Oxidation Resistance Characteristics of Silicon Thermal Nitride Films

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ABSTRACT

The oxidation resistance characteristics of silicon thermal nitride films are studied theoretically and experimentally. A four-layer model for the oxidation resistance kinetics has been developed in general, and the oxidation resistance time has been defined and used to evaluate the oxidation resistance of high structure density films on silicon in oxygen ambient. The thermal silicon nitride films prepared by nitridizing the silicon surface in ammonia ambient have been used to justify the developed oxidation resistance model, and reasonable agreement between the developed model and the oxidation resistance characteristics of the fabricated thermal silicon nitride films have been obtained. Based on the developed model, the diffusivity and diffusion length of the oxidant species in the thermal silicon nitride films have been deduced and their activation energies are estimated to be −2.091 and −0.672 eV, respectively.

Silicon nitride has been an important material in the fabrication of high performance integrated circuits and devices due to its higher structure density which exhibits strong oxidation resistance and barrier against diffusion of impurities (1-3). Recently, several investigators (4-6) have reported that higher structure density films can be prepared by directly nitridizing the silicon surface in ammonia gas or nitrogen. Some important applications of the as-grown thermal nitride films in MOSFET (7) and electrically alterable ROM (8) have also been reported.

The major difference between the thermal nitridation and the thermal oxidation is that the as-grown thermal nitride films have higher structure density, so "self-limiting" growth can easily occur for the thermal nitridation of the silicon surface in nitrogen or ammonia ambient. The growth kinetics of the as-grown thermal nitride film in ammonia or nitrogen gas has been proposed by us (9). It has been shown that the self-limiting growth of the thermal silicon nitridation in ammonia or nitrogen gas is mainly due to the fact that the characteristic diffusion length of the nitridant species in the as-grown thermal nitride film is much smaller than the thickness of the as-grown films. The characteristic diffusion length of the nitridant species has been estimated to be smaller than 10Å for nitridation temperatures below 1200°C.

In this paper an oxidation resistance model for the silicon thermal nitride films in oxygen ambient is developed to interpret the oxidation resistance characteristics observed from the silicon thermal nitride films oxidized in dry O_2 ambient. A characteristic time which is called the oxidation resistance time is defined and used to evaluate the structure density of the as-grown silicon thermal nitride films. Based on comparisons between the developed model and the oxidation resistance characteristics of the as-grown silicon thermal nitride films, the diffusivity and diffusion length of the oxidant species in the as-grown silicon thermal nitride films are deduced. It has been shown that the diffusivity of the oxidant species in the as-grown silicon thermal nitride films is much smaller than that of the oxidant species in the as-grown silicon dioxide and the diffusion length of the oxidant species in the as-grown silicon thermal nitride films is smaller than 12Å for dry O_2 oxidation below 1154°C.

Theoretical Model

For a high structure density film grown on a silicon surface, the transport of the oxidant species across this film can be represented by Fig. 1, in which this film can be a CVD Si_3N_4 or silicon thermal nitride. According to Fig. 1, there are four basic steps for the oxidation kinetics: (*i*) the oxidant species must be transported from the bulk of the oxygen ambient to the interface between the film and the bulk gas; (*ii*) some oxidant species may diffuse across the film and reach the interface between the film and the silicon dioxide. During this process, some oxidant species may react with silicon nitride film and then transform the silicon nitride film into silicon dioxide or oxynitride film; however, these transformed films are of lower structure density and are assumed to be transparent to the oxidant species; (*iii*) the oxidant species must transport across the previously as-grown silicon dioxide and reach the silicon surface; (*iv*) the oxidant species then react with silicon. Note that the four basic processes described above form the generalized oxidation resistance model, which can be used to describe some important special cases. For example, in the case of thick silicon nitride film, the oxidant species may not transport across the whole silicon nitride film, then $X_2 = 0$ and $C_{in} = 0$, so the oxidation processes are limited at the surface of the silicon nitride film. Moreover, this model may also be used to describe the chemical resistance properties of the silicon nitride film or others. According to the oxidation processes described above, the oxidant flux in each region can be separately described as follows:

