Material design of plasma-enhanced chemical vapour deposition SiCH films for low-\textit{k} cap layers in the further scaling of ultra-large-scale integrated devices-Cu interconnects

Hideharu Shimizu\textsuperscript{1,2}, Shuji Nagano\textsuperscript{1}, Akira Uedono\textsuperscript{3}, Nobuo Tajima\textsuperscript{4}, Takeshi Momose\textsuperscript{2} and Yukihiro Shimogaki\textsuperscript{2}

\textsuperscript{1} Taiyo-Nippon Sanso Co., Tsukuba-shi, Ibaraki 300-2611, Japan
\textsuperscript{2} Department of Materials Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 103-8656, Japan
\textsuperscript{3} Division of Applied Physics, Faculty of Pure and Applied Science, University of Tsukuba, Tsukuba-shi, Ibaraki 305-8577, Japan
\textsuperscript{4} National Institute for Materials Science, Tsukuba-shi, Ibaraki 305-0047, Japan

E-mail: Hideharu.Shimizu@tn-sanso.co.jp

Received 2 June 2013
Accepted for publication 26 August 2013
Published 27 September 2013
Online at stacks.iop.org/STAM/14/055005

Abstract
Cap layers for Cu interconnects in ultra-large-scale integrated devices (ULSIs), with a low dielectric constant (\textit{k}-value) and strong barrier properties against Cu and moisture diffusion, are required for the future further scaling of ULSIs. There is a trade-off, however, between reducing the \textit{k}-value and maintaining strong barrier properties. Using quantum mechanical simulations and other theoretical computations, we have designed ideal dielectrics: SiCH films with Si–C\textsubscript{2}H\textsubscript{4}–Si networks. Such films were estimated to have low porosity and low \textit{k}; thus they are the key to realizing a cap layer with a low \textit{k} and strong barrier properties against diffusion. For fabricating these ideal SICH films, we designed four novel precursors: isobutyl trimethylsilane, diisobutyl dimethylsilane, 1, 1-divinylsilacyclopentane and 5-silaspiro [4,4] nonane, based on quantum chemical calculations, because such fabrication is difficult by controlling only the process conditions in plasma-enhanced chemical vapor deposition (PECVD) using conventional precursors. We demonstrated that SiCH films prepared using these newly designed precursors had large amounts of Si–C\textsubscript{2}H\textsubscript{4}–Si networks and strong barrier properties. The pore structure of these films was then analyzed by positron annihilation spectroscopy, revealing that these SiCH films actually had low porosity, as we designed. These results validate our material and precursor design concepts for developing a PECVD process capable of fabricating a low-\textit{k} cap layer.

Keywords: PECVD, interconnects, barrier dielectrics, cap layer, SiCH, precursor, material design
1. Introduction

Plasma-enhanced chemical vapor deposition (PECVD) is now widely used for fabricating insulating films such as SiO₂ and SiN in the production of ultra-large scale integrated devices (ULSIs). PECVD insulating films with target properties and structure have been developed by controlling the process conditions, sometimes empirically, using simple silicon-based molecules such as Si(OCH₃)₄ and SiH₄ [1, 2].

In the early 2000’s, PECVD SiOCH films with a lower dielectric constant (k-value) than 3.0 were adopted as insulating layers between Cu interconnect lines after the 90 nm node to reduce resistance–capacitance (RC) delay. Currently, to realize the potential performance of 22 nm node devices, the required k-value of the SiOCH films must be less than 2.4. However, Cu readily diffuses into SiOCH low-k films (k < 3.0), causing poor reliability [3].

Either PECVD SiN (k = 7.0) or PECVD SiCN (k = 4.8) have been used as insulating layers on top of Cu lines to prevent Cu diffusion [4, 5]. To cope with the decreasing dimensions of ULSI devices, thinner cap layer films with k < 4.0 are needed to improve effective k (or k_eq) of the Cu interconnect. More recently, PECVD SiCH (k = 2.8–4.0) films have shown potential as an alternative to conventional cap layers such as SiN and SiCN, because SiCH films have two unique characteristics [6–10]. (It should be noted that the notation relating to SiN, SiCN, SiOCH and SiCH in this report does not reflect atomic ratios.) The first characteristic is resistance to plasma damage [6]. In low-k bulk (SiOCH, k < 3.0) films, k increases substantially after the plasma-reactive ion etching process, whereas SiCH films with a high C content (C/Si ~ 4) show a very stable resistance against plasma damage. Moreover, the etching rate of SiCH with a high C content is four times slower than that of low-k bulk films (SiOCH). SiCH cap layers on low-k bulk films are thus expected to function both as a protection layer against plasma damage and as an etching stopper. Etching of a low-k bulk film on a cap layer for an overlaid interconnect should be stopped before the Cu line to prevent corrosion of the Cu line. The second characteristic of SiCH is its barrier properties against both Cu diffusion [7–10] and moisture diffusion [11, 12]. SiCH films formed from trimethylsilane (3MS) or tetramethylsilane (4MS) reportedly act as Cu diffusion barriers [7–9] and moisture diffusion barriers [11].

