

Dielectric and Passivation-Related Properties of PECVD PSG

(PECVD PSG의誘電 및 保護膜特性에 관한 研究)

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要 約

PECVD장비를 사용하여 PSG를 증착하고 막의 유전 및 보호막 특성을 조사하였다. X-선 형광분석으로 PSG내의 인 농도를 분석한 결과 약 8m/o에서 포화되었다. 인 함량에 대한 PSG의 적외선 흡수율, 식각속도 및 시트저항등의 변화도 비교하였다. APCVD와 PECVD에 대한 유전특성, 스텝 커버리지, 크랙저항과 게터링효과를 검토하였다. PECVD산화막은 비중 2.4 g/cm^3 , 굴절율 1.53, 항복전장 11-13MV/cm의 값을 가졌고 크랙저항도 APCVD산화막 보다 우수하였다. 2m/o의 인을 포함하는 PECVD PSG의 경우 양호한 스텝 커버리지와 게터링효과를 보였다. 공정변수에 대한 일련의 실험을 통하여 PECVD PSG 공정으로 보다 개선된 특성의 보호막을 얻을 수 있었다.

Abstract

The properties of plasma-enhanced CVD phosphorous silicate glass (PECVD PSG) for passivation layer are studied. Phosphorous concentration was analyzed with X-ray fluorescence. As a result, PECVD PSG has a limiting phosphous concentration of about 8 mole %. Curves relating to etch rate, infrared absorption ratio, and sheet resistivity were adapted to monitor phosphorous concentration indirectly. Dielectric properties, step coverage, crack resistance, and gettering effect are discussed in both of atmospheric pressure CVD (APCVD) and PECVD oxide. PECVD SiO_2 film have density of about 2.4 g/cm^3 at deposition rate of $450 \text{ \AA}/\text{min}$, refractive index of about 1.53, and breakdown at fields of 11-13 MV/cm. Crack resistance of PECVD oxide is greater than APCVD oxide. PECVD PSG films contained with 2 mole % phosphorous show good step coverage and gettering ability. The obtained results show more advantages in PECVD PSG than in APCVD PSG for device passivation.

I. Introduction

PECVD thin films have generated consider-

able interest in recent years. Much of this interest stems from the ability of high energy electrons in rf glow discharges (plasmas) to break chemical bonds and thereby promote chemical reactions at relatively low temperature ($< 400^\circ\text{C}$). Such considerations are particularly important when depositing films onto substrates which cannot withstand high temperatures. A further advantages, however, is that the highly reactive plasma atmosphere can re-

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sult in the formation of materials with unique chemical, physical, and electrical properties.

This paper, aimed for the improvement of passivation characteristics, describes the PECVD PSG deposition technique and effect of deposition parameters on various film properties.

PSG is widely used in silicon integrated devices as a passivation film providing mechanical protection and improving electrical stability and reliability. The control of phosphorous concentration in the glass film is crucial. A PSG with low phosphorous content may result in inadequate gettering of externally introduced contaminants such as sodium ions; it may also cause cracking of the glass because of excessive stress. Too high a concentration of phosphorous, on the other hand, may result in current leakage across the surface or in a hygroscopic glass, which may cause metal corrosion problems.[1] Therefore we placed primary consideration the analysis of phosphorous concentration in PSG film. These include; X-ray fluorescence, etch rate variation, infrared absorption, and sheet resistivity.

PECVD PSG application to the passivation is also discussed in respect of step coverage, crack resistance and gettering ability. Dielectric properties such as refractive index, film density, dielectric strength, particle and pinhole density of PECVD, APCVD, and thermal oxide are finally discussed.

II. Experiments

Figure 1. shows the basic design of the ASM America, Inc. PECVD system. It consists of a resistance-heated furnace with in which is placed a 165/171 mm quartz tube. Into the deposition region is inserted a boat assembly that rolls on wheels and consists of vertically oriented graphite slabs which carry the wafers in slots. Every other slab is connected to one rf power input with the other slabs alternately connected to the other rf power input, which operates at 410 KHz at a maximum of 1000 watt.

