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LTO - SiO₂ DEPOSITION IN A STAGNATION FLOW LPCVD SYSTEM

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Résumé

Un dispositif à parois froides à basse température, avec une configuration de flux d'arrêt, est utilisé pour le dépôt de SiO₂ sur des plaquettes de silicium, entre 280°- 400°C. Les propriétés suivantes des films ont été étudiées: vitesse de dépôt, distribution de l'épaisseur, indice de réfraction, vitesse de corrosion humide, caractérisation chimique par ESCA et infrarouge, caractéristiques électriques en fonction de la température du substrat, de la pression total, du gaz vecteur et du rapport O₂/SiH₄.

Abstract

A cold wall low temperature oxide (LTO) process, by a stagnation flow technique for the deposition of device quality SiO₂ on silicon wafers at temperatures of 280°- 400°C is reported. The following properties of the SiO₂ films were investigated: Growth rate, deposition profile, refractive index, wet etch rate, chemical characterization by XPS, electrical properties and IR - spectra have been studied as function of substrate temperature, reaction pressure, carrier gas and O₂/SiH₄ mole ratio.

I. Introduction

The growth of thin silicon dioxide layers by chemical vapor deposition (CVD) has become one of the most important methods for semiconductor device processing and has been investigated by several authors /1/-/6/. The main advantage of LTO depositions is their considerably lower process temperature as compared to high temperature oxide (HTO: SiH₂Cl₂ + N₂O; = 850°C) and the tetraethylorthosilicate process (TEOS: = 700°C). Unlike plasma enhanced CVD, LTO processes avoid high concentrations of bonded hydrogen (in the form of Si-H and of OH groups) in the oxides. H-bonds in the SiO₂ films can produce recombination centers and cause deep trapping /7/. The LTO process avoids plasma induced surface damage, which can also lead to high H-concentrations /7/. In particular LTO processes with stagnation flow technique attain deposition rates, which exceed the deposition rates of other processes as e.g. LTO processes with LPCVD quartz tubes, by an order of magnitude. Stagnation flow deposition systems with high deposition rates produce advantageously high yields and good film quality. Their low deposition temperature and high deposition rates make SiO₂ films suitable for final passivation after aluminium metallization. Furthermore the high deposition rate and the option to use a vacuum loadlock make a throughput as high as in batch systems possible. Especially for R&D applications these systems provide a number of advantages like quick processing, high efficiency, easy investigation of the reaction products and simplified numerical simulation /8/.

In a stagnation flow reactor the deposition results depend mainly on: Gas flow, convection, diffusion and chemical reactions in the gas phase and at the wafer surface. Optimisation of these parameters is a crucial requirement for manufacturers (reactor design, process control and development) and for users (deposition profile, film properties). This work describes the dependency of the deposition results on variation of the process parameters.

1. Experimental

A specially designed cold wall reactor (Fig.1) was used for these investigations. The reactor consisted of a rotating infra-red heated wafer support and a shower head type gas inlet system. A two stage rotary pump (Leybold TRIVAC 40 BCS) in connection with a roots blower (Leybold RUVAC 250 WSU) provided the necessary low pressure (< 5000 Pascal) in the CVD reactor. The flow rates of the reaction gases (SiH_4 , O_2 and N_2 for inert gas) were adjusted by thermal mass flow controllers. The gas flow was led through a shower head perpendicular onto the silicon wafer. Four halogene infra-red lamps generated the required wafer temperature, which was stabilized by feedback via a thermocouple and a self optimizing PID Eurotherm power controller. A purge gas was applied to expel reactive gases from the heat module in order to avoid deposition on the hot lamp surfaces. The reactor chamber and the shower head were made from stainless steel, and the wafer support from fused silica.

Fig. 1 Arrangement of the LTO deposition reactor

The SiO_2 films were deposited onto one-side polished $0.01 - 0.02 \Omega\text{cm}$ (100) silicon substrates. Electronic grade chemicals (Merck, Selectipur) were used for substrate cleaning. The silicon substrates were cleaned by the following procedure:

◦ Successive washing (10 minutes each step) in:

1. trichlorethylene
2. acetone
3. isopropanole
4. deionized water ($\approx 18 \times 10^6 \Omega\text{cm}$)
5. HNO_3 65% (at room temperature)
6. deionized water ($\approx 18 \times 10^6 \Omega\text{cm}$)
7. HF dip (5%)
8. deionized water ($\approx 18 \times 10^6 \Omega\text{cm}$)

