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6. Effect of Additive in Barrier CMP Slurries on the Polishing Selectivity of Low-k Layers

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The effect of saccharide based additive in Barrier CMP slurry was investigated to control the removal rate and selectivity of TEOS and SiOC films for Cu/Low-k integration applications. We have developed various slurry compositions to achieve desired polishing selectivities. In the case of polishing a dielectric stack that has a Low-k layer with cap TEOS, we have prepared several types of slurry variation available to achieve desired results. The polishing properties of the obtained slurries were evaluated to exhibit excellent planarization on patterned wafer.

1. Introduction

CMP (Chemical Mechanical Polishing) is an indispensable process step in semiconductor device fabrication, especially the Cu wiring and interconnect formation. For preventing Cu ion migration into interlayer dielectrics (ILD) films, a barrier film composed of Ta/TaN is used to isolate the Cu from the surrounding ILD film. Therefore, in the portions except those corresponding to Cu-embedded wirings, the exposed barrier film must be removed by CMP. However, since the barrier films is harder than Cu, it is difficult to achieve significant removal rate. Accordingly two steps polishing method has been proposed, which includes 1st polishing step of removing Cu and 2nd one of removing barrier film, as shown in **Fig. 1**.

Figure 1 shows a cross sectional view on various stages of Cu interconnect formation in CMP process. **Fig.1(a)**: the wiring cross section before polishing, **(b)**: the state after the 1st polishing step where excess Cu film is removed, **(c)**: the cross section after 2nd polishing step where excess barrier Ta film is removed, **(d)**: the cross section after over polishing after Barrier CMP to achieve the desired interconnect thickness.

Figure 2 shows the definition of terms as for planarity. The barrier film is not shown. Dishing is likely to occur in a wide wiring portion, and signifies a state where Cu film in wiring portion is over polished so that the central part thereof is concaved (red arrow in **Fig.2**).

Erosion tends to occur in high density pattern, and signifies a phenomenon that the ILD film is over polished and becomes thin. In a conventional polishing compound, the increase of dishing and erosion in Cu embedded wiring can give rise to problems that cause lower planarity.

Barrier CMP requires that Ta / TaN, Cu and ILD films are polished simultaneously during planarization process. Ta layer is hard to be polished. However, by adding hydrogen peroxide to the slurry a thin oxidized layer is formed on the Ta surface. Mechanical abrasion removes the oxidized layer, then Ta layer can be polished uniformly. Unless enough amount of hydrogen peroxide is present in the slurry to promote the formation of a thin oxidized layer on the surface, fine crack and inhomogeneous polishing occur on the Ta surface. Cu is polished chemically and its removal is promoted by the effect of oxidizer and a chelating agent in the slurry. On the other hand, ILD film is polished mechanically by the action of abrasive present in the slurry. Colloidal silica is typically used as the abrasive for polishing ILD film in barrier slurries. However the use of CeO_2 based slurries

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has been increased for a polishing oxide layers for STI (shallow trench isolation) process in recent years. In this case removal rate of oxide film is accelerated by chemical interaction between CeO_2 abrasive and silica film. It is well known that CeO_2 has interaction with SiO_2 which has the different surface potential [(1)]. This suggests that introduction of chemical effect by additive in barrier slurry can be useful in controlling the removal rate and selectivity of oxide films during Barrier CMP process.

Recently to meet the demand of the reduced dielectric constant, Low-k material such as Black diamond™ (SiOC) has been introduced as ILD. Due to the inferior mechanical properties of typical Low-k material, it is required that a silicon dioxide film is deposited on the Low-k material as a protection layer. Typically, plasma CVD process with TEOS (tetraethoxysilane) as a source material is used. Polishing at low pressure is required due to the fragile nature of the Low-k film. Also, polishing selectivity between different types film materials are needed to adapt to variety of film design. So it is desired that the required removal rates are achieved at 7 k or 14 kPa (1 or 2 psi) as a down force and polishing selectivity can be arbitrarily controlled.

