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Belt Transport CVD Processing

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ABSTRACT

Belt transport CVD processing, a simple but useful technique applied widely in wafer fabrication, is evaluated in this work. An empirical relation, (T_{ox}) (belt speed)$^n = K$, where T_{ox} is the oxide thickness, is established. The value of n is found to be 1.09 experimentally and 1.0 as analyzed theoretically. A simple deposition model is discussed. The effects of belt speed on film thickness and the effects of flow rate on characteristics are also studied in detail.

Chemically vapor deposited SiO_2 and doped SiO_2 are widely used in IC fabrication due to the low deposition temperature. Three applications, namely, as masking materials for diffusion and etching, as coating material for protective passivation, and as field oxide material, are frequently employed (1, 2). Therefore, it is very important to obtain stable processing conditions for the fabrication of CVD films.

There are many kinds of CVD reactors (3-6). However, two types of reactors are classified. The first is the chemical vapor transport (CVT)[1] reactor. The wafers in this type are fixed inside the furnace; the chemical vapor is conducted into the inlet and forms the solid product on the wafer surface (Fig. 1a). The solid product may also be formed in the vapor phase other than on the wafer surface, and the particulates may fall on wafer surface and result in passivation defects. Generally, CVT is applied in low pressure and/or higher temperature CVD processing.

The second is the belt transport (BT) CVD reactor. In this system, the wafers are placed on a hot plate which is traversed under a nozzle head by a moving belt (Fig. 1b). The nozzle head is cooled by chilled water; the chemical vapor flows into the nozzle head and spreads over the hot plate. The solid chemical product can be formed more dominantly on the surface of the hot area due to thermal activation. Furthermore, the particle contamination problem on the wafer surface can be minimized, and the deposition rate and uniformity are more stable.

The effects of variables on CVD processing in the BT reactor have been studied.

Theoretical Analysis

When SiH_4 is mixed with oxygen gas, chemical reactions occur to form the solid products such as SiO_2, SiO, and Si.

The following possible chemical reactions should be considered

$$SiH_{4(g)} + 2\,O_{2(g)} \xrightarrow{k} SiO_{2(s)} + 2H_2O_{(g)} \qquad [1]$$

$$SiH_{4(g)} + O_{2(g)} \xrightarrow{k_1} SiO_{(s)} + 2H_2O_{(g)} \qquad [2]$$

$$\xrightarrow{k_2} SiO_{2(s)} + 2H_{2(g)} \qquad [3]$$

$$SiH_{4(g)} \xrightarrow{k_3} Si_{(s)} + 2H_{2(g)} \qquad [4]$$

In the case of higher O_2 concentration during the oxidation of silane, reaction [1] will dominate and SiO_2 is the major component of the silox film. Conversely, the Si content will be higher due to the larger contribution of Eq. [2], if the O_2 concentration is decreased.

Consider Eq. [1], *i.e.*, high oxygen-to-silane ratio, all the silane molecules are to be reacted fully into $SiO_{2(s)}$

$$R = \rho A \left[\frac{dT_{ox}}{dt} \right] \qquad [5]$$

Chemically, the rate in weight per unit time is

$$R = k \cdot P_{SiH_4} \cdot P_{O_2}^2 \qquad [6]$$

where ρ is the density of the silox film, A is the deposition area including the whole surface under the nozzle head, k is the reaction rate constant, P_{SiH_4} is the partial pressure of SiH_4, and P_{O_2} is the partial pressure of O_2. According to Eq. [5] and [6]

$$dT_{ox} = \left[\frac{kP_{SiH_4}P_{O_2}^2}{A\rho} \right] dt \qquad [7]$$

On integrating the time from 0 to t

$$T_{ox} = \left[\frac{kP_{SiH_4}P_{O_2}^2}{A\rho} \right] t \qquad [8]$$

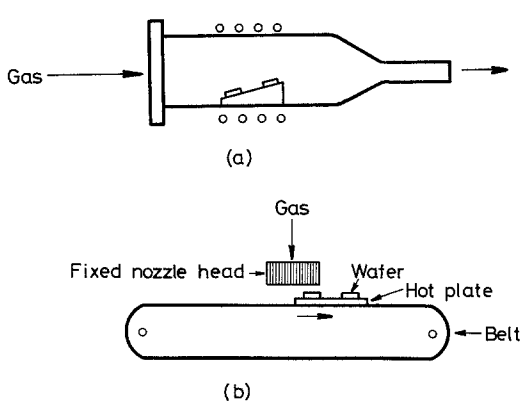

Fig. 1. (a) The CVT deposition reactor. (b) The BT deposition reactor.

