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Deposition of PSG Film by Photo-CVD

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The deposition characteristics of phospho-silicate glass by mercury-sensitized photo-CVD method are investigated. Also evaluated are the electrical, chemical and physical properties of as-deposited and of annealed photo-CVD PSG.

It is shown that phosphorus is easier doped into the film under the smaller N_2O/SiH_4 ratio, which is opposite tendency to that of conventional CVD method.

Formation of P_2O_5 in the as-deposited film is not sufficient for the photo-PSG and the variety of annealing ambience affects the properties of densified film strongly.

Step coverage of photo-PSG is conformal and the residual stress is compressive typically.

1. Introduction

Chemical vapour deposited silicon oxide of good quality , prepared at low temperature, has been desired in the field of multilevel wiring techniques as interlayer insulating film between aluminum wiring. Phospho-silicate glass (PSG), which has been widely used as reflow glass, is thought to be attractive for this application from the view point of crack resistance despite the lack of humidity resistance and of stability of electric performance. Atmospheric pressure CVD technique (APCVD) using $SiH_4+O_2+PH_3$ system , up to the present, mainly has provided the PSG film in spite of its essential problems; poor step coverage decisively lowers the reliability of metal wiring over the PSG layer and relatively high process temperature ranging from 400 °C to 450 °C has a tendency to cause Al-hillocks.

Though the plasma-deposited PSG is expected to overcome the above difficulties, there seem to be other troublesome problems such as radiation damage, undesirable surface heating by gas plasma and instability of a deposited film probably caused by the non-uniformity of electric field from the morphorogy of underlayer materials and patterns in LSI. Recently, the photo-CVD technique is expected as a low temperature and radiation-damage free proccessing with good step coverage, and many studies on the deposition of silicon oxide, silicon nitride and silicon by this method have been reported.

However, there are no detailed studies on the preparation of PSG film by this method. Feasibility study on the preparation of PSG film by photo-CVD (photo-PSG) is of very interest in developing a reliable fine line multilevel metallization.

In this paper, a study on the deposition and the characterization of photo-PSG, which is sufficiently P-doped, is reported.

2. Experimentals

The photo-PSG was deposited by the mercury-sensitized photo-CVD technique using a low pressure mercury lamp as 2537 Å and 1849 Å photon source.

The irradiation intensity of 2537 Å line at the center of the substrate was $\sim$ 6 mw/cm^2. 100 % SiH_4, 1 % PH_3/H_2 and N_2O were employed as silicon source, phosphorus source and oxidant, respectively. Argon gas of several SLM was admitted to introduce near the UV light window for restricting the undesirable deposition onto it. The deposition pressure ranged from 1 to 10 Torr and the deposition temperature was below 400 °C. Phosphorus concentration in the deposited film was measured by means of fluorescent X-ray analysis. Deposition characteristics for the variety of deposition parameters such as substrate temperature, gas mixing ratio and so on were examined. Also evaluated were the electric performance and physical characteristics of as-deposited and annealed photo-PSG.

2. Results and Discussions

Figure 1 shows the dependence of phosphorus concentration in the deposited film on the flow rate of 1 % PH_3/H_2 . The phosphorus concentration in the figure is given expressin to mole % of P_2O_5 on the assumption that all the phosphorus in the photo-PSG are incorporated in the form of P_2O_5.

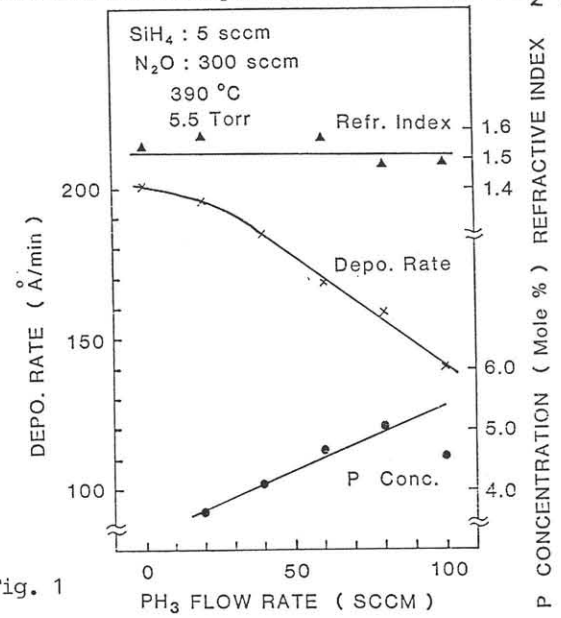


Fig. 1

It is shown that phosphorus concentration increases almost monotonously as 1 % PH_3/H_2 flow rate increases. Decreasing feature of deposition rate, shown in Fig. 1, is similar tendency to that of plasma-PSG and and is quite different from APCVD -PSG.

