A study on the structure of Si-O-C thin films with nano size pore by ICPCVD

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ABSTRACT

Si-O-C(-H) thin film with a low dielectric constant were deposited on a p-type Si(100) substrate by an inductively coupled plasma chemical vapor deposition (ICPCVD). Bis-trimethylsilylmethane (BTMSM, H₂C₂-Si-CH₃-Si-C₃H₃) and oxygen gas were used as precursor. Hybrid type Si-O-C(-H) thin films with organic material have been generated many voids after annealing. Consequently, the Si-O-C(-H) films can be made a low dielectric material by the effect of void. The surface characterization of Si-O-C(-H) thin films were performed by SEM(scanning electron microscope). The characteristic analysis of Si-O-C(-H) thin films were performed by X-ray photoelectron spectroscopy (XPS).

KEYWORD
Si-O-C thin films, low-k, XPS, pore, reaction mechanism

I . INTRODUCTION

A low dielectric material has been required for the multilevel interconnection of the ULSI (ultra large scaled integrated circuits) device as a device performance. Low temperature deposition is required for multilevel interconnection interlayer dielectric because thermal stress affects device characteristics and wirability reliability. A low dielectric material is used to reduce propagation delay times, cross-talk
noise between metal layers, and power dissipation from RC coupling \cite{1-3}. Low temperature deposition techniques using organic sources such as H2O-TEOS (tetraethylorthosilicate) plasma-enhanced chemical vapor deposition (PECVD), biased electron cyclotron resonance (ECR) chemical vapor deposition (CVD) and helicon wave plasma CVD have been investigated \cite{4}. Since the development and integration of those new low dielectric materials have been examined recently, the hybrid-type film mixed with organic and inorganic materials is being examined as possible candidates suitable to low dielectric material in ultra high density of device integration. There is still an ongoing discussion on the best choice of the low-k dielectric between spin-on and plasma-enhanced chemical vapor deposited materials. However, it becomes generally known that plasma-enhanced chemical vapor deposition method can offer better low-k films than spin-on method. The hybrid type film between organic and inorganic material is a promising candidate for low-k material with stable thermal properties \cite{5}. One of the hybrid-type low dielectric material is Si-O-C(-H) thin films. In this work, Si-O-C(-H) thin films were deposited by an inductively coupled plasma chemical vapor deposition (ICP-CVD). High plasma density of about 1012cm\(^{-3}\) was obtained at low pressure (<450mTorr) with the rf power of about 300\text{ W} in ICPCVD \cite{6}. Si-O-C(-H) thin films were investigated by a chemical analysis and the structure of the film with voids was discussed.

II. Experiments

The Si-O-C(-H) thin-film was deposited on the p-type Si(100) substrate by ICPCVD with rf power at 13.56MHz. Precursor mixed with BTSM and O\(_2\) was used. The total flow rate of precursor was 20 sccm while the flow rate ratio of BTSM(Ar):O\(_2\) was varied 9sccm:11sccm, 8sccm:12sccm, 7sccm:13sccm and 6sccm:14sccm, respectively. Working pressure was 450 mTorr and the substrate was not heated and the annealing process was performed at temperature of 300\textdegree C, 400\textdegree C and 500\textdegree C, respectively for 30 minutes in vacuum. The BTSM was vaporized and carried by argon gas with a thermostatic bubbler at 35\textdegree C and all of the gas delivery lines were heated and kept at a constant temperature of 40\textdegree C. The dielectric constant of the film was measured by C-V measurement using a MIS (metal-insulator-semiconductor) structure. The structural study of Si-O-C(-H) thin film mixed with organic and inorganic materials with nano-pore was performed by XPS. Finally the reciprocal relationship between relative dielectric constant and the chemical structure before and after annealing was investigated.

III. Results and Discussion

Fig. 1 shows the XPS survey scan spectra of as-deposited film and annealed films at different temperatures, respectively.

