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Effects of fluorine implantation on the kinetics of dry oxidation of silicon

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Kinetics of dry oxidation of silicon after implantation of fluorine in the oxide layer are investigated. It appeared that implanted fluorine can result in negative values of the linear oxidation rate constant. Fluorine profiles obtained by the nuclear reaction analysis (NRA) method using a resonant $^{19}\text{F}(\alpha, p)^{22}\text{Ne}$ nuclear reaction will be presented. At 1200 °C the fluorine moves to the interface of Si and SiO_2 , both in dry oxidizing and inert atmospheres. Based on these findings, a model is presented that explains quantitatively the observed anomalous behavior of the linear oxidation rate constant.

I. INTRODUCTION

In this article we present some oxidation data of silicon after fluorine implantation in the oxide layer. Fluorine depth profiles are obtained by a new, sensitive method.

So far, only a few investigations have been published on the effect of fluorine on oxidation of silicon. The pioneering work by Schmidt and Michel¹ in 1957 showed an increase of the anodic oxidation rate by adding fluorine (NH_4F) to the oxidizing solution. In 1973 Croset and Dieumegard² reported that during anodic oxidation fluorine piles up at the interface. In 1978 Tarantov, Kas'yanenko, Konorov, and Romanova³ reported the electrical effects of fluorine and chlorine after anodic oxidation. An important conclusion was that chlorine is immobile in the oxide, whereas fluorine is mobile. This is in agreement with the results of an experiment of Williams and Woods⁴ in 1975. They showed that at room temperature an electric field of about 1.2×10^7 V/cm made fluorine migrate through thermally grown SiO_2 , whereas chlorine remains fixed.

Today, plasma oxidation can be used for low-temperature oxidation. In order to accelerate the oxidation rate one can also use halides (Chang, Chang, and Darach, 1980⁵). At 600 °C the oxidation rate is linear, indicating that the reaction at the Si- SiO_2 interface is rate determining. Apparently, the CF_4 added to the plasma influences this interface, and indeed a pileup of fluorine at the interface was found. The concentration of fluorine in the oxide film was estimated to be less than 0.5 at. %.

Greeuw and Verwey⁶ showed in 1983 that implantation of silicon with fluorine or chlorine also increases the oxidation rate. The oxidation in this case generates donor centers, probably complexes of halides and implantation-induced defects.

In 1984 Morita, Kubo, Ishihara, and Hirose⁷ showed that an addition of NF_3 to the oxidizing ambient increased the oxidation rate during dry oxidation. Temperatures used were in the range of 600–800 °C. Here a temperature-dependent critical concentration of NF_3 above which etching starts is observed, just as with plasma oxidation. In the former case, however, no pileup of fluorine at the Si- SiO_2 interface was found.

It is of great interest to know where the fluorine is located. Fluorine profiles are obtained in various ways. Croset

and Dieumegard² determined the total fluorine content by means of the broad $^{19}\text{F}(p, \alpha)^{16}\text{O}$ resonance at 1270-keV proton energy. Successive etching and measuring gave a rough estimate of the depth profile. Williams and Woods⁴ used SIMS; Chang, Chang, and Darach⁵ used the Auger electron signal as a function of sputter time, a technique comparable with SIMS. However, at interfaces sputter rates change, which makes SIMS less accurate at those regions. The chemical state of fluorine can be determined by means of XPS. Morita, Kubo, Ishihara, and Hirose,⁷ showed with this technique that all fluorine atoms in their SiO_2 are incorporated as Si-F bonds.

In view of the articles listed above, much is unknown about fluorine in silicon dioxide during oxidation. In order to concentrate on the interaction of fluorine with silicon dioxide, no contaminant other than F should enter the oxide; therefore, implantation of the fluorine seems to be the best start of this research.

In 1980 Isomae, Tamura, and Tsuyama⁸ implanted BF_2 in the oxide and showed that after reoxidation for 15 min at 1150 °C a broadened implantation profile and a little peak at the Si- SiO_2 interface occurred. The boron profile was not determined; the technique used here was SIMS.

