Effects of NH₃-Plasma Nitridation on the Electrical Characterizations of Low-κ Hydrogen Silsesquioxane with Copper Interconnects

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Abstract—The interaction between copper interconnects and low-κ hydrogen silsesquioxane (HSQ) film was investigated using a Cu/HSQ/Si metal insulation semiconductor capacitor and NH₃ plasma post-treatment. Owing to serious diffusion of copper atoms in HSQ film, degradations of the dielectric properties are significant with the increase of thermal stress. The leakage current behavior in high field conduction is well explained by the Poole–Frenkel (P–F) mechanism. By applying NH₃-plasma treatment to the HSQ film, however, the leakage current is decreased and P–F conduction can be significantly suppressed. In addition, the phenomenon of serious Cu penetration is not observed by means of electrical characteristic measurements and secondary ion mass spectroscopy (SIMS) analysis even in the absence of diffusion barrier layers. This indicates the copper diffusion in low-κ HSQ film can be effectively blocked by NH₃ plasma post-treatment.

Index Terms—Copper, diffusion processes, insulator contamination, integrated circuit interconnections, low-permittivity dielectrics, MIS devices.

I. INTRODUCTION

As ULSI circuits are scaled down, interconnect structures with two or more metal levels have become the dominant tendency to produce high-density circuits and enhance device performance. In these designs, the linewidth and spacings between metal interconnects are also made smaller. The smaller line dimension increases the resistivity (R) of the metal lines and the narrower interline spacing increases the parasitic capacitance (C) between the lines. Therefore, copper with low resistivity (1.67 μΩ-cm for bulk) and high electromigration resistance and new intermetal dielectric (IMD) materials with low dielectric constant (κ) are required to reduce the crosstalk capacitance, power consumption and RC delays associated with the metal interconnect system [1]. These candidates for low-κ dielectric films have been deposited based either on spin-on deposition [2] or chemical vapor deposition (CVD) [3]. One of the most promising low-κ materials is siloxane-based hydrogen silsesquioxane (HSQ) [4], [5] having the general formula \((\text{HSiO}_3)_{2n}\), \(n = 2,3\), etc. available as flowable oxide (FOX) from Dow Corning Inc. HSQ is an inorganic material that can be considered as a derivative of \(\text{SiO}_2\) in which one of the four oxygen atoms bonded to every silicon atom is replaced by hydrogen. This class of inorganic spin-on dielectric has a low dielectric constant (about 2.8), available nonetchback process, planarization, and good gap-filling characteristics. Furthermore, the low dielectric properties can be achieved if the formation of O–H bonds and moisture absorption in the film is minimized [6]. Therefore, the integration of HSQ film as an IMD into multilevel interconnects has received much attention [7], [8]. However, the use of copper interconnects has some issues in integrated circuit (IC) application because it is easy for copper to diffuse into the dielectric films degrading the reliability [9]. For this reason, copper interconnects formed by damascene process need the deposition of some barrier layers (e.g. Ta, TaN, or Si₃N₄) at the interface between dielectric films and copper lines forming a cladding structure to prevent Cu from penetrating through dielectric films [10], [11]. These barrier layers have usually high resistivity or high dielectric constant (for Si₃N₄), which cause a higher via resistance and higher equivalent parasitic capacitance. For example, the sheet resistance of 0.3 μm Cu metal line is about 0.048 Ω/□. For the via size of 0.28 μm, the via resistance of the cladding structure with Ta barrier is about 1.0 Ω, and that with TaN barrier is about 1.3 Ω in a thickness of 400 Å for Ta and TaN [12]. These barrier layers would tend to the increase in the RC delay and offset partial advantages of the copper interconnect system. Mikagi et al. described a barrier metal free copper damascene technology using NH₃ plasma-treated SiOF film for improvement of RC delay [13]. The efficiency of NH₃ plasma treatment on other kinds of low-κ dielectrics against Cu diffusion has been not reported extensively.