The system exhibits good film uniformity for low temperature oxide, both doped and undoped. These films typically have better

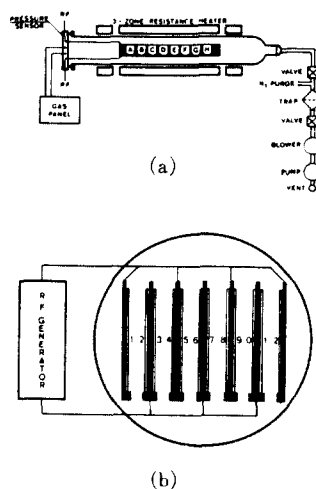


Fig. 1. PECVD system (a) Side view cross-section of system; (b) Front view cross-section of reactor internals.

than $\pm 10\%$ thickness uniformity with growth rates in the 200-700 $\text{\AA}/\text{min}$ range. Investigations of PSG film were undertaken based on these results. (2)

The gas system was composed of SiH_4 , N_2O , O_2 and PH_3 (5% in N_2). A silicon carbide coated graphite boat with a capacity of seventy 100 mm wafers was used for this work. The wafers used were 6-9 ohm-cm, (100) and p-type having 100 mm diameter. The thickness and refractive index of the films were measured with a nanospec, and an ellipsometer respectively.

PECVD oxides were deposited under the fixed conditions; $\text{SiH}_4=78\text{SCCM}$, $\text{N}_2\text{O}=1500\text{SCCM}$, $\text{O}_2=14\text{SCCM}$, tube pressure of 0.78 Torr, at 380°C . The variable conditions were PH_3 gas flow rate and rf power. Under these fixed conditions and rf power of 150watt, phosphorous concentration versus PH_3 gas flow rate was observed using x-ray fluorescence analysis. x-ray fluorescence analysis was carried with standard sample which was prepared by mixing SiO_2 and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ powder.

With the method reported by Levin, infrared absorption analysis was done. (3) Fourier Transform Infrared (FTIR) spectrometer (Nicolet-3600C) was utilized in this work. The ratio of the P=0 absorption at 1320 cm^{-1} and

the Si-O absorption at 810 cm^{-1} is calculated. This ratio is compared to the phosphorous concentration obtained from x-ray fluorescence.

Samples are etched at 25°C using pad etchant ; HF (48.8%) : NH_4F (40%) : CH_2OH : $\text{CH}_2\text{OH} = 1:6:7$. Etch rate is determined by plotting film thickness measured by nanospec vs. etch time.

PECVD PSG are heated at 1100°C for 20 and 120 minutes in 1% O_2 in N_2 . The films are removed by etching in hydrofluoric acid and sheet resistivity of the n-type diffused layers are measured using a 4 point probe.

Prior to varying the phosphorus concentration, we checked the reproducibility and uniformity of sheet resistivity of 6.5 mole % PSG for 3 runs, day after day. For each wafer, sheet resistivity was measured for about 100 points. Sheet resistivity shows excellent uniformity of 5%. The effects of rf power on the deposition rate, refractive index, and etch rate were investigated. RF power was varied from 100 to 400 watt. The film density was obtained by using the Lorentz-Lorentz equation which relates refractive index to film density of SiO_2 .(4)

To enhance the visual inspection of pinholes, plasma etching technique(5) was applied with ETE 425-D equipment. The etching conditions so as to maximize the Si-to- SiO_2 etch rate ratio were obtained at total pressure of 0.35 Torr, rf current of 0.23A, O_2 of 30 SCCM and CF_4 of 270 SCCM. Oxide thickness was $\sim 7000\text{\AA}$.

The intrinsic breakdown voltages were measured on 0.004 cm^2 area, one hundred capacitors made from 1000 \AA oxide films deposited on silicon wafers.

For the crack observation, APCVD oxide on silicon wafer was formed with $1\text{ }\mu\text{m}$ thickness and patterned by photolithography. On the APCVD oxide with $1\text{ }\mu\text{m}$ height topology, metal (Al, 1% Si) was deposited by a sputter for on the entire wafer surface. And APCVD or PECVD oxide was deposited on the metal layer. In this step, three types of glass were prepared; single, double and triple-layer. The single-layer glass was a $1\text{ }\mu\text{m}$ -thick PSG or SiO_2 film, and double-layer consisted of a 4000 \AA -thick SiO_2 top layer over the 6000 \AA -thick PSG mainlayer, while the triple-layer film

consisted of a 6000 \AA -thick PSG film with a 2000 \AA -thick SiO_2 film deposited on either side. Phosphorous concentrations were varied between 2 to 4 mole %. After deposition of CVD glass, the samples were alloyed at 450°C in H_2 ambient for 30 minutes. These samples were dipped into metal etchant for three hours and observed metal discolor at crack.

Glass passivation efficiency was studied from the bias temperature stress capacitance voltage (B-T-S, C-V) plots using aluminum dots, 500 \AA PECVD PSG, 500 \AA thermal oxide, silicon, capacitors. In PECVD PSG process, phosphorous concentrations were varied between 1 to 6.5 mole %. Thermal oxide was grown in O_2 of 4500 SCCM for 20 minutes at 1000°C . B-T-S was carried with +10V bias for 4 minutes at 250°C .

