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Low Dielectric Constant Fluorinated Oxide Films Prepared by Remote Plasma Chemical Vapor Deposition

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Low dielectric constant SiOF films were deposited using $SiF_4/SiH_4/O_2$ mixtures by a remote plasma chemical vapor deposition. The refractive index and relative dielectric constant decrease with increasing SiF_4 flow rate. The fluorine content in the SiOF film was increased by increasing SiF_4/SiH_4 ratio. With increase of fluorine content in the SiOF film, the peak position of Si-O stretching mode shifts to higher wave number. The SiOF film, deposited with SiF_4/SiH_4 mixture (SiF_4/SiH_4 =40), exhibited a F content of 12 at. % and a dielectric constant of 3.38.

1. INTRODUCTION

As advanced IC's approach sub-half micron geometries, the challenge of the interlevel dielectric process becomes filling narrow gaps with a high aspect ratio and global planarization. On the other hand, in device-switching performance, high performance devices are approaching speed limitations due to the interconnect dielectrics of conventional silicon oxide. The dielectric constant impacts significantly the clock frequency, and devices operate through the RC time delay of the interconnect wiring.[1] Recently, many fabrication techniques of low dielectric constant films have been investigated. In particular, fluorine doped into silicon oxide has been studied by various techniques in order to get low dielectric constant, such as conventional tetraethoxysilane (TEOS)-based PECVD using hexafluoroethane (C_2F_6), room-temperature catalytic CVD using fluoro-triethoxy-silane (FTES)-H_2O and ECR-CVD using tetrafluorosilane (SiF_4)-O_2.[2,3,4]

In our present work, we have studied the deposition of SiOF films using gas mixtures of SiF_4, SiH_4 and O_2 by remote plasma chemical vapor deposition (RPCVD). The structural and dielectric properties of fluorinated silicon oxide (SiOF) films are described.

2. EXPERIMENTAL DETAILS

The SiOF films were deposited in a RPCVD reactor using He and O_2 as the exciting species. The substrate materials for SiOF deposition in this study were (100) oriented p-type silicon wafer. To deposit SiOF films, the He and O_2 were passed through the plasma generating region contained inside a cylindrical quartz tube. The plasma was generated by applying RF power to an induction coil, wrapped around the outside of quartz tube. In the deposition area, silane diluted in He and SiF_4 was introduced from the circular ring in the reactor that was attached below the discharging tube for the deposition of SiOF films.[5,6]

Table I shows the deposition conditions of SiOF films by RPCVD. The flow rates of He, O_2, SiH_4 were fixed at 100 sccm, 50 sccm, and 0.5 sccm, respectively, and SiF_4 flow rate was varied. The substrate temperature was fixed at 300 °C.

Table I. The deposition parameters for the SiOF films by RPCVD.

Gas pressure	0.5 mbar
RF power	100 W
T_s	300 °C
Gas flow rates (sccm) :	
He	100
O_2	50
SiH_4	0.5
SiF_4	0-20

The film thickness and refractive index were measured by Rudolph AutoEL-3 Ellipsometer operated at 632.8 nm. The structural variations and compositions of SiOF film were evaluated using Fourier transformation infrared spectroscopy (FT-IR), and x-ray photoelectron spectroscopy (XPS). The FT-IR and the XPS measurements were carried out by Bomem 100 series FT-IR spectrometer and V.G. Scientific ESCALAB 200R spectrometer, respectively. Dielectric constant was evaluated by C-V measurement at 1 MHz with metal-oxide-semiconductor (MOS) structures formed on the p-type silicon wafer with a resistivity 0.85 ~ 1.15 Ω/cm using aluminium dot electrode.

3. RESULTS AND DISCUSSION

Figure 1 shows the refractive index of SiOF film as a function of flow rate ratio of SiF_4 to SiH_4, denoted by $[SiF_4]/[SiH_4]$. The refractive index decreases with increasing $[SiF_4]/[SiH_4]$, due to the incorporation of F into

SiO_2 film. This result indicates that some change in the film structure, such as transformation of film composition and variation of film density, are arisen by incorporation of F. The F atoms were bonded with Si atoms and bonding cleavages were occured in the local environment of Si-O bonds. It seems that the $SiO_{2-x}F_x$ configuration is generated and thus microvoid is appeared in the film.