In the cap layer, however, good diffusion barrier properties and a low k have a tradeoff relation [13–15]. Most dielectrics with a low k are obtained by decreasing the density of the films, mostly by introducing multiple pores, which in turn results in inferior barrier properties. In fact, the diffusion barrier properties of SiCH films formed from 3MS or 4MS degrade when k < 4.0. We have therefore chosen a different approach to obtain a lower k without degrading the barrier performance [16]. We used quantum mechanical simulations to estimate the Cu diffusion coefficient in various insulating materials and found that the porosity is the dominant factor in controlling Cu diffusion. The results suggest that the Si–C₃H₈–Si network structure is the most promising to realize good barrier performance and a low k. Based on these strategies, we therefore developed four precursors (figure 1) for PECVD SiCH films to control network structure: isobutyl trimethylsilane (iBTMS), disobutyl dimethylsilane (DiBDMS), 5-silaspiro[4,4]nonanone (SSN) and 1,1-divinylsilacyclopentane (DVSnP) [17].

The performances of SiCH films prepared using these precursors were demonstrated in our previous reports [14–16]. SiCH films with k = 3.5 using iBTMS and DiBDMS exhibited strong barrier properties against Cu diffusion. SiCH films with k = 3.0 using SSN and DVSnP also exhibited strong barrier properties. The relationship between porosity and the barrier properties of SiCH films was not clarified in our previous reports [14–16]. In this report, the porosity of SiCH films with a high carbon content (C/Si ~ 4) deposited using these four precursors was examined using positron annihilation spectroscopy (PAS) [18–25]. The results confirmed that a lower porosity of the SiCH film improved the barrier properties against Cu diffusion; a relation consistent with our material design [14–16, 26].

2. Materials design and experimental

2.1. Origin of the barrier properties

As mentioned above, a cap layer should have both a low k and strong diffusion barrier performance. Several materials have been investigated as candidates. Although SiO₂ and SiOCH films can realize a low k (k ~ 2.7), they also show poor barrier performance against Cu diffusion. In contrast, SiN films exhibit barrier properties, but have a rather higher k (k ~ 7.0) than SiOCH. We expect SiCH to have both a low k and good barrier performance. To optimize these competing properties, here we investigated the atomic mechanism that controls these properties by considering two factors that determine the barrier performance of a film against Cu diffusion.
Figure 2. Activation energies of Cu⁺ migration in (a) SiO₂, (b) SiN, (c) SiCH and (d) SiOCH estimated by quantum chemical calculations.

The first factor is chemical interaction, which is defined as the barrier height when a Cu⁺ ion migrates from a trapped site to another site in SiN, SiOCH, SiCH or SiO₂ films. Figure 2 shows the cluster model we developed to calculate the barrier height of Cu diffusion. We estimated the transition state (TS) of a Cu⁺ ion’s migration from a trapped site to another trapped site in the model structures of SiN, SiOCH, SiCH and SiO₂. The differences of energy between a trapped site and the TS are estimated to be the barrier height of Cu⁺ diffusion in this cluster model. In figure 2, the value of barrier height is shown under the TS state. The figure reveals no significant difference in the activated barriers of a Cu⁺ ion migration in SiN, SiOCH, SiCH and SiO₂ films, whereas these materials have entirely different barrier properties experimentally. Neither a Cu atom nor a Cu⁺ ion interacts with lone pairs in nitrogen or oxygen, because all of the 3d-orbitals in Cu atoms and Cu⁺ ions are occupied by electrons. In addition, the calculated activation energies of Cu⁺ ions were much lower than those previously reported (SiO₂: 13.6 – 32.6 kcal mol⁻¹, SiN: 29.9 kcal mol⁻¹) [27, 28]. Therefore, the activated barrier of migration, namely the chemical interaction, such as the coordination bond between Cu–N or Cu–O, was not the dominant factor in Cu diffusion. In this model, the electrostatic interaction between Cu⁺ and dipoles in a dielectric film was also taken into account. Si–O and Si–N have a larger dipole moment than Si–C, which however did not seem to affect the barrier properties. Neither N nor O are thought to be necessary atoms for a Cu diffusion barrier.