III. Results and Discussion

1. Phosphorous concentration

The phosphorous concentration increases almost linear as the ratio of PH_3/SiH_4 in the region from 0 to 16% as shown in Fig.2.

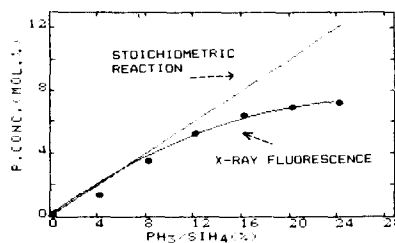


Fig. 2. Phosphorous concentration as a function of PH_3/SiH_4 gas ratio.

The data agree reasonably well with the planar plasma system data of Hollahan which indicate a limiting phosphorous content of about 6 mole % at much higher PH_3 flows rate. (6) Dopant incorporation mechanism in PECVD oxide is not clear yet. (7)

Figure 3. shows the FTIR spectra for the as deposited PECVD PSG. Five absorption peaks are clearly observed at about 455 , 810 , 1060 , 620 , and 1320 cm^{-1} . The first three peaks result from the Si-O bonds, 620 cm^{-1}

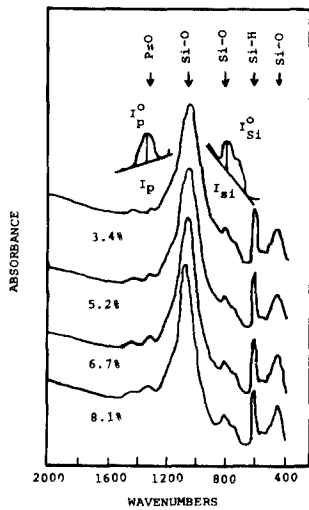


Fig. 3. FTIR absorption spectra of PECVD PSG.

from Si-H bond, and the last one from the P=O bond. Using the absorption bands at 1320 cm^{-1} and at 810 cm^{-1} the absorption ratio

$$R = \log(I_p/I_p^0) / \log(I_{si}/I_{si}^0)$$

is defined (I_p , I_p^0 , I_{si} , and I_{si}^0 are defined in Fig. 3). (3)

The ratio is approximately linear with the concentration of phosphorous in the glass in Fig. 4. Using this figure the phosphorous concentration can be obtained indirectly from the infrared absorption spectra.

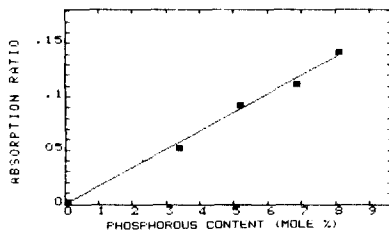


Fig. 4. Calculation curve showing the absorption ratio vs. phosphorous mole % obtained from x-ray fluorescence.

The dependence of the etch rate of PSG film on phosphorous concentration is given in Fig. 5.

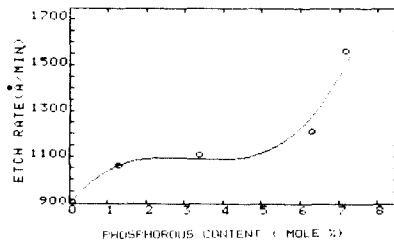


Fig. 5. Etch rate vs. phosphorous mole %.

As seen in fig. 5, the etch rate of PSG films increased markedly in the ranges of phosphorous contents less than 1.5 mole % and greater than 5.5 mole % which it showed nearly flat increase in the range between 1.5 and 5.5 mole %. The increase in etch rate with addition of phosphorous is assumed that the dopant tends to be removed from the glass more rapidly than SiO_2 dose. (8)

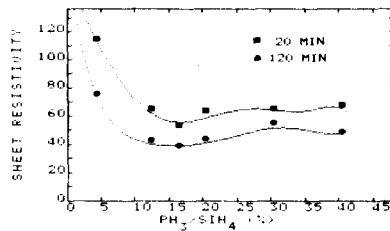


Fig. 6. Sheet resistivity vs. PH_3/SiH_4 gas flow ratio.

Figure 6 shows sheet resistivity versus PH_3/SiH_4 gas ratio. Sheet resistivity began to saturate at PH_3/SiH_4 ratio of 16%.

Above this ratio this film appeared precipitation as shown in Fig. 7.