(*i*) In region (I), the oxidant flux can be expressed by the conventional form for the thermal oxidation, which can be written as (10)

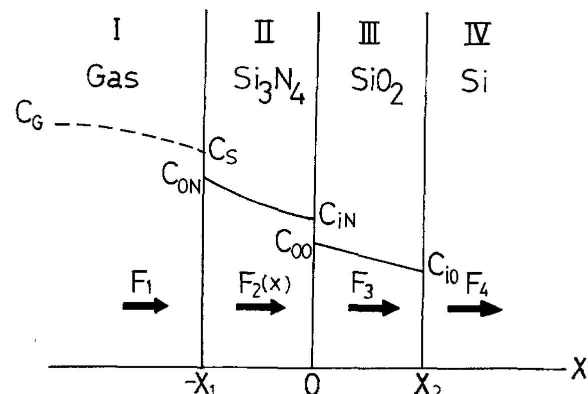

Fig. 1. Schematic diagram of the oxidation resistance model

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$$F_1 = h\,(C^* - C_{on}) \quad [1]$$

where C^* is the concentration of the oxidant species, which is in equilibrium with the partial pressure in the bulk of the oxygen gas P_G; C_{on} is the concentration of the oxidant species at the outer surface of the silicon nitride, which is proportional to the partial pressure of the oxidant species right next to the silicon nitride surface P_s, *i.e.*, $C_{on} = HP_s$, where H is the Henry law constant.

(*ii*) In region (II), the oxidant flux can be assumed to be a diffusive flux and is written as

$$F_2(X) = -D_{on}\frac{dC_o(x)}{dx} \quad [2]$$

where D_{on} is the diffusivity of the oxidant species in the silicon nitride layer. As described before, the oxidant species does react with silicon nitride and form silicon dioxide or oxynitride film at the outer surface of the silicon nitride film. However, this oxidized film has lower structure density and can be assumed to be transparent to the oxidant species. If the oxidant species across the silicon nitride film are characterized by a lifetime τ_{on}, then the diffusion equation for the oxidant species across the silicon nitride film can be written as

$$\frac{d^2C_o(X)}{dX^2} - \frac{C_o(X)}{L_{on}^2} = 0 \quad [3]$$

where $L_{on} = (D_{on}\tau_{on})^{1/2}$ is the diffusion length of the oxidant species in the silicon nitride film.

Solving Eq. [3] by using the boundary conditions $C_o(-X_1) = C_{on}$ and $C_o(o) = C_{in}$ we obtain

$$C_o(X) = \frac{C_{in}\sinh\left(\frac{X+X_1}{L_{on}}\right) - C_{on}\sinh\left(\frac{X}{L_{on}}\right)}{\sinh\left(\frac{X_1}{L_{on}}\right)} \quad [4]$$

The diffusive flux in region (II) can then be written as

$$F_2(X) = -D_{on}\frac{dC_o(X)}{dX} = \left(\frac{D_{on}}{L_{on}}\right) \left\{\frac{C_{on}\cosh\left(\frac{X}{L_{on}}\right) - C_{in}\cosh\left(\frac{X+X_1}{L_{on}}\right)}{\sinh\left(\frac{X_1}{L_{on}}\right)}\right\} \quad [5]$$

(*iii*) In region (III), the as-grown silicon dioxide layer has lower structure density, the diffusion length of the oxidant species in the oxide layer can be assumed to be much larger than the oxide thickness, then the flux of the oxidant species can be expressed by

$$F_3 = D_{oo}\frac{C_{oo} - C_{io}}{X_2} = \text{Constant} \quad [6]$$

where D_{oo} is the diffusivity of the oxidant species in the oxide layer; X_2 is the thickness of the as-grown silicon dioxide; C_{oo} is the concentration of the oxidant species at the outer surface of the as-grown silicon dioxide; C_{io} is the concentration of the oxidant at the silicon surface.

(*iv*) In region (IV), the rate of the oxidation at the silicon surface can be expressed by the conventional form for the thermal oxidation, which can be expressed by

$$F_4 = K_{so}C_{io} \quad [7]$$

where K_{so} is the chemical surface-reaction rate constant for the thermal oxidation.

