4 References

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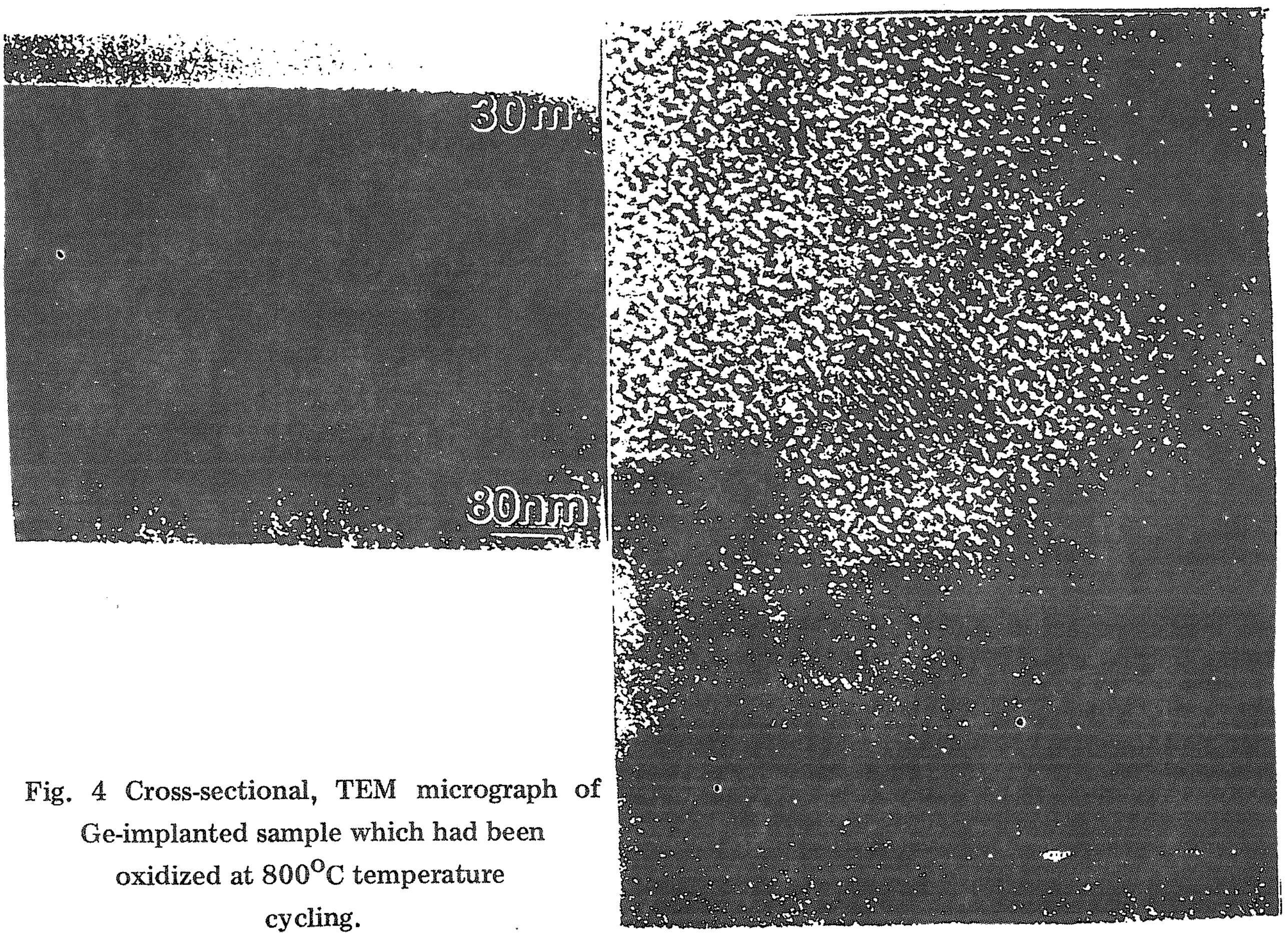

Fig. 4 Cross-sectional, TEM micrograph of Ge-implanted sample which had been oxidized at $800^{o}C$ temperature cycling.

