行政院國家科學委員會專題研究計畫成果報告

極大型積體電路元件相關耐火金屬化物及電介質技術

Study on Refractory Metals and Dielectric Materials for VLSI Integral Circuits Technology

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一、中文摘要

一種由道康寧公司提供，名爲流動性氧化物(FOx-16)的 hydrogen silisequioxane (HSQ) 可旋轉塗佈的低介電材料，若經過氨氣電漿處理後可以成功的阻止銅原子的擴散，HSQ 膜經過氨氣電漿處理不但可以降低漏電流，而且可以增加阻止金屬擴散進入介電層的能力，氨氣電漿處理後幾乎不會對此 HSQ 膜的低介電常數造成明顯的影響。隨氨氣電漿處理的時間增加，漏電流遞減的原因可能由於 HSQ 膜在氨氣電漿處理後更加緊密化。而增加阻止金屬擴散進入介電層的能力是由於 HSQ 經過氨氣電漿處理後，HSQ 表面被氮化而形成一層氮化物的原故。

關鍵詞：可旋轉塗佈、低介電材料、電漿處理

Abstract

A flowable oxide, supported by Dow Corning Corporation (FOx-16), is one kind of hydrogen silisequioxane (HSQ) low dielectric constant material, which can successfully suppress Cu diffusion without barrier metal by using NH_3 plasma treatment. After NH_3 plasma treatment, the hydrogen silisequioxane film with lower leakage current and better barrier ability was achieved. This film almost keeps the same dielectric constant after different plasma exposure times. The decrease in leakage current with more exposure time is due to a higher density of HSQ film is achieved after NH3 plasma treatment. The better barrier ability is due to a thin nitride film formed on the dielectric.

二、緣由與目的

Smaller feature size devices fabricated on large dies, longer transmission lines and more closely spaced interconnects, result in longer resistance-capacitance (RC) time delays which will bring further challenge on the semiconductor industry. Integration of materials with lower dielectric constant and copper film with lower resistance into device is needed to reduce interconnection delay and to improve device performance. Currently, the leading candidate for the metal alternative is Cu, and perhaps hydrogen silisequioxane (HSQ) for the dielectric. However, the diffusivity of Cu in HSQ is rather high. The degradation and transport of copper is through its oxidation and diffusion/migration of ions. Cu interconnects need a barrier layer around them to prevent the diffusion to the interlayer dielectric. The Cu diffusion will cause dielectric to failure and lead to significantly increase in leakage current. The improvement of reducing Cu diffused into dielectric is our goal in this study.

The H_2 annealing and H_2 plasma treatment are used to improve the leakage current of low-k materials.[1] However, the barrier ability against Cu is still unsatisfactory. An excellent barrier ability is achieved by formation of a thin barrier layer of SiON on the surface of SiOF film.[2] Numerous authors[2-3] showed that the barrier metal free structure especially reduced the resistance in fine patterns. D.S. Gardnes et al.[4] also showed that using a thin SiN layer as a barrier layer could obtain a lower RC delay time than using a refractory metal.

Flowable oxide (FOx-16), a kind of spin-on HSQ, is a low k material used in this study. In this letter, a thin nitride film on the surface of HSQ by NH_3 plasma treatment is achieved. The results will show much greater improvement than as-cured sample.

三、結果與討論

Figures 1 (a) and (b) show the Fourier transform infrared (FTIR) spectra of cured FOx-16 after NH_3 and H_2 plasma treatment in different exposure times, respectively. This figure indicates that the cage-like Si-O bond starts to convert to network structure after NH_3 or H_2 plasma treatment, i.e., HSQ film becomes densier after plasma treatment.

Figure 2(a) shows the leakage current density of MOS capacitors. A decrease in leakage current after NH_3 plasma treatment can be observed. This result is similar to the samples after H_2 plasma treatment in Fig. 2(b). After more plasma treatment, the leakage current decreased further with increasing plasma exposure time. The passivated dangling bonds in the SOG cause a decrease in leakage current with increasing plasma exposure time. Hydrogen passivated played a major role of decreased leakage current, while the previous work1 found an increase in leakage current after N_2 plasma treatment.