Using the continuous conditions for the flux at each boundary, *i.e.*, $F_2(-X_1) = F_1$, $F_2(0) = F_3 = F_4$, and letting $C_{oo} = mC_{in}$ with m the solubility ratio of the oxidant species between these two regions, we obtain

$$C_{on} = hC^*\left\{\frac{D_{on}}{L_{on}}\coth\left(\frac{X_1}{L_{on}}\right) + h - \frac{D_{on}^2}{L_{on}}(1 + k_{so}X_2/D_{oo})\,\text{csch}\left(\frac{X_1}{L_{on}}\right) \times\left[mk_{so}L_{on}\sinh\left(\frac{X_1}{L_{on}}\right) + \left(1+\frac{k_{so}X_2}{D_{oo}}\right)D_{on}\cosh\left(\frac{X_1}{L_{on}}\right)\right]^{-1}\right\}^{-1} \quad [8]$$

$$C_{in} = C_{on}\left[\cosh\left(\frac{X_1}{L_{on}}\right) + \frac{mk_{so}L_{on}\sinh\left(\frac{X_1}{L_{on}}\right)}{D_{on}\left(1+\frac{k_{so}X_2}{D_{oo}}\right)}\right]^{-1} \quad [9]$$

If the number per unit volume of the oxidant species needed to replace nitrogen radicals in silicon nitride is N_1 and the number per unit volume of the oxidant species incorporated into a unit volume of oxide is N_2, then we obtain

$$-N_1\frac{dX_1}{dt} = \Delta F = F_2(-X_1) - F_2(0) = \left(\frac{D_{on}}{L_{on}}\right)\left\{\frac{(C_{on} - C_{in})\left[\cosh\left(\frac{X_1}{L_{on}}\right) - 1\right]}{\sinh\left(\frac{X_1}{L_{on}}\right)}\right\} \quad [10]$$

$$N_2\frac{dX_2}{dt} = k_{so}C_{io} = \frac{k_{so}mC_{in}}{1+\frac{k_{so}X_2}{D_{oo}}} \quad [11]$$

Putting Eq. [8] and [9] into Eq. [10] and [11] we obtain two simultaneous first order differential equations which can be solved by using a computer. However, if the silicon nitride film is thicker than the diffusion length of the oxidant species, *i.e.*, $X_1 >> L_{on}$, then $F_3 = F_4 = 0$. In this case, Eq. [8] and [9] can be simplified to be

$$C_{in} = 0 \quad [12]$$

for $X_1 >> L_{on}$

$$C_{on} = \frac{hC^*}{h + \frac{D_{on}}{L_{on}}} = \text{Constant} \quad [13]$$

and Eq. [10] and [11] can also be expressed as

$$-N_1\frac{dX_1}{dt} = \frac{hC^*}{1+\frac{hL_{on}}{D_{on}}} = \text{Constant} \quad [14]$$

for $X_1 >> L_{on}$

$$N_2\frac{dX_2}{dt} = 0 \quad [15]$$

From Eq. [14] and [15] it is clearly seen that the oxidation rate of the silicon nitride is a constant and that of the silicon surface is zero if the thickness of the silicon nitride film is much larger than the diffusion length of the oxidant species in the silicon nitride. The oxidation resistance time of the silicon nitride can be defined as the time that the thickness of the residual nitride film approaches to half of the diffusion

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length L_{on}. This definition will cause the hyperbolic terms in Eq. [8] and [9] to have greater changes so that the oxidation rate increases very rapidly. Based on this definition, the oxidation resistance time t_{or} can be expressed as

$$t_{or} = \frac{X_1 - \dfrac{L_{on}}{2}}{\left|\dfrac{dX_1}{dt}\right|} = \frac{\left(X_1 - \dfrac{L_{on}}{2}\right) N_1}{hC^*} \left(1 + \frac{hL_{on}}{D_{on}}\right) \quad [16]$$

From Eq. [16] it is shown that the oxidation resistance time is linearly dependent on the thickness of the silicon nitride film for $X_1 >> L_{on}/2$. Note that there are a total of nine variables in two simultaneous differential equations as shown in Eq. [8]-[11]; some of them can be chosen from the pure oxidation of silicon and the others can be deduced from the experimental curves of the oxidation resistance experiments, which will be discussed later.

