액상증착법에 의한 산화막 형성에 관한 연구

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Study on the Formation of SiO2:F films Using Liquid Phase Deposition

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Abstract - We formed SiO_2:F films by low-temperature process called Liquid Phase Deposition(LPD) and investigated its electrical and physical properties. Because of the use of room-temperature and no special vacuum apparatus for forming SiO_2:F films, this technique can have some advantages related with the application to dielectric interlayer for multilevel structure in ULSI devices.

The growth rate 100nm/hr was obtained at the growth solution of 2.5mol/l. The P-etch rate showed a similar or better tendency compared with SiO_2 films formed by CVD, Sputter, E-beam evaporator etc.. The fourier transform infrared(FTIR) spectra revealed that the contained fluorine atoms exist uniform throughout the formed SiO_2 films. The Scanning Electron Microscope images showed that LPD-SiO_2 films could be stably grown on silicon substrates and the good step-coverage could also be obtained, which indicates that the LPD-SiO_2 films have some possibility of the application to planarization and interlayer dielectric films which are vitally necessary to achieve the multilevel interconnection in ULSI. The I-V characteristics has some distinct differences according to the concentration of growth solution.

1. Introduction

A multilevel interconnection is necessary for improving the performance of ULSI devices. However, this interconnection inevitably causes an increased interconnection delay coming from a parasitic capacitance, which is more troubling than a conventional gate delay. The signal delay has been reduced largely in two ways. The one is related with the wiring materials and the other is tied with the parasitic capacitance of an interlayer dielectric insulator.

Concerned with the parasitic capacitance, many groups have been studying to reduce the capacitance of the interlayer insulator, for example, by incorporating fluorine into the insulator films or by using CH_2-SiO_2 and MHSQ-SOG[1-2]. For the introduction of fluorine into SiO_2 films could improve their electrical characteristics[3]. Even the fluorinated SiO_2 films showed a dielectric constant around 3.5, which is not small enough to satisfy the requisites of a quarter-micron LSI. Even though organic polymers have a lower dielectric constant than inorganic materials, some problems such as poor adhesion with silicon substrates, poor thermal stability and the production difficulties have prevented their widespread use in microelectronics[4].

Some CVD techniques have a few advantages related with interlayer dielectric materials. For instance, the fluorinated amorphous carbon(a-C:F)films by Kendo et al. showed a dielectric constant under 3.0[5]. But the a-C:F films process is so complicated to carry out and also the films requires another films such as SiO_2 as an intermediate because of the weak points related with some process such as CMP. In regard to multilevel interconnection process, another fatal drawback is a thermal stress, which could lead to the regression of some device characteristics and wiring reliability. Several techniques such as TEOS-ozone APCVD and H_2O-TEOS PECVD and so on have been investigated for use in multilevel interconnection applications[6-7]. However, all of these methods require a substrate temperature over 300℃ for polymerization and dehydration.

Recently some researchers have attempted to develope a low-temperature method to get over the above mentioned problems. The Liquid Phase Deposition(LPD) method has been developed and examined as a low-temperature process to form silicon dioxide films on various kinds of substrates. And also the LPD technique was originally introduced for the application to Liquid Crystal Display(LCD) by some researchers at Nippon sheet glass Co. Ltd. Because the temperature required for the growth of LPD-SiO_2 films is room-temperature and no vacuum system is necessary, there have been some continuous studies about the characteristics and the applications of LPD-SiO_2 films such as a selective growth and a Metal-Insulator-Semiconductor(MIS)solar cell[8-9]. Another important characteristics of LPD method is that the formed SiO_2 films by the technique contain -F as well as -OH controlled by the concentration of the growth solution because an equilibrium reaction between Hydrofluorosilicic acid(H_2SiF_6) saturated with silica and deionized water is used in the growth process. The property of LPD-SiO_2 films depend critically on the incorporated amount of -F and -OH bonding.

2. Experimental

The LPD-SiO_2 growth method could be roughly divided into two steps. The first step is to make a necessary growth solution supersaturated with silica from an original 4.0mol/l solution. The solution making process is so important in that the characteristics of the formed LPD-SiO_2 films is absolutely dependent on the states of the growth solution. The growth solution is kept under 4-5℃ until the deposition process starts. The second is the growth step by immersing the pretreated substrates into the prepared growth solution. Because some contaminants are also produced during the growth which could result in the decrease of electrical and physical characteristics of the formed SiO_2 films and low growth rate, a unique filtering system is used in the process, which contributes considerably to the improvement of the formed films in both electrical and physical aspect.

