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Photo-CVD Silicon Nitride and Silicon Oxide Films for VLSI Application

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Silicon nitride and silicon oxide films deposited by photo chemical vapor deposition(Photo-CVD) technique are characterized. Both films are grown at low temperature from room temperature to 400°C. The basic physical, chemical and electrical properties of these films are investigated. In particular, the characteristics of the breakdown voltage, the current conductance, etch rate, stress, step coverage and so on are investigated in details from view point of VLSI application.

§1 Introduction

A photo-CVD is a novel technique to deposit thin films at a relatively low temperature. In Photo-CVD process, UV light (2537 Å and 1849 Å) emitted from a low pressure mercury lamp is currently used to activate or decompose the reactant gases like SiH_4 by a direct or indirect absorption of the resonant light energy, and enhance the chemical reaction at the surface of the substrate to deposit the films. Therefore, photo-CVD process is considered essentially to be a radiation-damage free process compared with a current plasma-enhanced CVD. In this paper, the basic deposition characteristics of silicon nitride and silicon oxide films will be reported in details, in which the depositions are carried out by the indirect photo-induced decomposition process with the aid of mercury vapour in a newly designed reaction chamber. The characterizations of the deposited films will be discussed on their stoichiometric, chemical and electrical properties in contrast with those of films deposited by the conventional CVD method.

Further, some experimental results will be discussed on its capability for application of the films to the devices.

§2 Experimentals

Reactant gases such as SiH_4, NH_3 and N_2O were introduced through the temperature-controlled mercury reservoir into the aluminum chamber. Ar gas was used as a carrier gas. In the case of the deposition of silicon nitride films, 100% SiH_4 was admitted into the reaction chamber at the flow rate of 2~10 SCCM and mixed with NH_3 at the flow rate of 80~400 SCCM. Total gas pressure in the reaction chamber was controlled to be 0.1~10 torr by APC (Automatic Pressure Controller) followed by mechanical booster pump and rotary pump. UV light was emitted through the quartz window, which is transparent to λ=2537Å and 1849Å lines, to the substrate surface, at where the illumination intensity was about 6 mW/cm^2. The temperature of the sustrate was controlled in the range of room temperatue to 400°C. The deposition rate, refractive index and infrared spectra were investigated as functions of UV light intensity, substrate temperature, gas flow rate, total pressure and mercury reservoir temperature. Leakage current characteristics and breakdown voltage of silicon nitride films were measured with the structure of Al-Nitride-Al in the dark and evacuated cell. C-V measurements were also carried out. Thermal crack resistance as well as step coverage from the view point of application, was investigated with PSG-Al-Silicon Nitride structure under the thermal stress at 450°C, N_2, 60 minutes.

§3 Results and Discussions

Fig.1 shows the thickness of silicon nitride film as a function of deposition time. As can be seen from Fig.1, the film grows linearly with the deposition time, which means the growth of silicon nitride film in photo-CVD process is limited by surface reaction process. Fig.2 shows the deposition rate of the film as a function of the illumination intensity of 2537 Å line. The deposition rate was found to increase almost linearly with increasing light intensity. Both deposition rate and refractive index vs. substrate temperature are shown in Fig.3. Deposition rate decreases gradually with the increment of substrate temperature, while the refractive index increases. These results are very similar to those of plasma-CVD. As is shown in Fig.5, there is a strong correlation between the number of Si-H bond in photo-CVD silicon nitride film and its refractive index. The deposition rate of silicon nitride film, as illustrated in Fig.4, was found to saturate around 3~4 torr of total pressure. The high vapor pressure of mercury plays a role to enhance the deposition.