3 Conclusion

It has been shown that, over most of the range of temperature and ambient studied, the effect of Ge-implantation on Si oxidation rates can be accounted for by a modified interfacial reaction rate, and oxide strain relief. An anomalous behavior was observed during $800^{o}C$ oxidation in steam. Rates were greatly enhanced over their intrinsic and can be explained by interface strain relief. These conditions, which produce the largest differential growth rates between implanted and virgin Si, seem ideally suited for masking applications. It should be noted that the effect of Ge-implantation on the interfacial reaction was observed for dry oxidation or temperatures $> 1000^{o}C$ were the oxide is already viscoelastic.

3.1 Acknowledgment

The authors gratefully acknowledge Dr. A.A. Bidokhti for many helps in preparing this manuscript.

the interface is shown in fig. 3 indicating an smoother interface in the case of Ge implanted samples. An interesting morphology, was observed in samples with a thick Ge layer which had undergone multiple oxidations at 800°C. The oxidations were done by cycling the sample in and the out of the furnace.

A TEM micrograph of a sample cycled three times at 800°C is shown in fig. 4(b). crystal islands of Ge is observed within the oxide corresponding to the location of the oxide/Si interface after each cycle. Also, a continuous Ge layer (epitaxial on Si) is seen at the final oxide/Si boundary. The presence of Ge precipitates within the oxide can be a result of Ge precipitation with stable sizes in the Ge–Si layer. due to supercooling effect.

These Ge precipitates from at the interface where the Ge concentration is highest. These islands are left inside the oxide by the preferential oxidation that takes place at the Ge–Si during the cooling cycle are shown in fig. 4. It must be mentioned at this stage that Ge trapping in the oxide only occurs in temperature cycling.

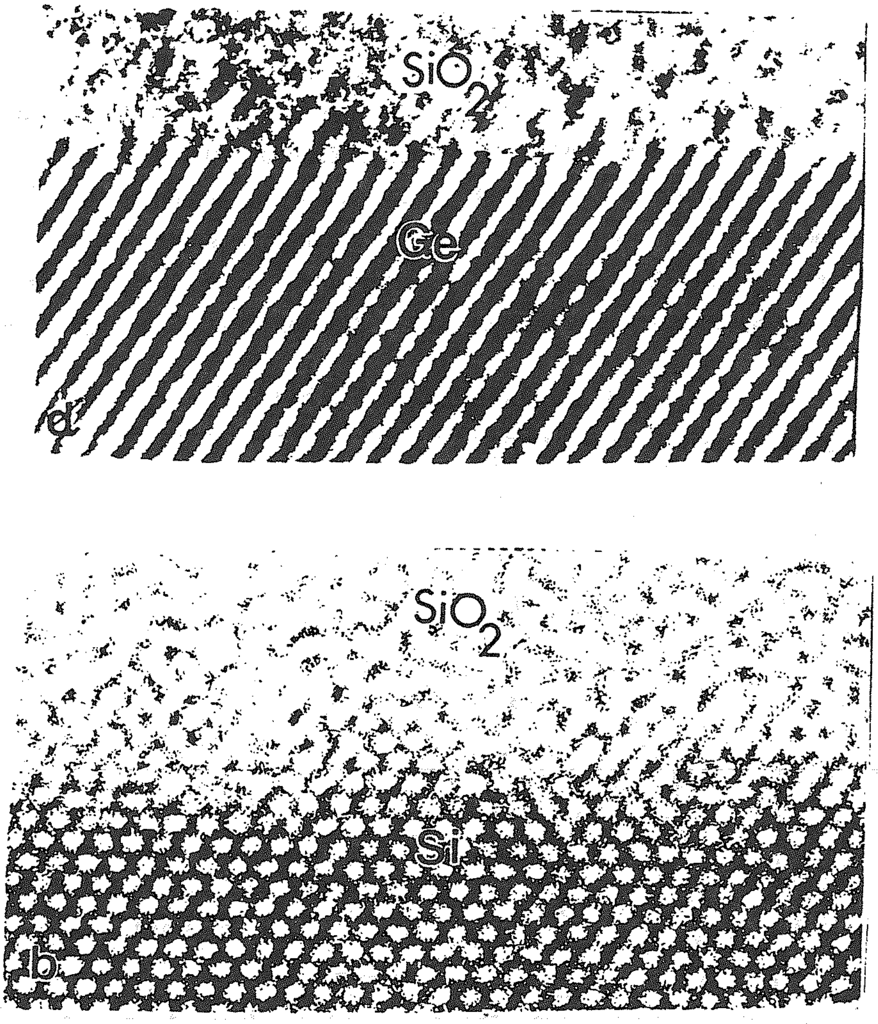

Fig.3 High resolution image of oxidized samples under the same condition but
a) Ge-implanted b) virgin

relieved by the viscous flow should be considered.

