A Novel Simulation Method for Oxynitridation and Re-oxidation

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Abstract – **We proposed a novel model to enable accurate and practical simulations for a growth of oxynitride film on a Si substrate. In the growth of the oxynitride film, oxidation of the Si surface and the incorporation of nitrogen atoms in the oxynitride film occur simultaneously. Due to the nitrogen atoms in the oxynitride film, the growth rate of the oxynitride film is quite different from that of SiO_2 film. We extended an oxidant diffusion model that depends on the nitrogen concentration in the oxynitride film. In the present model, the oxidant diffusivity is a function of the nitrogen concentration. We apply the present model to the simulations of several oxynitride processes and re-oxidation of the oxynitride films. The simulation results show quite good agreement with the experimental ones.**

I. INTRODUCTION

Oxynitride (SiON) film is indispensable for MOSFET gate insulator, because it blocks dopant penetration from gate to Si substrate. The thickness of the gate insulator is one of the most important parameters for determining device characteristics of MOSFETs. Furthermore, re-oxidation and/or post-oxidation are frequently used in LSI fabrication. Therefore, it is an important task to develop an accurate model to simulate the further oxidation of the SiON film as well as the thickness of the SiON film during the primary oxynitride formation.

The oxynitride growth model for N_2O oxynitridation was previously suggested on the basis of the Deal-Grove model, which is widely used for simulation of SiO_2 growth [1-2]. The previous model reproduces experimental results for the thickness of the SiON film. It is, however, quite difficult to adopt the model for a two-dimensional (2D) simulation, such as re-oxidation or the post-oxidation process, since the Deal-Grove model is suitable for one-dimensional calculation of the thickness of the oxide film. In the present paper, we propose a novel method to deal with the growth of the SiON film during the oxynitride process and re-oxidation of the SiON films.

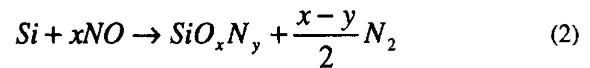
In the following section II, we describe the content of the present model of SiON growth. In section III, we apply the present model to the simulations for several oxynitride processes and re-oxidation process. Section IV, the final section is devoted to summary and conclusion.

II. MODELING

It is reported that the growth rate of the SiON film during the N_2O oxynitridation process is significantly reduced, since the nitrogen atoms incorporated in the SiON film suppress oxidant diffusion [3]. Therefore, it is necessary to consider the effect of nitrogen on oxidant diffusivity (D_{ox}). We propose an empirical formulation for the oxidant diffusivity with parameters α and β as follows:

$$D_{ox} = \frac{D_i}{1+\alpha(C_N / N_0)^\beta} \tag{1}$$

where D_i is the oxidant diffusivity in the SiO_2 film, C_N is the nitrogen concentration in the SiON film, and N_0 (=6.6× $10^{22}cm^{-3}$) is the total atomic number in unit volume of SiO_2. In the present study, we deal with two kinds of oxidant molecules, O_2 and NO. In the NO oxynitridation, the oxidant is NO molecules, since the oxynitride reaction at the SiON/Si interface is shown as follows:



$$Si + xNO \rightarrow SiO_xN_y + \frac{x-y}{2}N_2 \tag{2}$$

Therefore, the NO oxynitride process is a self-limiting growth by the oxidation of the Si surface with incorporation of nitrogen atoms in the SiON film.

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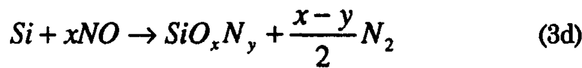
In the case of N_2O oxynitridation, however, the oxidation-oxynitridation kinetics is rather complicated. The N_2O molecules dissolve to NO, O_2 and N_2 [4]. The reactions at the SiON/Si interface in the case of N_2O oxynitridation are expressed as follows,