◦ Treatment in a rinser dryer (15 minutes each step):

9. deionized water ($\approx 18 \times 10^6 \Omega\text{cm}$)
10. hot N_2

II. Results and Discussion

1. Influence of Temperature

Deposition experiments were carried out with the following parameters:

- total pressure 1000 Pascal
- reactive gases 10 sccm SiH_4 , 160 sccm O_2
- carrier gas 500 sccm N_2
- deposition time 50 sec

During the heat up time, (approximately 2 min.) reactive gas was led through a bypass and adjusted to a constant flow rate. After the temperature had risen to the required value, the bypass was closed and the deposition started. Directly after the deposition process the system was pumped down to $<1 \times 10^{-1}$ Pascal. Afterwards the system was purged with N_2 until the wafer was cooled down below 40°C and then refilled to atmospheric pressure. Subsequently a new wafer was placed into the reactor and the next deposition could be started. The dependence of growth rate on the wafer temperature is shown in Fig. 2. In the temperature range between 300°C and 370°C the deposition rate increases by a rate of $\approx 0.02 \text{ nm sec}^{-1}/^\circ\text{C}$ proportionally to the temperature. Above 370°C the growth rate vs. temperature curve flattens out.

Fig. 2 Deposition rate vs. temperature

2. Influence of oxygen-to-silane ratio (γ)

The oxygen-to-silane ratio γ was varied, while the total gas flow, the pressure, and the temperature was kept constant (720 sccm, 1000 Pa, 400°C). The results for γ -values from 1 to 32 are plotted in Fig. 3. For γ -ratios up to 8, the growth rate vs. γ -curve shows a steep rise; for higher γ ratios the growth rate comes to saturation at a value of about 2.9 nm/sec. The film thickness uniformity deteriorates considerably with decreasing γ -values, as is shown in Fig. 4.

Fig. 3 Deposition rate vs. γ

Fig. 4 Film thickness profiles for different γ - values

3. Pressure Influence

The deposition rate versus total pressure (with gas flow, wafer temperature and carrier gas flow kept constant) is depicted in Fig. 5; the maximum rate is approximately 3.6 nm/sec at 1200 Pa. Fig. 6 shows ellipsometrically measured thickness profiles, for different total pressures. The thickness profiles show the best uniformity ($\approx 2\%$ deviation from the mean value, within a distance of 9 mm from the edges) at a pressure of 1200 Pa. Thickness uniformity and growth rate are thus simultaneously optimized. Operation at pressure levels higher than the optimum value (1200 Pa) lead to deteriorated thickness profiles. At lower pressures than 800 Pa the deposition rate becomes small and some particulate contamination can be observed.

Fig. 5 Deposition rate vs. total pressure

Fig. 6 Ellipsometrically measured thickness profiles for different total pressures

4. Influence of Carrier Gas

The carrier gas flow is another important parameter which effects the deposition rate and particulate contamination. The formation of particulate SiO_2 -deposits is well known /9/ and can be suppressed with optimized process parameters. In order to reduce the concentration of the reactive gas, N_2 was applied as diluting gas. We used highly pure nitrogen (H_2O and O_2 contents <0.1 ppm) to optimize deposition results and to suppress homogeneous gas phase nucleation. At high flow rates the SiO_2 deposition rate decreases and a film thickness deviation of greater than 12% from the mean value (measured at a distance of 9 mm from the edges) occurs. Fig. 7 shows the influence of the carrier gas on the deposition rate. We found that lower particulate contamination of the reactor walls, adequate deposition rates and profiles can be obtained at about 500 sccm carrier gas flow. Examples for SiO_2 profiles at different carrier gas flows are shown in Fig. 8.

Fig. 7 Deposition rate vs. flow rate of carrier gas

Fig. 8 Thickness uniformity for different carrier gas flows

5. Shower Head Variation

The film uniformity depends strongly on the gas flow from the gas inlet shower head. For instance the distance between substrate and gas shower head had a strong impact on the deposition results. A homogeneous distribution of holes over the shower head resulted in a poor uniformity of the layer thickness (Fig. 9a). To compensate this effect one can use an inhomogeneous distribution of holes. The resulting film uniformity is shown in Fig. 9b.

Fig. 9 Thickness profiles for different gas nozzels distribution

6. Etch Rate

A sensitive characterization of the silicon dioxide quality is the determination of the etch rate. Chemical structure of the films, mechanical stress, resistivity and breakdown field are in most cases related to the etch properties /10/. Etch rates of the SiO_2 films in 1.8 M HF are nearly constant for all applied deposition temperatures (300°C, 350°C, 400°C). We found an etch rate of $\approx 3\text{nm/sec}$, which is approximately the fourfold value of the etch rate of thermal oxides. This value is comparable to the case of PECVD films /11/.