Conventionally, the removal of ILD film during successive Cu removal and Barrier CMP process including Ta removal and ILD over polishing (**Fig.1**) is attributed to the mechanical action. Recently, we have found that the removal rate of SiOC (carbon doped silicon oxide) film during CMP can also be controlled by the chemical effect of the CMP slurry in addition to the mechanical action.

In Cu CMP process several researchers have investigated the relationship between slurry pHs and their polishing properties [(2) (3)]. However there are only very few information available on the influence of slurry pH and chemical effect to the polishing behavior of barrier slurries on TEOS and Low-k films. In recent times the requirement for ILD loss has been getting smaller as the technology node becomes narrower. Therefore the development of a barrier slurry with excellent control over the removal rate of ILD films becomes very important.

2. Experimental

Barrier slurries were produced by mixing abrasive and chemicals. Slurry pH was adjusted by adding alkali hydroxide while keeping the acid concentration in the slurry to be constant. Colloidal silica was used as an abrasive in the slurry. Hydrogen peroxide solution for oxidizer was mixed just before polishing wafers. Polishing experiments were carried out using APPLIED MATERIALS Mirra Polisher. The wafers (Φ200mm) were polished on IC pad provided by Rohm and Haas. Down force of 7k and 14 kPa (1 and 2 psi) and

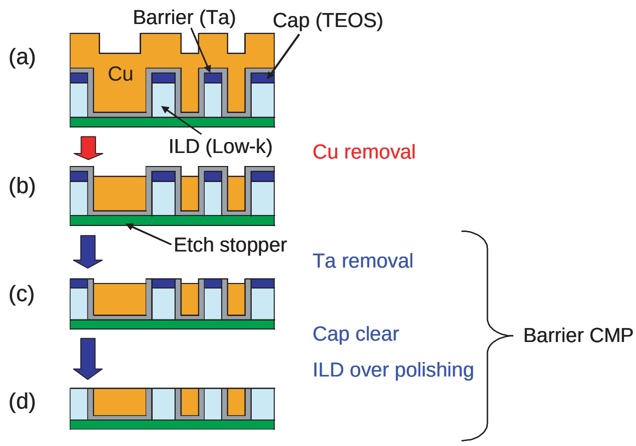

Fig. 1 CMP process.

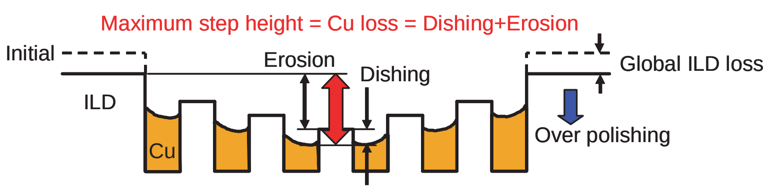

Fig. 2 Definition of terms.

Platen/Head rotation speed of 103/97 and 143/137 rpm were applied in this work.

The removal rate was calculated from the thickness change of the film before and after polish. The removal rates were measured for Ta and Cu wafers by sheet resistance measurement, and they were measured for TEOS and SiOC films by optical measurement. Black diamond™ wafer was used for evaluating the polishing behavior on Low-k material. It is one of the carbon doped oxide which is produced by CVD (chemical vapor deposition) with TMS (tri-methylsilane). Its k value is around 2.7 and lower enough compared to SiO_2 whose k value is around 4.

Polishing performance was evaluated using patterned wafers for SEMATECH 800Az which can also be used for monitoring the electrical properties after polishing. Planarity was measured by surface profiler (KLA tencor HRP). Dynamic light scattering particle size analyzer was used for the evaluation of particle size distribution and dispersion stability of the slurries.

