Modeling of the Self-Limiting Oxidation for Nanofabrication of Si

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ABSTRACT

The self-limiting oxidation method has been frequently used to fabricate the nano-scale (e.g., sub-5 nm) Si columns and widely reported in the recent literature [1, 2]. However, few theoretical modeling has been carried out to quantitatively describe the observed oxide growth behavior in such a small scale.

Under an incompressible-oxide assumption, we extend a conventional 2-D model to give a closed-form solution for the nanoscale oxide growth. The model predicts the self-limiting growth behavior quite well.

1 INTRODUCTION

The early work on self-limiting oxidation by Liu et al. [1] combined the electron-beam lithography and dry thermal oxidation to yield nanowires in different feature size. In the dry oxidation at $T = 875^{o}C$, four different starting radii of Si column were chosen in their experiment. The Si cores shrank due to the consumption of Si by O_2 and their column radii finally saturated to four different asymptotic values which depend on the starting radii.

A model developed by Kao et al. [3] to describe the stress effects in wet oxide is found suitable for studying the self-limiting dry oxidation after some extensions. The experimental results are quantitatively explained in this paper by suggesting that the accumulated stress slows down the chemical-reaction rate.

2 THEORETICAL ANALYSIS

Extending the Deal-Grove model to 2-D conditions with appropriate boundary conditions in cylindrical coordinate, the oxidation rate for a Si column can be expressed as:

$$N\frac{d(b-a)}{dt} = C^*/(\frac{1}{k_s} + \frac{1}{h}\frac{a}{b} + \frac{a}{D}\ln\frac{b}{a}) \qquad (1)$$

where all the symbols are following the definitions in [3]. The geometry is shown in Fig. 1. On the other hand, Si core radius a and the column (including SiO_2 layer) radius b are not independent variables.

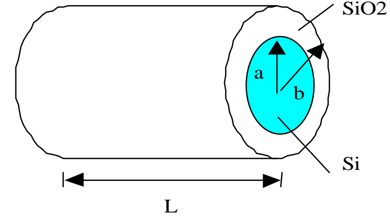

Fig. 1. Oxidized Si Column.

We assume an incompressibe fluidic oxide and the relation between a and b can be derived using volume conservation of the produced SiO_2. The ratio of produced SiO_2 volume to the consumed Si volume is known about **2.25:1** [3]. If the initial radius of Si core is a_0 and the initial radius of column is b_0, then we have:

$$\pi(b^2 - a^2)L - \pi(b_0^2 - a_0^2)L = 2.25\pi(a_0^2 - a^2)L \qquad (2)$$

which leads to a simple relation,

$$b^2 + 1.25a^2 = b_0^2 + 1.25a_0^2 = A \qquad (3)$$

Combining (1) and (3), we have the following equation,

$$\begin{aligned}&(\frac{0.625}{\sqrt{y-1.25}} + 0.5)\sqrt{A}\,y^{-3/2}N\frac{dy}{dt} = \\ &C^*/(\frac{1}{k_s} + \frac{1}{h}\frac{1}{\sqrt{y-1.25}} + \frac{1}{D}\sqrt{\frac{A}{y}}\ln\sqrt{y-1.25})\end{aligned} \qquad (4)$$

where $y = A/a^2$. To take the mechanical stress effects into account, Kao's model is introduced as below:

$$\begin{aligned}&k_s = k_{s0}Exp(-\sigma V_k/K_BT) = k_{s0}Exp[-\sigma 25(\overset{o}{A})^3/K_BT],\\ &\sigma = 2\eta\zeta(\frac{1}{a^2} - \frac{1}{b^2}).\end{aligned} \qquad (5)$$

From the data for dry oxidation process [4], the linear rate constant at $T = 875^{o}C$ is about:

$$k_{s0}C^*/N = 0.0125(um/h) \qquad (6a)$$

provided that h is much larger than k_{s0}. Here k_{s0} is the reaction rate constant without mechanical stress effects. And we also have below approximation [4]:

$$2D(\frac{1}{k_{s0}}+\frac{1}{h}) \approx 2D\frac{1}{k_{s0}} = 0.303(um) \qquad (6b)$$

Combination of (4), (5), (6a) and (6b) yields the following equation:

$$80(\frac{0.625}{\sqrt{y-1.25}}+0.5)\sqrt{A}\,y^{-3/2}\frac{dy}{dt}=$$
$$\{Exp[S(a_0)\frac{y}{A}(1-\frac{1}{y-1.25})]+\frac{1}{1000\sqrt{y-1.25}}+6.6\sqrt{\frac{A}{y}}\ln\sqrt{y-1.25}\}^{-1} \qquad (7)$$

Integrating above equation leads to:

$$t=\int_0^t dt = \int_{y_0}^{y} 80(\frac{0.625}{\sqrt{y-1.25}}+0.5)\sqrt{A}\,y^{-3/2}$$
$$\{Exp[S(a_0)\frac{y}{A}(1-\frac{1}{y-1.25})]+\frac{1}{1000\sqrt{y-1.25}}+6.6\sqrt{\frac{A}{y}}\ln\sqrt{y-1.25}\}dy \qquad (8)$$

where $y_0 = A/a_0^2 = 2.25$ is the initial value of y obtained from equation (3). Even equation (8) is complex, it is in closed-form and can be used to calculate y as a function of t. This will further lead to the values of a and b. The only parameters involved are A and $S(a_0)=\frac{2hz25(\overset{o}{A})^3}{k_B T}$, both of which depend on the starting Si radius.