The second factor is the physical interaction, which means that the barrier against Cu diffusion is controlled by the atomic arrangement of the film structure. A highly packed material might have a strong barrier property against Cu diffusion. The relationship between the atomic arrangement of a dielectric film and Cu diffusion was investigated by classical molecular dynamics simulation. In our molecular dynamics (MD) simulation, Cu–film–matrix interaction is represented by elastic collisions of van der Waals spheres of Cu⁺ ion with those of film atoms. Compositions and densities of SiO₂, SiN, SiCH and SiOCH films, reported by us and other groups, were employed to establish a model structure for MD simulation [29–31]. Figure 3 shows the model structures used in these simulations. Table 1 summarizes the simulation results for the diffusion coefficient, density, porosity and k-value. The results indicate that a lower porosity, i.e. a highly packed atomic arrangement, improves the barrier properties against Cu diffusion, as evidenced by the lower diffusion coefficient. Also revealed are various-sized pores, such as nanometer-sized vacancies (micropores) that exist in porous SiOCH and sub-nanometer-sized voids that exist even in a close packing crystal. In polymer science, these latter vacancies are sometimes called free volume [32, 33]. In this study, ‘pore’ or ‘porosity’ includes pores of all sizes and porosity is defined as the summation of the volume of all pores in a unit volume of a dielectric material.

Based on these calculations and simulation results, the barrier properties of dielectrics are controlled mainly by the porosity. The chemical composition actually caused the differences of the barrier properties between various films, because the chemical composition also affects the porosity of the films. The chemical interactions, such as coordination interaction and dipole–ion interaction, are not necessary for barrier performance. Therefore, we focused on the porosity of dielectrics hereafter to design a cap layer with a lower k-value.

2.2. Design of SiCH films and their precursors

Based on the above-mentioned calculations and simulations, we developed SiCH films with both a low porosity and density.
The local dipole moment increases the electro-negative atoms such as N, O and F. The polarization or local dipole moment, which is a consequence of the oxygen atoms in SiO\textsubscript{2}.5 polarizability. As shown in figure 4, in this method, the spaces were pores. Finally, we estimated the porosities of the materials by applying the hard sphere estimation are reported in our previous reports [14, 16].

The third method involves modifying the material composition. We estimated the relationship between the porosity and the k of SiCH films with a C/Si ratio of 4.0 and 6.0 using a quantum chemical calculation for two different material compositions: SiC\textsubscript{2}H\textsubscript{4} and SiC\textsubscript{2}H\textsubscript{2}, as is the case with Si(CH\textsubscript{2})\textsubscript{2} [37] (see footnote 5). Figure 4 indicates that increasing the C/Si ratio of a SiCH film should reduce the k without increasing the porosity. Therefore, in this study, we focused on SiCH films with as high C/Si ratio as 4. Compared with a terminated structure, the network structure is thought to be more favorable for retaining a low porosity [38]. The distance between two Si atoms is expected to be reduced by forming networks such as Si–CH–Si or Si–C–H–Si. Consequently, SiCH films with these network structures are more favorable for achieving strong barrier properties.

Therefore, we developed precursors iBTMS and DiBDMS for a Si–CH\textsubscript{2}–Si network and C-rich SiCH films [14, 15], and SSN and DVScP for a Si–C\textsubscript{2}H\textsubscript{2}–Si network and C-rich SiCH films [14, 16]. These precursors were designed based on their reactions in plasma estimated by quantum-chemical calculations. The details of the reaction estimation are reported in our previous reports [14, 16].

### 2.3. Experimental

Table 2 summarizes the deposition conditions for the SiCH films. For this low-k film deposition, we used a conventional anode-coupled PECVD apparatus with a 300 mm Si wafer using an RF frequency of 13.56 MHz. SiCH films with k = 2.9–4.5 were fabricated using 4MS, iBTMS and DiBDMS at 400–670 Pa using an RF power of 450–950 W at a substrate temperature of 350 °C. Conventional precursor, 4MS, was used as a reference for comparison. SiCH films with k = 2.7–4.5 were fabricated using DVScP and SSN at 67–260 Pa using an RF power of 100–600 W at a substrate temperature of 350 °C. In the deposition, precursors were supplied to the reaction chamber by direct injection without using a carrier gas.
The barrier properties of each SiCH film against Cu diffusion could be evaluated based on the I–V characteristics, in which the leak current measured using a Cu electrode was compared with that using an Al electrode [14–16]. The drift rate (diffusion velocity in an electric field) of Cu⁺ into each SiCH film was evaluated based on the difference in the leak current between using an Al electrode and that using a Cu electrode. A lower drift rate indicates better barrier performance against Cu diffusion [39, 40]. Moreover, each SiCH film with 50 nm thickness was formed on an electroplated Cu film (1500 nm). Then we annealed it at 200 °C in an air atmosphere for 12 h. The oxidation of the Cu substrate was checked visually. If SiCH films acted as barrier against O₂ diffusion, the surface of the under-laid Cu was not oxidized and its color did not change.