Experimental Results and Theoretical Comparisons

Silicon p-type wafers of <100> orientation and the resistivity of 10 Ω-cm were used as the starting materials. After standard cleaning processes, the wafers were dipped into buffered HF acid for 1 min in order to remove the native oxide on the silicon surface and then were rinsed in deionized water for 10 min. After drying using a nitrogen gun, the cleaned wafers were then put into the quartz tube prepurged with nitrogen. Hydrogen gas was then used to replace the nitrogen gas in order to remove the residual native oxide on the silicon surface. After several minutes of hydrogen gas flow, the ammonia gas was introduced into the reactor tube for thermal nitridation and the hydrogen gas was then turned off. The thickness of the as-grown silicon thermal nitride films was measured by ellipsometer (Rudolph 436-200E). The growth rate of the as-grown thermal nitride films at different nitridation temperature has been discussed in detail (9), and will not be repeated here. However, it has been shown that the "self-limiting" growth of the as-grown thermal nitride films is mainly due to the fact that the characteristic diffusion length of the nitridant radicals in the as-grown thermal nitride films is always smaller than 10Å for nitridation temperatures below 1200°C, and the activation energy of the characteristic diffusion length is measured to be about 0.181 eV. The structure density of the as-grown thermal nitride films has been tested by the chemical resistance method, which shows similar properties to those of silicon nitride. The oxidation resistance studies of the as-grown silicon thermal nitride films are another test for structure density. In this paper, the as-grown silicon thermal nitride films were oxidized in dry O_2 ambient at three temperatures, 1000°, 1050°, and 1154°C. The thickness of the oxidized silicon thermal nitride films was measured by ellipsometer.

Figure 2 shows the characteristic curves of the fabricated silicon thermal nitride in 1000°C dry O_2 ambient, in which the solid curves are calculated by the developed model and the parameters used are cited in Table I. It is clearly seen that general agreement between the experimental measurements and the theoretical calculations has been obtained although some experimental data are slightly out of the theoretical curves. From Fig. 2, it is shown that thicker thermal nitride films do give stronger oxidation resistance, and longer nitridation time does give higher structure density for the silicon thermal nitride film, which, in turn, shows stronger oxidation resistance. Similarly, Fig. 3 and 4 show the oxidation resistance characteristics of some silicon thermal nitride films oxidized in dry oxygen for the oxidation temperatures of 1050° and 1154°C, respectively, in which the parameters used

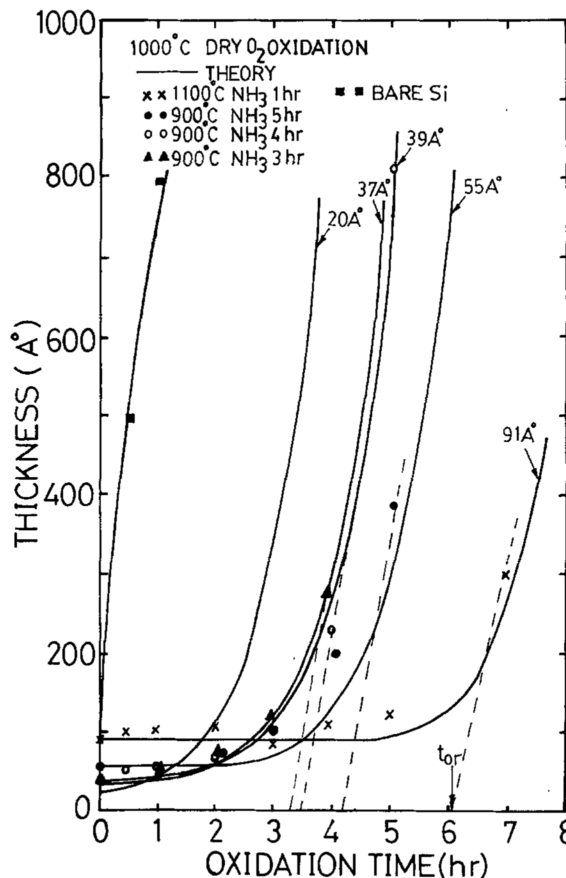

Fig. 2. Oxidation resistance characteristics of thermal nitride films oxidized in 1000°C dry O_2 ambient. Solid lines represent theoretical calculations; *, ●, ○, ▲, ■ represent experimental data.

