

ICPCVD방법에 의한 나노기공을 갖는 Si-O-C 박막의 형성에 관한 연구

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

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요 약

ULSI(ultra large scaled integrated circuits)의 고집적화와 고속화를 위한 다층 배선 기술 중에서 층간 절연막의 특성을 향상시켜주는 것은 매우 중요한 요소이다. 소자의 소형화에 따른 절연층의 용량에 의한 신호의 지연을 방지하고 급속배선간의 상호간섭을 막아주기 위해서 현재 요구되는 $0.13\mu\text{m}$ 급 소자의 경우에는 유전율이 매우 낮은 $k \leq 2.0$ 인 층간 절연막이 필요하게 된다. 이러한 차세대 반도체 소자의 층간 절연물질로서 사용될 유력한 저유전 물질로 Nanoporous silica($k=1.3 \sim 2.5$)를 적용하려는 연구가 진행되고 있다(1)-(3). 그러한 물질 중에 하나가 organosilicate films이 있는데 carbon-doped oxides, silicon-oxycarbides, carbon-incorporated silicon oxide film, organic-inorganic hybrid type Si-O-C thin films 혹은 organic-inorganic hybrid silica materials 등으로 불린다. 이에 본 연구에서는 nano-pore를 갖는 유무기 하이브리드 구조의 저유전 박막을 BTMSM/ O_2 의 혼합된 precursor를 사용하여 ICPCVD 방법에 의해 형성하였다. 총 유량을 20sccm이 되도록 하여 O_2 :BTMSM(Ar)의 유량비를 변화시키며, 작업진공도는 300mTorr였다. 기판은 가열하지 않고, p-type Si(100) 위에 Si-O-C-H 박막을 형성하였다. 열적안정성을 조사하기 위하여 300°C, 400°C, 500°C에서 30분간 열처리하여 비교 분석하였다. 형성된 박막의 특성은 XPS로 분석하여 유전상수와 상관계수를 조사하였다.

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, $\text{H}_3\text{C}_3\text{-Si-CH}_2\text{-Si-C}_3\text{H}_9$) 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

1. INTRODUCTION

A low dielectric material has been required for the multilevel interconnection of the ULSI (ultra large scaled integrated circuits) devices as a device

performance. Low temperature deposition is required for multilevel interconnection interlayer dielectric because thermal stress affects device characteristics and wiring reliability. A low dielectric material is used to reduce propagation delay times, cross-talk

noise between metal layers, and power dissipation from RC coupling [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 [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 [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 (ICPCVD). High plasma density of about 10¹²cm⁻³ was obtained at low pressure (<450mTorr) with the rf power of about 300W in ICPCVD [6]. Si-O-C(-H) thin films were investigated by a chemical analysis and the structure of the film with voids was discussed.

II. Experimentals

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 BTMSM and O₂ was used. The total flow rate of precursor was 20 sccm while the flow rate ratio of BTMSM(Ar):O₂ 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°C, 400°C and 500°C, respectively for 30 minutes in vacuum. The BTMSM was

vaporized and carried by argon gas with a thermostatic bubbler at 35°C and all of the gas delivery lines were heated and kept at a constant temperature of 40°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.

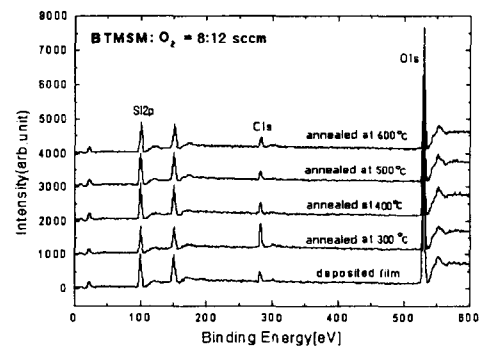


Fig. 1. The XPS survey scan spectra of as-deposited film and annealed films of the BTMSM:O₂ flow rate ratio

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 98cm⁻¹ to 102cm⁻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°C, 400°C, 500°C and 600°C are 101.05eV, 101.21eV, 101.49eV and 101.69eV, respectively.

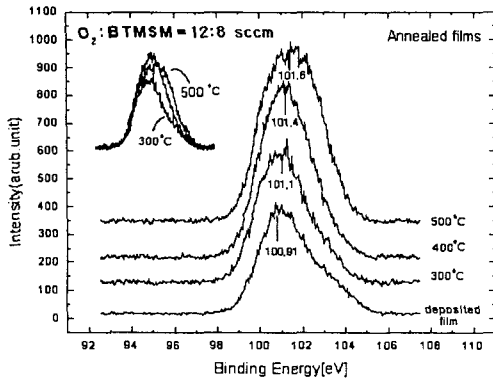


Fig. 3. The Si2p narrow scan spectra of the films in the range from 98cm-1 to 102cm-1 at 300°C, 400°C, 500°C and 600°C, respectively.

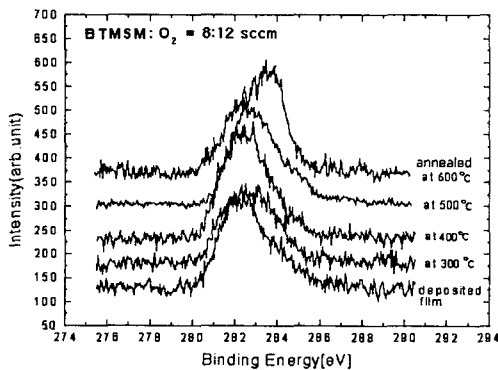


Fig. 4. The C1s narrow scan spectra of the range from 280cm-1 to 285cm-1.

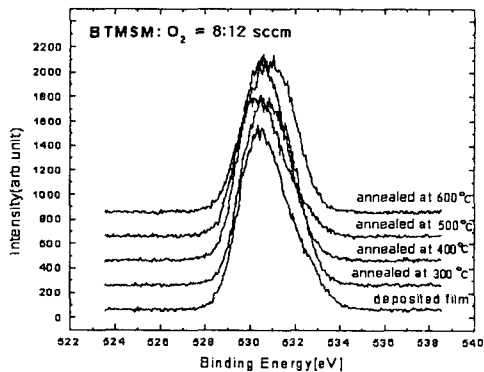


Fig. 5. The O1s narrow scan spectra of the range from 528cm-1 to 534cm-1.

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.

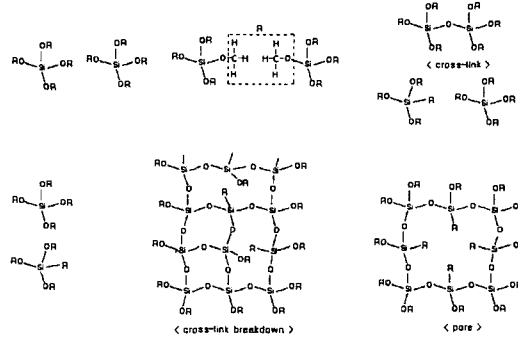


Fig. 6. The reaction mechanism using the chemical shift of Si-O-C(-H) thin film by XPS.

The OH related groups are made from Si-CH3 alkyl 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.

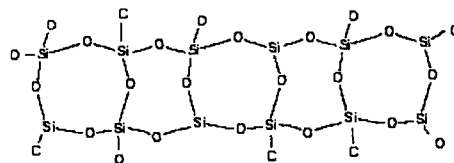


Fig. 7. Pore structure of a ladder type in Si-O-C(-H) thin films.

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.

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