In this work, we have investigated the influence of copper on the intrinsic dielectric properties of inorganic low-κ HSQ film. Leakage current behavior also were intensively studied, since a relatively high electric field may be produced even for a low applied operation voltage in deep subquarter micron interconnection devices. In addition, NH₃ plasma post-treatment was applied to the HSQ film instead of conventional high-resistivity or high-dielectric-constant barrier layers, minimizing the increase in RC delay in order to obtain a better performance in the copper interconnect system.
stretching cage-like peak near 1130 cm\(^{-1}\), Si-O stretching network peak near 1070 cm\(^{-1}\), Si-O bending cage-like peak near 863 cm\(^{-1}\), and Si-O bending network peak near 830 cm\(^{-1}\). Most of the solvent is eliminated up to 150 °C, then the HSQ film melts at a baking temperature of 200 °C. At 300 °C baked temperature, flow occurs and additional bond rearrangement gives film greater strength to resist cracking and decreased surface roughness. During the baking process, the FTIR spectra of HSQ are almost the same. After a 400 °C curing process, however, the peak of Si-O stretching vibration and that of bending vibration significantly change. It is clearly shown that the chemical structure of the HSQ film changes from cage-like to a 3-D network structure to provide sufficient mechanical integrity to withstand subsequent processing.

To investigate the impact of copper on low-\(k\) HSQ film, control samples were fabricated following the same processing sequence of Cu/HSQ/Si capacitors except that an Al electrode instead of Cu metallization. Fig. 2(a) and (b) show the leakage current density and dielectric constant of HSQ with Al-electrode and Cu-electrode capacitors after being subjected to a thermal stress ranging from 425 °C to 500 °C for 30 min, respectively. It is observed that both the leakage current and dielectric constant of HSQ film are significantly increased with the increase of annealing temperature. In addition, the leakage current density of Cu-electrode capacitor is higher than that of Al-electrode capacitor. Especially in the high field conduction region, the diversity of leakage current between capacitors with Cu-electrode and Al-electrode is even larger as much as one order of magnitude when capacitors being subjected thermal stress at 500 °C. This seems to indicate that some kinds of degradations occurred in HSQ film. When stressing HSQ films at temperatures above 400 °C the HSQ film properties will be degraded due to the pyrolysis of the HSQ film. During thermal stress, Si-H bonds in HSQ film are easily broken at the elevated annealing temperature, which causes the generation of dangling bonds and moisture absorption in the HSQ film [14]. This is well explained for the increase of both leakage current and permittivity in the case of Al-electrode capacitors. However, the dielectric properties of HSQ with Cu-electrode capacitors are worse than that of Al-electrode capacitors. This suggests that the pyrolysis and copper diffusion play important roles in the degradation of the Cu/HSQ/Si capacitors, simultaneously. This inference can be confirmed further by the measurement of SIMS depth profiles and the investigation on the mechanism of leakage current conduction. Fig. 3 shows the SIMS depth profiles of copper in the HSQ film with Cu-electrode capacitors after subjected to the thermal stress at 425 °C and 500 °C for 30 min. The copper profile shows a high level of copper is observed at the copper/HSQ interface and an exponential-like decay in the HSQ film. In addition, the copper content in HSQ film is increased with the increase of annealing temperature. The leakage current behaviors of HSQ film with the Cu-electrode can be investigated further on the leakage current density \((J)\)-electric field \((E)\) characteristics such as a \(\log J\) versus \(E^{4/2}\) plot, as shown in Fig. 4. It is found that the leakage current density is linearly related to square root of the applied electric field. The linear variations of the current correspond either to Schottky emission [15] or to Poole–Frenkel mechanism [15]. The Schottky–Richardson emission generated by the thermionic...
Fig. 2. Dielectric properties of HSQ film with Al-electrode and Cu-electrode capacitors after various thermal annealing temperature (425–500 °C) for 30 min. (a) Leakage current density of HSQ film as a function of electric field. (b) Dielectric constant of HSQ film as a function of thermal annealing temperature.

Fig. 3. SIMS depth profiles of copper in HSQ film with Cu-electrode after being subjected to thermal stress at 425 °C and 500 °C for 30 min.

Effect is caused by the electron transport across the potential energy barrier via field-assisted lowering at a metal-insulator interface. The current density in the Schottky emission can be quantified by the following equation:

\[
J = A^*T^2 \exp \left( \frac{\beta_E E^{1/2} - \phi_b}{k_B T} \right)
\]

where \( \beta_E = (e^3/4\pi\varepsilon_0\varepsilon)\) effective Richardson constant, \( \phi_b \) the contact potential barrier, \( k_B \) the Boltzmann constant, \( e \) the electronic charge, \( E \) the applied electric field, \( \varepsilon_0 \) the dielectric constant of free space, and \( \varepsilon \) the high frequency relative dielectric constant. The Poole–Frenkel (P–F) emission is due to field-enhanced thermal excitation of trapped electrons in the insulator into the conduction band. The current density is given by