$$2N_2O \rightarrow 2NO + N_2 \quad (3a)$$

$$2N_2O \rightarrow 2N_2 + O_2 \quad (3b)$$

$$Si + O_2 \rightarrow SiO_2 \quad (3c)$$



$$Si + xNO \rightarrow SiO_xN_y + \frac{x-y}{2}N_2 \quad (3d)$$

The O_2 molecules are the main component of the oxidation of Si through the reaction (3c). Although NO molecules contribute to the oxidation of Si surface, the amount of NO molecules is much less than that of O_2 molecules [4]. It is, therefore, considered that the NO molecules are responsible for the incorporation of nitrogen in the SiON film, and have little affect on the oxidation. Ignoring the effect of NO molecules on the growth of SiON film, we deal with O_2 molecules as oxidant molecules.

In order to describe the modeling of nitrogen concentration, we briefly refer to the behavior of nitrogen atoms during the oxynitride process [5-7]. In Figure 1, we schematically illustrate the distributions of nitrogen atoms according to three kinds of oxynitride/re-oxide processes, namely thermal annealing in NO, N_2O or NH_3 ambient, and re-oxidation of the oxynitride films. From this figure, it is seen that the behavior of nitrogen atoms in the N_2O oxynitridation is similar to that in the NO oxynitridation. In the N_2O and NO oxynitridation, nitrogen atoms are unevenly distributed near the SiON/Si interface region. Taking into account these features, we employ an empirical model to formulate C_N in (1) for NO and N_2O oxynitridation.

In both oxynitridaion mechanisms, the NO molecules efficiently incorporate nitrogen into the newly grown SiON region. We assume that the relation between the oxidant diffusivity and the nitrogen concentration is dependent on the areal density of nitrogen in the SiON film rather than on the

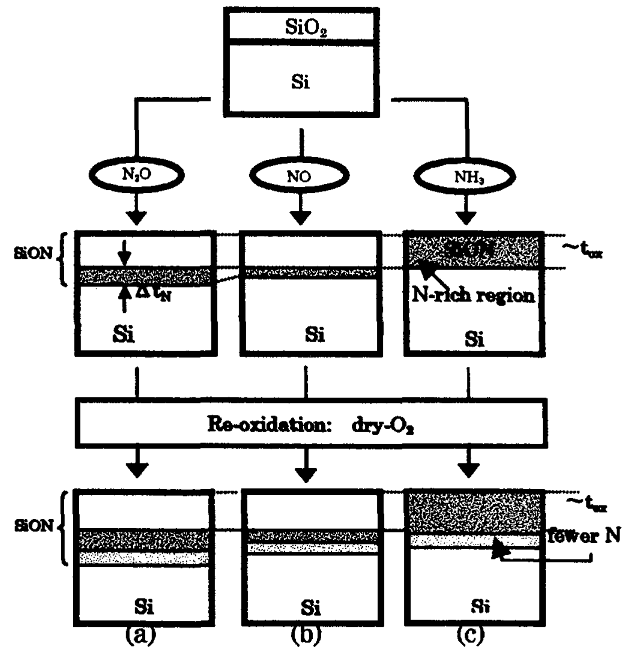


Fig.1. Schematic illustration of N distribution during oxynitride and re-oxidation process. In the N_2O and NO oxynitridation, nitrogen atoms are distributed near the SiON/Si interface region. In the NH_3 nitridation, nitrogen atoms are distributed in the whole SiON region. In the re-oxidation, newly oxidized region contains fewer N atoms.

nitrogen distribution profile, because the newly grown SiON layer is small. Then, we approximate that the nitrogen distribution is uniform in the newly grown SiON region (thickness is Δt_N in Fig.1) so that C_N is a function of temperature, ambient, and pressure[8-9]. We propose an Arrhenius equation for nitrogen concentration with parameters A, B, and C.

$$C_N = A\exp\left(-\frac{B}{k_BT}\right) \times p_{ox}{}^{C} \quad (4)$$

where p_{ox} is oxidant pressure. C_N is determined so as to reproduce the areal density of nitrogen that is experimentally obtained.

