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〈연구논문〉

Room Temperature Fabrication of Silicon Oxide Thin Films by ECR PECVD

Ho-Young Lee, Yoo-Chan Jeon and Seung-Ki Joo

Department of Metallurgical Engineering, Seoul National University,
Seoul 151-742, Korea

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ECR PECVD에 의한 상온 실리콘 산화막 형성

이호영 · 전유찬 · 주승기

서울대학교 금속공학과

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Abstract – Silicon oxide thin films were deposited at room temperature on (100) Si substrates by ECR PECVD (Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition) system. Effect of gas flow rate ratio (SiH_4/O_2) on the film properties was investigated and the optimum deposition condition was extracted. When SiH_4/O_2 flow rate ratio was 0.071, the irreversible dielectric breakdown field was 9~10 MV/cm and the leakage current density was an order of 10^{-11} A/cm^2 even at the field of 4~5 MV/cm. These values are suitable for device fabrication which requires low temperature process such as thin film transistors for liquid crystal display.

요 약 – ECR PECVD(Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition) 장치를 이용하여 (100) 실리콘 기판 위에 실리콘 산화막을 상온에서 증착하였다. 기체 유량비(SiH_4/O_2)가 막의 성질에 미치는 영향을 고찰하여 최적의 증착 조건을 도출하였다. 기체 유량비가 0.071일 때 비가역 파괴 전장은 9~10 MV/cm이었고, 4~5 MV/cm의 전장하에서도 누설 전류는 ~10^{-11} A/cm^{2}이었다. 이러한 수치들은 액정 표시 소자용 박막 트랜지스터와 같이 저온의 제조공정이 요구되는 소자를 만들기에 충분하다.

1. Introduction

Insulating films deposited at low temperature with good electrical properties are in demand for microelectronics and thin film transistor technology among other applications [1]. Low temperature process is necessary to prevent the diffusion of shallow junctions and interdiffusion of metallic layers in silicon-based intergrated circuits. In the case of thin film devices on amorphous silicon, good insulating layers are reauired to be deposited at below temperatures at which hydrogen diffuses out of the *a*-Si (Ca. 300℃). Plasma-enhanced chemical vapor deposition (PECVD) is one of the techniques that have been introduced to deposit insulating films such as silicon oxide and silicon nitride [1-6]. Deposition of silicon oxide films at low temperatures using PECVD method has a serious surface damage problem due to energetic ions in the plasma and, what is worse, the deposited films are generally porous and of poor electrical properties [7, 8] with a high concentration of water-related impurities [1-3]. In recent work, however, it has been reported that high quaility, low temperature plasma silicon oxide films have been deposited by remote plasma-enhanced chemical vapor deposition (RPCVD) process using very dilute helium [9 11] and photochemical vapor deposition (photo-CVD) [12, 13]. The improvement in quality of silicon oxide films deposited by dilute helium plasma has been attributed to cooler plasma, more controllable reaction pathways by Penning reaction between helium and reactant gases and supressed gas phase reactions between reactive species. The deposition rates of these processes are generally very low (5~100 Å/min) at low r.f. power and very dilute helium plasma, thus possibly limiting their use to device gate dielectric applications.

ECR PECVD has been known to be suitable for low temperature process due to its intermediate energy of incident ions and high density plasma even at low pressure ($<10^{-3}$ torr). In this work, silicon oxide thin films were formed by ECR PECVD at room temperature. Gas flow rate ratio (SiH_4/O_2) was varied systematically to study the effects on the electrical and physical properties of the films.