The chemical formula expressing the reaction during the growth solution could be roughly written as follows.

$$H_2SiF_6 + 2H_2O \Leftrightarrow SiO_2 + 6HF + Q \quad \text{-------}(1)$$

The formula (1) seems quite a little simple. As a matter of fact, so many intermediate processes happen during the growth solution making process. But it is no use to consider all the formula in this study, except that ,besides SiO_2, fluorine ions are produced simultaneously during the deposition process, which affects the states of the formed SiO_2 films to a considerable degree. N-type(100)substrates with 550㎛ thick and 5Ωcm are used. The substrates are pretreated using two different cleaning methods, Semico-Clean 23 and buffered HF(HF:H2O = 1:40) respectively, for the comparison related with their growth rates. In the study, a unique filtering system is used to improve the growth rate and the electrical characteristics of LPD-SiO_2 films. The growth process was done under the atmosphere while the growth solution is kept at around 35℃. To investigate I-V and C-V characteristics by KEITHLEY 617 I-V Meter and HEWLETT PACKARD4280A 1MHz C-Meter respectively, Al-electrodes with a diameter of 7×10^{-4} cm^{-4} are formed by resistance-evaporator at the base pressure of 3×10^{-7} Torr and back sides are also evaporated for forming Ohmic contact. a DVA 362 Ellipso-Meter and Scanning Electron Microscope were used for the thickness and the cross-sectional view, respectively.

3. Results and discussion

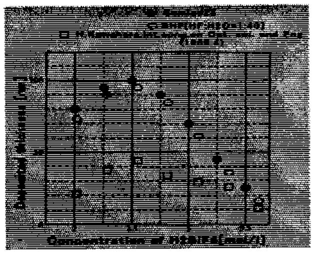


Fig. 1. The growth rate of LPD-SiO_2:F film for the first 1hr according to the concentration of solution.

Fig.1 shows that the growth rate of LPD-SiO_2 films depend on the concentration of the growth solution. The highest deposition rate, 100nm/hr is obtained at the 2.5 mol/l of the growth solution. It seems quite difficult to grow the LPD-SiO_2 films at the concentration over 3.5mol/l because the amount of fluorine in the solution tends to increase in proportion to the concentration of the solution and the increased fluorine attack the substrate surface, which hinders the growth of the SiO_2 films. Moreover, in case of over 3.5mol/s, sometimes etching-away of the surface by Fluorine happens instead of the growth of LPD-SiO_2 films. There is not so big difference of the growth rate between the pretreatment of Semico-Clean23 and that of buffered HF. The small difference of deposited thickness probably comes from the fact that the substrates with the pretreatment of buffered HF is passivated by -H and the -H bonding ought to be taken away by fluorine before the growth of LPD-SiO_2 films[10].

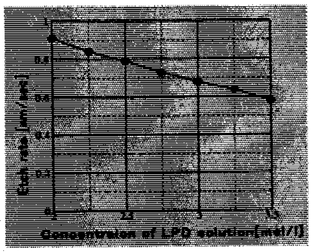
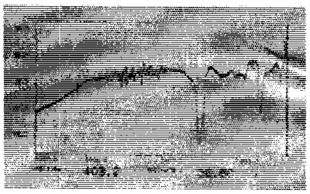


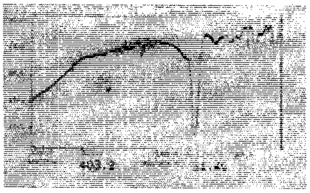
Fig. 2. The P-etch rate of LPD-SiO_2 film as a function of the concentration of the growth solution.

The P-etch rate of LPD-SiO_2 films is shown in Fig.2. The LPD-SiO_2 films showed a comparable value with SiO_2 films except dry oxide. It is a little exciting to see that the P-etch rate tends to decrease in inverse ratio to the increase of the concentration of the growth solution, which could be explained as follows. As the concentration of the growth solution becomes higher, the amount of the contained fluorine in the formed films increases. As well, because the P-etchant contains fluorine as an element playing a critical role in the etching process, the

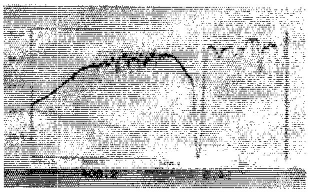
LPD-SiO_2 films grown at the higher concentration is hard to be attacked by the etchant.



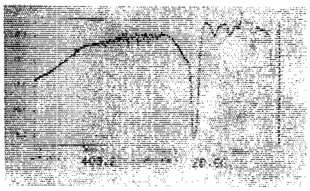
(a) 760Å



(b) 1300Å



(c) 1900Å



(d) 2200Å

Fig. 3. The FTIR spectra of LPD-SiO_2 films formed at 2.5mol/l. (Si-O : 1094cm^{-1}, Si-F : 928.8cm^{-1})

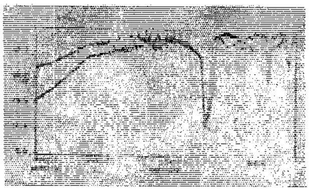


Fig. 4. The comparison of FTIR spectrum of LPD-SiO_2 film and thermal SiO_2 film.