The apparatus and analyses used for structural evaluation were as follows. The composition and structural information of each SiCH film were evaluated using X-ray photoelectron spectroscopy (XPS; ULVAC PHI-1600 system) and Fourier-transform infrared adsorption (FTIR; PerkinElmer Spectrum 400 FTIR spectrometer). The C content of each SiCH film was evaluated by measuring the Cls and Si2p XPS spectra intensity. The quantities of Si–CH₂–Si networks, Si–C₃H₆–Si networks and Si–C₅H₂₆+1 fragments in each film were evaluated based on the FTIR peak intensity normalized by the film thickness.[14–16] The density of each film was evaluated by Rigaku x-ray reflectometry (XRR) and the pore structure by PAS. For PAS, 300 nm thick SiCH films were deposited on silicon substrates.

PAS is an effective method to directly evaluate a nano-sized pore and the sub-nano-sized void in SiCH films [18–25]. A positron is generated by the beta plus decay of ²²Na to ²²Ne. In the PAS measurement on the SiCH films in this study, the positrons were accelerated by an electric field toward the film; their penetration depth depended on the acceleration energy. Ellipsometric porosimetry (EP) is known as another method to evaluate the porosity and pore sizes in solid state materials. EP can analyze the amount of nano-sized pores and the free volume (sub-nano-sized voids). The V/T parameter only reflects the quantity of nano-sized pores. Because the penetration depth of a positron depends on the acceleration energy (E) of irradiating positrons, we can obtain the depth profile of these two parameters by varying E, thus yielding S–E and V/T–E curves.

### 3. Results and discussion

#### 3.1. Performance of SiCH films

Table 3 shows the drift rate of Cu⁺ into each SiCH film. We found that the barrier properties of the SiCH films prepared using DVScp or SSN were better than those using DiBDMS, iTMS or 4MS and that SiCH films with k = 3.5 using 4MS had the poorest barrier properties against Cu⁺ diffusion (i.e. the highest Cu drift rate). Moreover, the film with k = 3.5 exhibited good barrier properties against Cu and moisture, whereas that with k = 3.0 exhibited poor barrier properties, as summarized in table 3. Comparison between the two SiCH films prepared using DiBDMS reveals that a reduction in the k-value in a SiCH film caused these poor barrier properties.

#### 3.2. Composition and density of SiCH films

The differences in the properties of the structure of the SiCH films were evaluated by measuring the composition of each
SiCH film by XPS. Table 3 summarizes the results. The C/Si ratio of the SiCH film fabricated with DVScP was the highest of the five precursors, whereas that of SiCH with 4MS was the lowest. Newly designed organic silanes, iBTMS, DiBDMS, SSN and DVScP, were confirmed to be favorable for forming SiCH with a high C content. The high C content in SiCH films prepared using iBTMS or DiBDMS was thought to be derived from the iso-butyl fragment, as reported previously [15].

The density of SiCH with \( k = 3.5 \) prepared using each precursor measured by XRR is shown in table 3. The density of a SiCH film is generally affected by both its composition and porosity. The weight of a C atom is less than that of a Si atom, whereas the van der Waals radius of a carbon atom is 0.17 nm and that of a Si atom is 0.21 nm. We could not use the film density to directly compare the pore structures of SiCH films fabricated with 4MS, iBTMS, DiBDMS, SSN or DVScP, because the film density of C-rich SiCH is thought to be lower than that of Si-rich SiCH, while their porosities are similar.

### 3.3. Structure of SiCH films

The relationship between \( k \) and the structure of each SiCH film was investigated by FTIR spectroscopy to evaluate the amount of alkyl fragments, such as Si–CH\(_3\) and Si–C\(_2\)H\(_5\), and networks such as Si–C\(_2\)H\(_5\)–Si and Si–CH\(_3\)–Si. In the FTIR spectra (see the supporting information), the alkyl fragments, Si–CH\(_2\)–Si networks and Si–C\(_2\)H\(_5\)–Si networks peaked at 1250, 1350 and 1410 cm\(^{-1}\), respectively [41–43].