Other studies have shown an increase in oxidation rates on annealing thick oxides (9). Relieving the compressive stress, would increase interface kinetics by satisfying the volume requirements for conversion of Si to SiO_2. Also, a crossover is observed in oxidation rates for viscous flow point of the virgin oxide (10). This accounts for the difference in the activation energies measured at low (780-930°, 2.2 eV) and high ($>950°$ C, 1.3 eV) temperatures.

The change in the binding energy of Si–Si (78.1 kCal/mole) to that of Ge–Si (72 kCal/mole) accounts for implanted samples stress relaxation at lower temperatures. It is an acceptable fact at this stage to assume that the associative effect with the viscous flow can lead to the total 40% enhancement rates observed. A Maxwell viscoelastic flow properties (5,6) explain occurrence of increasing stress at reduced oxidation temperatues ($< 950°$ C) for virgin Si. A 120% volume required in Si conversion to SiO_2 leads to limiting factor specially at lower temperature which is also in agreement with the observation of lower oxidation rate of virgin Si in our experiments. Similarly we have observed that at temperatures above 1000° C no enhancement takes place. Therefore the major role of Ge is in strain relief.

Kinetic data for steam oxidation is given in fig. 2 for two different temperatures. The figure shows that at the higher temperature, the implanted data parallels that from virgin Si. This indicates that the diffusion rate constant is the same in both samples but the interfacial reaction rate is different. However, a totally different behavior is observed in samples oxidized at 800°C. The plot in fig. 2 shows that both the slopes and intercept of the two data sets (implanted and non-implanted) differ. The reason for this behavior as discussed is due to reduced strain in the oxide and at the interface. a similar low-temperature oxidation effect in As^+-implanted Si was recently reported (7).

A comparison of the high resolution images of

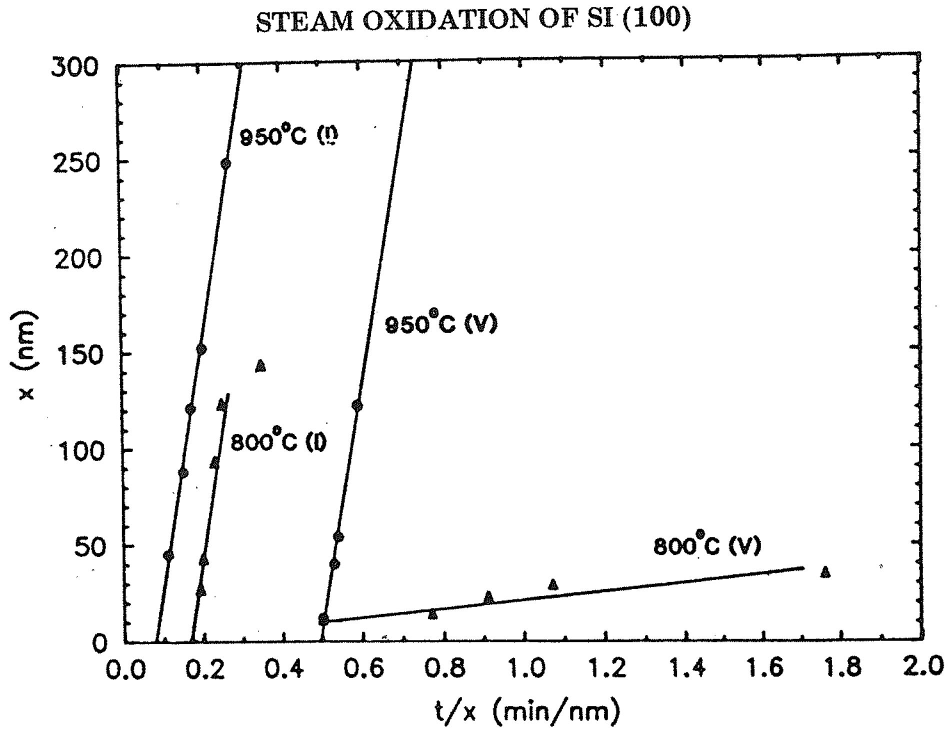

Fig. 2 Kinetic data at 800 and 950°C for steam oxidation of implanted and virgin Si.

through the screen oxide at this energy placed the peak of the implant profile near the Si surface and therefore resulted in a high surface concentration of Ge.

