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Study of the Influence of Temperature on the Deposition of SiO_2 Films from Reaction of Silicone Oil Vapor and Ozone Gas

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Abstract

This work reports the influence of deposition temperature on the deposition of SiO_2 films on silicon substrate by using chemical reaction of silicone oil vapor andozone gas at low temperature. An organic solution as a catalyst at atmospheric pressure has been used to enhance the deposition rate of SiO_2. The deposition rate of SiO_2 films was found to vary with the variation of the concentration of the catalyst and deposition temperature (160°C ~ 260°C). The deposited SiO_2 films were confirmed by Fourier transform infrared (FT-IR) spectroscopy. The thickness and refractive index of the as-deposited films were measured by the laser ellipsometry. FT-IR spectra of the as-deposited films were very much similar to those of SiO_2 films found in literature. The deposition temperature was found to influence the deposition rate of SiO_2strongly. The maximum deposition rate was found to 17.2 nm per minute for the case of 220°C. The deposition temperature also influenced the refractive index of the films. Experimental results showed that thedeposition temperature could be a major parameter for the enhancement of the deposition rate.

Keywords: Low-Temperature SiO_2 deposition, APCVD, FT-IR spectroscopy.

INTRODUCTION

Advanced very large scale integrated (VLSI) devices require high aspect ratio topography on semiconductor substrates. SiO_2 films have been widely applied in the production of electronic devices, integrated devices, optical thin film devices, sensors, and so on [1-9]. Moreover, low temperature deposition of SiO_2 film on a silicon substrate is desired for high quality gate oxide films to obtain high performance thin film transistors (TFTs) and to form interlayer dielectric (ILD) to suppress the disconnection of interconnect metal [10]. Recently special attention has been paid to thin-film transistor (TFT) technology because it is used for large area flat panel displays such as liquid crystal displays (LCD) [11-12]. TFT performance strongly depends on the SiO_2 / Si interface properties [13-15].

Conventionally, oxidation [16-17], Plasma Enhanced Chemical Vapor Deposition (PECVD) [18-21], Low Pressure CVD (LPCVD) [22-24] and Atmospheric Pressure CVD (APCVD) [25, 26] are used for deposition of SiO_2 on silicon substrate. In oxidation method, silicon dangling bonds are formed due to lattice mismatch between Si/SiO_2 interfaces which degrade the device performance[27]. LPCVD is used to deposit a wide range of possible film compositions with good conformal step coverage but an extra low

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pressure system is required to attain the pressure of 10-1000 Pa (the available pressure LPCVD). PECVD method has some advantages that the advantages of a low deposition temperature as well as controlling the deposition rate quickly and accurately to obtain high-quality SiO_2 film [28]. However, the setup of this system is very complicated and also, sometimes the deposited films damaged due to plasma.

In this study, APCVD methods have been used to deposit SiO_2 films at low temperature with taking advantage of their easy set-up and lower cost (no extra setup is required for pressure control). In this method, silicone oil has been used as starting materials used to deposit SiO_2 films. It is a promising materials because of their low cost, high thermal stability and high safety[29,30], compared with tetra-ethyl-ortho-silicate [TEOS:$Si(OC_2H_5)_4$] [31, 32], a widely used as a common source materials to deposit SiO_2 films. TEOS is also toxic to human eyes and throats. Moreover, deposition of SiO_2 films in controlled ambient requires temperature in excess of 600 °C. In this work, we have been able to deposit SiO_2 films at relatively lower temperature by adding a more aggressive oxidant into silicone oil. In particular, we have used ozone (O_3) as aggressive oxidant. In addition, an organic solution has been added to the system to enhance the deposition rate of SiO_2 films.

EXPERIMENTAL

Figure 1 shows a schematic diagram of the atmospheric pressure chemical vapor deposition (AP) CVD system used for the deposition of silicon oxide films. Here, the conventional APCVD system has been slightly modified by introducing a new line partwhich facilitates to add anorganic solution to the main stream of the system.