On the other hand, nitrogen atoms are distributed in the whole SiON region and accumulated at the SiON/Si interface by NH_3 nitridation since NH_3 molecules diffuse in the SiO_2 film and nitrogen distribution proceeds by an exchange of oxygen for nitrogen in the SiO_2 network. Therefore, we assume that C_N is determined by solving the diffusion equation of NH_3 in the SiON film with constant surface

concentration (N_{surf}). Here N_{surf} is a function of temperature and pressure. The nitrogen diffusivity, N_{surf}, and other relevant parameters are determined so as to reproduce the areal density of nitrogen that is experimentally obtained. Re-oxidation of these samples reveals that fewer nitrogen atoms are contained in the newly oxidized region [6,7].

Finally, we use a simple approximation for surface reaction of the oxidant molecules at the Si surface. Surface reaction has an effect on the SiON film growth as well as the oxidant diffusion. However, in the case that C_N is larger than 1.0at.%, the blocking effect of oxidant in the SiON region has the predominant role in the SiON growth [10]. Therefore, we assume that the chemical surface reaction constant k_s for silicon oxidation is not affected by the nitrogen atoms, since modulation of k_s gives raise to a minor contribution to the SiON growth rate.

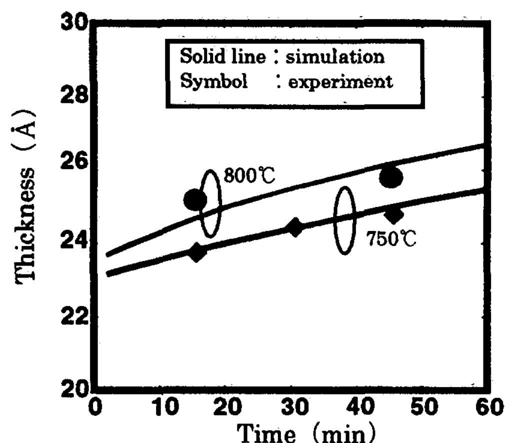


Fig.3. Simulation results for thickness of the SiON films grown at low temperature in NO ambient.

III. Results of Simulation

In Fig.2, we demonstrate the simulation results for the thickness of the SiON film grown at 1050℃ in NO ambient. The result for the present method is in good agreement with the experimental one. It is found that the growth rate in NO ambient is much smaller than that of the corresponding oxidation in dry O_2. The difference in the growth rate between dry O_2 oxidation and NO oxynitridation is ascribed to the effect of nitrogen atoms in the oxyniride film, as is previously discussed in section II. Due to the effect of the nitrogen, the time dependence of the oxynitride thickness shows a diffusion-limited feature. In Fig.3, we show the simulation results for low-temperature NO oxynitridation. From Fig.2 and Fig.3, it is seen that the thickness of oxynitride film is accurately simulated for a wide range of temperature and time of NO oxynitridation.

In Fig.4, we show the simulation results for N_2O oxynitridation. Jut as for the NO oxynitridation, it is seen that there is good agreement between the experimental data and simulation results.

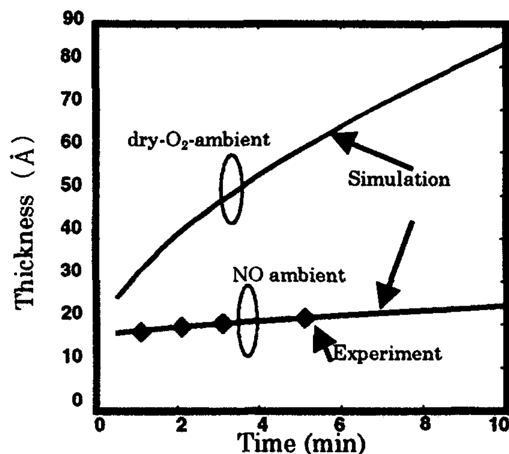


Fig.2. Simulation result for thickness of the SiON film grown at 1050℃ in NO ambient.