3. Results and Discussion

As shown in **Fig. 3**, the slurry pH affects on the removal rates of TEOS and SiOC films. The removal rate in acidic condition was relatively high for TEOS film and was low for SiOC. On the contrary, in basic condition the removal rate was very high for SiOC film, especially at range of around 10, and was low for TEOS. TEOS film and SiO_2 abrasive have a small charge in acidic solution and a negative one in neutral to basic. We estimate that

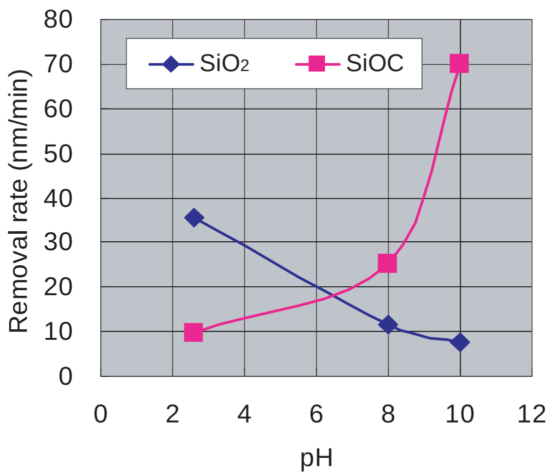

Fig. 3 Influence of pH on removal rates of TEOS and SiOC films. Down force: 14 kPa Rotation speed: Platen/Head = 103/97rpm

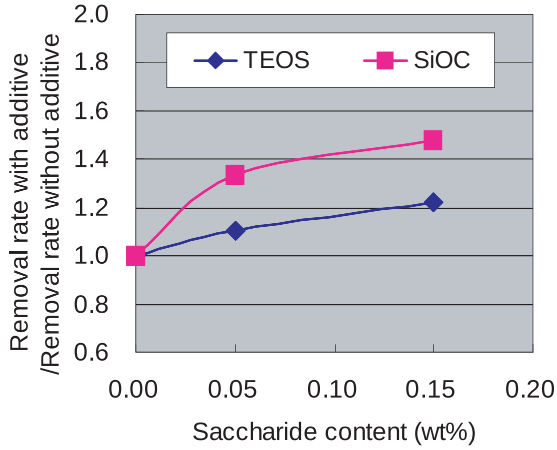

Fig. 4 Effect of saccharide content on removal rates of TEOS and SiOC films. Polishing condition is the same as Fig.1

the removal rate of TEOS film with SiO_2 abrasive was decreased in neutral to basic because the static repulsive force became strong by negative charges of both compounds. As a result, the reason for the high removal rate of SiOC film in basic condition might be attributed to chemical reaction.

Recently, the pH influence for polishing Low-k material; SOD (spin on dielectric) of MSQ (methylsilsesquioxane) was reported [4], showing that the removal rate of Low-k material in acid solution is much higher than in basic. The result might indicate that polishing performance of Low-k material by CVD with TMS is different from that of Low-k material by SOD of MSQ. Additionally, the difference of the polishing behavior between TEOS and SiOC films might depend on their chemical reactivity.

The above information promoted us to study the effect of an additive for modification of polished surface circumstance, especially focusing on chemical interaction. After screening several compounds, we have found a novel additive based on saccharide. The removal rate of TEOS and SiOC films increase with the saccharide content as shown in **Fig. 4**, indicating that SiOC film is heavily influenced than TEOS one probably due to the higher chemical activity on the surface.

Generally a larger abrasive causes higher removal rate than smaller abrasive while polishing ILD film. In this study it was confirmed by particle size analysis that there is no difference in the mean particle size of the abrasive due to the introduction of saccharide additive in the slurry. This probably indicates that the increase in removal rate observed here under the presence of additive do not mainly stem from a mechanical effect, but from a chemical interaction caused by both OH groups on the wafer and additive saccharide in the slurry.

Hydrogen bond may be very effective for the promotion of the removal rate.

Estimated model for polishing SiOC film is shown in **Fig. 5**. The affinity of the slurry to the surface of the wafer is originally very low because of the existence of the hydrophobic site on the surface of SiOC film. However a saccharide in the slurry can affect to change the character of SiOC film and can support the interaction between abrasive and the surface of the wafer. As it is generally known, SiOC film is weaker than TEOS film. Young's modulus of Black diamond™ is very low compared to that of TEOS. This may be one of the reasons why the additive in the slurry accelerates the removal rate of SiOC compared to TEOS.