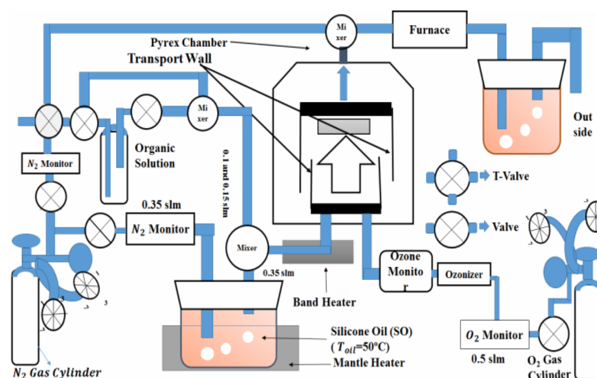
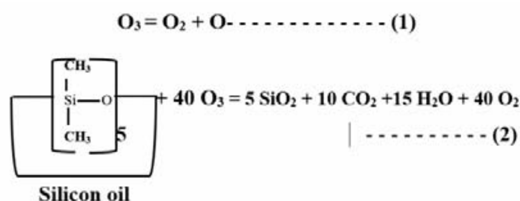


Fig 1: Schematic diagram of APCVD method.

The chemically cleaned substrates were loaded into the chamber, which was uniformly heated by heater at a deposition temperature. The silicone oil (SO) (TSF-405) was heated to about 50 ºC and vaporized directly by bubbling with N_2 gas at a flow rate of 0.35 standard liter per minute (slm) through a stainless tube heated to about 55 °C to avoid the condensation of SO vapor. The organic solution was heated to three different temperatures of 21.9 ºC, 28.1 ºC and 34.1 ºC by another heater and vaporized by bubbling with N2 gas at five different flow rates of 0, 0.05, 0.1, 0.15 and 0.2 slm. After that, the

organic solution was mixed with silicon oil vapor and then flown into the chamber. The ozone was generated by anozonizer from O_2 gas at the flow rate of 0.5 slm and then introduced into the chamber together with the silicone oil and organic solution vapor.
The substrates were n-type single crystals silicon with a resistivity of 5-15 Ω-cm. The crystallographic orientation of the substrate was [111]. The dopant of the wafer is phosphorus. The thickness of the substrate = 525 ± 25 μm. They were chemically cleaned by hot ammoniacal solution ($NH_4OH : H_2O_2 : H_2O = 1 : 1 : 4$) and hot acid solution (HCl: $H_2O_2 : H_2O = 1 : 1 : 4$). After each chemical solution treatment, the chemical oxide was removed by 1% HF solution.

In our experimental process,O_3 is decomposed to O_2 and reactive O shown in equation (1). This decomposition is dependent on deposition temperature [33, 34]. Oliver R.Wulf& Richard C. Tolman specified the range of decomposition temperature that is 148 ºC to 179 ºC [34].Since the O is very chemically active, the overall reaction of the process of reactive oxygen and SO is shown in equation (2). In the first stage, the chemically reactive oxygen atoms are reacted with the methyl (-CH_3) bond of theSOin the gas phase and broken the methyl bond to form hydroxyl (-OH) bond then intermediate products of deca-hydroxyl-cyclo-penta-silaxane (precursors) are formed together with by-products of H_2O and CO_2. In other words, -CH_3 side groups are replaced with hydroxyl (-OH) and silanol bonds of Si-OH cover the sides of the siloxane chains. In the second stage, the –OH groups on the surface are eliminated the by the dehydration reaction with the –OH groups on the precursors.