Fig. 1. The XPS survey scan spectra of as-deposited film and annealed films of the BTSM:O\(_2\) flow rate ratio

Si2p, C1s and O1s electron orbital spectra consist of peak centered at approximately 102eV, 282eV and 531eV, respectively. To research chemical shift as a function of annealing temperature, Fig. 2 shows Si2p electron orbital spectra of the range from 986cm\(^{-1}\) to 1036cm\(^{-1}\). The main peak of Si2p of the as-deposited film is shown in Fig. 4(a) at 100.91eV. Fig. 2 shows that the main peak of Si2p electron orbital spectra shift to high binding energy as a function of annealing temperature. The main peak of the annealed films at 300\textdegree C, 400\textdegree C, 500\textdegree C and 600\textdegree C are 101.05eV, 101.21eV, 101.49eV and 101.68eV, respectively.
Fig. 3. The Si2p narrow scan spectra of the films in the range from 98cm-1 to 102cm-1 at 300°C, 400°C, 500°C and 600°C, respectively.

Fig. 4. The C1s narrow scan spectra of the range from 280cm-1 to 285cm-1.

Fig. 5. The O1s narrow scan spectra of the range from 528cm-1 to 534cm-1.

The C1s and O1s narrow scan spectra are shown at the Fig.4 and the Fig. 5. The main peaks of C1s shifted chemically as increasing the annealing temperature, but the main peaks of O1s were almost unchanged. From these result, we can confirm that Si–O–C(–H) thin films become chemically stability because of shifting to higher binding energy after annealing. Fig.6 shows that Si–O open link was changed into Si–O ring link by annealing.

Fig. 6. The reaction mechanism using the chemical shift of Si–O–C(–H) thin film by XPS.

The OH related groups are made from Si–CH3 alkyd group and oxygen recombination during the deposition, and then Si–O open link increase. Two OH bonds recombine H2O and oxygen, and then Si–O ring link increase during the annealing. H2O are evaporated after annealing. Binding Energy of SiO3 and C–Si are small than that of SiO4 and C–O(1,2). About H9C3–Si–CH2–Si–C3H9 (BTMSM) as a precursor, major feature of this precursor is a very strong Si–CH2–Si bond between two silicon atoms. The Fig. 7(d) shows that the bonding structure changes to CO(1,2) after annealing. Consequently, Chemical bonding of Si–O–C(–H) thin films becomes stable and the bonding structure is stronger than that of as-deposited film by annealing. From these result, it can be suggested a pore structure of Si–O–C(–H) thin films like a ladder type of Fig. 7.

Fig. 7. Pore structure of a ladder type in Si–O–C(–H) thin films.
The dielectric constant of as-deposited film is higher than that of annealed film because of OH bonds. As increasing the annealing temperature, the dielectric constant of film decreased because of the reduction of the OH groups due to evaporating of H2O. The thickness and the capacitance of film were measured FE-SEM and HP 4280A C-V meter. The dielectric constant of as-deposited film was 5.3. The dielectric constant of films annealed at 300°C, 400°C and 500°C were 3.5, 3 and 2.4 as shown Si2p in Fig 2(a), respectively. The dielectric constant of annealed films at 600°C is lower than 2.4 because of large chemical shift of Si2p in Fig 4(b).

IV. Conclusion

The bonding structure of the Si-O-C(-H) thin films was investigated from XPS spectra analysis. It can be verified that chemical shift of the Si2p increase as a function of annealing temperature. The Si–O open link was formed by combination of CH3 groups and oxygen during the deposition. The Si–O open link changed into stable bonding structure of the Si–O ring link by annealing. The dielectric constant of annealed film becomes smaller than that of as-deposited film, because of the reduction of OH groups by H2O evaporation and the void formation during the annealing. Therefore, Si-O-C(-H) thin films formed by O2/BTMSM inductively coupled plasma CVD is a very promising low-k material due to chemical and thermal stability.

Reference

[6] Shou-Young JING and Chi Kyu CHOI JKPS.