II. EXPERIMENTS AND RESULTS

A. Oxidation data

Silicon wafers (Wacker) FZ, $\langle 100 \rangle$ *p*-type B-doped, 1–30 Ω cm were used for all experiments. After a 30-min oxidation at 1200 °C (dry oxygen, 1 l/min), the samples were implanted with 40-keV F^+ ions in an Extrinsic 200-kV implanter. Doses were 0, 10^{15} , 7×10^{15} , and 4×10^{16} F^+/cm^2 ; projected range in the 155-nm oxide was 66.9 nm, standard deviation 25.2 nm. Reoxidations at 1050, 1100, 1150, or 1200 °C were performed during 10, 30, 90, and 270 min. Oxide thicknesses were measured either by means of a Gaertner L-116 Automatic Ellipsometer or by hand with ellipsometric tables, taking 1.46 as the refractive index of the oxide. A graphical extrapolation was made to obtain the initial oxidation times, and these six pairs of data of each experiment were fitted with the least-squares criterion on a linear-parabolic law as suggested by Deal and Grove.⁹ The output of these fits are the parabolic rate constants B and the linear rate constants B/A , as given in Table I.

It is striking to see negative linear constants. Although in the literature no negative values of A are reported, there is some more evidence for the peculiar behavior of halides. Deal, Hess, Plummer, and Ho,¹⁰ who added Cl_2 to the oxidizing ambient, refer to their constants as being "erratic."

B. Fluorine profiles

Sputtering of oxide and determining the yield of fluorine with a mass spectrometer or an Auger signal monitor are fairly easy ways to obtain profiles. A disadvantage of these methods is the unknown sputter rate and the fact that the sputter rate changes on passing interfaces. Especially in our case, where we expect fluorine at the interface, it is not an appropriate method.

What one really wants is to probe the fluorine as a function of depth in the SiO_2 without sputtering or removing material. The appropriate technique is the nuclear reaction analysis method (NRA), using a reaction with a narrow resonance. With this technique, the yield of a nuclear reaction is measured as a function of beam energy. The beam energy is varied in small steps through a narrow resonance. The yield is, in our case, determined by the depth distribution of fluorine. The depth scale is obtained via the stopping power of the oxide; the depth resolution is determined by the width of the resonance and the straggling in the stopping. The depth profile is derived from the measured yield curve by a deconvolution with the shape of the resonance and the straggling in the stopping.

The most suitable reaction for our purpose was the $^{19}\text{F}(\alpha, p)^{22}\text{Ne}$ reaction at 2443 keV, with, according to our measurements, a width of 3.2 keV.¹¹ Spectra were deconvoluted via a new procedure preventing negative solutions to obtain a depth profile of fluorine in SiO_2 .¹² The maximum film thickness that can be probed is about 250 nm, due to a neighboring resonance.

An implantation profile measured in this way of a dose of $2 \times 10^{15} \text{ F}^+/\text{cm}^2$ is shown in Fig. 1(a). One observes a peak at about 90 nm and some fluorine at the surface. Most,

TABLE I. Parabolic rate constant B and linear rate constant B/A , for reoxidation of silicon after fluorine implantation in the oxide, at various temperatures.

T (°C)	F^+ dose (cm^{-2})	B ($10^{-2} \mu\text{m}^2/\text{h}$)	B/A ($10^{-1} \mu\text{m}/\text{h}$)
1050	0	1.92	1.48
1050	10^{15}	1.55	15.0
1050	7×10^{15}	1.42	-1.81
1050	4×10^{16}	2.04	-2.02
1100	0	2.49	3.23
1100	10^{15}	2.20	-90.7
1100	7×10^{15}	2.23	-2.85
1100	4×10^{16}	2.67	-2.22
1150	0	3.47	6.79
1150	10^{15}	3.33	11.3
1150	7×10^{15}	3.18	-7.45
1150	4×10^{16}	3.40	-2.86
1200	0	4.11	-630
1200	10^{15}	3.92	-11.4
1200	7×10^{15}	3.80	-4.82
1200	4×10^{16}	4.03	-3.09

but not all, samples showed such a surface peak, so it is likely to be contamination. After 10-min oxidation at 1200 °C we obtain the profile depicted in Fig. 1(b). The fluorine dose in this case was $10^{16}/\text{cm}^2$. Apparently no fluorine is detectable within the oxide, and peaks can be seen at the interface and the surface. Longer oxidation times give the same results, although it seems that the fluorine content of the interface peak decreases. It appeared that fluorine also moves to the interface during inert anneals. A fluorine profile after an inert anneal of 10 min at 1200 °C is depicted in Fig. 1(c).

