Investigation into the Structural and Electrical Properties of a-SiCO:H as a Diffusion Barrier to Copper

Jaeyeong Heo and Hyeong Joon Kim*
School of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

In this study, we attempted to deposit low dielectric constant a-SiCO:H as a copper diffusion barrier by the plasma-enhanced chemical vapor deposition method using an organosilicon precursor, bis(trimethylsilylmethane) (BTMSM, C7H20Si2). The dielectric constant of the a-SiCO:H films increased from 2.54 to 3.25 as the deposition temperature was increased from room temperature to 280°C. The refractive index increased gradually with increasing deposition temperature, indicating that the film has a denser structure as well as a higher dielectric constant at higher deposition temperatures. The Fourier transform infrared and X-ray photoelectron spectroscopy analyses indicated that the chemical structure of the Si atoms in the films changed from the D moiety to the T moiety with increasing deposition temperature. The electrical conduction mechanism of the a-SiCO:H films was determined to be a Schottky emission current in the high field region ($E > 0.4$ MV/cm).

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Interest in the development of reliable low-$k$ thin films has increased over the past few years because of their pivotal role in ultralarge scale integration (ULSI) intermetal dielectric (IMD) materials. As the circuit feature size shrinks below 0.18 μm, the increase in the signal propagation delay due to the interconnects becomes important. The smaller line dimensions increase the resistance ($R$) of the metal lines and the narrower interline spacing increases the parasitic capacitance ($C$) between the lines. To reduce the $RC$ delays, low-$k$ dielectrics ($k < 3.0$) are being considered to replace the currently used SiO2 ($k \sim 4.2$) for interlayer dielectric insulation. It is also desirable to replace the etch stop material, silicon nitride, with low-$k$ dielectric materials, in order to further reduce the effective dielectric constant of the Cu interconnect system. The etch stop material acts as a copper diffusion barrier and protects the copper during the processing steps. In a previous study, amorphous low-$k$ carbide ($k < 5.5$) deposited using trimethylsilane gas was used as a highly insulating hard mask or etch stop layer. Considerable effort has recently been made to develop etch stop materials by plasma enhanced chemical vapor deposition (PECVD) using various organosilicon precursors, such as trimethylsilane (3MS), octamethylcyclotrisiloxane (OMCTS), and trimethoxysilane. Although the bis(trimethylsilylmethane) (BTMSM) precursor is known to be an attractive candidate for the deposition of low-$k$ materials, its use as a precursor for the deposition of a diffusion barrier or etch stop layer has not yet been reported.

In this study, a-SiCO:H films with a relatively lower $k$ value (2.5–3.2) were deposited by inductively coupled plasma (ICP)-type PECVD using BTMSM as the precursor. Argon was used as a dilute gas, whose role is to increase the dissociation efficiency of the precursor. The deposition and structural properties of the films were investigated by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements. The carbon contents in the film were compared by atomic emission spectroscopy (AES) and XPS, and the film roughness was checked by atomic force microscopy (AFM) measurements. The leakage conduction mechanism of the a-SiCO:H films was also determined by measuring the current density–voltage ($J$–$V$) characteristics of the fabricated metal-insulator-semiconductor (MIS) capacitors.

Experimental

Low-$k$ a-SiCO:H films were prepared on p-type silicon (100) substrates by radio frequency (13.56 MHz) ICP PECVD using a CH3-containing organosilane source, namely, the BTMSM (C7H20Si2) precursor. The chamber was pumped to a base pressure of $10^{-3}$ Torr using a booster and a dry pump, and the processing pressure and plasma power were fixed at 0.2 Torr and 700 W, respectively. The precursor was vaporized and carried to the reaction chamber with inert Ar gas at a flow rate of 50 sccm from a thermosublimation bubbler maintained at 30°C. The oxygen content in all of the films was maintained at about 15–20 atom %, which was confirmed by the XPS measurement. The temperature of the substrate was varied from 25 to 280°C.