The ratio of fragments to networks (fragment/network ratio) was estimated as the FTIR peak intensity of networks divided by the peak FTIR intensity of fragments. Figure 5 shows this estimated ratio for SiCH films with \( k = 3.0–4.0 \) for each precursor. This ratio is thought to indirectly correspond to the amount of pores or voids, because there are larger spaces between alkyl fragments than between the network structure and because fragments have more freedom of movement, such as intra-molecular rotation. In other words, a lower fragment/network ratio is thought to indicate a lower porosity.

We found that the fragment/network ratio in SiCH films was lower for the novel precursors iBTMS, DiBDMS, SSN and DVScP that we designed than for 4MS. The SiCH film with \( k = 3.5 \) prepared using conventional 4MS showed a significantly higher fragment/network ratio than the other films. However, as we reported previously, controlling the composition of SiCH films with 4MS is so difficult that the C/Si ratio of SiCH films with 4MS was approximately constant at 2.0. These results indicate that the lower \( k \)-value in SiCH–4MS films was caused by an increased porosity, which is consistent with our material modeling shown in figure 4. In contrast, SiCH films with DVScP or SSN showed the lowest fragment/network ratio among the studied samples. Consequently, their porosity apparently decreased due to a higher C content, which is caused by the larger amount of Si–C\(_2\)H\(_5\)–Si networks.

In summary, our results on the barrier origin and material design reveal the successful fabrication of ideal SiCH films with a lower \( k \) and stronger barrier properties by effectively overcoming the trade-off relationship between the \( k \)-value and the barrier properties.

### 3.4. PAS analysis on SiCH films

Using PAS analysis, we directly evaluated the porous structures of SiCH films with \( k = 3.0–3.5 \) formed from iBTMS, DiBDMS, SSN, DVScP and 4MS. All of these SiCH films were 300 nm thick. Figure 6 shows the obtained \( S–E \) curve (figure 6a) and \( V/T–E \) curve (figure 6b) of the SiCH films from DiBDMS, iBTMS and 4MS with \( k = 3.5 \) (note that the \( S \) and \( V/T \) parameters at \( E > 10 \) keV reflect the pore structure of the silicon substrate). The SiCH films fabricated from SSN and DVScP with \( k = 3.5 \) were evaluated by PAS for pore structure analysis, as shown in the \( S–E \) curve (figure 7a) and \( V/T–E \) curve (figure 7b). Also shown are the results for the SiCH film with 4MS for reference. Table 4 summarizes the averages of the \( S \) parameter and the \( V/T \) parameter from \( E = 0.1 \) to 10 keV of the SiCH films from DVScP, SSN, DiBDMS, iBTMS and 4MS with \( k = 3.5 \). Among all of the SiCH films evaluated by PAS, the film from 4MS showed

### Table 3. Properties and structure of deposited SiCH films.

| Precursor | DVScP | SSN | iBTMS | DiBDMS | DiBDMS | 4MS |
|-----------|-------|-----|-------|--------|--------|-----|
| Dielectric constant, \( k \) | 3.5 | 3.5 | 3.5 | 3.5 | 3.0 | 3.5 |
| \( \text{Cu}^+ \) drift rate (ions cm\(^{-2}\)s\(^{-1}\)) | \( 1 \times 10^{10} \) | \( 1 \times 10^{10} \) | \( 5 \times 10^{10} \) | \( 5 \times 10^{10} \) | \( 8 \times 10^{10} \) | \( 1 \times 10^{11} \) |
| Barrier against \( \text{Cu} \) | Good | Good | Good | Good | Poor | Poor |
| Barrier against \( \text{O}_2 \) | Good | Good | Good | Good | Poor | Poor |
| C/Si ratio | 4.3 | 4.0 | 3.4 | 3.6 | 4.0 | 2.0 |
| Density (g/cm\(^3\)) | 1.53 | 1.47 | 1.48 | 1.50 | 1.40 | 1.45 |

**Figure 5.** Fragment/network ratio of SiCH films evaluated by FTIR spectroscopy.
the highest $S$ parameter, indicating that this film had more pores and/or voids than the other films. In the $V/T$ parameter, there was no difference between the DVScP, SSN, iBTMS, DiBDMS and 4MS films. Therefore, SiCH films from 4MS with $k = 3.5$ had more free volume (sub-nano-sized voids) than those from DVScP, SSN, iBTMS or DiBDMS, thus resulting in poor barrier properties of SiCH films prepared using 4MS.