Key words: belt, transfer, CVD.

[1] Not to be confused with chemical transport reactions in which deposition results from transport (usually by diffusion) between zones of different temperature in a reversible equilibrium (4).

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However, in the belt transport system

$$t = \left[\frac{L}{\text{belt speed}}\right] \quad [9]$$

where L is the width of the nozzle head. Using Eq. [8] and [9], we thus obtain

$$(T_{ox})\,(\text{belt speed}) = \left[\frac{kP_{SiH_4}P_{O_2}^2}{A\rho}\right] L = K \quad [10]$$

And then, for a given apparatus (A and L constant)

$$K = K(P_{SiH_4}, P_{O_2}, \rho, T) \quad [11]$$

Therefore, K is a function of reactant partial pressure, film density, and wafer surface temperature.

However, at a high oxygen-to-silane ratio, the partial pressure of oxygen can be thought of as constant even though the O_2 gas is further increased. And therefore, at high O_2/SiH_4 ratios

$$\frac{dT_{ox}}{dt} = K'(T) \cdot P_{SiH_4} \quad [12]$$

or

$$(T_{ox})\,(\text{belt speed}) = K''(T) \cdot P_{SiH_4} \quad [13]$$

i.e., the deposition rate is linearly dependent on the partial pressure of SiH_4, where K' in Eq. [12] and K'' in Eq. [13] are temperature dependent factors. Thus, SiH_4 partial pressure and wafer surface temperature will affect the deposition rate.

Experimental

A Pacific Western System (PWS) Model 2000 CVD reactor was used in this work. The temperature of the wafer surface was measured by a Wahl International Model 392/°C thermometer. The oxide thickness was measured by a Beckman Model 26 spectrophotometer. The index of refraction was measured by a Princeton Applied Material Ellip 7610 ellipsometer. The wafers were cleaned by a standard acid/H_2O_2 process prior to depositing the CVD film. The layout of gas lines is shown in Fig. 2. O_2, SiH_4, and N_2 were conducted and controlled by Brooks Tube flowmeters. The wafer surface temperature was kept high enough so that deposition can occur.

Results and Discussion

Effect of belt speed on film thickness.—By following the specified deposition parameters, $N_2(O_2) = N_2(SiH_4) = 5900$ cm³/min; $O_2 = 640$ cm³/min; $SiH_4 = 48$ cm³/min, and the wafer surface temperature of 415° ± 5°C, it is observed that the deposit thickness varies inversely with belt speed (Fig. 3). The empirical reaction between the film thickness and belt speed was established as

$$(T_{ox})\,(\text{belt speed})^{1.09} = 6.79 \times 10^{-4}\ \text{cm}^2/\text{min}$$

This result is approximately consistent with that theoretically analyzed in Eq. [10],

Effect of oxygen-to-silane ratio on film characteristics.—The observed refractive index of CVD films depends strongly on the deposition parameters. Also, the thermal annealing of as-deposited CVD films (7) in an ambient of nitrogen gas at 1100°C changes the refractive index. Figure 4 indicates that the refractive index of as-deposited CVD films of higher oxygen-to-silane ratio (greater than 12:1) is abnormally low. However, after thermal annealing for 30 min, the refractive index becomes normal at a value of 1.45. Interestingly, the refractive index at lower oxygen-to-silane ratio changes from 1.45 to 1.50 after annealing treatment. Therefore, two phenomena are implied in accordance with the above observations, First, there may exist oxygen and/or nitrogen in as-deposited CVD films at larger oxygen-to-silane ratios, *i.e.*, faster deposition due to a higher concentration of oxygen in the gas mixture may cause oxygen and/or nitrogen to be trapped in the as-deposited CVD film. The trapped gas will be evolved on thermal annealing. Second, the CVD film exhibits a silicon-rich phenomenon at lower oxygen-to-silane ratio, *i.e.*, the silicon content of the CVD film will be higher as reaction [2] becomes more important in the formation mechanism of the film. Consequently, the deposition model described in Eq. [10] will not fit well for deposition at lower oxygen-to-silane ratios.