The films were postdeposition-annealed (PDA) for 30 min at 450°C in an N2 atmosphere in a conventional furnace, and a Pd/a-SiCO:H/p-Si MIS capacitor structure was fabricated by depositing Pt-top electrodes using the electron beam evaporation method through a shadow mask. All of the films were deposited to a thickness of about 50 nm to preclude the dependency of the dielectric constant on their thickness. After depositing aluminum as a back contact metal, annealing was performed at 400°C for 30 min under a forming gas (5% H2 + 95% N2). A Hewlett-Packard 4194A impedance meter and a 4140B picoammeter were used for the capacitance-voltage (C–$V$) and J–$V$ measurements, respectively. The C–$V$ measurement frequency was fixed at 1 MHz. We elucidated the structure of each film by XPS (Sigma Probe, ThermoVG) and FTIR (JASCO FT/IR-660 plus).

Results and Discussion

The a-SiCO:H films were deposited in the temperature range from 25 to 280°C, in order to study the dependence of their structural and electrical properties on the deposition temperature. Figure 1a shows the dependence of the deposition rate on the deposition temperature. As the deposition temperature increases, the deposition rate gradually decreases. The inverse proportionality of the deposition rate to the deposition temperature conforms to the general behavior observed for the growth of organosilicate glass (OSG) thin films. In order to study the variation of the deposition rate behavior with temperature, an Arrhenius plot of the deposition rate was constructed, as shown in Fig. 1b. It shows linear behavior with (1/$T$), and its activation energy is ~0.077 eV. This negative activation energy indicates that the film formation reaction is controlled by the absorption and desorption steps. Because the reactive species involved in the deposition of the film are CH3, related, it is considered that their desorption increases with increasing deposition temperature.

Figure 2a shows the variation in the refractive index and thickness loss with the deposition temperature after PDA. As the deposition temperature increases, the refractive index slightly increases to 2.5 at 180°C and then increases sharply as the deposition temperature is further increased. After PDA, the refractive index is lowered in the low-deposition temperature region but increases slightly above...
180°C. This lowering of the refractive indices of the films in the lower temperature region can be explained as follows: thermally unstable CH radicals, which can exist in the films and are removed during N$_2$ annealing, can be pumped out with ease so that the PDA makes the film more loose. In the higher deposition temperature region, however, the number of unstable CH radicals in the film is so small that the high-temperature PDA makes the film denser. Gray et al. reported similar behavior for trimethylsilane-based a-SiC:H films; in their study, the $k$ value of the a-SiC:H film at 350°C dropped considerably after the forming gas anneal process ($\Delta k = 0.8$), but interestingly that of the a-SiC:H film deposited at 400°C increased by 0.1.9

The thickness loss shows a drastic variation with the deposition temperature; it is as high as 13.5% for the film at room temperature and it decreases first to 7–8% and eventually to about 3% as the deposition temperature increases. This thickness loss of the film of almost 14% seems unusual, but Grill reported that a thickness loss of over 20% could be obtained in the deposition of low-$k$ films.10

The compositional change of the films measured by XPS shows that the carbon concentration in the film decreases from 52.5 to 46.7%, while the silicon concentration increases from 31.6 to 34.5%, as the deposition temperature is increased from room temperature to 280°C. This result also supports the above explanation of the change in the refractive index.

The dielectric constant and the contribution of the electronic polarization to the dielectric constant for the a-SiCO:H films after PDA measured by the C–V method are illustrated in Fig. 2b. The dielectric constant gradually increases as the deposition temperature increases, which is consistent with the behavior of the refractive index and thickness. The lowest $k$ value of 2.54 is observed for the film prepared at room temperature and it increases and seems to reach a saturated value of 2.75 at 150°C; however, it increases sharply again at around 180°C and then increases to 3.25 at 280°C. Considering the above results for the refractive index, thickness, and dielectric constant, the deposition temperature range of 150–180°C seems to represent the transition point of the deposition behavior in our system. The dielectric constant comprises three components arising from the contributions of the electronic, ionic, and dipolar polarizations.11 The ionic and dipolar $k$ value, obtained by subtracting the electronic contribution ($n^2$) from the $k$ value at 1 MHz, increases from 0.24 to 0.55 with increasing deposition temperature. The relatively low ionic and dipolar $k$ value (0.24) of the film deposited at 25°C is attributed to the low polarizability of the C–C and Si–C bonds, as confirmed by the XPS measurements described later.