7. Film Composition

The physical properties of the SiO_2 layers were investigated by IR - absorption, X-ray photoelectron spectroscopy (XPS) and ellipsometry. A Perkin-Elmer 597 spectrometer (wave number 200 - 4000 cm^{-1}) was used for infra-red measurements. The film composition, was determined by XPS (ESCA LAB MK2 V.G. Scientific). IR and C-V measurements were carried out on films deposited on-to one-side polished (111) 40 - 65 Ωcm wafers. In order to remove surface contaminants like carbon and oxygen, the as-deposited films were sputtered for 30 minutes with argon ions (corresponding to $\approx 30\text{ nm}$ film depth). After this treatment the observed composition of 31.8 at.% Si and 68.2 at.% O_2 corresponds closely to stoichiometric SiO_2 . This agrees well with ellipsometric measurements of the refractive index for the 400°C sample, which gave a value of 1.462, close to the value 1.456 of thermal oxide. Fig. 10 shows typical IR-spectra for different deposition temperatures. For a deposition temperature of 400°C the SiO_2 spectra resemble the spectra from thermally grown SiO_2 , except of an O-H stretching peak at 3620 cm^{-1} . For lower deposition temperatures like 300 C an additional peak appeared at 880 cm^{-1} . This peak is well known as corresponding to Si-H vibrations /12/. Si-H groups generate localized states within the energy gap of silicon dioxide /13/ and impair the quality of SiO_2 films.

Fig. 10 Infra-red spectra for two different deposition temperatures

8. Electrical Measurements

(C-V characteristics and dielectric breakdown strength)

MIS capacitors were utilized to characterize the electronic properties of as-deposited and thermally annealed (30 min, 450°C, forming gas) films. Aluminium dots were sputtered onto deposited SiO₂ films and structurized by photolithography to form MIS capacitors. Dots with an area of $1.0 \times 10^{-2} \text{ cm}^2$ were sputtered on films of about 200 nm thickness. The depositions were performed on a (100) n-Si substrate with a resistivity of 40-65 Ωcm . A resulting 1 MHz (at room temperature) C-V plot for an as-deposited sample is shown in Fig. 11. A flatband voltage shift of $\approx -4 \text{ V}$ can be observed, caused by oxide and surface charges. The C-V curve shows a small amount of hysteresis this indicates mobile ion drift or occurrence of interface states [14/-/15/. After the described annealing procedure the interface damage is evidently reduced. The resulting C-V curve (Fig. 12b) is now comparable to the C-V characteristics of thermally grown SiO₂ (Fig. 12a).

Fig. 11 C-V curve of a SiO₂ film deposited at 400°C (as-deposited). Using the formular $V_{FB} = \phi_{MS} + Q_F/C_I$ [15/ and the measured value of C_I the density of fixed interface charges was determined to be $Q_F/e = 9 \times 10^{11} \text{ cm}^{-2}$.

Fig. 12 C-V curves of a post metallization annealed SiO₂ film (B) the fixed interface charges (see formular Fig. 11) was determined to be $Q_F/e = 1.4 \times 10^{11} \text{ cm}^{-2}$. For comparison a thermal grown SiO₂ film is shown in curve (A).

Breakdown data were taken on similar MIS structures with sputtered aluminium dots (area of $1.5 \times 10^{-3} \text{ cm}^2$). A slowly increasing voltage was applied to the capacitors till they broke down. Typically 70 measurements were taken for each sample. Histograms of the breakdown fields are plotted for two different deposition temperatures (300° and 400°C) in Fig. 13. The breakdown histograms of the two processes show a shift to higher breakdown voltages at higher deposition temperatures (400°C).

Fig. 13 Breakdown histograms of SiO₂ films deposited at 300° and 400°C

III. Summary and Conclusions

High-quality low temperature oxide has been deposited at high deposition rates (up to ≈ 4 nm/sec) by a stagnation flow reactor. The advantages of the stagnation flow gas kinetics, in comparison to diffusion limited processes like quartz tube reactors, are enhanced deposition rates and adequate thickness uniformity ($\approx 2\%$ deviation from the mean). Breakdown experiments, C-V data, IR-spectra, refractive index and XPS results all demonstrate a good film quality, comparable to thermally grown oxides.

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