GROWTH KINETICS OF LOW-TEMPERATURE OXIDE FILMS ON SILICON

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Experiments on oxidation of monosilane by oxygen have been used to examine the growth rate of films on n-type silicon.

Silicon dioxide insulating films are widely used in semiconductor devices and integrated circuits; they are used in masks to prevent dope from entering certain parts of the semiconductor during diffusion and also to produce p—n-junctions, as well as for passivating and protecting surfaces. In addition, they are used in active and passive parts of functional units.

Pyrolytic SiO_2 films have recently been widely used in semiconductor devices; there are several papers [1, 2] on the production and testing of low-temperature SiO_2 films, but the growth on single-crystal silicon has not been examined in detail.

One of the simplest ways of producing such oxide films is to deposit SiO_2 by pyrolysis of silane, with oxygen as the oxidant and nitrogen as the carrier gas. The following reaction occurs:

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O.$$

We have examined the growth of pyrolytic SiO_2 films and the choice of optimal deposition conditions by varying the reagent concentrations, the gas flow speed, and the deposition temperature. The SiO_2 was deposited with a horizontal epitaxial-growth equipment.

The films were made on n-type silicon of specific resistance 0.01 ohm•cm; before the SiO_2 was deposited, the surface was polished in HCl for 3 min at high temperatures with an etch rate of about 1 μm /min. The temperature was monitored via standard alloys: PbSn (31.7), Zn (9), Cd (8), Cu (0.3) T_m = 250°C; SnPb (28.5), Zn (21.5) 340°C; AgCu (7), Zn (38) 534-548°C; Al 660°C and also with an experimental optical pyrometer working over the range from 20 to 600°C and reading to ± 10°C. The film thickness was measured with an LEM-2 ellipsometer to ± 5 Å.

The growth of the SiO_2 was examined as in [3]; Fig. 1 shows growth rate vs deposition temperature for molar reagent ratios between 1 : 5 and 1 : 20. The rate increases fourfold as the O_2 concentration increases from 1.5 to 6.0 mg/liter. Several characteristic regions can be distinguished. Region *a*b extends from 270 to 340°C, and represents transition from the kinetic region to growth controlled by surface processes. The activation energy is about 4 kcal/mole. The growth in region bc (340-550°C) is controlled by surface processes, and the rate is almost independent of temperature. In region cd there is a fall in growth rate in the range 550-1050°C, which appears to be due to the following factors: 1) the monosilane decomposes [4], which produces inclusions in the oxide film, which substantially reduces the etch rate in the etching agent (for instance, the rate changes from 8-10 Å/sec for films made at 340°C to 3-5 Å/sec for 900-1000°C); 2) the rate falls because the monosilane is oxidized in the bulk gas.

Figure 1b shows the growth rate vs gas flow rate; the relation at 340°C (curve 1) is the same as that at 550°C (curve 2), where the rate is higher by 200 Å/min under otherwise identical deposition conditions. The rate also increases rapidly for flow rates between 3 and 15 liter/min, so the rate-limiting step

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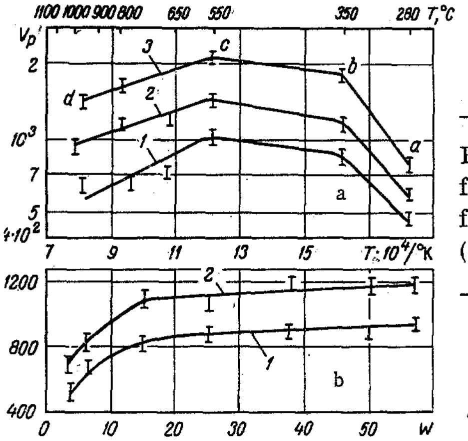

Fig. 1. Growth rate V_p (Å/min) of SiO_2 as a function of: a) deposition temperature; b) gas flow rate W (liter/min) for SiH_4/O_2 ratios (molar) of: 1) 1 : 5; 2) 1 : 10; 3) 1 : 20.

is transported in the flow. Between 15 and 55 liter/min the growth rate is almost independent of the flow speed at 340°C (curve 1) and at 550°C (curve 2). At these speeds, the film grows in the kinetic region, where surface reactions control the process.

The monosilane is substantially oxidized at low gas flow speeds, and amorphous SiO_2 is deposited on the reactor walls; above 30 liter/min, there is far less of this SiO_2, and virtually none at 50 liter/min.

Figure 2a shows the growth rate vs silane concentration; between 0.14 and 0.9 mg/liter (340°C, curve 1) there is a rise from 500 to about 1300 Å/min. The SiO_2 films have a homogeneous structure in this growth-rate range. Films produced at concentrations above 0.9 mg/liter contain inclusions of amorphous SiO_2, which cause the film to crack even before cooling. The oxidation in the bulk gas producing this SiO_2 is probably facilitated by the ready decomposition of silane at low concentrations, since there is excess O_2. The hydrogen atoms released by the decomposing silane diffuse from the substrate and are carried away by the gas. At high silane concentrations, molecules diffusing from the substrate decompose in the bulk gas to produce amorphous SiO_2. Also, H_2O may be formed as a secondary product at high silane concentrations, which produces additional hydrolysis and increases the number of SiO_2 inclusions in the film. The increase in growth rate at 550°C (curve 2) is due to increased diffusion of silane to the substrate, followed by decomposition in the surface layer and loss of the decomposition products from the reaction zone. The balance between the reactions in the bulk and at the surface is displaced into the heterogeneous region.

Figure 2b shows the growth rate vs O_2 concentration; the oxygen concentration where the reaction becomes the rate-limiting step is higher at 550°C (curve 2) than that at 340°C (curve 1). The growth rate falls at 340°C when the O_2 concentration is 11-15 mg/liter because the silane concentration is reduced, while the balance shifts in favor of the homogeneous reactions (bulk hydrolysis). At 550°C, there is more rapid and complete formation of the SiO_2 film on the substrate.

These results on SiO_2 film growth in controlled oxidation of silane indicate the optimum deposition conditions. The film growth rates are closely reproducible in the range 340-550°C and are about 500-1200 Å/min for gas flow rates W of 25-30 liter/min, silane concentrations of 0.3-0.35 mg/liter, and oxygen

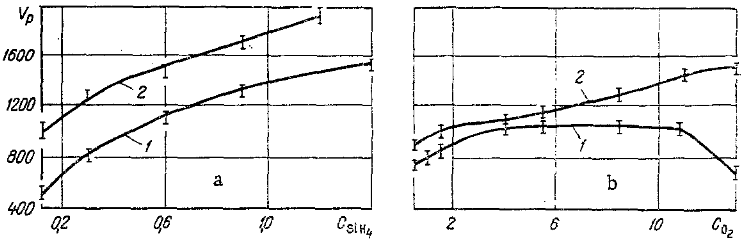

Fig. 2. Growth rate V_p (Å/min) of SiO_2 as a function of: a) monosilane concentration at CO_2 = 5.8 mg/liter; b) oxygen concentration at C_{SiH_4} = 0.29 mg/liter.

concentrations of 5.5-6.0 mg/liter. The SiO_2 films made under these conditions have good structural and electrical features.

LITERATURE CITED

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