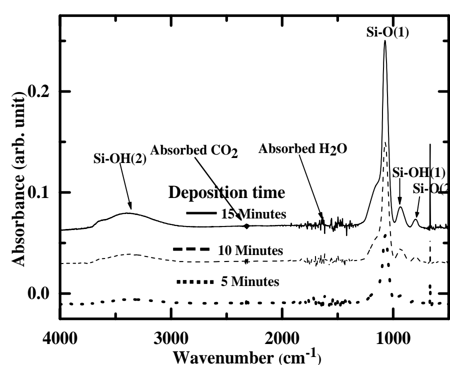


Thickness and Refractive index were measured by laser ellipsometry (ULvac ESM 1A) at a wavelength 632.28 nm, spot size of about 1 nm, angle of incidence 70 º, sampling time 20 ms as well as measured 10 times at the same location.Chemical structures of as-deposited films were studied by Fourier Transform Infrared Spectroscopy (Perkin Elmer (Spectrum 100) FT-IR Spectrometer) of wave number range 500 to 4000. When the deposited films are investigated by FT-IR spectrophotometer, the deposited film is kept into the holder and waits 5 to 6 minutes for removing unwanted H_2O and CO_2, which are absorbed in the films.

RESULTS AND DISCUSSION

Figure 2showstheFT-IR spectra that were obtained from the as-deposited films with different deposition time, in the range between 500 and 4000 cm^{-1}. Unless otherwise stated all the data was taken at ~28.1 ºC and 160 ~ 260 ºC for the organic solution and substrate respectively. The flow rate of N_2 gas was kept at 0.1 slm for the organic solution. The deposition time was also constant at 10 minutes. For the sake of simplicity, spectra are divided into two frequency regions: low frequency region between 500 and 2000 cm^{-1} and high frequency region between 2000 and 4000 cm^{-1}. In the low frequency

region, they consist of three broad bumps in the range between 500 and 1250 cm^{-1}, showing quite different shape and width, but the comparable absorption amplitude. The line widths and the peaks position are same for all the deposition films. The broad absorption band for Si-O-Si bonds are 1010 – 1090 cm^{-1} and 730 – 860cm^{-1}, which are attributed to the Si-O-Si stretching and bending vibrations, respectively [35-37]. Thus, The peaks at the wavenumbers of 1075 cm^{-1} and 810 cm^{-1} are labeled as Si-O(1) and Si-O(2), respectively. Another feature is observed in the range between bands 1500 to 1800 cm^{-1}, which is due to the absorbed H_2O in the deposited films [35, 37, 38].On the other hand, in high frequency region of the FT-IR spectra a broad absorption band between bands 3000 – 3600 $cm^{-1}$are observed. A weak band at about 2300 cm^{-1} is attributed as absorbed CO_2 in the films [39-40].



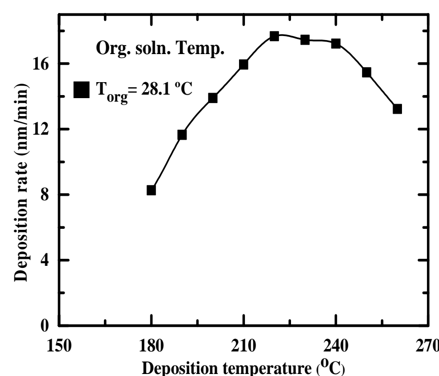


Fig 2: FT-IR spectra of silicon oxide films at temperaturedifferent deposition time.

Fig 3: Deposition rate vs. deposition curve with catalyst.

Hydrogenated silicon oxide thin films are characterized by the absorption bands at 850 – 990 cm^{-1} and 3000 – 3600 cm^{-1}, which are attributed to the Si-OH stretching vibrations [40, 41].It is observed from the figure that the amplitude of these two peaks is increased with the deposition time. The maximum peaks at the wave numbers of 950 and 3350 cm^{-1} are labeled as Si-OH (1) and Si-OH(2), respectively. The FT-IR spectra showed that the films deposited from 160 to 260 ºC are almost stoichiometric Si oxides without signals related to carbon, although small signals of Si-OH.

The deposition time was kept constant at 10 minutes and N_2 flow rate for oil was kept constant at 0.5 slm as well as O_2 flow rate was 0.5 that was also constant. The catalyst concentration was $3.05x10^{-5}$ moles/cm^3. As can be seen from Figure 3, the deposition rate increases with the deposition temperature until certain temperature, and then it starts to decrease.Increase in deposition rate with the increase in deposition temperature is a common phenomenon particularly at a low deposition temperature. At lower temperature, molecular energy of the reagents increases with increasing the deposition temperature which in turn overcomes the activation energy of the reaction. Consequently the reaction rate and deposition rate increases [42-43]. But, the saturation of the deposition rate and decline nature with the higher temperature suggests that a different chemical reaction occurs in the pathway.