The dependence of deposition parameters on the source gas mixing ratio are shown in Figs. 2 & 3.

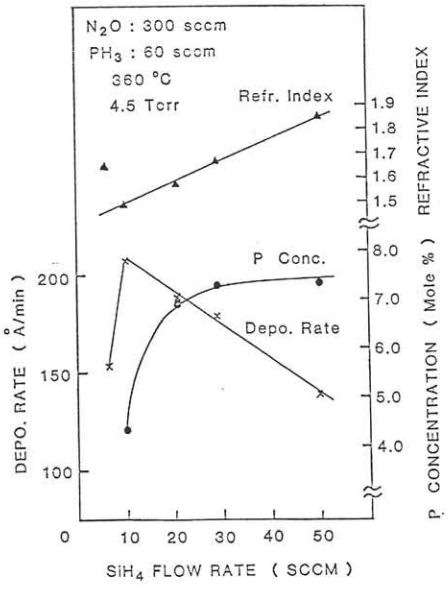


Fig. 2

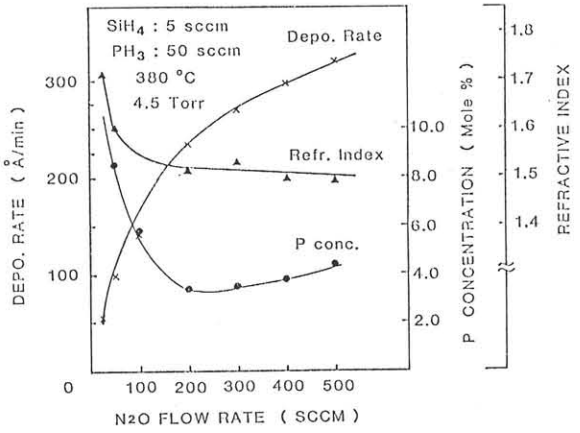


Fig. 3

These figures are characterized by that the amount of incorporated phosphorus is strongly affected by the N_2O/SiH_4 ratio and that the low partial pressure of N_2O results in the high concentration of phosphorus , which is opposite tendency to that of conventional CVD technique. In the APCVD system using $SiH_4+O_2+PH_3$ as source gas, PH_3 is decomposed into P_2O_5 through the oxidation by O_2 , and the phosphorus concentration is apt to increase with the increase of O_2 flow rate.

The above result implies that a phosphorus atom does not combine with oxygen in as-deposited photo-PSG and that PH_3 has a tendency to be photo-decomposed directly rather than is oxidized by nascent oxygen derived from N_2O.

Figure 4 shows the temperature dependence.

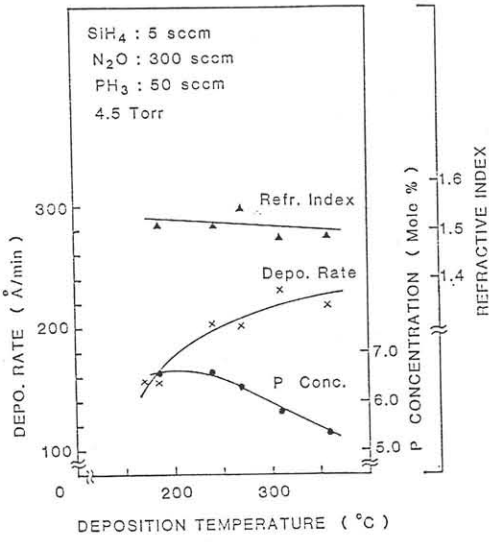


Fig. 4

It is shown that phosphorus is easier doped into the film at lower temperature, while the increase of substrate temperature enhances the deposition of photo-PSG, which is simillar to that of undoped photo-CVD silicon oxide.

Remarkable feature was observed in infrared absorption spectra. Figures 5 & 6 show the FTIR spectra of as-deposited and annealed photo-PSG film. As can be seen in the spectrum of as-deposited film in Fig. 5, P=O absorption band around 1300 cm^{-1} is considerable weak even for the sufficient N_2O flow rate (500 sccm) , which is quite different from that for the conventional CVD technique. This result reveals that , as mentioned before, P_2O_5 is not formed sufficiently in the as-deposited photo-PSG and that phosphorus is incorporated into the film in a different form from that of the conventional CVD technique. This will be due to the lack of sufficient supply of oxidant.