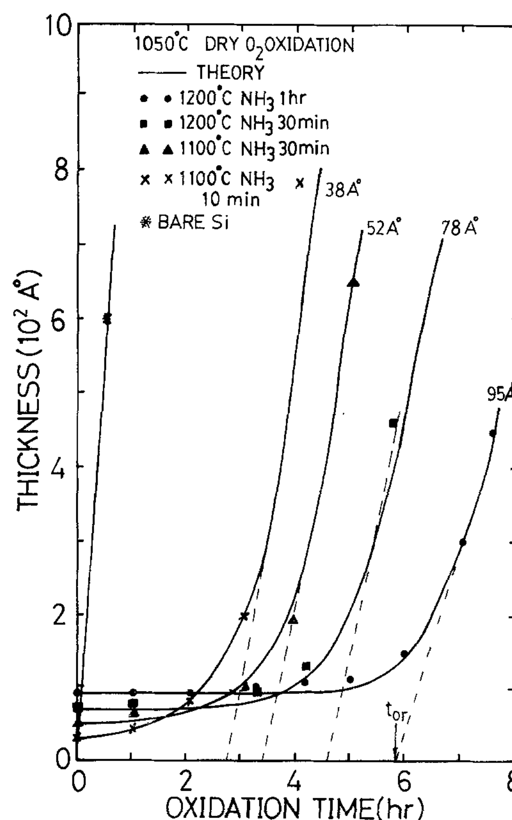

Fig. 3. Oxidation resistance characteristics of thermal nitride films oxidized in 1050°C dry O_2 ambient. Solid lines represent theoretical calculations; ●, ×, △, ■, * represent experimental data.

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Table I. Parameters used for theoretical calculations

Parameters oxidation temp,	D_{on} (μm^2/hr)	L_{on} (Å)	D_{oo} (μm^2/hr)	h (μm/hr)	k_s (μm/hr)
1000°C	0.12	6.2	2.11×10^3	1.39×10^6	3.6×10^4
1050°C	0.20	8	3.135×10^3	10^6	3.6×10^4
1154°C	0.98	12	1.023×10^4	9.217×10^5	3.6×10^4

$N_1 = 6.674 \times 10^{22}/cm^3$, $N_2 = 2.2 \times 10^{22}/cm^3$, $m = 12$, $C^* = 5.47 \times 10^{17}/cm^3$.

in the theoretical calculations are also cited in Table I. Again, general agreement between the experimental measurement and the theoretical calculations has been obtained, and the oxidation resistance properties of the as-grown silicon thermal nitride films with respect to the film thickness and nitridation temperature are similar to those discussed for the silicon thermal nitride films oxidized at 1000°C.

If the diffusion lengths of the oxygen species in the silicon thermal nitride films as cited in Table I are plotted as a function of the inverse temperature, the straight line using the least square fitting is shown in Fig. 5, which gives the activation energy of −0.672 eV for the diffusion length of the oxygen species in the silicon thermal nitride films. It is shown that the diffusion length of the oxygen species in the silicon thermal nitride films is smaller than 12Å when the oxidation temperature in dry oxygen is below 1154°C, which is the major reason that the as-grown silicon thermal nitride films have stronger oxidation resistance when the thickness of the as-grown thermal nitride films is larger than the diffusion length of the oxygen species. Note that the diffusion length of the oxygen species in the silicon thermal oxide is much longer than that in the silicon thermal nitride films, which is mainly due to the fact that the silicon thermal oxide films are less dense in structure when compared to that of the as-grown silicon thermal nitride films. Similarly, the diffusivity of the oxygen species in the silicon thermal nitride films as a function of the inverse temperature is shown in Fig. 6, the straight line using the least squares method is plotted, which gives the activation energy of −2.091 eV. From this plot, it is shown that the diffusivity of the oxygen species in the as-grown silicon thermal nitride films is much smaller than that of the oxygen species in the silicon thermal oxide. However, the activation energy of the diffusivity for the oxygen species in the as-grown silicon thermal nitride films is larger than that of the oxygen species in the as-grown thermal oxide films. This shows that the oxidation resistance of the as-grown silicon thermal nitride films becomes poor at higher oxidation temperature, which is mainly due to larger diffusion length and diffusivity of the oxygen species in the as-grown nitride films as the oxidation temperature is increased. In the last, the oxidation resistance time as a function of nitride thickness deduced from the extrapolation of the oxidation characteristics of Fig. 2-4 is plotted in Fig. 7. It is shown that the oxidation resistance time is linearly dependent on the thickness of the silicon thermal nitride film, which is