Figure 3 indicates that the electrical breakdown field (E_{BD}) distribution of the samples after NH_3 and H_2 plasma treatment HSQ shows a great improvement of breakdown voltage after NH_3 plasma treatment. From secondary ion mass spectrometer (SIMS) analysis (not shown here), we found that the copper diffused into HSQ at 400℃. On the other hand, after NH_3 plasma treatment for 10 min, the HSQ film almost keeps the same profile as as-deposited sample. We also measured the electric field of Al gate. In this case, the as-cured HSQ sample shows the same level of electric field as NH_3 plasma-treated HSQ. When the electrode was changed to Cu, the as-cured sample demonstrated significant degradation as shown in Fig. 3. Therefore, we suggested that the Cu must be a major cause of leakage current. The formation of nitride film on the surface of SOG causes a higher breakdown voltage and better barrier ability. SIMS analysis shows that the thickness of nitride film on the HSQ is 35 nm after NH_3 plasma treatment for 10 min. Nitride film is the best barrier material against the impurity diffusion. From x-ray photoelectron spectroscopy (XPS) analysis, we found a strong peak of N_{1S} at 398 eV and a weak peak of N_{1S} at 403.5 eV. We suggest that the mechanism of our nitride should act as passive diffusion barriers.[5]

Figure 4 shows that the dielectric constant varies with different plasma exposure times. It also shows that the dielectric constant of HSQ increases at beginning from the as-cured value of 2.7 and follows a slight decrease with more exposure time. This implies that the thin nitride film only formed on the surface of SOG and the NH_3 plasma treatment provides hydrogen to passivate the dangling bonds in the SOG resulting the reduction of dielectric constant.

The time to failure (TTF) stress can be used as an indicator of barrier quality. The effect of electric field on copper transport when the temperature was measured at 150℃. Initial decrease in the leakage current is similar to the samples of Cu on oxide or nitride as shown in Fig. 5.[6,7] This decrease in leakage current is due to the injection of mobile ions of Cu into the dielectric. The injection of ions leads to charge build-up in the dielectric and to oppose further injection. It results that the leakage current reduces continuously until it matches with the electron injection from backside electrode. In this figure, the TTF stress of SOG was found that the sample after NH_3 plasma treatment shows much greater improvement than as-cured sample. Even applying two times electric filed to the NH_3 plasma sample, it still shows much longer TTF time than the as-cured and H_2 plasma samples. Finally, in the breakdown stage, the NH_3 plasma treated sample shows an abrupt breakdown without gradual increase in leakage current which is similar to oxynitride in the other reports.[4] The "self-healing" phenomena (the leakage current spikes up and down) are sometimes observed in TTF testing. These phenomena are due to non-uniform diffusion of copper.[6] Based on the above data, the NH_3 plasma treatment is an excellent method to improve the quality of HSQ.

四、計畫成果自評

本計畫成功的研究出以可旋轉塗佈的低介電材料 HSQ，經過氨氣電漿處理之後，證明在此種應用下，低介電材料 HSQ 成功的阻止銅原子的擴散，並且可降低漏電流，因此本計畫執行可謂相當成功，在學術上的應用也相當有價值，本計畫之成果已被國際學者肯定並即將在國際期刊上發表

論文，論文發表資料請參閱參考資料[8,9,10,11]。

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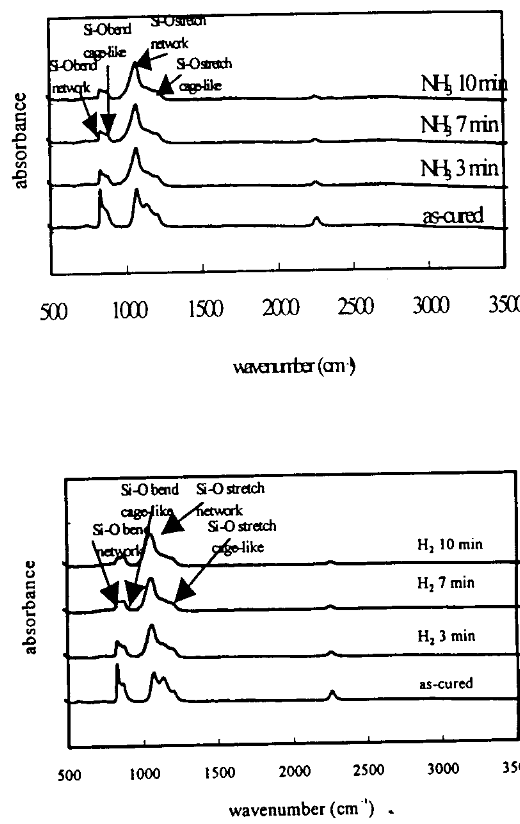
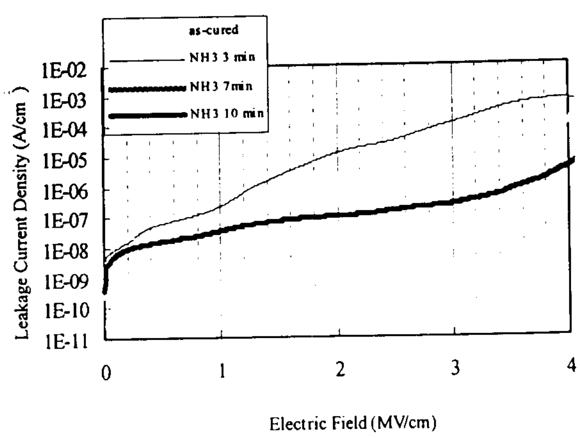