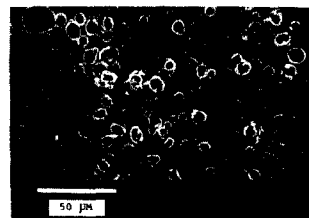


Fig. 7. SEM photograph of a 5000 \AA PSG film with phosphorous contents after heating in N_2 at 1100°C for 2.5 hr.

The reason of these phenomena is assumed that the impurity (phosphorous) in SiO_2 acts as a nuclei seed at high phosphorous concentration. (9) It is needed to study precipitation composition and mechanism in PECVD PSG.

x-ray fluorescence analysis is very tedious and time consuming. Consequently, it is unsuitable for routine use; however, it is useful for the absolute calibration of other techniques. Calibration curves which relate this absolute phosphorous concentration to absorption ratio, etch rate, and sheet resistivity were also obtained in this work. Using these calibration curves, phosphorous concentration could be easily monitored in routine PECVD PSG process.

2. Dielectric Properties

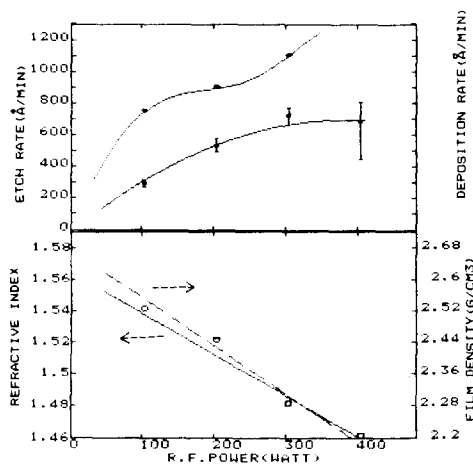


Fig. 8. Effects of R.F. power on dielectric properties of PECVD oxide.

The effects of rf power on the deposition rate, refractive index, film density, and etch rate are shown in Fig. 8. Deposition rate is nearly linear with rf power less than 300 watt. Film thickness uniformity becomes poor as RF power increases over the 300 watt.

The faster the deposition rate, the less chance there is for the atoms to reach their lowest energy state and the most dense structure and, thus, the resulting films can be quite porous with a good deal of bond strain in the films.(4) The porosity and strain in

the films will result in lower refractive indices, faster etch rate as show in Fig.8. At 150 watt, O/Si ratio is about 2 according to the curve studied by reinberg. (10)

Under the condition of this rf power, PH_3/SiH_4 gas flow ratio was varied. There was no trend in the refractive index variation, and its value is near to 1.53.

The various radical are generated in the case of CF_4 plasma etching. Among them, fluorine radical F^* and fluorocarbon ion such as CF_3^* selectively etch silicon and silicon dioxide, respectively. The addition of oxygen to CF_4 caused the etch rate of silicon to increase because of the increase of F^* . Using a $\text{CF}_4\text{-O}_2$ mixture gas in rf plasma etching, we applied this technique to the detection of the pinhole density in the SiO_2 film by the etching of underlying Si substrate with F^* .

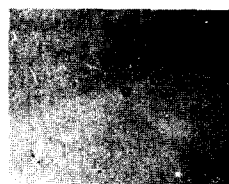


Fig. 9. Etch pit revealed by plasma etching method.

Figure 9 shows etch pit formed by plasma etching method. Pinhole densities of thermal, PECVD and APCVD oxide are $2/\text{cm}^2$, $6/\text{cm}^2$, and $40/\text{cm}^2$ respectively.

In the case of PECVD oxide deposition, homogeneous reactions must be minimized to reduce particulate formation and to enhance heterogeneous reactions. Thus, relatively low power density and high $\text{N}_2\text{O}/\text{SiH}_4$ ratios are generally used (11) Oxygen is not typically used in such processes because of the rapid (and sometimes homogeneous) reaction of O_2 with SiH_4 . Relative to N_2O is the preferred oxidizer for SiH_4 in SiO_2 deposition because of the low bond dissociation energy (1.7eV) of N-O in this molecule. (10, 11) But O_2 flow is the most critical parameter for fine adjustment of the oxide thickness uniformity. To get good thickness uniformity and reduce particles, SiH_4/O_2 ratio was adjusted near 5

and rf power of 150 watt.

Another particle source is due to thermal stress cracking of the chamber wall, electrode materials and depositing film layer. To minimize the stress of film, the system was cleaned in situ for 1 hr in plasma containing C_2F_6 and O_2 gas ambient with the substrate heater on. Subsequent to the cleaning operation a pre-deposition run was made with the desired flow and thickness. Particle densities of the $1 \mu m$ thickness PECVD SiO_2 and APCVD SiO_2 are about $1.13/cm^2$ and $5/cm^2$ respectively.