In Deal and Grove model (3), oxide thickness is related to oxidation time by

$$t = \frac{x}{B/A} \ X \ \frac{x^2}{B}$$

where x is the oxide thickness, t the time, and A and B are the constants specific to a given set of oxidation conditions.

Two different regimes of growth are generally identified, a linear regime when $t \ll \frac{A^2}{4B}$ which leads to the relation $x = t\frac{B}{A}$, and a parabolic regime when $t \gg \frac{A^2}{4B}$ which gives $x^2 = Bt$. The constant B, referred to as the diffusion rate constant, and $\frac{B}{A}$, the linear rate constant, express the rates of the two limiting processes which control the thermal oxidation. Plots of x verses t/x are shown in fig. 1 for oxidation of both implanted and virgin Si.

This manner of plotting allows the kinetic parameters to be determined. The diffusion rate constant B is given by the slope of the curves and the y-intercept gives the value of (– A). A consistent behavior is observed over the temperature range investigated. The kinetic data from each sample lies along a straight line which is expected from Eqn. (1) so long as the rate constants do not vary with time (i.e., oxide thickness). The absence of non-linearity in the implant data shows that the oxidations were "well-behaved" at each temperature with constant reaction rates. Implanted and non-implanted data at each temperature have the same slopes but different intercepts which demonstrates that the interfacial rate constants are substandially affected by implantation but not the diffusion rates. The rate parameters determined from the data in fig. 1 are tabulated in table 1.

Arrhenius plot of the interfacial reaction in both implanted and virgin samples generally is a simple activated process; exp (-Ea/kT), characterizing different slops for various temperatures (fig.3). But plot of the data for implanted and virgin Si at low temperature indicates different slope at 800°C. The slope of 800°C implanted sample is the same as 950°C virgin sample. Therefore not only the activation energy but also other factors such as the tension free energy

Table 1. Rate Constants for Wet Oxidation of Si.

Oxidation Temp.(°C)	A(μm)	Parabolic rate constant B(μm^2 /hr)	Linear rate constant B/A(μm/hr)
1000 (I)*	0.094	0.160	1.702
1000 (V)	0.196	0.162	0.826
950 (I)	0.061	0.081	1.328
950 (V)	0.183	0.080	0.437
900 (I)	0.120	0.043	0.358
900 (V)	0.206	0.040	0.194

* "I" denotes implanted and "V", virgin.

which additional accumulation of Ge at the interface produces no effect.

The use of Ge-implantation to modify thermal oxidation rates raises interesting possibilities, since Ge is isoelectric in Si. Thermal oxides are extensively used in the fabrication of integrated circuits in Si for isolation, masking purposes. It is anticipated that both processes could benefit directly from the effects of Ge-implantation. Also, the differential rate of oxide growth between implanted and non-implanted Si is used to selectively mask against subsequent process steps.

In this paper, the influence of Ge-implantation on thermal oxidation is investigated over a range of temperature and oxidation ambient. Kinetic data is generated over this range and is related to the mechanisms for oxidation enhancement by Ge-implantation. Oxidation is shown to be consistent with the mechanism described (4), except for steam oxidation at low temperature 800°C, where a lower compressive strain in the oxide layer and lower binding energy at the interface together increases the oxidation rate. A high resolution comparison is made in order to qualitatively determine the influence of Ge intermediate layer on the roughness of the SiO_2/Ge_xSi_{1-x} compared to that of Si/SiO_2 interface.

2 Experimental Procedure

Rutherford backscatteirng spectroscopy (RBS) was used to determine oxide thicknesses and characterize the behavior of Ge during oxidation. The detailed microstructure in the oxidized samples were determined by cross-sectional, transmission-electron microscopy (TEM). Oxidations were done in a standard tube furnace in both steam and wet ambient. The wet ambient was produced by bubbling O_2 through 95°C water. Single crystal, n-type Si $<100>$ were used in this investigation. A 20 m screen oxide was grown on the Si before implantation to passivate the surface and also reduce the effective range of the implanted Ge-ions in Si. Samples were implanted with 30 Ke V Ge-ions to a dose of 10^{16} atoms/cm^2. Implantation