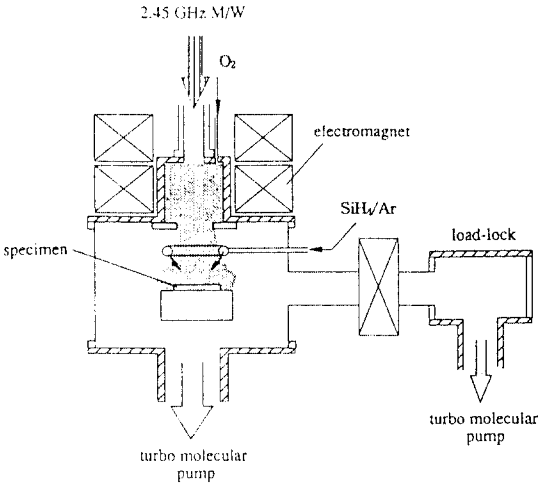

Fig. 1. Schematic diagram of ECR PECVD system.

Table 1. Deposition conditions for the experiment

M/W power	500 W
SiH_4/O_2 flow rate	0.03~0.5
Total flow rate	9 sccm
Total pressure	2 mtorr
Deposition time	10 min

2. Experimental

Schematic diagram of ECR PECVD system used in this work is shown in Fig. 1. Electromagnet which can generate axially symmetric magnetic field more than 875 Gauss was placed around the plasma chamber and the plasma was generated and sustained by 2.45 GHz microwave. 25% SiH_4 diluted with Ar and high purity (99.999%) O_2 were used as source gases. O_2 was introduced into plasma chamber to generate ECR plasma and SiH_4 was introduced into the deposition chamber through a gas distribution ring for uniform feeding. The deposition chamber was pumped with a turbo molecular pump. The initial chamber pressure was lower than 1×10^{-7} torr. Silicon oxide thin films were deposited on (100) Si wafer, which was not heated during deposition. Thickness and refractive index of the deposited films were measured by ellipsometer. The bonding properties of films were analyzed using Fourier transform infrared (FT-IR) spectroscopy of which resolution was 1 cm^{-1}. The etch rate of films was evaluated by using 10 : 1 buffer HF solution. Circular aluminum electrodes of 2.38×10^{-3} cm^2 were deposited onto the films for electrical characterization. I-V ca-reases as SiH_4/O_2 flow rate ratio increases, so the deposited film is expected to be oxygen-rich and the Si/O ratio in the film increased with increasing SiH_4/O_2 flow rate ratio. In conventional PECVD, SiH_4 and O_2 or N_2O are mixed before they are introduced into the chamber, but in this work, only oxygen gas was passed through ECR zone to be ionized or excited. The excited oxygen species were to react with SiH_4 to form silicon oxide on the substrate. Therefore, it is expected to have enough oxygen species to react with SiH_4. As the SiH_4/O_2 flow rate ratio increases, the increasing rate of reactive hracteristics were measured with a programmable voltage source and picoammeter. The leakage current density was measured when the electric field was 1 MV/cm and the breakdown field was defined as the electric field forcing a current density of 1×10^{-6} A/cm^2.

3. Results and Discussion

Effects of SiH_4/O_2 flow rate ratio on the refractive

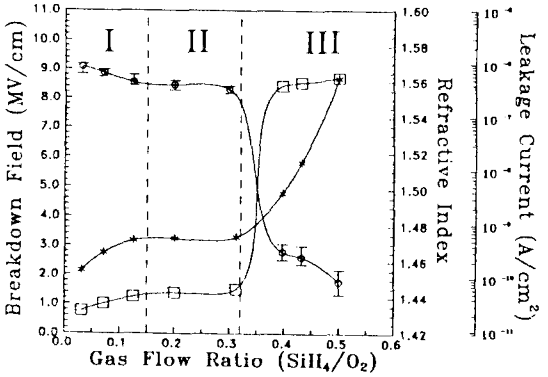

Fig. 2. Properties of silicon oxide thin films with respect to gas flow rate ratio. Three regions are distinguished as I, II and III (○: Breakdown field, ∗: Refractive index, □: Leakage current).

index, leakage current and the breakdown field of silicon oxide films are shown in Fig. 2. Depositon conditions are listed in Table 1. As the SiH_4/O_2 flow rate ratio increased, the refractive index, leakage current and the breakdown field were changed respectively in a certain way. Three regions can be identified in this figure. In region I, the refractive index and leakage current are increasing monotonically, while the breakdown field is decreasing linearly. In region II, all these three properties are almost constant and in region III, the refractive index is increasing very rapidly, while the breakdown field is decreased monotonically and the leakge current is nearly constant. The overall insulating properties are undesirable in region III.

