創新的腐蝕抑制劑於化學機械研磨之清洗對銅導線電性之研究

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摘要

隨著元件線寬愈做愈小，金屬線寬及間距也必須跟著縮小，如此會產生較大的延遲時間。為了降低訊號傳遞的延遲時間，在目前極大型積體電路的發展中，銅導線已成為先進元件的主要導線材料。晶圓經過化學機械研磨處理後，會在表面殘留大量的污染物，例如：研磨時所使用的研磨粉體、金屬離子以及其他不純物之污染。假如沒有將這些污染物去除掉的話，則會影響後續製程的良率。甚至殘留於介電層表面的銅離子擴散至主動元件區，則會使元件特性劣化，故研磨後之清洗製程格外的重要。

利用螯合劑去移除介電層表面的銅離子是最常見的方法，檸檬酸是最常使用的螯合劑。在本論文中，我們將比較檸檬酸和醋酸移除銅離子的能力。首先，我們會探討這兩種螯合劑浸潤的能力，用來評估晶圓表面在清洗過程中是否可均勻的移除銅離子。然後我們再探討這兩種螯合劑對銅金屬的蝕刻率，以確保晶圓經過清洗製程之後，銅導線表面沒有腐蝕現象發生。最後，我們也會改變螯合劑的 pH 值，並觀察其清洗能力的變化情形。

另外一種污染物是研磨液中的研磨粉體。由於研磨粉體會與銅導線表面形成化學鍵結，故一般的清洗製程很難完全移除掉。使用硝酸和BTA的混合水溶液進行磨光(buffing)的製程能有效移除研磨粉體，並在銅導線表面形成Cu-BTA的保護層。這層保護層可防止銅導線表面被腐蝕，同時又能降低漏電流。不過，Cu-BTA保護層在 150℃以上將會被破壞。因此，在本論文中，我們想利用鋼鐵產業所使用的腐蝕抑制劑（DNNS和$PBTC-Na_4$）來取代BTA在銅導線表面形成保護層，並觀察DNNS和$PBTC-Na_4$保護層對銅導線漏電流的影

響。除此之外，我們也會探討DNNS和PBTC-Na_4保護層的熱穩定性以及金屬螯合劑在清洗過程中是否會破壞DNNS和PBTC-Na_4保護層也將在本論文中討論。

Study on Electrical Properties of Cu Interconnect

with Novel Corrosion Inhibitors after Post CMP Cleaning

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Abstract

We know that the metal linewidth and spacing decreases with the device scaling, resulting in large RC time delay. Copper has been used as the interconnect material in the fabrication of advanced ultra-large scale integration circuit. The damascene process is regarded to be an essential and critical step for manufacturing copper interconnects. After CMP process, wafer surface leaves a large amount of contaminants, which must be eliminated. There are two major contaminants. One is the abrasive from the polishing slurry, and the other is the metallic impurity contamination on the wafer surface. If these contaminants still left on wafer surface in next process, chip yield would be reduced. Hence, post CMP cleaning is a very important process.

Metal chelators are commonly carrier out to remove Cu ions. Citric acid is one of the organic acids commonly used as chelators. In this study, we would compare with cleaning efficiency between citric acid and acetic acid. Firstly, we would investigate wetting ability of metal chelators in order to sure cleaning uniformly. Next, we would investigate corrosion rate for copper with metal chelators. Finally, the effect of different pH for chelating capability would be discussed.

Particle is another contamination from the polishing slurry. As polishing with colloidal silica based slurry, there was a strong tendency of the absorption of colloidal silica on Cu surface. It was difficult to remove the chemisorbed colloidal silica by conventional chemical cleaning. Buffing with HNO_3 and BTA aqueous could remove colloidal silica abrasives and formation Cu-BTA passivataion on Cu surface that could prevent copper surface be corroded and reduce surface leakage current. However, Cu-BTA passivation would be decomposed above 150^{o}C. Hence, another effective corrosion inhibitor should be used instead of BTA to formulated buffing solution. In this study, we would choose amine salt of Dinonylnaphthalene sulfonic acid (DNNS) and 2-Phosphonobutane-1,2,4-tricarboxlic acid tetrasodium salt (PBTC-Na_4) to act as corrosion inhibitor in post CMP cleaning process. Passivation effect on surface leakage current would be studied. Furthermore, thermal stability and chemical durability of DNNS and PBTC-Na_4 passivation layers would be discussed in this study.