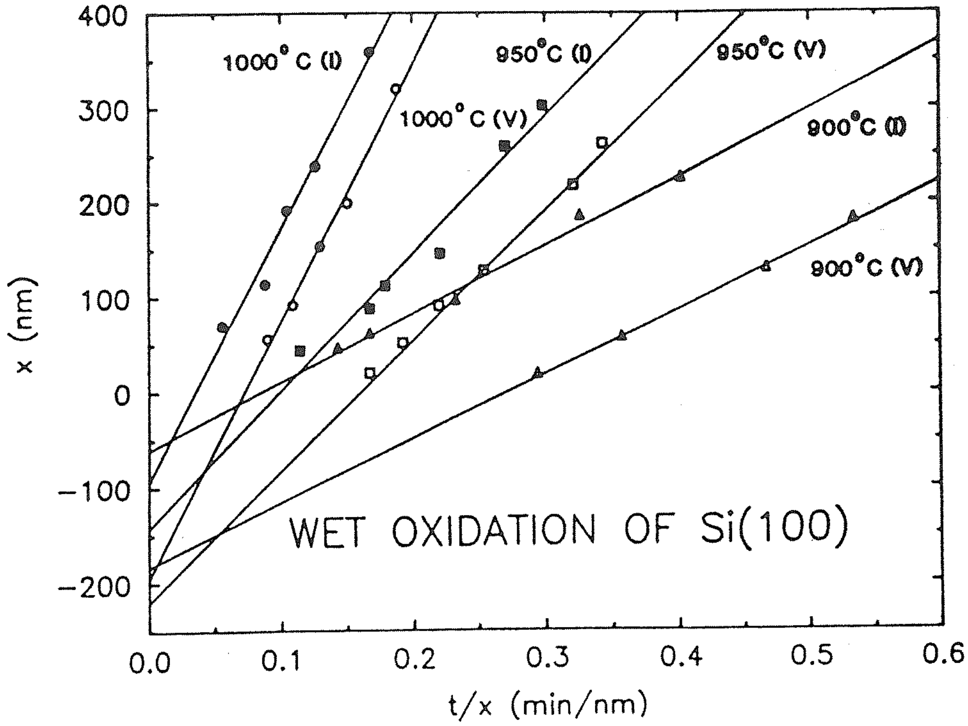

Fig. 1 Kinetic data at 900,950 and 1000°C for wet oxidation of implanted and virgin Si.

Defects and Interfacial Structure in GE/SI Layers.

D. Fathy, Ph.D.

Nuclear Materials Group, A.E.O.I.

&

M. Sayah, Ph.D.

Physics Dept. Amirkabir Univ. of Tech.

ABSTRACT:

During thermal oxidation of Ge–ion implanted Si, Ge is completely rejected from the growing oxide and forms an intermediate crystal layer between the Si and SiO_2*. The segregated Ge rich layer is epitaxial with the Si substrate and leads to enhanced oxidation rates. The increased oxidation rates are shown to arise because the segregated Ge modifies the interfacial growth kinetics and lowers strain in the oxide layer. Kinetic and interfacial structure information are provided over a range of temperatures and oxidation embients. Enhanced oxidation rates studied were found to be consistent with a modified reaction at the oxide/Si interface. An anomalous behavior is exhibited for steam oxidation at* 800^oC*, due to the viscous flow of the intermediate Ge layer. This behaviour is characterised and the mechanisms responsible are discussed. Also a comparison using HRTEM is made between* Ge/SiO_2 *and* Si/SiO_2 *interface. This shows that the undulations at the interface is different indicating a reduced binding energy due to the presence of substitutional Ge atoms.*

1 Introduction

It has recently been shown (1,2) that an epitaxial film of Ge forms on Si during thermal oxidation of Ge-ion implanted Si. During oxidation Ge is completely rejected at the growing oxide interface, where it accumulates forming a distinct, Ge-rich layer. The presence of this intermediary layer between the oxide and Si substrate leads to substantially enhanced oxidation rates.

Deal and grove (3) modeled oxidation of Si using rate-limiting process: (a) diffusive process which transports oxidant from the surface to the growing oxide boundary and (b) reaction at the oxide/Si interface which forms the oxide phase. In this case it was shown that a greatly increased interfacial reaction due to Ge-implantation accounts for the enhanced oxidation (4). Successful modeling of this effect was achieved by assuming a step-function dependence of the interfacial reaction rate on the amount of segregated Ge–Si of lower binding energy than that of Si–Si. No dependence was observed until approximately a single mono-layer of Ge is segregated after