\[
J = J_0 \exp \left( \frac{\beta_{PF} E^{1/2} - \phi_{PF}}{k_B T} \right)
\]

where \( J_0 = \sigma_0 E \) is the low-field current density, \( \sigma_0 \) the low-field conductivity, \( \beta_{PF} = (e^3/\pi\varepsilon_0\varepsilon)\) and \( \phi_{PF} \) the height of trap potential well. For trap states with coulomb potentials, the expression is virtually identical to that of the Schottky emission. The barrier height, however, is the depth of the trap potential well, and the quantity \( \beta_{PF} \) is larger than in the case of Schottky emission by a factor of two [15].

Distinction between the two processes can be done by comparing the theoretical value of \( \beta \) with the experimental one obtained by calculating the slope of the curve \( \log J - E^{1/2} \). The various values of the constant \( \beta \) are shown in Table I. The slope \( (=\beta/k_B T) \) of the straight line portion of curve in Fig. 4 gives a value of \( 6.475 \times 10^{-24} \) at 425 °C, \( 6.393 \times 10^{-24} \) at 450 °C, and \( 5.42 \times 10^{-24} \) J/(mV)^{1/2} at 500 °C for \( \beta \), respectively, closer to \( \beta_{PF} \) than \( \beta_s \). These results are strongly reasonable to believe that carriers are transported through the Cu/HSQ/Si capacitors by the field-enhanced P–F mechanism. Therefore, from all the above observations, the leakage current behavior in HSQ film with Cu electrode can be summarized as followed. Comparison with Al-electrode capacitor, elevated temperatures cause the increase in leakage current of Cu-electrode capacitor. This is due to the pyrolysis of HSQ and the enhancement in thermal excitation of trapped electrons in the HSQ film. Under higher thermal stress, large amounts of copper will diffuse into HSQ film and generate a lot of defects in HSQ film with the increase of annealing temperature. In addition, the increasing copper content in the HSQ film tends to lower the potential drop...
across the surface region causing a larger fraction of applied voltage to drop across the rest of the HSQ film. This can be modeled as a thinning in the effective HSQ thickness. The increase in electric field and the generation of defects (or traps) will enhance the P-F conduction mechanism. As a result, the leakage current is significantly increased with the increase of annealing temperature when compared with that of Al-gate. Furthermore, the thinning in the effective thickness leads to larger capacitance according to the relation of \( C = \varepsilon_0 \varepsilon (A/d) \), where \( A \) is the area of top electrode, and \( d \) is the film thickness. As a result, a higher dielectric constant derived from the capacitance of MIS capacitors would be obtained if the effect of thinning in effective thickness were not considered. Based on the accelerated degradation and thickness thinning resulted from copper diffusion, the dielectric constant of HSQ with Cu-electrode is higher generally than that of HSQ with Al-electrode. This is consistent with the increased dielectric constant as shown in Fig. 2(b).

To alleviate these degradations, NH\(_3\) plasma treatment was applied to the as-cured HSQ film. First, the analysis of XPS was carried out to investigate the modification at the surface of HSQ film before and after NH\(_3\) plasma treatment. Fig. 5 shows XPS spectra of N 1s in HSQ film with and without NH\(_3\) plasma treatment. It is found that a significant signal of nitrogen elements appears in the NH\(_3\) plasma-treated HSQ. The concentration of nitrogen on the surface of HSQ film with NH\(_3\) plasma treatment for 3 min, 6 min, and 9 min is 8.94, 13.56, and 17.97 at.%, respectively. This indicates that the nitrogen is doped into the HSQ film, and forms thin SiN\(_x\) layer on the surface of the HSQ film. The SiN\(_x\) is known as a diffusion barrier against Cu [16]. The electric characteristics of NH\(_3\)-plasma nitridated HSQ film are also studied as followed. Fig. 6(a) and (b) show the dielectric properties of NH\(_3\)-plasma treated HSQ film with Al and Cu electrode after subjected to thermal stress at 425 °C and 500 °C for 30 min, respectively. Both the leakage current and dielectric constant of Cu/HSQ/Si capacitor are decreased with the increase of NH\(_3\) plasma treatment time within 9 min. It is observed especially that the reduction of leakage current at high electric field region is significant. Especially, leakage current behavior of the NH\(_3\) plasma-treated HSQ film after subjected to thermal stress at 500°C keep almost the same as that of NH\(_3\)-plasma treated HSQ at 425 °C. Comparison with untreated HSQ, a reduction in leakage current of approximately two orders of magnitude is observed for NH\(_3\) plasma-treated samples. In addition, the dielectric constant of HSQ with NH\(_3\)-plasma treatment for 9 min maintains a low value (about 3.0). It is clearly shown that NH\(_3\) plasma treatment can effectively restores the properties of a damaged film to similar state as an as-cured HSQ film. In our work NH\(_3\)-plasma treatment within 10 min is an appropriate condition, or more nitridation would raise the dielectric constant of HSQ film. The short period NH\(_3\)-plasma treatment can prevent moisture uptake in HSQ from increased leakage current and dielectric constant due to film pyrolysis during the elevated thermal stress. As a result, the leakage current of NH\(_3\)-plasma treated HSQ with Cu-electrode is lower