Fig. 3 shows the effect of SiH_4/O_2 flow rate ratio on the deposition rate. Depositon conditions are identical with the Table 1. As the SiH_4/O_2 flow rate ratio increased, deposition rate increased monotonically and became saturated. This can be thought that the deposition rate is much dependent on the supply of SiH_4.

It is known that the refractive index increases with increasing Si/O ratio in the film [14]. In this experiment, from overall trend of view, the refractive index increases as SiH_4/O_2 flow rate ratio increases, which indicate that the Si/O ratio in the film increased with increasing SiH_4/O_2 flow rate ratio. In region I, where SiH_4/O_2 flow rate ratio is small, the refractive index of film is small and increases as SiH_4/O_2 flow rate ratio increases, so the deposited film is expected to be oxygen-rich and the Si/O ratio in the film increased with increasing SiH_4/O_2 flow rate ratio. In conventional PECVD, SiH_4 and O_2 or N_2O are mixed before they are introduced into the chamber, but in this work, only oxygen gas was passed through ECR zone to be ionized or excited. The excited oxygen species were to react with SiH_4 to form silicon oxide on the substrate. Therefore, it is expected to have enough oxygen species to react with SiH_4. As the SiH_4/O_2 flow rate ratio increases, the increasing rate of reactive silicon species activated by excited oxygen species will be larger than that of oxygen species activated by electrons in the plasma so that the Si/O ratio in the film will increase monotonically with the increase of SiH_4/O_2 flow rate ratio. This situation is quite different from conventional PECVD, where silicon concentration is pretty high to react with O_2 because SiH_4 is easier to be decomposed with r.f. plasma than O_2. Therefore, in conventional PECVD the refractive index of silicon oxide films always decreases with increasing SiH_4/O_2 flow rate ratio. In region II, it is expected to obtain the stoichiometric oxide films because there will be enough silicon to react with oxygen plasma. It can be noticed that the breakdown field and refractive index remained constant value of 8.5 MV/cm and 1.47 respectively.

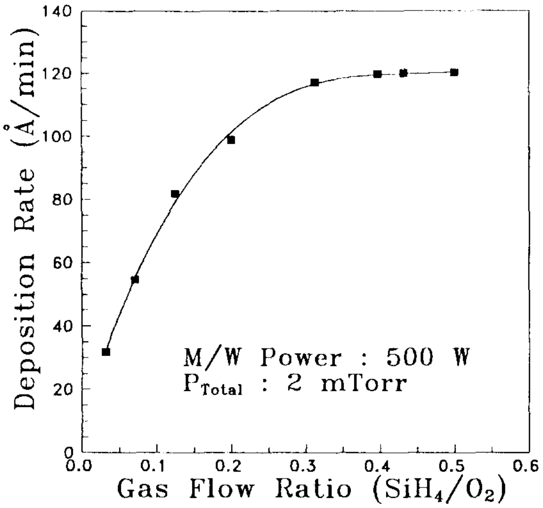

Fig. 3. Depositon rate characteristics of silicon oxide thin films with respect to gas flow rate ratio.

If more SiH_4 which is sufficient amount to form stoichiometric films is supplied to the reaction chamber (region III), deposited films became silicon-rich. In region III, the refractive index increased very rapidly as SiH_4 increased. Considering that the refractive index of amorphous silicon film is much higher than that of silicon oxide film, the properties of films are approaching to those of amorphous silicon films. This may account for the very low breakdown field and high leakage current density of the films obtained in this range. Deposition rate, in this region, does not change much. This can be explained as follows.

