annealed for the formation of the network and the pores due to the porogen removal. All samples were treated in an annealing process at 450°C for 90 min, in N_2 at atmospheric pressure. FIB analytics on cured samples reveal the deficiency of this integration concept. The picture (Fig. 4d) is showing a cross section of a cured sample. The materials Cu, TaN and ULK are clear visible. Around the copper line an additional material seems to have emerged. In some structures the Cu was completely removed from the line (Fig. 7). To clarify the composition of this undefined material additional analytics like EDX, EELS and diffraction images were executed and prepared. The material mapping of this strip shows a high amount of copper and oxide (Fig. 9), since the diffraction image shows a structure which corresponds closely to Cu_2O (Fig. 10). During the annealing of MSQ a rearrangement of the network is occurring, hydroxyl groups will be removed. This mechanism of cross-linking is mainly explained by the condensation of silanols with the byproduct water [3, 4]. These processes promote the oxidation of Cu and Cu^{2+} ions will incorporated in the network. Therefore, Cu surfaces must be protected by a cap layer [J. Calvo et al., “Porous Ultra Low-k Material Integration Through An Extended Dual Damascene Approach: Pre-/ Post-CMP Curing Comparison” Advanced Metallization Conference, in press (2015)] to hinder the incorporation in the dielectric network and the formation of Cu_2O.

4. Summary

In this study a new ultra low-k integration concept based on a sacrificial approach was investigated. Principle experiments were done to show the compatibility of the materials to the sacrificial dielectric removal. A gab fill process was developed to fill the spaces between the metal lines. These experiments have shown excellent results regarding to the gap fill behavior also for 30 nm gaps. The mean challenge at this moment is the formation of Cu_2O during the curing process of the MSQ. This accentuates the need for a cap layer if such indirect ULK integration concept should be successful.

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EFRE

Europäischer Fonds für regionale Entwicklung

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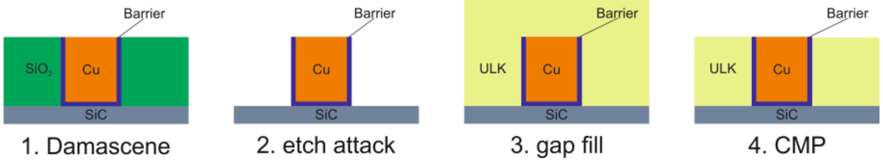

Fig. 1 process flow of the alternative indirect integration concept of ultra low-k. Starting with a single damascene structure a wet etch creates free standing metal lines, which will filled with ULK via Spin On followed by chemical-mechanical polishing

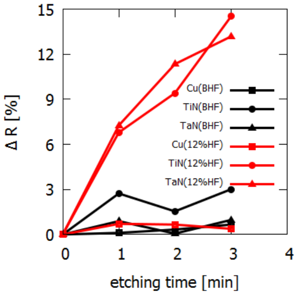

Fig. 2 Relatively changes of sheet resistance affected by an etch attack with BHF (black) and 12 % HF (red) on the materials Cu (square), TiN (circuit) and TaN (triangle)

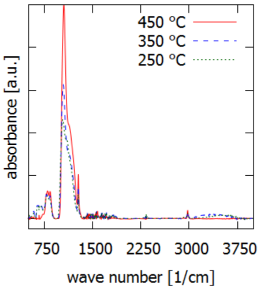

Fig. 3 FTIR spectra of ULK films cured at different temperatures. The spectra are normalized to the film thickness. The cross linking becomes better by increasing temperature, visible on the OH-peak

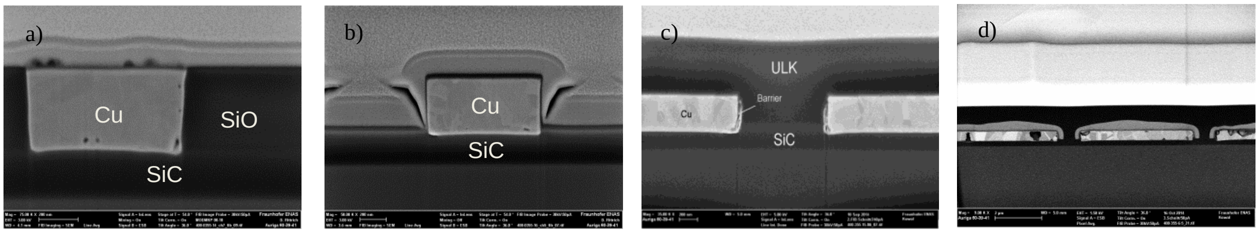

Fig. 4 single process steps of the concept: a) Damascene structure with SiO$_2$ sacrificial layer and SiC etch stop; b) sacrificial layer removed by BHF, Cu und TaN are not affected, (the material around the metal line is Pt needed for the FIB cut); c) gap fill; d) cured sample, the destruction of the copper lines and the formation of an additional material are clear visible.

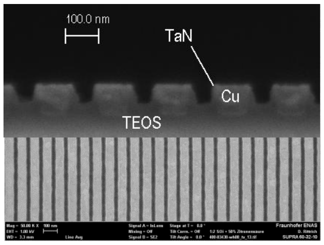

Fig. 5 removal of the sacrificial layer of 50 nm structure; cross section and top view

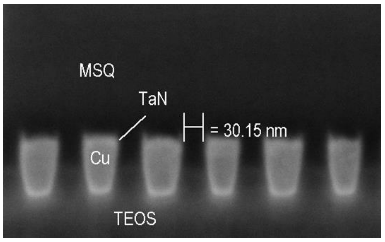

Fig. 6 excellent gap fill process without any defects in the non cured MSQ, defect free TaN layer is visible

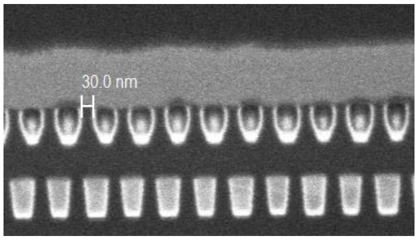

Fig. 7 cured sample with 30 nm line space. The formation of Cu$_2$O caused by the curing above the metal lines is visible

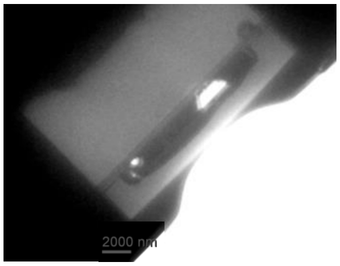

Fig. 8 TEM lamella of a cupper line after the curing process

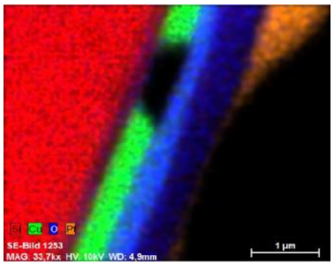

Fig. 9 Material mapping of a TEM lamella with the materials Si (red), O (blue), Cu (green) and Pt (orange)

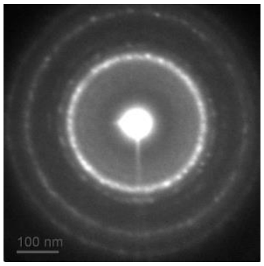

Fig. 10 diffraction images of the material formed during the curing process, the structure corresponding with Cu$_2$O