The SiCH film from DVScP showed the lowest $S$ parameter, indicating that this film has the lowest number of pores and/or voids. The film from DVScP also had the lowest free volume (sub-nano-sized voids) than that from 4MS, and thus had strong barrier properties against Cu diffusion.

Based on table 4, SiCH films deposited using these newly developed precursors, iBTMS, DiBDMS, SSN and DVScP, have less free volume (sub-nanometer-sized voids) compared with the SiCH film deposited using the conventional precursor, 4MS.

Figure 8 and table 4 also show the $S$ parameter and $V/T$ parameter for the SiCH films prepared using DiBDMS with $k = 3.0$ and 3.5. At the interface between the SiCH film and the Si substrate, as shown in figure 8, both the $S$ and $V/T$ parameters of SiCH films with $k = 3.0$ were found to be higher than those with $k = 3.5$. This indicates that these $k = 3.0$ films had comparatively more nano-sized pores and free volumes around the SiCH/Si interface, which in turn caused a reduction in $k$ and a degradation in the barrier properties. On the other hand, the SiCH structure close to the surface might be rearranged during deposition to reduce the surface energy of SiCH films.

Figure 9 shows schematics of the pore structure of SiCH films based on the PAS results summarized in table 4. SiCH films with $k = 3.5$ using DVScP are thought to have few sub-nano-sized voids (figure 9(a)). In contrast, SiCH films with $k = 3.5$ using 4MS are thought to have a large number of sub-nanometer-sized voids (figure 9(b)). The SiCH film using DiBDMS with $k = 3.5$ had few sub-nano-sized pores (figure 9(c)), whereas those with $k = 3.0$ had both nano-sized and sub-nano-sized pores at the SiCH/Si interface (figure 9(d)).

The amount of free volume (sub-nano-sized pores) can be revealed by the $S$ parameter measurement. The comparison of the $S$ parameter in table 4 reveals that the SiCH film from DVScP had the lowest value, those from SSN and DiBDMS
Figure 8. (a) $S$–$E$ and (b) $V/T$–$E$ curves of SiCH films with $k = 3.0$ and 3.5 using DiBDMS.

Table 4. The results of PAS measurement.

| Film            | Precursor | $S$ parameter | $V/T$ parameter |
|-----------------|-----------|---------------|-----------------|
| SiCH ($k = 3.5$) | 4MS     | 0.543         | 0.588           |
| SiCH ($k = 3.5$) | iBTMS  | 0.539         | 0.588           |
| SiCH ($k = 3.5$) | DiBDMS | 0.533         | 0.588           |
| SiCH ($k = 3.5$) | SSN    | 0.535         | 0.587           |
| SiCH ($k = 3.5$) | DVScP  | 0.529         | 0.587           |
| SiCH ($k = 3.0$) | DiBDMS | 0.536         | 0.590           |

both had the second lowest, that from iBTMS had the third lowest and that from 4MS showed the highest value. This order is approximately consistent with the fragment/network ratios shown in figure 5. The comparison of the C/Si ratio results summarized in table 3 reveals that to realize SiCH films with a low $k$, the films need a higher C/Si ratio and thus yield only a small amount of free volume. The $S$ parameter of the SiCH film using DiBDMS was similar to or slightly lower than that using SSN, although DiBDMS were poorer for forming a network structure in SiCH films. The porosity of our SiCH films measured by PAS mainly depended on the network ratio. The $S$ parameter also became lower when high-hydrocarbon fragments were included in the films, because those fragments contributed to the lower $k$-value without a large increase of porosity. Owing to the larger content of high-hydrocarbon fragments such as $-\text{CH}_2\text{CH}(\text{CH}_3)_2$, SiCH films prepared using DiBDMS are thought to show a smaller $S$ parameter.

These results are consistent with our material design concept. The poor barrier properties of SiCH films was due to the high porosity, which includes both nano-sized and sub-nano-sized pores. To develop a SiCH film with good barrier properties and a low $k$, a high C/Si ratio utilizing the Si–C$_2$H$_4$–Si network structure is favorable. The newly developed precursor, DVScP, might be the best candidate for this purpose.