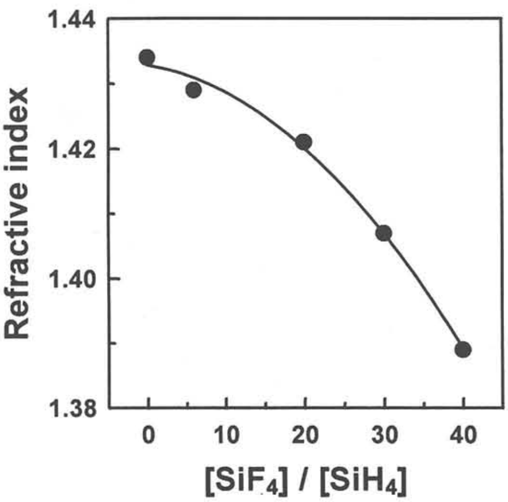

Fig. 1. Refractive index of SiOF films as a function of $[SiF_4]/[SiH_4]$.

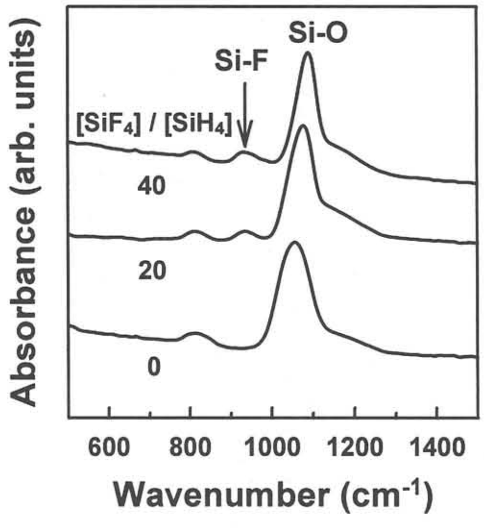

Fig. 2. FTIR absorption spectra for SiOF films.

Figure 2 shows the typical FT-IR absorption spectra for the SiOF films. For comparison, SiO_2 film was deposited with no SiF_4. The SiO_2 film shows absorbance peaks at 1055 cm^{-1} and 810 cm^{-1}, corresponding to stretching and bending modes of Si-O vibration, respectively. The SiOF films deposited with SiF_4 show Si-F stretching modes at 935 cm^{-1}, [7] and the peak intensity of Si-F modes increases slightly with $[SiF_4]/[SiH_4]$. These results mean that Si-F bonds are formed by SiF_4 addition and the significant amounts of fluorine atoms are incorporated in the Si-O bonding network. The peak position of Si-O stretching modes at 1055 cm^{-1} is gradually shifted to higher wave number with increase of $[SiF_4]/[SiH_4]$. These results indicate that Si-O bonding configurations is influenced by Si-F formation. And Si-O bonds become stronger with the addition of fluorine, caused by high electronegativity of F atoms. The variation of vibration frequency is similar to the shift in the hydrogen bonding configuration from SiH to SiH_2 by the addition of fluorine in hydrogenated amorphous silicon (*a*-Si:H).[8] Absorption peaks corresponding to silanol (Si-OH) at 940 cm^{-1} and ~3400 cm^{-1}, and H_2O at ~3700 cm^{-1} were not found for the SiOF films. The SiOF film deposited with $[SiF_4]/[SiH_4]=40$ shows a Si-O peak at 1087 cm^{-1}.

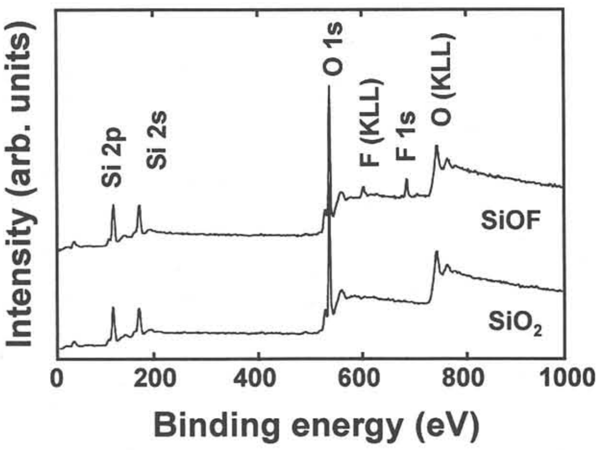

Fig. 3. Comparison of XPS spectra between SiOF and SiO_2 films.

The typical XPS spectra of the deposited films are shown in Fig. 3. The SiOF film shows an F 1s peak at 690 eV, corresponding to Si-F, and the Si 2p peak shifts to higher binding energy with the increase of F 1s peak intensity. This result is in agreement with the Si-O peak shift in FT-IR data.