Reaction model.—If it is assumed that the partial pressure of the i-component gas in gaseous mixture is

$$P_i = \left[\frac{r_i}{r_{total}}\right] P_{atm} \quad [14]$$

where r denotes the flow rate of gas read from the flowmeter, and r_{total} denotes the summation of flow rates of all gases during the deposition period. Then, Eq. [10] can be written as

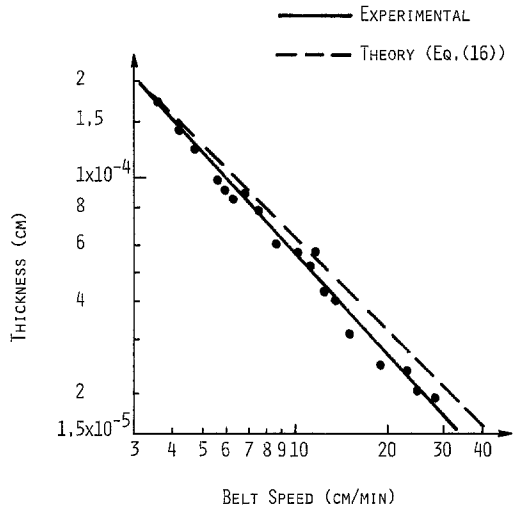

Fig. 3. The effect of belt speed on film thickness

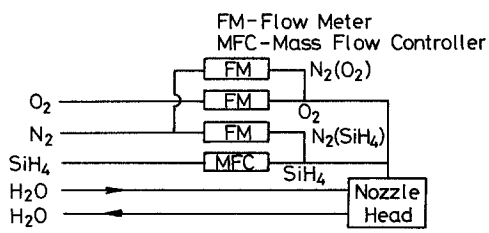

Fig. 2. The layout of gas lines in the BT CVD system

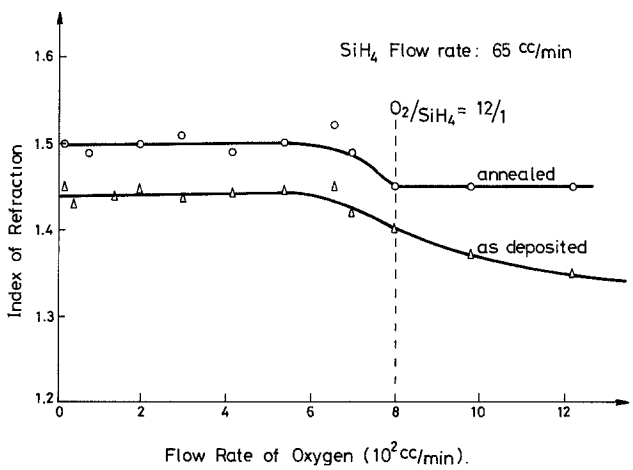

Fig. 4. The effect of thermal annealing at 1100°C in N_2 on the refractive index of CVD silicon oxide films.

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$$(T_{ox})\,(\text{belt speed}) = K(T)\cdot\left[\left(\frac{r_{SiH_4}}{r_{O_2}}\right)\left(\frac{r_{O_2}}{r_{total}}\right)^3\right] \quad [15]$$

$$= K(T)\cdot S \quad [16]$$

The logarithm (T_{ox}) (belt speed) is plotted *vs.* the logarithm of the S factor as shown in Fig. 5. It is obvious that the (T_{ox}) (belt speed) product varies approximately linearly with respect to the S factor, (T_{ox}) (belt speed) $= KS^{0.90}$. This fact implies that in high oxygen-to-silane ratio CVD processing, Eq. [1] dominates the deposition reaction and $SiO_{2(s)}$ is the major component in the silox film as explained previously.

Effect of gas-flow on film thickness.—At fixed parameters of belt temperature, belt speed, flow rate of cooling water, flow rate of nitrogen, etc., silox films were deposited with various flow rates of SiH_4 and O_2. The results are shown in Fig. 6 and 7. It is observed that excessive flow of O_2 reduces the film thickness. This phenomenon is similar to that reported by Kern *et al.* (8) and Baliga *et al.* (9). The reason given by Baliga *et al.* is that adsorption of oxygen on the silicon substrates retards the chemical reaction. However, Fig. 8 indicates that the value, (T_{ox}) (belt speed), is linearly decreased with the decreasing partial pressure of SiH_4 which resulted from the further increase of oxygen flow, *i.e.*, the effect is consistent with that described previously in Eq. [13].