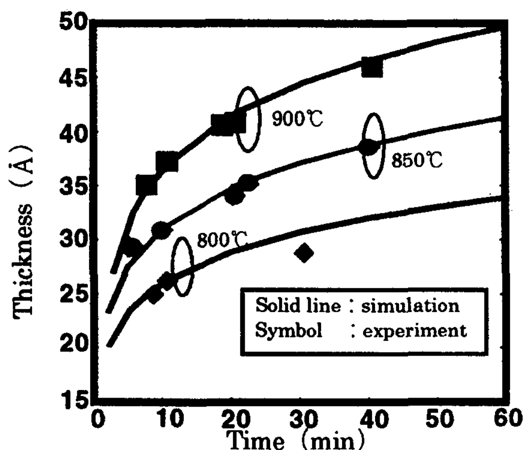


Fig.4. Simulation results for thickness of the SiON films in N_2O ambient.

In actual simulations for device fabrication, it is necessary to simulate the oxynitridation process for two-dimensional structure. Fig.5 illustrates the result of sidewall oxidation after poly-Si etching deposited on a SiON film. The gate oxide is nitrided in NH_3 ambient. We use the empirical formulation of oxidant diffusivity with parameter $\alpha = 1.254 \times 10^3$ and $\beta = 1$. The present method (Fig.5(b)) reproduces the experimental configuration well (Fig.5(a)), although the usual oxidation procedure (Fig.5(c)) leads to a large bird's beak. Thus, the present method is also appropriate for 2D simulation including the oxynitride process.

Note that the present method is efficient for the modeling of the recently reported anomalous diffusion during the oxynitride process [7,11], since the generation of point defects at the SiON/Si interface during the oxynitride process is strongly related with the growth rate of the SiON film

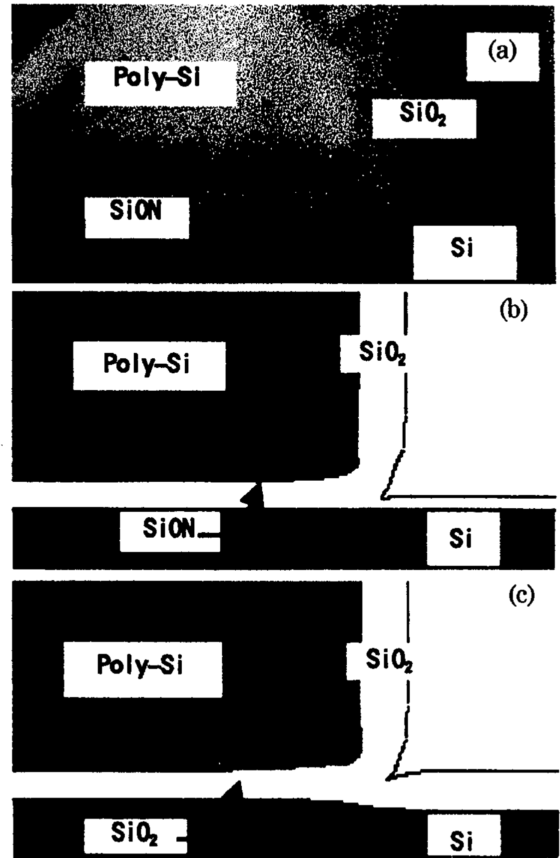


Fig.5. The sidewall oxidation after poly-Si patterning on the SiON film. (a) TEM (transmission electron microscope) micrograph (b) simulation result with the present method (c) the sidewall oxidation against SiO_2 film.

IV. Conclusion

We developed an oxynitridation model taking into account the effect of nitrogen concentration in the SiON region. We proposed an empirical formulation for the oxidant diffusivity that decreases with the increase of nitrogen concentration in the SiON film. We showed that the simulation results for the thickness of the SiON films in NO and N_2O ambient are in good agreement with the experimental ones. Furthermore, it was seen that the simulation result for the sidewall oxidation reproduces the shape observed by TEM measurement. Making use of the present method, accurate simulations can be performed for a wide range of oxynitride and re-oxidation processes.

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