The influence of stress on the diffusion constant and solid solubility is supposed to be less important than the influence on reaction constant. From fluid dynamic analysis in [3], $2hz$ value varies with the starting radius while remains constant everywhere in the oxide (from $r=a$ to $r=b$). For starting radius of $a_0 = 1um$, $2hz$ at $875^\circ C$ is estimated using the results of [3], e.g., the pressure p, a and h_0 as a function of temperature along with the relation of $h = h_0 \exp(a \times p)$,

$$2hz = 2hv(r)\,r = 2hv(a)\,a \approx 2.627\times10^{-4}\,(N)$$

However, no similar calculation is performed in [3] for nanoscale thermal oxide. To simplify this problem, we apply scale analysis to estimate $2hz$ for four different starting radii. It's assumed that $v(a) \propto a_0$ and thus $v(a)a \propto a_0^2$. Then $2hz(a_0)$ decreases by a factor of $(1mm/a_0)^2$ from $2hz(a_0 = 1mm) = 2.627\times10^{-4}(N)$. We have checked this assumption with the available calculations in [3], e.g., three starting radii of $0.5mm, 0.75mm$ and $1.0mm$ at $800^\circ C$, and a close agreement is found. In order to compare our simulation with experimental data, we chose four starting radii, as [1] did, $a_0 = b_0 = 10, 15, 20, 25\ (nm)$ in the calculation. The estimation is listed below:

$$\begin{aligned} 2hz(a_0 = 10nm) &= 2.627\times10^{-8}(N)\\ 2hz(a_0 = 15nm) &= 5.91\times10^{-8}(N)\\ 2hz(a_0 = 20nm) &= 10.51\times10^{-8}(N)\\ 2hz(a_0 = 25nm) &= 16.42\times10^{-8}(N) \end{aligned} \qquad (9)$$

Above estimation is only approximate, but it will make the calculation easier and still grasp the involved physics.

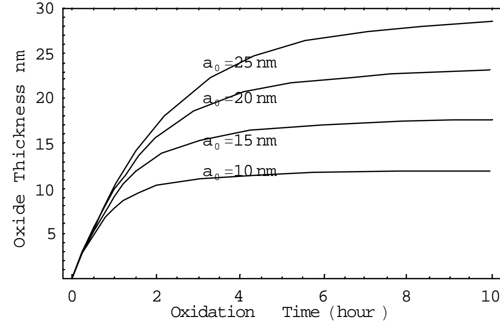

Fig.2. The column oxide thickness as a function of time predicted by the model. The starting radii are 10, 15, 20, and 25 nm respectively.

The oxide growth rates for four different starting radii are calculated using equation (8) and the parameters in (9), and shown in Fig. 2. Basically, the final asymptotic values predicted by the model are close to those observed. This is a strong support of the validity of our simulation. We also notice the model's deviation from the experiment at the beginning of oxidation. When $t < 1h$, there is no significant difference in oxide growth rate among four different curves from our model. However, the data show that noticeable difference exists. Also, the predicted asymptotic oxide thickness is smaller than that observed. Since the growth behavior is sensitive to the value of $2hz$ which is only approximately estimated using scale analysis, above deviations are not surprising.

3 CONCLUSION

In this paper, we present a simulation for the nanoscale self-limiting oxidation. Under an incompressible-oxide assumption, an extended 2-D model is applied to interpret the observed data. The

effects of accumulated stress on the reaction rate constant for different starting radii in nanoscale are estimated. A closed-form equation is obtained and the oxide growth rates are shown. It is found that the model predicts the self-limiting behavior of oxide growth quite well.

REFERENCES

[1] H. L. Liu, D. K. Biegelsen, F. A. Ponce, N. M. Johnson, and R. F. W. Pease, “Self-limiting oxidation for fabricating sub-5 nm silicon nanowires,” *Appl. Phys. Lett. 64,* 1383 (1994).

[2] C. Single, F. Zhou, H. Heidemeyer, F. E. Prins, D. P. Kern and E. Plies, “Oxidation properties of silicon dots on silicon oxide investigated using energy filtering transmission electron microscopy,” *J. Vac. Sci. Technol.* B 16(6),1998, pp. 3938-3941.

[3] D. B. Kao, J. P. Mcvitte, W. Nix, and K. C. Saraswat, “Two-dimensional thermal oxidation of silicon-II. modeling stress effects in wet oxides,” *IEEE Trans. Electron Devices,* vol. ED-35, No.1, 1988, pp.25-36.

[4] S. Wolf and R. N. Tauber, *Silicon Processing, Vol.-1.*, Sunset Beach, Lattice Press, 1986.

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