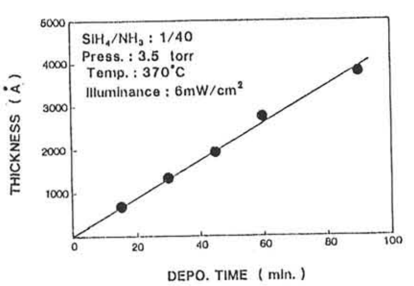

Fig. 1

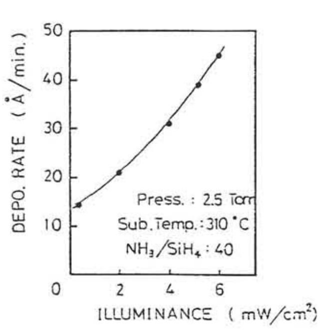

Fig. 2

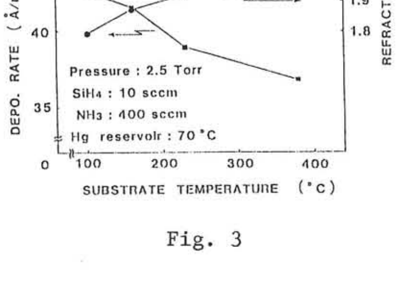

Fig. 3

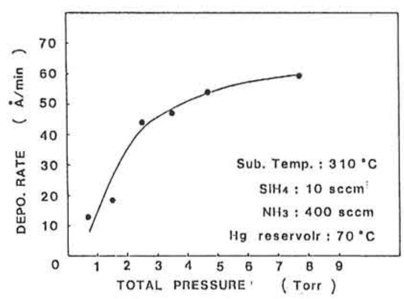

Fig. 4

The deposited films are characterized as follows. In Fig.5, FTIR spectra of the silicon nitride films of about 1300 Å thick, which are deposited on P-type silicon substrate. The films are deposited at the several substrate temperature at the constant illuminance. As can be seen from Fig.5, the large absorption peak at around 2170 cm^{-1} is observed, which assigns to Si-H bond. Other absorption peaks around 1160 cm^{-1} and 3160 cm^{-1} are due to the absorption by N-H bond. These absorptions by Si-H and N-H bonds have been reported on plasma-CVD silicon nitride film.[4]

The absorption peak height of Si-H bond as well as that of N-H bond decreases rapidly with the increasing deposition temperature. This means the number of Si-H and N-H bonds depends on the deposition temperature.

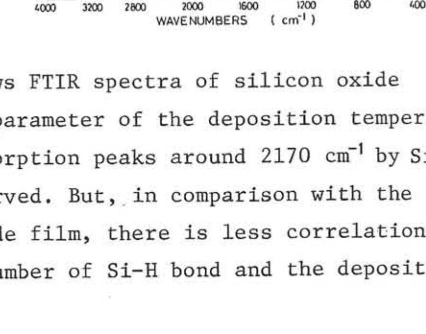

Fig. 5

Fig. 6 shows FTIR spectra of silicon oxide films as the parameter of the deposition temperature. The absorption peaks around 2170 cm^{-1} by Si-H bond are observed. But, in comparison with the silicon nitride film, there is less correlation between the number of Si-H bond and the deposition temperature.

Thus, even in photo-assisted CVD process as well as the case of plasma-assisted CVD, both Si-H and N-H bonds are contained in the silicon nitride and silicon oxide film during growth of the film.

From the view point of application of these insulators to the devices, their electrical prop-

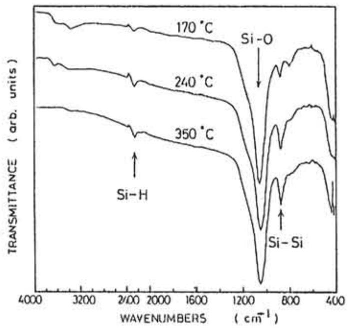

Fig. 6

erties are essentially important. A leakage current characteristics are measured. The thickness of the measured film was 3500 Å, which was deposited at 370°C to reduce the content of Si-H bond and its refractive index was 1.98. The Poole-Frenkel plots of the I-V characteristics of Al-Silicon Nitride- Al showed two stages of conduction at low electric field and high electric field. Further, a small injection type of hysteresis was observed on I-V characteristics. This hysteresis is known to arise from charge trapping. Thus, the above results mean that the trap density of photo-CVD silicon nitride film may be rather small.(Fig. 7)