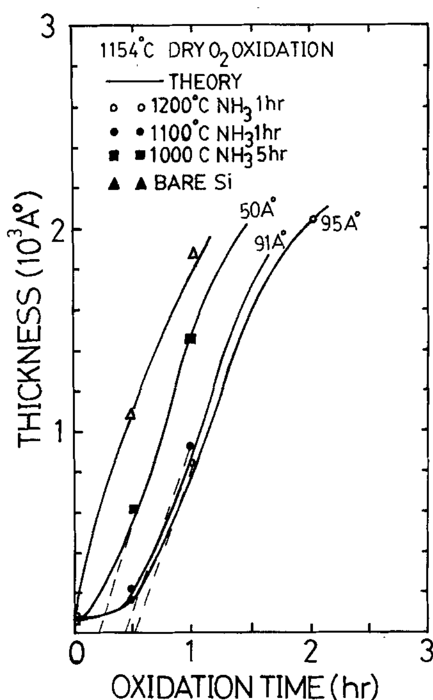

Fig. 4. Oxidation resistance characteristics of thermal nitride films oxidized in 1154°C dry O_2 ambient. Solid lines represent theoretical calculations; ●, ○, ■, ▲ represent experimental data.

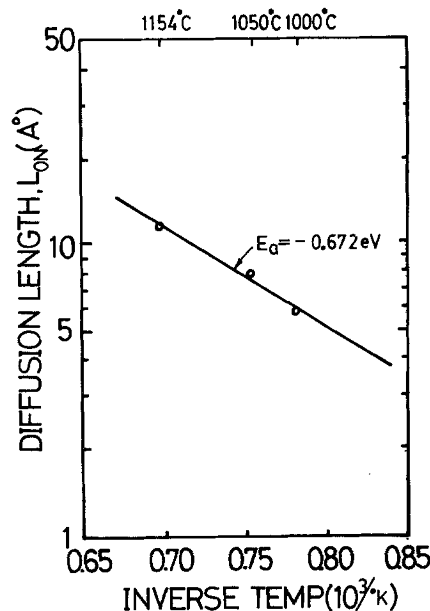

Fig. 5. Diffusion length of oxygen species in thermal nitride film as a function of inverse temperature.

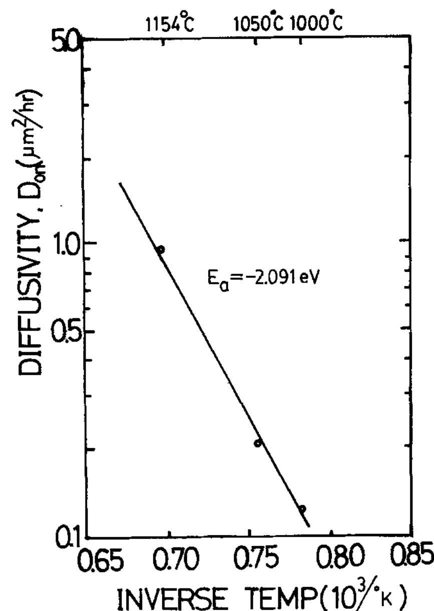

Fig. 6. Diffusivity of oxygen species in thermal nitride films as a function of inverse temperature.