Fig.3 shows the fourier transform infrared(FTIR) spectra of LPD-SiO_2 films with different thickness grown at 2.5mol/l. The thickness is 760Å for (a), 1300Å for (b), 1900 Å for (c), 2200Å for (d). The FTIR spectra have the absorption bands with the peaks at around 1094cm^{-1} and 928.8cm^{-1}, corresponding to the presences of Si-O bond and Si-F bonding respectively. The peak of Si-F bonding at about 928.2cm^{-1} tends to increase uniformly in proportion as the thickness increases according to the deposited time, which indicates that the Si-F bonding exists uniform throughout the formed films and therefore as is the F atom.

Fig.4 reveals that there is a distinct difference between the FTIR spectrum of LPD-SiO_2 film(2500Å at 2.5mol/l) and that of dry-SiO_2 film(2600Å at 1000℃). The FTIR spectrum of thermal SiO_2 film does not have any peak corresponding to 931.2cm^{-1} existing at the spectrum of LPD-SiO_2 film, which is the distinguished difference caused by the existence of Si-F bonding.

Fig. 5. The SEM cross-sectional image of LPD-SiO_2 film(9000Å at 2.5mol/l) on N-type(100) silicon substrate.

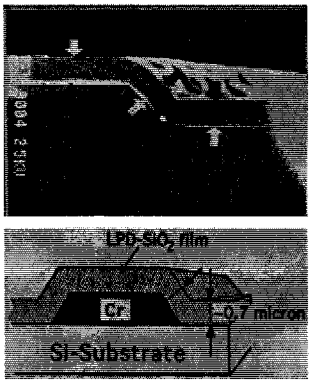


Fig. 6. The SEM cross-sectional view of LPD-SiO_2(7000Å, 2.5mol/l) formed on the patterned Cr stripe.

A LPD-SiO_2 film(90000Å at 2.5mol/l) was grown on n-type(100) silicon substrate in Fig.5 showing a good interface. Fig.6 shows a LPD-SiO_2 film grown on the patterned Cr stripe and it has a good step-coverage, which means that LPD-SiO_2 films have some possibility of the application to planarization materials and interlayer dielectric insulator related with multilevel interconnection in ULSI.

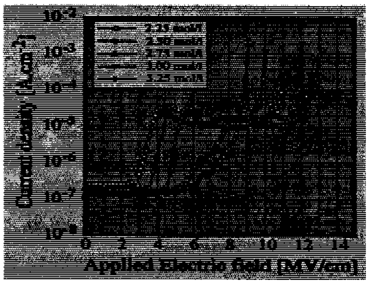


Fig. 7. The I-V characteristics of LPD-SiO_2 film as a function of the concentration of the growth solution.

The Current versus Voltage characteristics as a function of the concentration of the growth solution is shown in Fig.7. We found that low concentration of the growth solution usually causes the formed films to have two-step process related with I-V property while the high concentration of the growth solution makes the formed films have the similar pattern which is found in usual SiO_2 films. It is obvious that LPD-SiO_2 films contain -OH bonding inside the films like other methods such as CVD etc. because the growth of LPD-SiO_2 experiences $Si(OH)_4$ sol agglomeration process near the silicon substrate[11]. In case of OH-rich LPD-SiO_2 films which are grown at the low concentration, the I-V characteristics has two-step process. The first part is due to F-N tunneling and Poole-Frenkel mechanism and the second is brought out by emission and drift current just when a voltage is applied sufficiently. Unlike this case, F-rich films obtained at the high concentration do not show the first part compared with OH-rich films because the traps of OH-rich films are reduced by the fillment of fluorine. The lowest 8.5Mv/cm of breakdown voltage is seen at 3.25mol/l and the leakage current caused by direct tunnel shows a little larger value ranging from 6×10^{-6} to 1×10^{-7} $A\cdot cm^{-2}$, which could be lessened by some post-annealing.

4. Conclusions

We formed LPD-SiO_2 films by Liquid Phase Deposition(LPD)method and investigated their basic characteristics. The room-temperature and no necessary vacuum system are two of the prominent characteristics of LPD technique. To improve the growth rate, a unique filtering system was used in the study and the highest growth rate, 100nm/hr was obtained in case of 2.5mol/l of growth solution. The P-etch rate showed a decrease in inverse ratio to the increase of the growth concentration, which is caused by fluorine contained in both P-etchant and the F-rich films.

The FTIR spectra revealed that the existence of fluorine is uniform throughout the LPD-SiO_2 films and Scanning Electron Microscope cross-sectional views showed a good step-coverage and also a good interface, which indicates that LPD-SiO_2 films have some possibility of the application to planarization materials and interlayer dielectric insulator related with multilevel interconnection in ULSI.

We found that I-V characteristics of Metal-LPD:SiO_2-Semiconductor structure has some distinct differences according to the concentration of the growth solution. The LPD-SiO_2 films grown at the low concentration have two-step I-V process. And the first part is caused by F-N tunneling and Poole-Frenkel mechanism and dose not appear in case of the films of the high concentration because the traps of the low concentration playing a critical role in the Poole-Frenkel mechanism is filled by fluorine to some extent. And the breakdown which is enough for the common application is caused by emission and a drift current when an electricity is applied sufficiently.

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