III. MODELING THE OXIDATION

A. Introduction

The Deal and Grove⁹ model applies to a system which consists of three parts: a surface, a homogeneous layer, and an interface. For "steady state oxidation" a flux balance can be set up, and the well-known linear parabolic oxidation law is obtained;

$$x_0^2 + Ax_0 = B(t + \tau), \quad (1)$$

where x_0 is the oxide thickness at time t , τ is the oxidation time needed to get the oxide thickness at $t = 0$, B is the parabolic rate constant, and A is a constant related to the linear rate constant B/A . These constants are by definition positive.

In view of our results, see Table I, one must state that our system is more complex. Therefore, we have to look more closely at our data. There are many ways to display oxidation data. A very clear one is oxide thickness versus total oxidation time divided by the oxide thickness. From Eq. (1):

$$x_0 = B \frac{t + \tau}{x_0} - A, \quad (2)$$

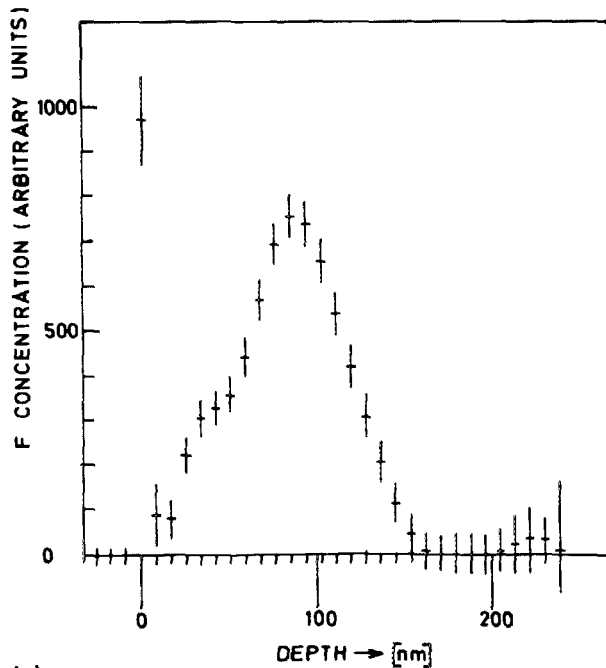
so the slope of the plot x_0 vs $(t + \tau)/x_0$ equals B , and the intercept with $(t + \tau)/x_0 = 0$ yields $-A$.^{10,13}

Figure 2 gives a plot according to this method. At high temperatures the curves are almost parallel, indicating that the parabolic rate constant does not change much with fluorine added, while the intercept with $(t + \tau)/x_0 = 0$ shifts upward until it even changes sign. Any memory effects^{14,15} on A and B are incorporated in the kinetics of the unfluorinated samples. The deviation from this behavior is due to the implanted fluorine.