Fig. 1 FTIR spectra of cured HSQ after (a) NH_3 plasma treatment (b) H_2 plasma treatment for different exposure times.



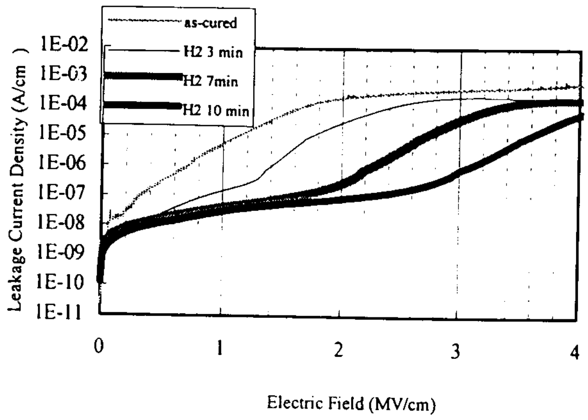


Fig. 2 The leakage current density of HSQ after (a) NH_3 plasma treatment (b) H_2 plasma treatment for different exposure times.

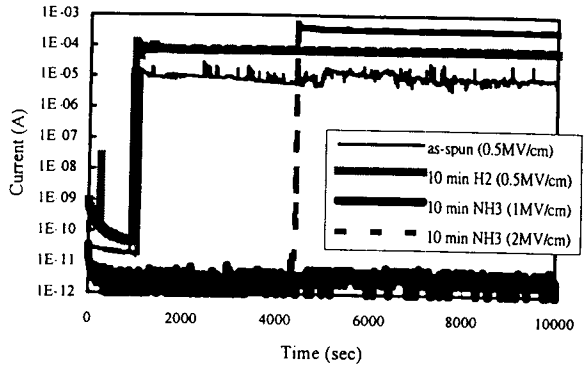


Fig. 5 The RBS spectra of two annealed structures. (a) Cu/typical CVD-W/Si, (b) and Cu/WNx/W/Si multilayers.

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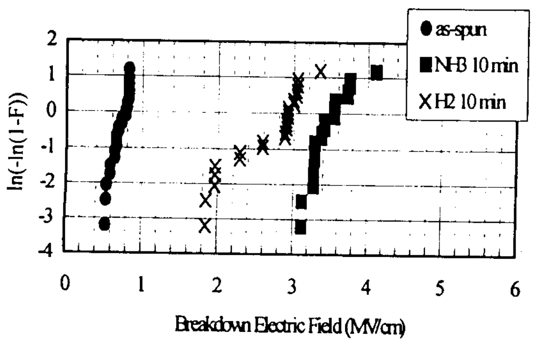

Fig. 3 Weibull plot of MOS structure's electrical breakdown field (E_{BD}) distribution after different plasma treatment conditions.

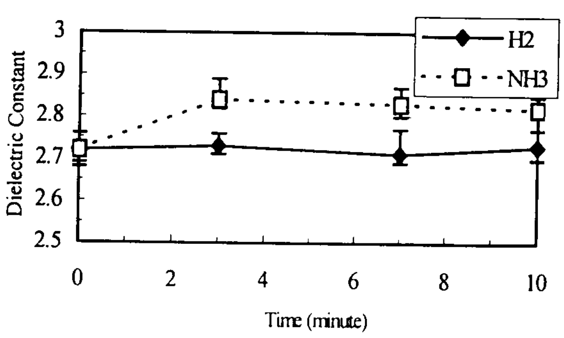

Fig. 4 The variation of dielectric constant after different plasma treatment conditions.