Saccharide used in this study is nonionic, being neutral and water soluble, and does not exhibit understandable influence on the slurry stability.

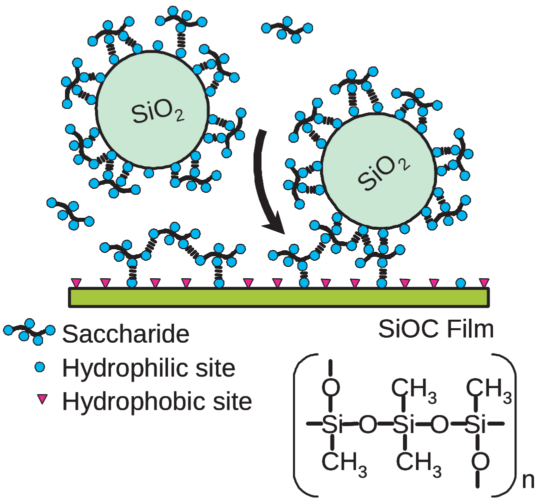

Fig. 5 Estimated model for polishing SiOC.

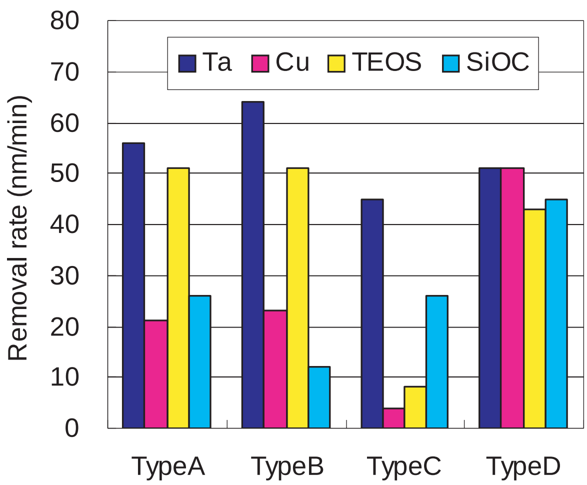

Fig. 6 Selectivity of slurry.
Down force: 7 kPa (Type D: 14 kPa)
Rotation speed: Platen/Head = 143/137 rpm

The above results indicate that saccharide is an excellent additive for removal ILD film.

Then we have studied to prepare various kinds formulation for effective and selective barrier slurries with above novel additive. The results for several applications are summarized in **Fig. 6**, showing excellent selectivity.

Type A: Slurry with high TEOS removal rate and adjustable Cu one to retain a thin TEOS cap at the end of Barrier CMP, and to be applicable to baseline composition.

Type B: Slurry, modified Type A, with high TEOS and low SiOC removal rates to removal completely the TEOS cap and stop on SiOC film.

Type C: Slurry with low TEOS removal rate to retain the TEOS cap with minimal loss at the end of Barrier CMP and stop on TEOS film.

Type D: Non selective slurry having similar removal rate for Ta, Cu, TEOS and SiOC films.

In recent years, non selective slurry which can polish all films at the almost same rate like Type D is highly demanded. **Figure 7** shows good uniformity of removal rate on blanket wafers of Ta, Cu, TEOS and SiOC films from center to edge were obtained. The removal rate for Cu can be controlled by the content of hydrogen peroxide. Cross sectional view of SEMATECH 800Az patterned wafer and planarity change from Cu CMP to Barrier CMP were shown in **Fig. 8** and **9** respectively. SiOC (Low-k material) loss means ILD loss after clearing Cap TEOS (**Fig. 1**). Maximum step height (sum of dishing and erosion) (**Fig. 2**) was depend on the wiring width, but that of the widest line (L/S 100 nm) was less than 30nm at the point of clearing cap.