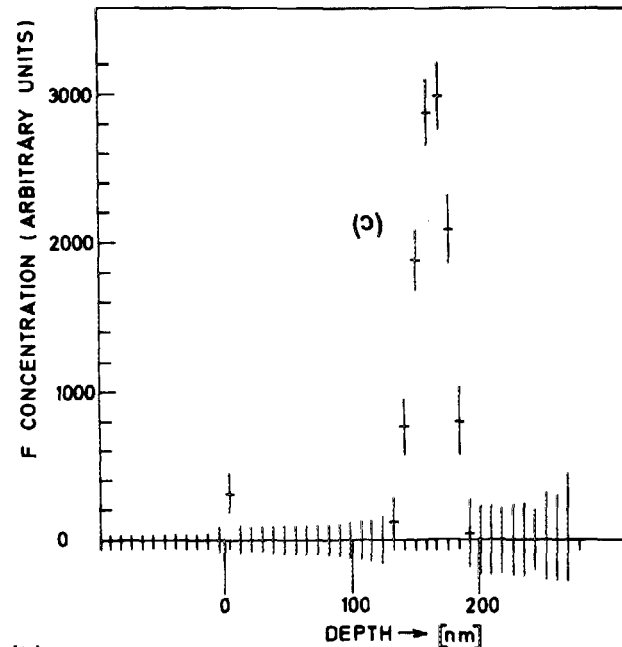
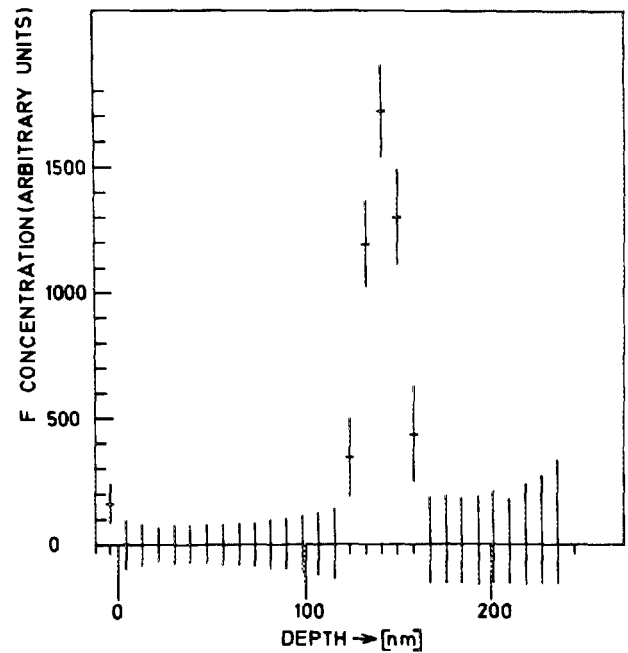
In Sec. II B we observed that fluorine moves to the interface and is not detectable within the oxide layer. This must be taken into account in a model. We also know that the Deal and Grove model applied to a surface, layer, and interface system cannot yield negative values of A . Hence, we have to construct a more complicated structure or use another theory.

B. Extension of the Deal and Grove model

In this section we introduce an extension of the Deal and Grove system in which, see Fig. 3, we incorporate implantation damage. Implantation results in a layer with a different diffusion coefficient D_2 from the undamaged oxide diffusion coefficient D . Fluorine moves to the interface and is not incorporated. The damaged layer of thickness x_d does not con-



(a)



(b)

FIG. 1. (a) Depth profile of 40-keV-implanted $2 \times 10^{15} \text{ cm}^{-2} \text{ F}^+$ ions in 154-nm SiO_2 . (b) Depth profile of 40-keV-implanted $1 \times 10^{16} \text{ cm}^{-2} \text{ F}^+$ ions in 154-nm SiO_2 after reoxidation for 10 min at 1200 °C. Oxide thickness is 180 nm. (c) Depth profile of 40-keV-implanted $4 \times 10^{15} \text{ cm}^{-2} \text{ F}^+$ ions in 154-nm SiO_2 after an inert anneal of 10 min at 1200 °C. Oxide thickness is 161 nm.

tain fluorine either. On the structure of this layer we will elaborate in Sec. IV.

For this model we find, making a flux balance like Deal and Grove,¹⁰ for the oxidation rate:

$$\frac{dx_0}{dt} = \frac{C^*/N_1}{(x_0 - x_i/D) + x_i/D_2 + 1/k + 1/h}, \quad (3)$$

where x_0 is the oxide thickness at time t , C^* is the equilibrium concentration of the oxidant in the oxide, N_1 is the number of oxidant molecules incorporated into a unit volume of the oxide layer, x_i is the layer thickness, D is the oxidant diffusion coefficient in the undisturbed oxide, D_2 is the same in the modified layer, k is the interface reaction rate constant, and h is the gas-phase transport coefficient. Integration yields

$$x_0^2 - x_i^2 + (x_0 - x_i) \left(\frac{2D}{h} + \frac{2D}{k} - 2 \frac{D_2 - D}{D_2} x_i \right) = \frac{2DC^*}{N_1} t. \quad (4)$$

In this model, A can become negative if D_2 exceeds D . A higher interface reaction rate constant k also lowers A . In this model only oxidation rates higher than normal can be expected; in the parabolic limit normal growth rates are expected. During oxidation, the parabolic constant B does not change.