4. Conclusion

Cap layers for ULSI-Cu interconnects with lower $k$ and stronger barrier properties against Cu and moisture diffusion are required for further scaling of ULSIs. We developed novel precursors for PECVD to meet these demands. The difficulty is that lowering the $k$ value has a trade-off relationship with maintaining strong diffusion barrier properties. We used quantum mechanical simulations of Cu diffusion through SiO$_2$, SiN, SiOCH and SiCH films and found that the chemical composition of the films is not strongly correlated with the Cu diffusion but with the porosity of the films. The nitrogen and oxygen components of the films were expected to increase the $k$ of the films. Based on the results, we then designed the ideal dielectrics: SiCH films with Si–C$_2$H$_4$–Si networks. In our material design based on simulations, the porosity of the dielectrics should be kept lower for maintaining strong barrier properties. SiCH films with Si–C$_2$H$_4$–Si networks were estimated to maintain a lower porosity and a lower $k$. To fabricate ideal SiCH films, we designed novel precursors, iBTMS, DiBDMS, SSN and DVScP, based on quantum chemical calculations, because it was difficult to fabricate the ideal SiCH films by controlling only the process conditions in PECVD using conventional precursors.

We demonstrated in our previous report that newly designed precursors, DVScP and SSN, formed SiCH films with large amounts of Si–C$_2$H$_4$–Si networks and smaller amounts of fragments [16]. The precursor design based
on quantum chemical calculations and the performances of these SiCH films prepared using these precursors were demonstrated in our previous reports [15, 16]. Using iBTMS and DiBDMS, we could reduce the k of SiCH films as low as 3.5 while maintaining good barrier properties against Cu diffusion. SiCH films with \(k = 3.5\) using SSN and DVS\&P have better barrier properties than those using iTBMS and DiBDMS. Moreover, using SSN and DVS\&P, we could further reduce the k of SiCH film to 3.0 with the same barrier performance. The pore structure of SiCH films with \(k = 3.5\) were analyzed by PAS in this study, revealing that SiCH films with Si–C\(_2\)H\(_4\)–Si networks showed lower porosity, as we designed.

These results confirmed that our precursor design effectively generated the expected materials for ULSI-Cu cap layers that could overcome the trade-off relationship between low k and strong diffusion barrier performance. Moreover, our material design and precursor design concepts are extendable to the further development of PECVD processes for multi-functional requirements, as is the case with both a lower k and strong barrier properties.

These SiCH films and their precursors have not yet been applied to Cu-interconnects in commercial ULSI devices. The performances of the SiCH films were, however, examined and the RC delay time constant was reduced by 11.4% [6]. Further evaluations on the reliabilities of our SiCH films and the cost reduction of our precursors should be made for the practical use of this SiCH film as a cap layer in the future generation of ULSIs.