As shown in Fig. 1, O_2 is introduced into plasma chamber to generate ECR plasma and SiH_4 is introduced into the deposition chamber through a gas distribution ring. For that reason, O_2 is ionized or excited while passing through ECR zone and activates SiH_4 fed to deposition chamber. In the early stage of region III, the short supply of O_2 gives rise to the deficiency in activated oxygen to form the equal number of Si-O bonds in compared to the number of Si-O bonds in the final stage of region II so that this insufficient activated oxygen makes deposition rate lower, while the shortage in activated oxygen does not go down the amount of activated silicon, that is, once SiH_4 is introduced into the main chamber, most of SiH_4 is decomposed by excited oxygen and turns into activated silicon, in short, the more amount of SiH_4 is introduced, the more amount of activated silicon is generated. Hence, there must be the excessive activated silicon which did not form Si-O bond and this excessive activated silicon is deposited on the substrate as it is. So this additional activated silicon makes deposition rate higher. It can be said that the deposition rate is determined by amount of SiH_4 introduced into the deposition chamber. The two effects, namely the effect of deficiency in O_2 on the deposition rate and the effect of superabundance in SiH_4 on the deposition rate, are canceled out so that the deposition rate does not change in comparison to the final stage of region II.

While in the final stage of region III, the short supply of O_2 causes the insufficiency in activated oxygen both to form Si-O bond and to activate SiH_4, so there are two effects which deposition rate make lower. Some excessive SiH_4 which did not form Si-O bond is used up for deposition of amorphous silicon films and the other excessive SiH_4 is not excited and pumped out as it is. For that reason, the deposition rate does not change much in spite of the increment in SiH_4 flow rate in the final stage of region III.

FT-IR transmission spectra, scanning wave num-

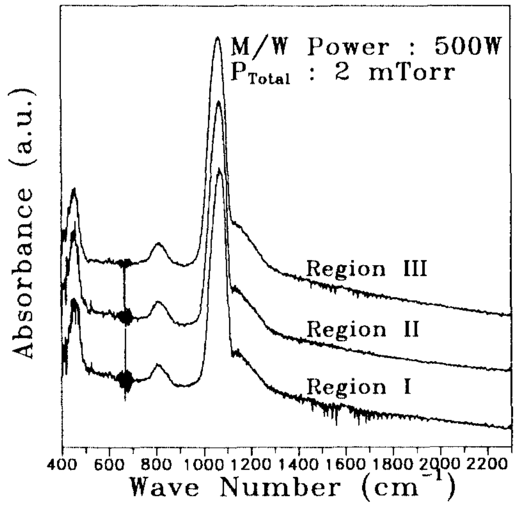

Fig. 4. FT-IR transmission spectra as a parameter of gas flow rate ratio.

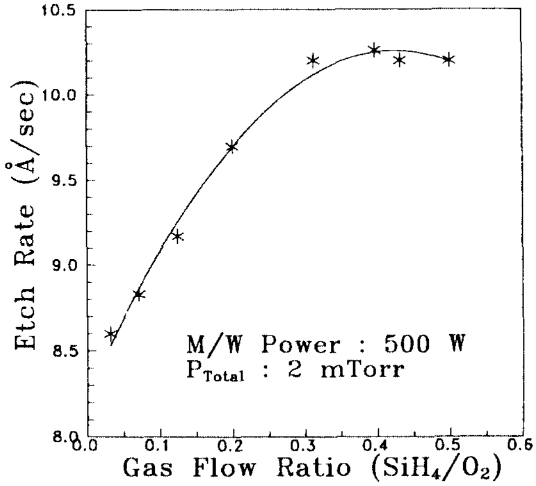

Fig. 5. Etch rate characteristics for 10 : 1 buffer HF solution as a function of gas flow rate ratio.