Figure 9 shows the effect of nitrogen on film thickness. It is observed also that the decrease of partial pressure of both SiH_4 and oxygen by the further addition of nitrogen gas reduces the deposition rate. On the other hand, heat will be carried away from the wafer surface by the increased flow of oxygen and nitrogen.

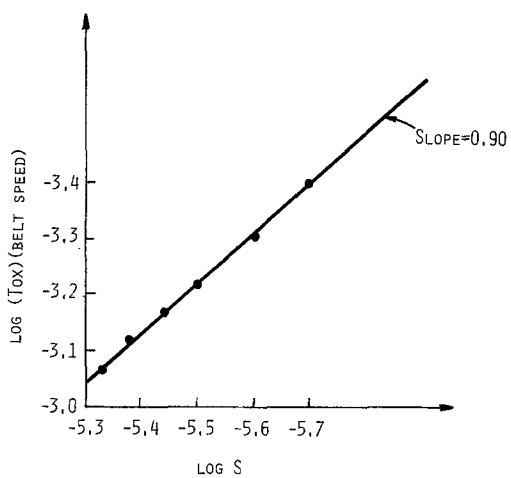

Fig. 5. The plot of log(T_{ox})(belt speed) vs. log S

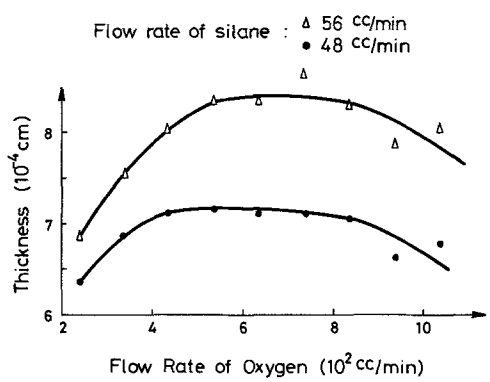

Fig. 6. The effect of oxygen flow rate on film thickness

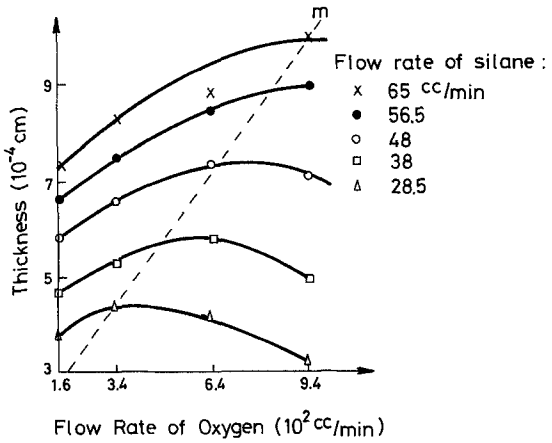

Fig. 7. The effect of oxygen flow rate on film thickness. Curve m denotes the optimum film thickness.

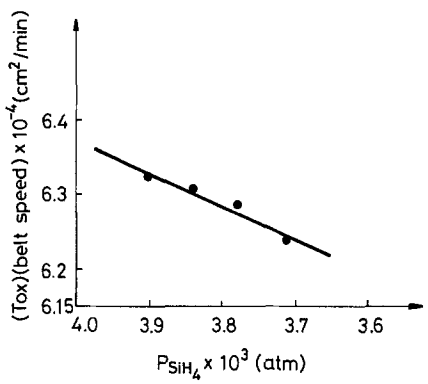

Fig. 8. The effect of further addition of oxygen on (T_{ox})(belt speed). The (T_{ox})(belt speed) factor is plotted vs. the partial pressure of silane.

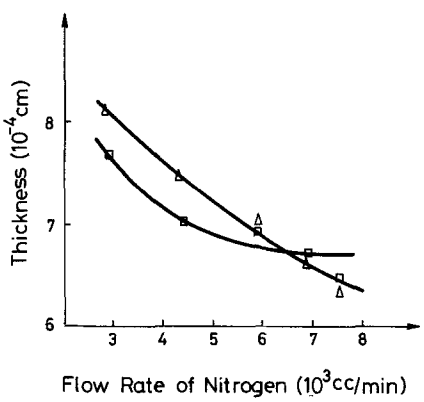

Fig. 9. The effect of nitrogen flow rate on film thickness. △ Varied $N_2(O_2)$ with $N_2(SiH_4)$ constant at 5900 cm³/min. ⊟ Varied $N_2(SiH_4)$ with $N_2(O_2)$ constant at 5900 cm³/min.