Figure 3 shows a comparison of the FTIR spectra of the a-SiCO:H film deposited at a temperature of 25°C ($k = 2.5$) and a typical low-$k$ a-SiOC:H film. We used the term a-SiOCH when O concentration is higher than that of C, of which the concentration was measured by XPS analysis; in the opposite situation, we used the term a-SiCO:H. The low-$k$ a-SiOC:H film ($k = 2.9$) was deposited in the same PECVD chamber at room temperature, a chamber pressure of 0.2 Torr, a plasma power of 80 W, and an O$_2$ flow rate of 50 sccm. The peak positions corresponding to the symmetric
stretching of the Si-(CH₃)₃ bonds that generally occur between 1250 and 1280 cm⁻¹ are shifted. The main building blocks for OSG materials are the “M,” “D,” “T,” and “Q” groups corresponding to the mono-, di-, tri-, and quad-oxygen-substituted silicon atoms, respectively. The first three groups appear at 1250, 1260, and 1270 cm⁻¹, respectively, and the Q group does not produce a CH₃ related peak. The symmetric stretching peak is located at 1255 cm⁻¹ for the a-SiCO:H film, but it is shifted to 1270 cm⁻¹ for the a-SiOC:H film. The peak at 1133 cm⁻¹ for the a-SiOC:H film is attributed to the existence of larger angle Si–O–Si bonds in a cage structure with a bond angle of approximately 150°, which are not present in the a-SiOC:H film. The absorption peaks at about 844 and 804 cm⁻¹ for a-SiOC:H film are attributed to M and D vibrations, respectively. They are shifted to 835 and 798 cm⁻¹ for a-SiCO:H film, respectively. As more carbon is incorporated in the film, it has been reported that absorption peaks of the Si–(CH₃)₃ and Si–O–Si bonds shift to lower wavenumbers (redshift). Did not directly refer to the same redshift of 844 and 804 cm⁻¹ peaks, but those peaks are well explained by the same mechanism. The relative intensity of the Si–O–Si bonds in the a-SiOC:H film is much stronger than that in the a-SiCO:H film, because the former is highly oxidated while the latter is not. This indicates that the structure of the a-SiCO:H film is different from that of the conventional low-k a-SiOC:H film.

The FTIR spectra of the films are shown in Fig. 4a as a function of the deposition temperature. The heights of the Si–(CH₃)₃ peaks at 1255 and 835 cm⁻¹ decrease with increasing deposition temperature. The position of the Si–(CH₃)₃ peak at 1255 cm⁻¹ is also shifted slightly to a higher wavenumber with increasing deposition temperature, as shown in Fig. 4b. The intensity ratios of Si–(CH₃)₃ to Si–O–Si and M to D are depicted in Fig. 4c. They are generally used as a reference for estimating the degree of polymerization of the film. The intensity ratio of Si–(CH₃)₃ to Si–O–Si decreases with increasing deposition temperature and the silicon moiety ratio of M to D also decreases from 90.6 to 78.4%, which is consistent with the previous results.