In this model it is possible to calculate A as a function of oxidation time and fluorine dose, because we may subtract the effect of the constant B ; that does not change on adding fluorine. The result of such a calculation is depicted in Fig. 4.

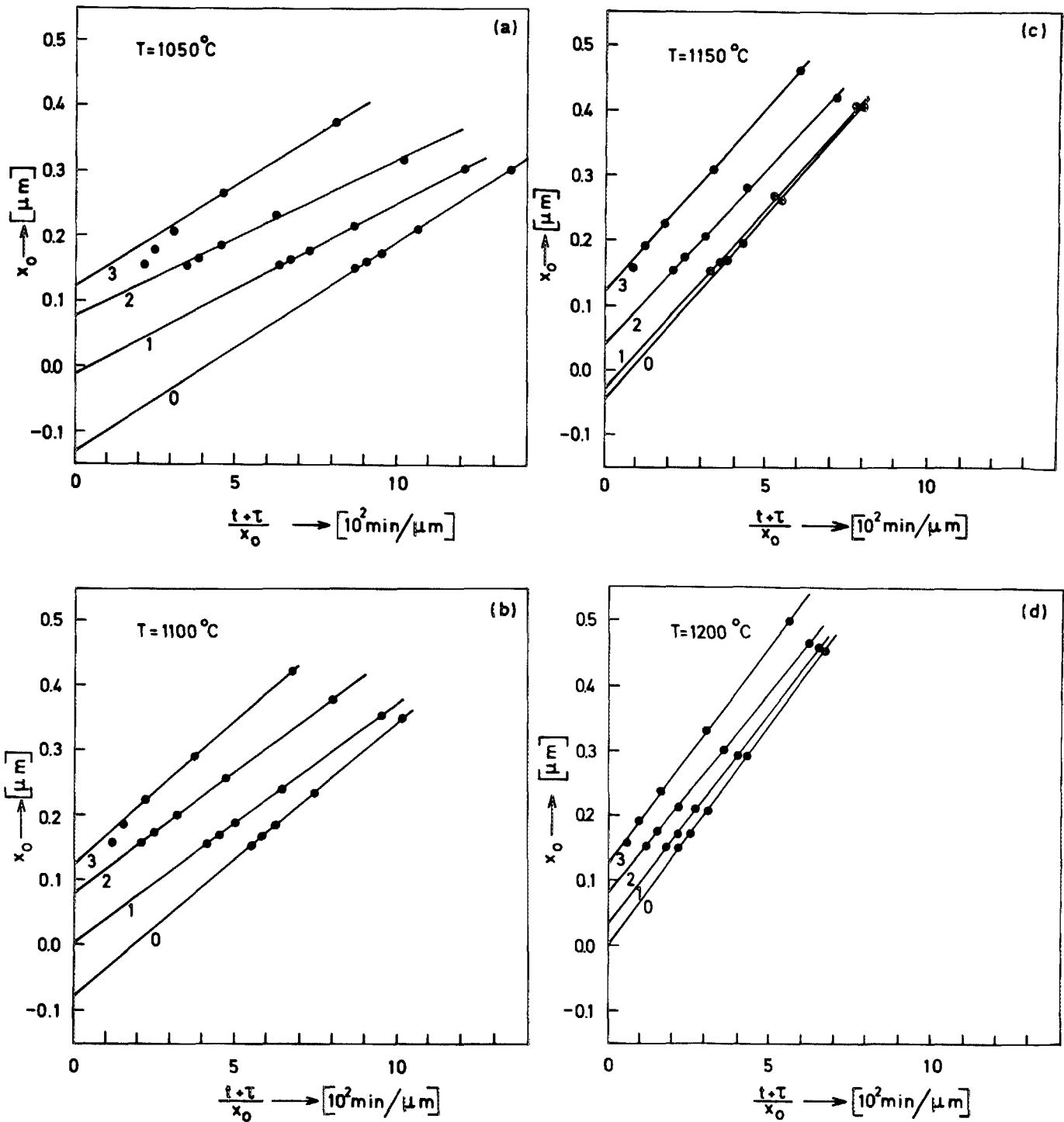


FIG. 2. The effect of fluorine on the reoxidation rate of silicon. 0 = unimplanted, 1 = 10^{15} , 2 = 7×10^{15} , and 3 = 4×10^{16} F^+ / cm^2 .