Therefore, excessive flow of oxygen or further addition of nitrogen lowers the wafer surface temperature, *i.e.*, $K'(T)$ or $K''(T)$ will be decreased if the heating power of the CVD system is kept constant.

Conclusions

With the belt transport CVD reactor used in this work, three conclusions on CVD silox formation are summarized : (*i*) The deposition rate is proportional to (T_{ox}) (belt speed), the product of film thickness and belt speed. (*ii*) The oxygen-to-silane ratio during the deposition period is very important for CVD process control. Too large a ratio will result in deposition rate decrease; however, too small a ratio will cause the CVD film to be silicon-rich. It is recommended that a

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ratio of 12/1 be employed for silox CVD processing. (*iii*) The deposition rate decrease with increased flow of nitrogen is attributed to two factors, depression of the silane partial pressure and lowering of the wafer surface temperature.

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Behavior of Pd/Sn and Pd Catalysts for Electroless Plating on Different Substrates Investigated by Means of Rutherford Backscattering Spectroscopy

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ABSTRACT

Two catalytic systems for electroless metal deposition have been investigated by means of Rutherford backscattering spectrometry (RBS). The well-known tin sensitizer, palladium activator, two-step catalyst had the main emphasis, but also a commercial one based on evaporated palladium was examined. The behavior of the two-step catalyst was largely dependent on the substrates used. On Al_2O_3, the Sn:Pd ratio was 1:1 with 1.3×10^{15} atoms/cm^2 each. On carbon substrates, the Sn:Pd ratio was 1:4 with 6×10^{15} tin atoms/cm^2 and 24×10^{15} palladium atoms/cm^2. Both these results violate the simple reaction mechanism described by the equation $Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0$. The commercial catalyst on polyimide containing 2.5×10^{15} palladium atoms/cm^2 on the surface behaved differently compared to the two-step catalyst by diffusing into the deposited layer and thereby influencing its deposition rate.

The catalyst systems used for initiating the deposits from autocatalytic Ni-P and Ni-P-W baths have been investigated by means of Rutherford backscattering spectrometry (RBS). The results thus obtained may contribute to the current discussion of this subject. This article reports on two types of catalysts, *i.e.*, the well-known two-step sensitizer-activator system containing Sn^{2+} and Pd^{2+} and a commercial method, where catalyzing takes place by means of a sparse layer of evaporated palladium atoms.

Previously, the two-step system has been investigated by Meek (1, 2) using RBS as well as the mixed catalyst system (3). Meek found results in agreement with those obtained by Cohen *et al.* (4), using Mössbauer spectroscopy; they stated that the simple reaction

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0 \qquad [1]$$

takes place to make the surface catalytically active. These findings were actually in disagreement with those of de Minjer *et al.* (5) as well as with those from the photosensitive sensitizers based on both Sn^{2+} and Sn^{4+}, neither of which could be explained by the simple Eq. [1] only. The latter results are mainly obtained by Schlesinger *et al.* (6-9).

The RBS Method

When a surface is bombarded with swift $^4He^+$ ions, the scattered particles can yield information on the stoichiometry *vs.* depth in the surface layer. The spectra consist of the number of particles as a function of the particle energy after scattering, shown in Fig. 1. From the width of a peak, the layer thickness may be determined, while the peaks stemming from the same layer contain information on the stoichiometry. As seen in Fig. 1, this is phosphorus and nickel in the top layer and aluminum and oxygen in the substrate. After a deposition time of 40 sec, the dotted spectrum in Fig. 1 indicates that a layer of a certain thickness has been formed on the substrate. The retrograde movement of the signals stemming from oxygen, aluminum, and Pd/Sn is due to their staying in-depth, whereas the nickel and phosphorus peaks always start at the same position, indicating signals from the surface. The tail is due to an in-depth deposition on the substrate.

In Fig. 1, the insert shows the experimental setup. An area of 1×1 mm^2 of the surface is irradiated by 2 MeV $4He^+$ ions to a dose of 40 μC. The investigation

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Key words: electroless, Rutherford backscattering, catalysis.

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