References

[1] Fracassi F, d’Agostino R and Favia P 1992 J. Electrochem. Soc. 139 2636
[2] Smith D L, Alimonda A S, Chen C-C, Ready S E and Wacker B 1990 J. Electrochem. Soc. 137 614
[3] Chen F, Bravo O, Chanda K, McLaughlin P, Sullivan T, Gill J, Lloyd J and Aitken J 2006 44th Proc. IEEE Reliability Physics Symp. p 46
[4] Wang Y H, Moitreyee M R, Kumar R, Shen L, Zeng K Y, Chai J W and Pan J S 2004 Thin Solid Films 460 211
[5] Chian C-C, Chen M-C, Ko C-C, Jang S-M, Yu C-H and Liang M-S 2003 Japan. J. Appl. Phys. 42 5246
[6] Nakahira J, Nagano S, Gawase A, Ohashi Y, Shimizu H, Chikaki S, Oda N, Hasaka S and Saito S 2010 Japan. J. Appl. Phys. 49 05FD04
[7] Loboda M J 2000 Microelectron. Eng. 50 15
[8] Chiang C-C, Chen M-C, Ko C-C, Wu Z-C, Jang S-M and Liang M-S 2003 Japan. J. Appl. Phys. 42 4273
[9] Cedric C-A and Vincent J 2007 Surf. Coat. Technol. 201 9260
[10] Cedric C-A, Vincent J, Agnes G and Barnes J-P 2008 Proc. Advanced Metallization Conf. p 381
[11] Chiang C-C, Wu Z-C, Wu W-H, Chen M-C, Ko C-C, Chen H-S, Jeng S-M, Yu C-H and Liang M-S 2002 Proc. of Advanced Metallization Conf. p 603
[12] Kobayashi C, Ohito K and Usami T 2010 Abstract of Advanced Metallization Conf. p P-21
[13] Lee S G et al 2001 Japan. J. Appl. Phys. 40 2663–8
[14] Shimizu H, Tajima N, Kada T, Nagano S, Ohashi Y and Hasaka S 2010 Japan. J. Appl. Phys. 49 05FF02
[15] Shimizu H, Tajima N, Kada T, Nagano S and Shimogaki Y 2011 Japan. J. Appl. Phys. 50 06EB01
[16] Shimizu H, Tajima N, Kada T, Nagano S and Shimogaki Y 2011 Japan. J. Appl. Phys. 50 08KA01
[17] Tajima N et al 2007 Japan. J. Appl. Phys. 46 5970
[18] Uedono A, Wei L, Tanigawa S, Suzuki R, Oghaki H, Mikado T and Ohji Y 1994 J. Appl. Phys. 75 3822
[19] Uedono A, Chen Z Q, Suzuki R, Ohdaira T, Mikado T, Fukui S and Shiota A 2001 J. Appl. Phys. 90 2498
[20] Uedono A, Suzuki T, Nakamura T, Ohdaira T and Suzuki R 2005 J. Appl. Phys. 98 043504
[21] Uedono A et al 2007 J. Appl. Phys. 102 064513
[22] Uedono A, Inoue N, Hayashi Y, Eguchi K, Nakamura T, Hirose Y, Yoshimaru M, Oshima N, Ohdaira T and Suzuki R 2009 Japan. J. Appl. Phys. 48 120222
[23] Oka Y, Uedono A, Goto K, Hirose Y, Matsuura M, Fujisawa M and Asai K 2011 Japan. J. Appl. Phys. 50 05EB06
[24] Sometani M, Hasunuma R, Ogino M, Kuribayashi H, Sugahara Y, Uedono A and Yamabe K 2012 Japan. J. Appl. Phys. 51 021101
[25] Uedono A, Verdonck P, Delabie A, Swerts J, Witters T, Conard T, Baklanov M R, Elshocht S V, Oshima N and Suzuki R 2013 Jpn. J. Appl. Phys. 52 106501
[26] Tajima N, Ohashi Y, Nagano S, Xu Y, Matsumoto S, Kada T and Ohno T 2009 IEEE Int. Interconnect Technology Conf. p 116
[27] McGrayer J D, Swanson R M and Sigmon T W, 1986 J. Electrochem. Soc. 133 1242
[28] Gupta D, Vieregge K and Sririkshan K V, 1992 Appl. Phys. Lett. 61 2178
[29] Favennec L, Jousseame V, Zenasni A, Bouchu D and Passeremond G 2006 IEEE Int. Interconnect Technology Conf. p 110
[30] Matz L M, Tsai T, Engbrecht E R, Taylor K, Haase G, Ajmera S, Kuan R, Kraft R and McKerrow A J 2005 Proc. of Advanced Metallization Conf. 437
[31] Tajima N, Hamada T, Ohno T, Yoned a K, Kobayashi N, Hasaka T and Inoue M 2005 IEEE Int. Interconnect Technology Conf. p 66
[32] Cohen M H and Turnbull D 1959 J. Chem. Phys. 31 1164
[33] Rouquerol J, Avnir D, Fairbridge C W, Everett D H, Haynes J, M, Pernicone N, Ramsay J D F and Unger K K, 1994 Pure Appl. Chem. 66 1739
[34] Sharmiryan D, Abell T, Iacopi F and Maex K 2004 Mater. Today 7 41
[35] Lim S W, Shimogaki Y, Nakano Y, Tada K and Komiyama H 1997 J. Electrochem. Soc. 144 2531
[36] Tajima N, Ohno T, Hamada T, Yoneda K, Kobayashi N, Shimr iki M, Miyazawa K, Hasaka S and Inoue M 2006 IEEE Int. Interconnect Technology Conf. p 122
[37] Shinriki M et al 2006 Proc. of Advanced Metallization Conf. p 339
[38] Loke A L S, Wetzel J T, Townsend P H, Tanabe T, Vrits R N, Zussman M P, Kumar D and Wong S S, 1999 IEEE Trans. Electron Devices 46 2178
[39] Chen Z, Prasad K, Li C Y, Lu P W, Lu S S, Tang S J, Gui D, Shu R and Kumar R 2004 Appl. Phys. Lett. 84 2442
[40] Birot M, Pilot J-P and Dunogues J 1995 Chem. Rev. 95 1443
[41] Rau C and Kulisch W 1990 Thin Solid Films 249 28
[42] Grill A and Neumayer D A, 2003 J. Appl. Phys. 94 6697
[43] Tsyba V T, Pushcheyeva K S and Vdovin V M, 1967 Chem. Heterocycl. Compd 3 782–3