Pinhole and particle density which weakens the dielectric strength could be reasonably reduced in this work under the low rf power, proper gas composition, and self plasma cleaning technique.

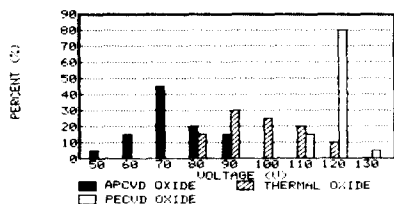


Fig. 10. Breakdown voltage distributions of thermal, PECVD and APCVD oxide.

Breakdown voltage distributions for 1000 \AA thickness capacitors were given in Figure 10. It shows that PECVD oxide has high breakdown voltage (average 110V) and narrow distribution comparing with other films. More detailed relation between pinhole density and dielectric strength will be studied.

3. Application to passivation process

In the recent studies, PECVD oxide (doped and undoped) is known to have compressive stress. (6,8,12) But APCVD oxide layers are in tensile intrinsic stress, that caused the crack. Through this experiment, there was no crack in PECVD oxide. In the case of APCVD oxide, we could observe crack as shown in Fig. 11. The detailed features of cracks of APCVD oxide were included in our another report. (13) This discussion indicates that PECVD oxide has better crack resistance than APCVD oxide.

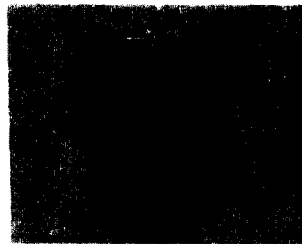


Fig. 11. Crack revealed in APCVD oxide.

Using this advantage, the effectiveness of a passivation layer in providing protection against metallization scratches could be increased with increasing PECVD film thickness ($1 \mu m$).

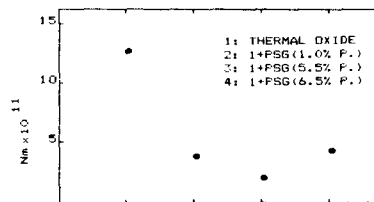


Fig. 12. Gettering effect of PECVD PSG.

Gettering effect of PECVD PSG film is shown in Fig. 12. Thermal oxide has mobile ionic charge number density (N_m) of 1.25×10^{12} . In the case of overcoating the PSG films at 5 mole % P., N_m is reduced to 8.3×10^{10} . These results show that PECVD PSG film can effectively getter mobile ions induced from oxidation process and metal deposition. Polarization was not found in this study. It is assumed that phosphorous concentration was relatively low (1.5-6.5 mole % P).

A thin SiO_2 top layer over the PSG main-layer is desirable for improved photoresist adherence and consequently improved pattern etching definition. (1)

For these reasons, we applied the combinations of PSG and SiO_2 films to passivation layer; for APCVD, 3000 \AA SiO_2 top layer over 4000 \AA 2% P. PSG and for PECVD, 4000 \AA SiO_2 and 6000 \AA 2% P. PSG.

Figure 13 shows SEM cross sections of these films over metal step ($1 \mu m$). Figure 13-a shows conformal step coverage of PECVD

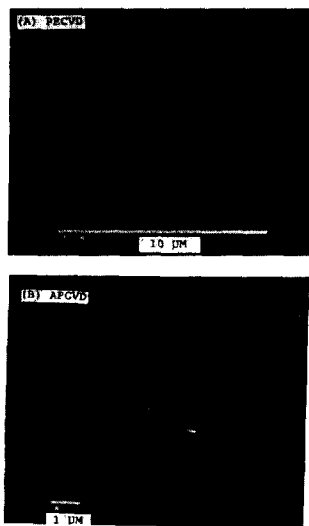


Fig. 13. SEM cross sections of APCVD and PECVD films.

oxide. In Fig. 13-b, APCVD oxide appears as a little negative slope.

IV. Conclusions

Phosphorous concentration was obtained from x-ray fluorescence. The etch rate, sheet resistivity, and absorption ratio to phosphorous concentration also have been demonstrated. Measurements based on these methods are proven to be more easy way to monitor the phosphorous concentration in routine PECVD PSG process.

In comparison with APCVD oxide, PECVD oxide has the less particle and pinhole density and the better characteristics of dielectric strength. In addition to these advantages, PECVD oxide was more dense film ($\sim 2.4 \text{ g/cm}^3$), if we take moderate deposition rate, 450 (\AA/min) . Applying to passivation layer, PECVD PSG films contained with 2 mole % phosphorous have good properties such as step coverage, crack resistance, and gettering ability.

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