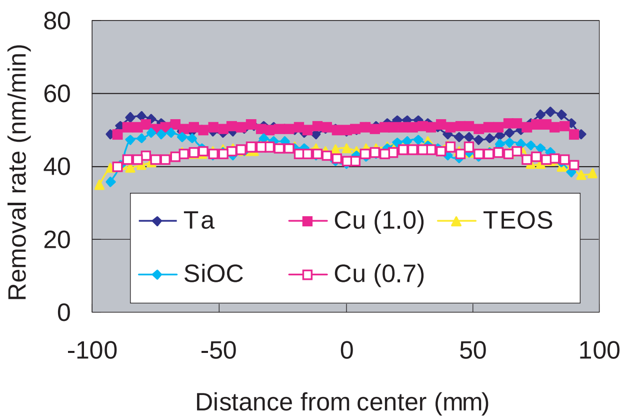

Fig. 7 Uniformity on Blanket wafer. (Type D)
Cu (H_2O_2 wt%)

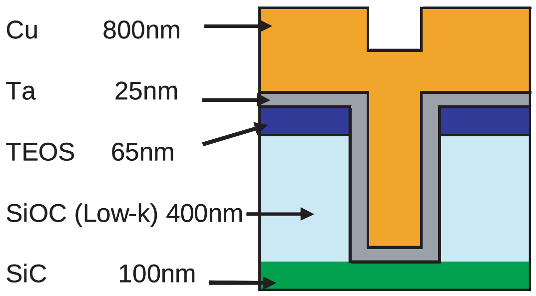

Fig. 8 Cross sectional view.

Over polishing refers to the extended polishing after clearing cap in order to accomplish planarization or to remove Cu residue. Although it is necessary to achieve good planarity within whole wafer, over polishing results in the loss of material and tend to cause dishing and erosion. For this reason, it is important to keep low dishing and erosion during over polishing. **Figure 9** indicates that Type D slurry has an excellent tolerance to over polishing.

It was also observed that the fang at array could be minimized as a desirable side effect by adding saccharide.

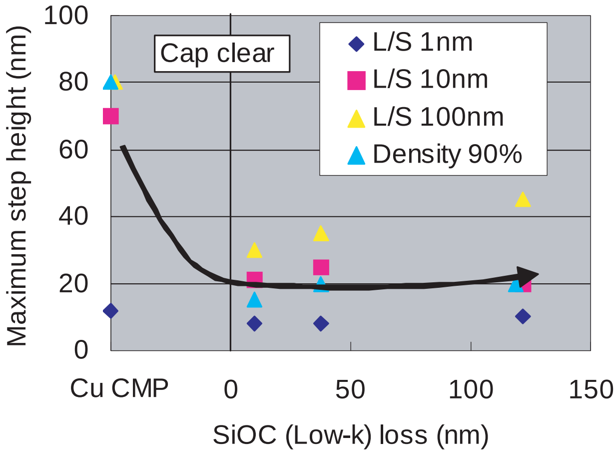

Fig. 9 Planarity change from Cu CMP to Barrier CMP using Type D.

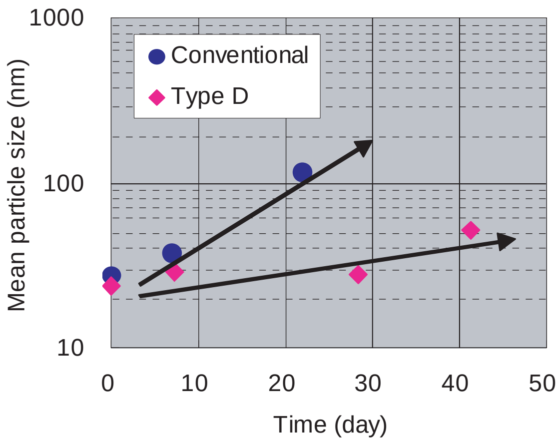

Fig. 10 Change of mean particle size at 55℃.

The slurry is very stable at room temperature, and then evaluated under an accelerated environment. **Figure 10** shows a mean particle size change at 55℃ to be more stable than conventional one which makes a gel for a long storage period.

4. Conclusion

Polishing properties of ILD films such as TEOS and SiOC was investigated in view point of chemical interaction. Novel additive based on saccharide compound was developed. Several kinds of selectivity and polishing performance for adopted film stack were studied using several kind of slurry composition. Excellent planarization and tolerance for over polishing are achieved.

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