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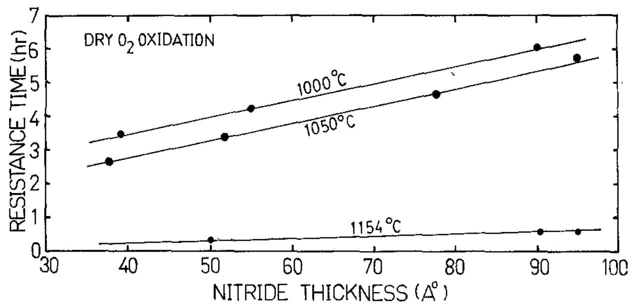

Fig. 7. Oxidation resistance time as a function of thermal nitride film thickness.

in agreement with the prediction of Eq. [16] for $X_1 >> L_{on}/2$.

Conclusions

This paper has developed an oxidation resistance model for the silicon thermal nitride films oxidized in dry oxygen ambient. The developed model has been formulated by using four-layer transport for the silicon thermal nitride films oxidized in oxygen ambient, in which the transport of the oxygen species across the silicon thermal nitride films has been characterized by a diffusion length. It has been shown that the developed model is in agreement with the experimental measurements. Moreover, based on comparisons between the developed model and the experimental data, the diffusivity and diffusion length of the oxygen species in the silicon thermal nitride films have been deduced and their activation energies are +0.672 and +2.091 eV, respectively. The most interesting result obtained is that the diffusion length of the oxygen species in the as-grown silicon thermal nitride films is smaller than 12Å for oxidation temperature below 1154°C in dry oxygen ambient. In addition, an analytic oxidation resistance time is defined and shown to be proportional to the thickness of the as-grown thermal nitride films when the diffusion length of the oxygen species is much smaller than the thickness of the as-grown silicon thermal nitride films, which is in agreement with the experimental data.

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REFERENCES

1. F. K. Heumann, D. M. Brown, and E. Mets, *This Journal*, **115**, 331 (1968).
2. S. M. Hu, *ibid.*, **113**, 693 (1966).
3. R. G. Frieser, *ibid.*, **115**, 1092 (1968).
4. S. P. Murarka, C. C. Chang, and A. C. Adams, *ibid.*, **126**, 996 (1979).
5. T. Ito, S. Hijiya, T. Nozaki, H. Arakawa, M. Shinoda, and Y. Fukukawa, *ibid.*, **125**, 3, 448 (1978).
6. T. Ito, T. Nozaki, and H. Ishikawa, *ibid.*, **127**, 2053 (1980).
7. T. Ito, T. Nozaki, H. Arakawa, and M. Shinoda, *Appl. Phys. Lett.*, **32**, 330 (1978).
8. S. Hijiya, T. Ito, T. Nakamura, N. Toyokura, and H. Ishikawa, IEDM Digest of Tech. Papers, 590 (1980).
9. C. Y. Wu, C. W. King, M. K. Lee, and C. T. Chen, *This Journal*, **129**, 1559 (1982).
10. A. S. Grove, "Physics and Technology of Semiconductor Devices," Chap. 3, John Wiley & Sons, New York (1967).

Physiochemical Effects of Heating Gold Thin Films on Gallium Arsenide

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ABSTRACT

The physiochemical effects of heating gold thin films on GaAs, namely, the arsenic evolution, gold-to-silver color transition, and microstructural changes, were investigated by *in situ* mass spectrometric evolved gas analysis and scanning electron microscopy. The gold-to-silver color transition was found to occur after a small amount of arsenic evolution. The transition temperature increased with increasing air pressure and gold film thickness. The relative quantities of arsenic species evolved followed the order $As_4 > As_2 > As > As_3$. We observed a new microstructure consisting of interconnected irregularly shaped protrusions which appeared after a small amount of arsenic evolution and changed to the previously reported microstructure of aligned rectangular protrusions near the completion of the arsenic evolution.

Gold has been used extensively as a contact metal for Schottky barrier diodes, Gunn diodes, IMPATT diodes, and as an ohmic contact metal for GaAs power microwave FET's and devices. The reliability and performance of the devices at high temperatures are of technological concern.

Various physiochemical effects of heating gold thin films on GaAs have been reported. They include ar-

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