One sees that A increases in time, toward the original value, suggesting that the damaged layer is being restored and that the interface effect of the fluorine decreases. Although the NRA method gives no reliable quantitative information, the latter suggestion seems to be confirmed by our experiments. One also sees that A saturates, independent of temperature. This will be discussed later; so far this model is not conflicting with our experiments.

In the model we can simulate a high fluorine dose by taking the high limit for k .

The expressions for A in this model become, if we assume that h is not rate determining as well:

$$A = -2[1 - (D/D_2)]x_r. \quad (5)$$

If the diffusion coefficient of the highly diffusive layer D_2 is very high compared to D , one finds the limit of A : $-2x_r$. This is independent of temperature: The value of x_r obtained from the limit in Fig. 4 is 65 ± 10 nm. If we model the implantation damage profile by a step profile with the same height and content as the actual Gaussian profile, its

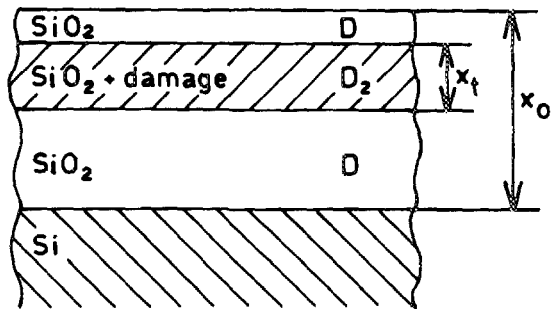


FIG. 3. Schematic view of the model of reoxidation after fluorine implantation in the oxide.

width is 63 nm, which corresponds well with our lower limit. So, we conclude that our results can best be explained by stating that the implanted oxide contains a highly diffusive layer within the oxide and that the oxidation reaction rate at the interface is enhanced by the presence of fluorine.

IV. DISCUSSION

A. The damaged layer

Basically there are three possible origins of this layer: implantation damage, positive charges, and fluorine. In order to check the first and second effects, we implanted SiO_2 with neon ions under conditions that were comparable with our fluorine implantations and measured the thickness of the SiO_2 film after reoxidation. It appeared that this implantation had no effect on the oxidation kinetics of the silicon. So the damaged layer is formed by the fluorine itself and remains damaged without the presence of fluorine, as we know that we still have this layer when the fluorine has already left the oxide layer.

The mechanism for the formation of the layer is considered to be the following. Some silicon atoms are displaced in the oxide by collision with a fluorine ion. A fraction of these silicon atoms will react with fluorine to stable gaseous compounds, e.g., SiF_4 . In analogy with gaseous chlorosiloxanes and chlorides,¹⁶ such a molecule diffuses through the oxide