Figure 4 shows the fluorine content with a variation of $[SiF_4]/[SiH_4]$. The fluorine contents were measured from the depth profile from XPS analysis. The fluorine content in SiOF film increases with $[SiF_4]/[SiH_4]$ and is 12 at.% when $[SiF_4]/[SiH_4]$ is 40. The fluorine content increases rapidly with SiF_4 flow rate at small $[SiF_4]/[SiH_4]$, and then increases gradually when $[SiF_4]/[SiH_4]$ is above 6. This result is consistent with FT-IR data shown in Fig. 3. It seems that there is some correlation between the fluorine content in the SiOF film and the peak position of the Si-O stretching vibration. With increase of fluorine content in the SiOF film, the $SiO_{2-x}F_x$ bonds are more generated and the peak position of Si-O stretching mode shifts to higher wave number due to more strong Si-O bonding network. It was found that the fluorine atoms are distributed uniformly in the film from the depth profile measurement.

The interlayer dielectric film should have a low dielectric constant. When p-type silicon wafer is used, the top metal electrodes are always biased by a negative voltage, which results in the accumulation of the majority carriers in the substrate and thus minimization of the effect of depletion capacitance is needed.

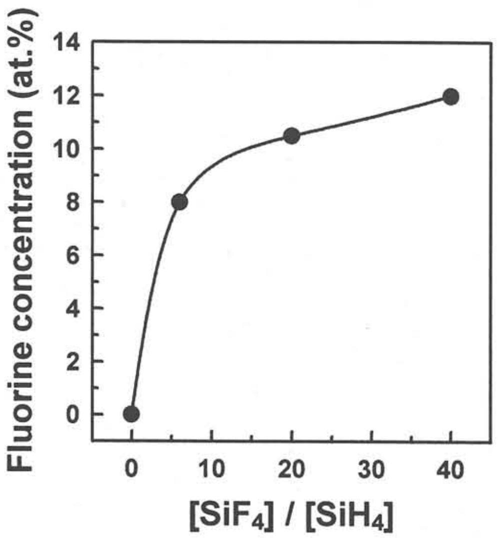

Fig. 4. Fluorine concentration of SiOF films as a function of $[SiF_4]/[SiH_4]$.

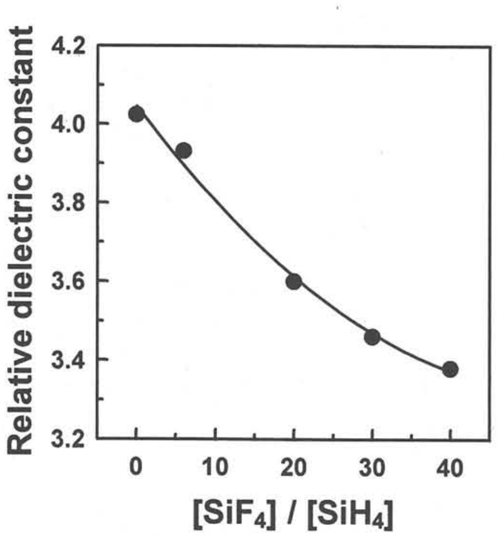

Fig. 5. Relative dielectric constant of SiOF films as a function of $[SiF_4]/[SiH_4]$.

Figure 5 shows the dielectric constant as a function of $[SiF_4]/[SiH_4]$. The relative dielectric constant of the SiOF film, obtained from high frequency (1 MHz) C-V measurements, decreases with increase of fluorine concentration. The relative dielectric constant, obtained from the SiOF with 12 at. % of fluorine content, is 3.38 and it is decreased by 16 % compared with SiO_2 with no F atom showing dielectric constant of 4.02.

4. SUMMARY AND CONCLUSIONS

A new technique to form interlayer dielectric film, fluorinated silicon oxide (SiOF), for VLSI multilevel interconnection was developed. The film was deposited by RPCVD using $SiF_4/SiH_4/O_2$ mixture. There is some correlations between the fluorine content in the SiOF film and the peak position of the Si-O stretching vibration. The fluorine content in the SiOF film was increased by increasing SiF_4/SiH_4 ratio. With increase of fluorine content, the $SiO_{2-x}F_x$ configuration is seems to be more generated and the peak position of Si-O stretching mode shifts to higher wave number. The relative dielectric constant of SiOF film with 12 at. % F was found to be 3.38.

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