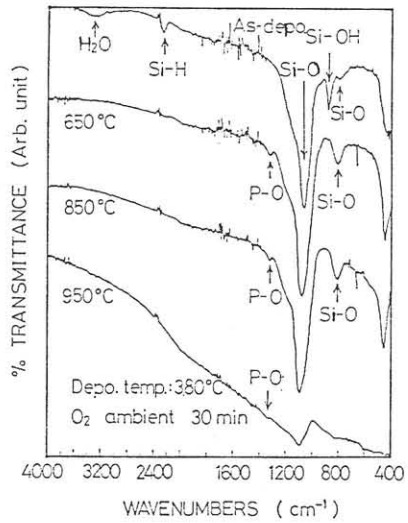


Fig. 5

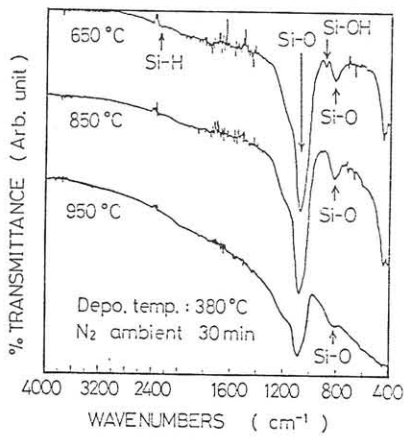


Fig. 6

In the spectrum of as-deposited film, also is shown the evident absorption peaks at around 3300 cm^{-1} , 2200 cm^{-1}, 900 cm^{-1} and 800 cm^{-1},which are ascribed to H_2O, Si-H, Si-OH and Si-O absorption , respectively. Distinctictive characteristics are recognized in the spectra of annealed films. Post-annealing in O_2 ambience brings about an appearance of P=O absorption band, which indicates that the oxidation of phosphorus occurs by annealing. Further, a breakaway of -OH or -H and the shift of peak position of Si-O at around 1100 cm^{-1} to the large wavenumber region can be also observed. On the contrary, annealing in N_2 ambience only causes the densification. (Fig. 6) The reason for the conspicuous lowering of transmittance at the low wavenumber region for 950 °C annealing, which can be seen in both N_2 and O_2 ambience , remains unexplained at present.

6 : 1 BHF etch rate was examined as a function of 1 % PH_3/H_2 flow rate. The etch rate of as-deposited film increases rapidly as 1 % PH_3/H_2 flow rate or phosphorus concentration increases, and the conspicuous reduction after densification in N_2 are shown in Fig. 7.

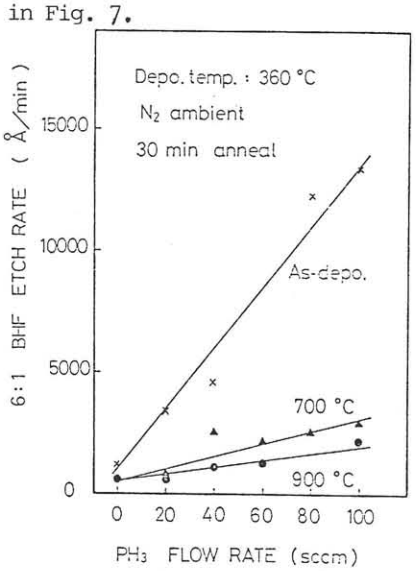


Fig. 7

In order to evaluate the electrical performance of photo-PSG, metal-oxide-semiconductor (MOS) structure were made of photo-PSG. Capacitance-Voltage (C - V)measurements were carried out at 1 MHz. Shift of flat-band voltage to the inversion region in bias voltage were observed especially for the specimens annealed in O_2 ambience, which will be due to the polarization phenomenon of photo-PSG film. Figure 8 shows the relative dielectric constant of as-deposited and annealed photo-PSG as

a function of 1 % PH_3/H_2 flow rate. The relative dielectric constant was calculated from the capacitance of the photo-PSG at 1 MHz. As shown in Fig. 8 , the dependence of the dielectric constant of as-deposited and of densified photo-PSG are weak. The values range 4.2∼4.8 for as-deposited film and 3.2∼3.6 for densified film, respectively. The reduction of the value after densification will be due to the breakaway of -OH or -H . On the other hand , annealing in O_2 ambience makes the dependence prominent and the relative dielectric constant increases for the specimen deposited under high flow rate of PH_3.