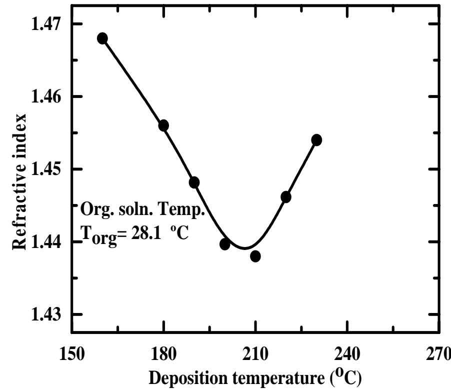


Fig. 4: Refractive index vs. deposition temperature curve at deposition time of 10 minutes.

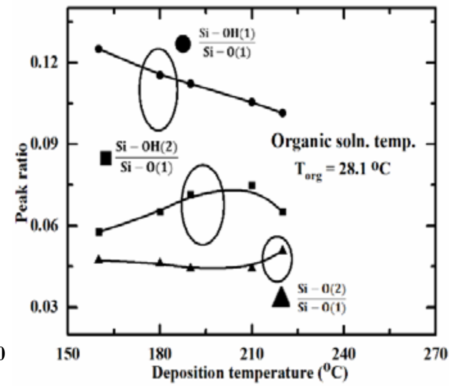


Fig. 5: Peak ratio vs. deposition temperature curve at deposition time of 10 minutes.

It can be observed from Figure 4 that the refractive index decreases with the deposition temperature and after a certain temperature the refractive index increases. The relative absorption peak intensities are plotted as a function of deposition temperature and are shown Figure 5. The peak ratios are required for qualitative discussion of refractive index.

When the amount of Si-OH(2) increases, the porosity of the film increases, because Si-OH(2) is the bond of SiO_2 and water. As a result decrease in density as porosity is increased in the structure. Now, from the Lorentz-Lorentz model [44-47], there is a physical relation between density and refractive index (the refractive index is directly proportional to the density of the film), So that, refractive index is inversely proportional to the Si-OH(2) bond.

It can be seen from Figure 5 that the ratio of Si-OH(1)/Si-O(1) decreases with the deposition temperature. As mentioned in experimental, -Si-O-Si- is produced from precursors. Dehydration reaction introduces production of –O-Si-O- from the precursors. It is known that, Dehydration is very active reaction. At the low deposition temperature, some of precursors are not reacted. But, when the deposition temperature increases thedehydration rate also increased, more precursors are reacted with their OH bond. So the ratio of Si-OH(1)/Si-O(1) decreases with deposition temperature.

CONCLUSIONS

The SiO_2 films were deposited on a silicon substrate at atmospheric pressure and temperature between 160 ºC and 260 ºC by using the chemical reaction between silicone oil vapor and ozone gas as well as an organic solution was used as a catalyst. The deposition rate was too low, e.g., 1 nm/min at 200 ºC for the case of without organic solution [33]. But in our study, the deposition rate was 11.85 nm/min at 200 ºC by using organic solution. The average deposition rate was found to be 13.2 whereas the maximum deposition rate was 17.2 nm per minutes at 220 ºC deposition temperature.The FT-IR spectra showed that the films deposited from 160 ºC to 260 ºC were almost

stoichiometricSi oxides. It is confirmed from FT-IR spectra of the as-deposited films. Although weak peaks from Si-OH related bond was found in the FT-IR spectra no peak related to Carbon was observed. The presence of Si-OH bond indicated the presence of small amount of pores in the deposited film that was responsible for the variation in refractive index of the deposited films. The amount of Si-OH were optimized with the help of tuning the deposition temperature that could be occurred due to increase dehydration reaction. From the experimental data it could be concluded that the deposition rate of SiO_2 from the chemical reaction between silicone oil vapor and ozone gas could be enhanced by optimizing the deposition temperature.

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