Figure 4a shows the XPS curve-fitting of the Si 2p core level of each film. The C–C bonds were set to 284.9 eV. All fits were obtained by constraining the full-width-at-half-maximum to be equal to 1.45 eV, which is commonly used for the spectra deconvolution of OSG thin films. We assume that the shift of the binding energy due to the various combinations of carbon and hydrogen atoms is smaller than the shift caused by an oxygen atom. The four chemically distinct Si atoms are assigned as follows: M (101.2 eV), D (101.9 eV), T (102.7 eV), and Q (103.4 eV). The Si 2p peak of the reference thermal oxide only fitted well with the Q moiety and the binding energies of the a-SiCO:H films are shifted toward a lower energy, as compared with the reference oxide. The shift of the binding energy is used to distinguish between silicon in the organic and inorganic state. It is clear that the main building block is D. The relative proportion of Si moieties, however, varies with the deposition temperature.

Figure 5a shows the XPS curve-fitting of the Si 2p core level of each film. The C–C bonds were set to 284.9 eV. All fits were obtained by constraining the full-width-at-half-maximum to be equal to 1.45 eV, which is commonly used for the spectra deconvolution of OSG thin films. We assume that the shift of the binding energy due to the various combinations of carbon and hydrogen atoms is smaller than the shift caused by an oxygen atom. The four chemically distinct Si atoms are assigned as follows: M (101.2 eV), D (101.9 eV), T (102.7 eV), and Q (103.4 eV). The Si 2p peak of the reference thermal oxide only fitted well with the Q moiety and the binding energies of the a-SiCO:H films are shifted toward a lower energy, as compared with the reference oxide. The shift of the binding energy is used to distinguish between silicon in the organic and inorganic state. It is clear that the main building block is D. The relative proportion of Si moieties, however, varies with the deposition temperature.
The proportion of the C moieties in the films. The relative proportion of C–Si increases with increasing deposition temperature, while that of the less polarizable C–C bonds decreases. The C 1s peak fit explains why the film deposited at low temperature had a low dielectric constant. The C–O/H20849/H20850/O/H20850 peak also decreases as the deposition temperature increases.

Figure 8a shows the leakage current density as a function of the applied electric field for the a-SiCO:H films deposited under different deposition conditions. The current densities at 1 MV/cm are about 1 × 10−7–1 × 10−8 A/cm2 and, exceptionally, that of the film deposited at 25°C is as low as 4 × 10−9 A/cm2. The electrical breakdown field is about 5 MV/cm for all of the films (not shown). In order to verify the conduction mechanism of the a-SiCO:H films in the high field region (E > 0.4 MV/cm), a plot of the leakage current density vs the square root of the applied field was made. The linear relation of ln(J) to the square root of the applied electric field corresponds to Schottky emission or Poole–Frenkel conduction.17 As shown in Fig. 8b, the k values derived from Schottky emission plot at room temperature correspond relatively well with those obtained from the C–V measurement of the MIS capacitors, while those derived from the Poole–Frenkel mechanism are greater than 20. Unfortunately, all of the samples, except for those deposited at 210 and 280°C, show a leakage current density which increases with increasing measurement temperature, and this could mislead us to obtain wrong k values for the films at higher measurement temperatures. The thermal instability of the films is presumably due to the less dense structure and thermally weak C–C bonds of the films deposited at low temperature.

Conclusions

In summary, a-SiCO:H films were deposited as a copper diffusion barrier by the ICP-type PECVD method using the organosilicon precursor, BTMSM. The dielectric constant of the a-SiCO:H films varied from 2.54 to 3.25 as the deposition temperature increased from room temperature to 280°C. The refractive index also gradually increased with increasing deposition temperature; the films fabricated at a higher deposition temperature have a denser structure and thus a higher dielectric constant. The FTIR and XPS analyses confirmed that the chemical structure of the films varies with the deposition temperature and that the T moiety of Si is preferred to the D moiety at higher deposition temperatures. The electrical conduction mechanism for the a-SiCO:H films was studied with MIS capacitors and it was found that Schottky-emission-type behavior is seen in the high field region (E > 0.4 MV/cm). It was verified that the deposition temperature plays a crucial role in determining the properties of the a-SiCO:H films, such as their composition, dielectric constant, and leakage current density.
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References