![Graph](image-url)
Fig. 6. Dielectric properties of various NH$_3$-plasma-treated HSQ films with Al-electrode and Cu-electrode capacitors after a series of thermal stress. (a) Leakage current density and dielectric constant of NH$_3$-plasma treated HSQ film after subjected to thermal stress at 425 °C for 30 min. (b) Leakage current density and dielectric constant of NH$_3$-plasma treated HSQ film after subjected to thermal stress at 500 °C for 30 min.

than that of Al-electrode HSQ without NH$_3$-plasma treatment. FTIR spectra can strongly evidence our statements, as shown in Fig. 7. It is found that the signal of Si-OH bonds appears in the spectrum of untreated HSQ. This cause is that defects (or dangling bonds) generated during the pyrolysis of HSQ at high stressing temperature will react with moisture forming Si-OH bonds in HSQ film. By the short period NH$_3$ plasma treatment, the surface nitridation layer prevents moisture absorption. As a result, no Si-OH bonds are observed in the NH$_3$-plasma treated HSQ film.

SIMS analysis was carried out to observe the distribution of copper atoms and nitrogen elements in the NH$_3$-plasma nitridated HSQ film. Fig. 8 shows the SIMS depth profiles of copper in HSQ film with Cu-electrode capacitors after subjected to thermal stress at 500 °C. In consistent with our electric characteristics, a significant amount of copper atoms are observed in the untreated sample. By contrast, the profile of the copper in the NH$_3$-plasma nitridated HSQ film revealed a very shallow copper distribution and only a slight amount of copper appearance at the near surface. The thickness of the SiN$_x$ is approximately 10 nm. Therefore, the phenomenon of copper diffusion into HSQ film was significantly reduced by NH$_3$ plasma treatment.

These above experimental results can be explained as followed. During the HSQ film curing process, a variety of bonding destruction and recombination occurred simultaneously. Si and O elements play important roles during the linking process. A great number of uncovered Si-bonds exist due to the small fraction of incomplete recombination of Si-O bonds and Si-H bonds broken during thermal curing process. The uncovered Si-bonding is an imperfect bond, which will result in unstable film properties. In the absence of diffusion barrier
layer between Cu and low-$k$ HSQ film, copper is easy to diffuse into HSQ film to degrade the dielectric properties resulting in increased leakage currents associated with the P–F conduction mechanism and raised dielectric constant. By applying short period NH$_3$-plasma treatment to as-cured HSQ film, the surface of HSQ can be modified to a thinner nitride layer (i.e., SiN$_x$ layer). The passivation layer effectively reduces moisture uptake and the diffusion paths of copper penetration through HSQ. Since the nitrogen remains in a top surface layer, the bulk $k$ value should not be significantly raised by this process.

IV. CONCLUSION

Dielectric degradation of a Cu/HSQ/Si structure was observed at elevated temperatures due to copper penetration into HSQ film. Even in the absence of diffusion barrier layers, however, the low-$k$ properties of HSQ film can be maintained by NH$_3$-plasma treatment. The NH$_3$-plasma treatment is capable of nitriding the surface and forming a passivation layer (SiN$_x$ layer) on the surface of HSQ film, which effectively prevent moisture uptake and block copper penetration in HSQ film. As a result, Poole–Frenkel type leakage current in HSQ film is effectively reduced. The higher-performance operation in a copper interconnect system can be achieved by applying NH$_3$-plasma treatment to HSQ associated with a rather thin barrier layer.

REFERENCES

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