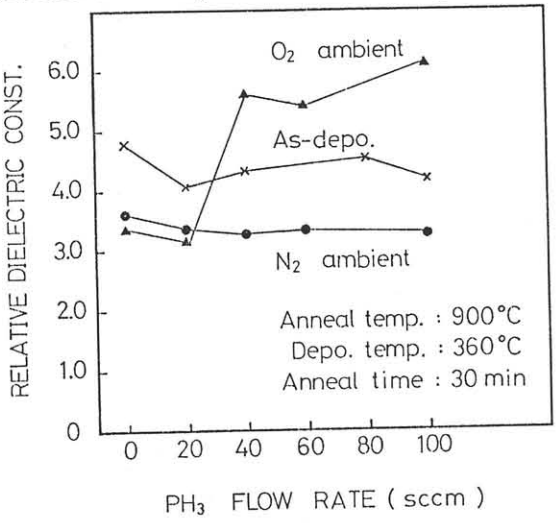


Fig. 8

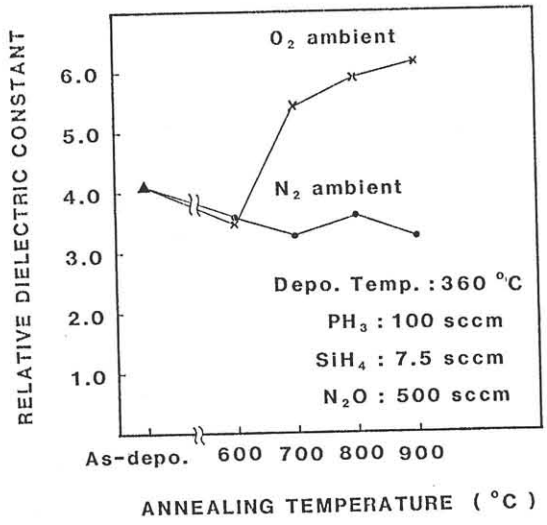
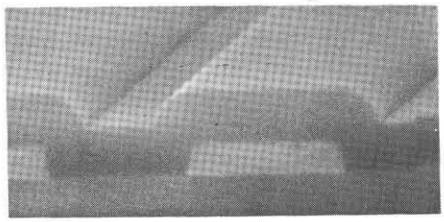


Fig. 9

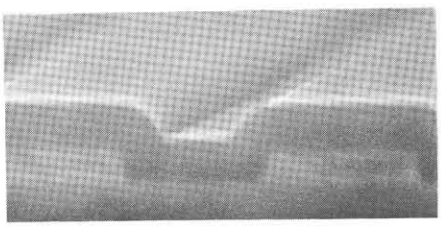
Similar feature on the annealing ambience can be seen in the dependence on the annealing temperature. (Figure 9) These will be related to the polarization of P_2O_5 formed under the annealing in O_2 .

The breakdown field strength of annealed photo-PSG was observed to be ∼ 8 MV/cm under the annealing condition of 900 °C , 30 min , N_2 (or O_2) The breakdown field strength of as-deposited photo-PSG is apparantly higher than that of annealed specimens, but this value depends strongly on the measurement condition such as the ramping rate of applied field.

Figure 10 shows the step coverage of photo-PSG ; (a) is the as-deposited and (b) the after annealing of 970 °C , 1 hr, O_2 .



(a) as-deposited



(b) after annealing of 970 °C O_2, 60 min

Fig. 10

Step coverage of photo-PSG is conformal as shown in Fig. 10 . Substantial reflow by annealing can not be observed, but this may be due to the insufficiency of phosphorus of the specimen.

The direction of residual stress was found to be compressive and varies in conjunction with phosphorus concentration, which suits the crack resistance

4. Summary

Phospho-silicate glass , which is sufficiently P-doped, was deposited by the mercury-sensitized photo-CVD using SiH_4+ N_2O + PH_3 as source gas.

Phosphorus is incorporated into the photo-PSG in a different form from that of the conventional preparation technique. The variety of annealing ambience affects the electric performance of photo-PSG. Step coverage of photo-PSG is conformal and the direction of residual stress of photo-PSG is compressive typically.

Reference

1. H. Itoh, M. Hatanaka, H. Abe and H. Nakata ; Proc. of 1983 IDPS p 85