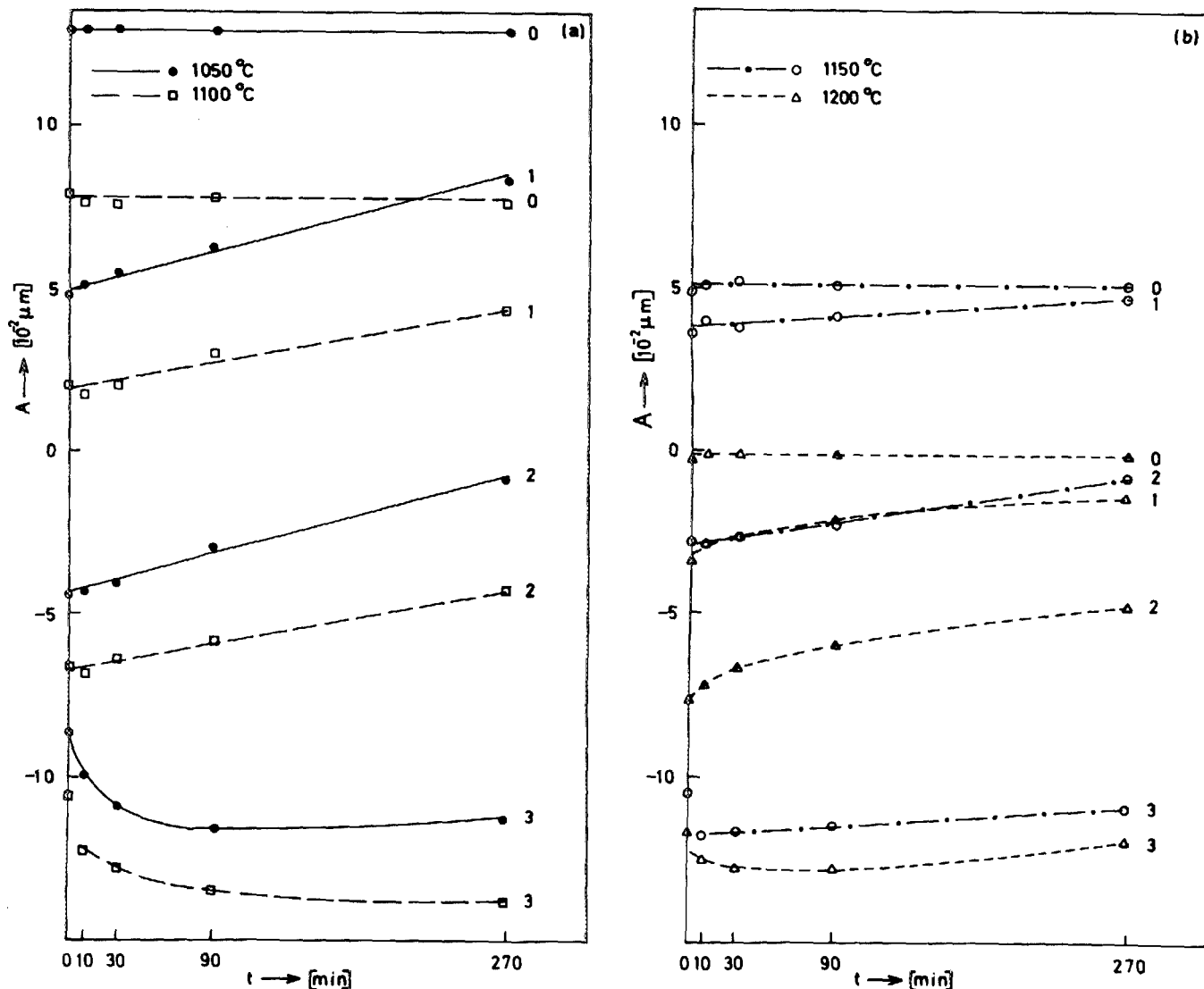


FIG. 4. Effect of the fluorine dose on the oxidation constant A vs oxidation time. 0 = unimplanted, 1 = 10^{15} , 2 = 7×10^{15} , and 3 = 4×10^{16} F^+/cm^2 .

and desorbs, leaving an oxide with a more open structure, due to the missing silicon atom. This damage will be restored very slowly, because there is no flux of silicon atoms through the oxide. The damage due to neon implantation is restored very quickly, because neon does not form gaseous compounds with silicon.

B. The interface

From Hamasaki¹⁴ it is known how important charges are at the interface. The interface reaction rate constant is influenced by a positively charged layer, 20 Å thick, probably consisting of excess Si. The compensation of these charges by F⁻ ions would result in a higher interface reaction rate constant. Moreover, it is likely that some silicon atoms react with fluorine to form molecules like SiF₄ that diffuse through the oxide and desorb.¹⁶ This accounts for an in-time decreasing interface concentration and a gradual restoring of the interface reaction rate constant to the original value.

V. CONCLUSIONS

The ¹⁹F(α, p)²²Ne reaction at 2443 keV proved to be a good probe for depth profiling of fluorine in SiO₂ layers up to 250 nm thick. We showed that at 1200 °C, implanted fluorine moves to the interface within 10 min, leaving no detectable fluorine within the oxide. This applies to inert anneals as well as to dry oxidations. Oxidation data analysis showed that the Deal and Grove model⁹ is too simple for implanted fluorine experiments. A model is presented consisting of a highly diffusive layer and a fluorine containing reactive interface between the silicon and its oxide, which explains our data well. The thickness of this layer is the same as the thickness of the implanted region. The origin of this layer lies in the desorption of silicon atoms, displaced by the implantation, in the form of molecules like SiF₄.

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