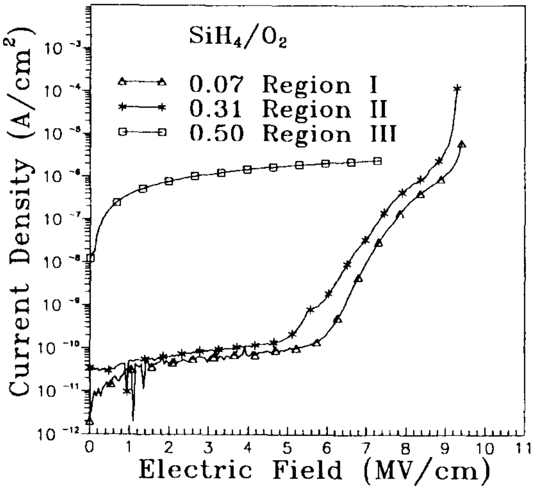

Fig. 6. I-V characteristics of silicon oxide thin films with respect to gas flow rate ratio.

ber range is from 400 to 4000 cm^{-1}, were obtained for all samples as a parameter of gas flow ratio. Typical spectra are shown in Fig. 4. The main peaks of Si-O bonds (1070, 805, 450 cm^{-1}) were observed. The spectra showed similar patterns to that of the silicon oxide film formed by thermal oxidation of silicon wafer It should be noted that the absorption peaks of hydrogen-related bonds (H_2O, SiOH, SiH) were not found at all, which demonstrate that the deposited films have no hydrogen atoms. In terms of FT-IR transmission spectra, judging from the fact that the intensity of main peak was not changed by varying the gas flow rate ratio from 0.031 to 0.5, the properties of the silicon oxide thin films does not changed by varying the gas flow rate ratio from 0.031 to 0.5.

Etch rate as a functuion of gas flow rate ratio is shown in Fig. 5. The etch rate of ECR PECVD silicon oxide thin films is comparable to that of thermal silicon oxide thin film (~10 Å/sec). The etch rate of films is closely related to the film density, film stoichiometry and the presence of weaker Si-H bonds [7]. The denser the film, the lower the etch rate and the more excess Si in the film, the lower the etch rate. The presence of weaker Si H bonds is another reason for the higher etch rate. The typical etch rate characteristic of ECR PECVD silicon oxide thin film is due to the complex effects of film density and film composition.

Table 2. Properties of silicon oxide thin films fabricated by various methods

	Dielectric strength	Leakage current
Thermal oxide	11 MV/cm	$\sim 10^{-11}$ A/cm^2
ECR PECVD	9~10 MV/cm	$\sim 10^{-11}$ A/cm^2
Conventional PECVD	8~9 MV/cm	$\sim 10^{-9}$ A/cm^2

I-V characteristics of silicon oxide thin films with respected to SiH_4/O_2 flow rate ratio are shown in Fig. 6. From the viewpoint of the breakdown field, leakage current density and deposition rate, it turned out that the optimum SiH_4/O_2 flow rate ratio for ECR PECVD silicon oxide films was 0.071 (corresponding to region I in Fig. 2). The silicon oxide thin films obtained in this range showed high catastrophic breakdown fields of 9~10 MV/cm and low leakage current density of $\sim 10^{-11}$ A/cm^2 even at the field of 4~5 MV/cm. These numerical values are much better than those of silicon oxide films prepared by conventional PECVD. Table 2 shows the properties of silicon oxide thin films fabricated by various method. Since the films were deposited at room temperature, it may be suitable for the device fabrication which requires low temperature process such as thin film transistors for liquid crystal display.

4. Conclusions

Silicon oxide thin films were fabricated by ECR PECVD at room temperature and the effect of SiH_4/O_2 flow rate ratio was investigated.

As SiH_4/O_2 flow rate ratio was varied from 0.031 to 0.5, three regions could be distinguished in terms of changes in refractive index, breakdown field and leakage current density. Changes in these properties could be explained by the characteristics of the ECR PECVD system. In region II (SiH_4/O_2=0.125~0.31), judging from refractive index, breakdown field and leakage current density, the film stoichiometry was kept.

Silicon oxide films, formed by ECR PECVD system under the optimum condition, showed refractive index as 1.465, breakdown field, defined as the electric field forcing a current density of 1×10^{6} A/cm^2, as 9 MV/cm and leakage current density, measured when the electric field was 1 MV/cm, as $\sim10^{11}$ A/cm^2.

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