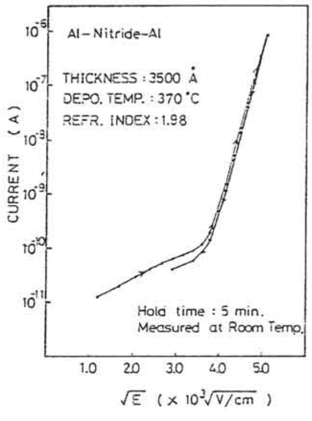

Fig. 7

In Fig. 8, a reciprocal temperature dependence of the leakage current is shown. In this case, applied electric field was fixed to be 1.3×10^{6} V/cm . As illustrated in Fig. 8, two types of the curve are obtained. At low temperature region, the current is independent of the temperature, which means the current tunnels from metal to silicon nitride. At high temperature, the measured current depends exponentially on the temperature and the activation energy associated with the trap depth of silicon nitride was calculated to be 0.25 eV.

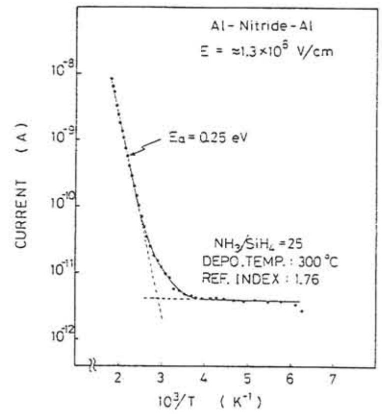

Fig. 8

The C-V measurement was made with the Al-Silicon Nitride-N type Silicon. The dielectric constant of silicon nitride film was measured to be 7.9 and the hysteresis of C-V curve was smaller compared with SiH_4 -NH_3 source plasma-CVD silicon nitride. C-V characteristics of MOS diode at low and high frequency are compared with the films deposited by photo-CVD , plasma-CVD and LPCVD methods. These measurements revealed that the photo-CVD oxide film shows small V_{FB} shift, small hysteresis curve and no feature of the radiation-induced damages.

From the view point of device application, for example, in the case of the intermediate insulating film between the first Al and the second Al, the insulating films have to be investigated on their breakdown voltage and crack resistance. The breakdown voltage of silicon nitride film, which was deposited at 370°C and its refractive index was 1.98, was about 3.4 MV/cm, as is shown in Fig. 9 .

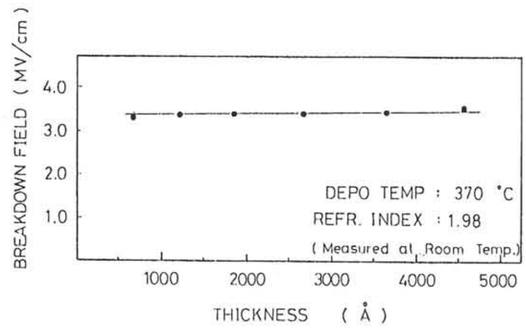

Fig. 9

This value is relatively high compared with the plasma-CVD silicon nitride. But the crack resistance was not enough.

$4 Conclusions

Mercury-sensitized photo-CVD process provides silicon nitride films of good quality compared with plasma-CVD silicon nitride. Refractive index of silicon nitride film is 1.8～2.0, which depends on deposition temperature and source gas ratio. Hysteresis of I-V and C-V characteristics is relatively small, which implies the number of traps in the film is small.

In the case of silicon oxide, stoichiometric and radiation-damage free film can be obtained by the photo-CVD process.

From the view point of application to the devices, silicon nitride and silicon oxide film show good step coverage and the etched profile of the films at the high step revealed to be isotropic and no enhanced etching phenomena at the steps.

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