Inorganic Materials, Vol. 36, No. 2, 2000, pp. 91–93. Translated from Neorganicheskie Materialy, Vol. 36, No. 2, 2000, pp. 135–137.

Effect of Laser Irradiation on the Oxidizer Transport and Self-Ogranization of the Interfacial Layer during Thermal Oxidation of Silicon

A. M. Khoviv and I. N. Nazarenko

Voronezh State University, Universitetskaya pl. 1, Voronezh, 394893 Russia

Received April 21, 1998

Abstract—The oxidation of silicon under mid- and near-IR laser irradiation was compared with thermal and combined (thermal + laser-enhanced) oxidation processes. The average rate of oxidizer transport through the oxide layer and the time taken for the formation and self-organization of the interfacial layer between SiO_2 and Si were evaluated from kinetic data for the three regimes studied. The processes influenced by laser irradiation were identified.

The mechanism underlying the influence of laser irradiation on the oxidation of single-crystal silicon is not yet fully understood. Thermal oxidation of silicon is commonly believed to involve three stages: oxidizer adsorption at the oxide surface, diffusion of neutral and/or charged species through the oxide film, and silicon oxidation at the SiO_2/Si interface. Earlier [1], we proposed a physicochemical model and a kinetic equation for thermal passivation of silicon with consideration for self-organization in the interfacial layer between silicon and silica.

In this work, we focus on the kinetics of thermal, laser-enhanced (LE), and combined (LT) oxidation of silicon in an oxygen atmosphere.

The experimental techniques used in this investigation were similar to those described earlier [2–4]. KDB-0.005 Si(100) wafers of dimensions 25 × 25 (thermal and LE oxidations) or 6 × 6 mm (LT), washed by standard peroxide–ammonia cycles and air-dried, were placed in a resistively heated quartz reactor. The flow rate of oxygen passed through the reactor was 40 l/h. During LE oxidation, the temperature of the reaction zone could be controlled by varying the output of the Nd:YAG laser operated at 1.064 μm (incident power density from 150 to 250 W/cm^2). During LT oxidation (Nd:YAG and CO_2 lasers, λ = 1.064 and 10.6 μm, respectively), the wafer was heated in a resistance furnace, and the incident power density was adjusted so as to raise the temperature in the beam spot by 20 K (35 W/cm^2 at λ = 1.064 μm and 5 W/cm^2 at λ = 10.6 μm). For comparison, we also carried out thermal oxidation, using the same setup but without laser irradiation. The temperature on the sample surface was measured with an accuracy of 3 K by a calibrated EOP-66 optical pyrometer. Oxide layer thicknesses were measured with an LEM-2 laser ellipsometer to an accuracy of 2–3 nm.

In the thermal and LT regimes, the thermal equilibration of the sample placed in the preheated reactor was assumed to take 60 s, and the oxidation time was corrected for this value. In the LE regime, the thermal equilibration time was taken to equal 30 s. During equilibration, the oxide layer (5–10 nm in thickness after peroxide–ammonia washing) grew as a result of nonisothermal oxidation and attained thickness l_1, which was determined by extrapolating the thickness vs. oxidation time data to $t = 0$.

The oxidation kinetics were fitted with an equation similar to that derived in [1] but modified to take into account l_1:

$$l^2 + 2(l_1 + v\tau_r)l = 2vl_0t,$$

where l is the oxide layer thickness, t is the oxidation time, v is the average velocity of oxidizer transport through the oxide layer, l_0 = 1 nm is the thickness of the interfacial layer between Si and SiO_2 in which self-organization develops, and τ_r is the time necessary for the formation and self-organization of the interfacial layer of thickness l_0.

Using the $l(t)$ data, we calculated v and τ_r and determined the apparent activation energies of mass transport and self-organization under the assumption that

$$v \sim \exp[-E_t/(RT)] \text{ and } 1/\tau_r \sim [E_s/(RT)],$$

where E_t is the activation energy of oxidizer transport through the oxide layer, and E_s is the activation energy of self-organization in the interfacial layer.

The results, displayed in the table, lead us to the following conclusions:

0020-1685/00/3602-0091$25.00

Kinetic parameters (v, nm/min, and τ_r, min) and activation energy of silicon oxidation

T, K	v	τ_r	v	τ_r	v	τ_r	v	τ_r
	thermal		LE (1.064 μm)		LT (1.064 μm)		LT (10.6 μm)	
1310					76	0.33		
1330	56	0.36					50	0.63
1340			427	0.31				
1350					105	0.39		
1375	75	0.37						
1390							64	0.40
1395					124	0.30		
1420			458	0.29				
1430	168	0.21					77	0.18
1450					194	0.20		
1470	190	0.19	587	0.26			117	0.33
1490					208	0.22		
1500			592	0.25				
1560			585	0.23				
1590			468	0.20				
1640			543	0.13				
Activation energy, kJ/mol	141	86	25	45	105	54	106	103

(1) The average velocity of mass transport in the LR regime is 3.1 to 7.7 times higher than that in the thermal regime, resulting in a higher oxidation rate. At T = 1330 K and t = 60 min, the oxide layer thickness is 143 nm in the LT regime and only 91 nm in the thermal regime. The increase in the oxidation rate can be accounted for by two effects:

the high incident power density has a significant nonthermal effect on the transport of oxygen-containing species through the oxide layer [5];

the mechanical inhomogeneity of the film, resulting from the large in-plane thermal gradient on the film surface in the LE regime, facilitates oxidizer diffusion to the SiO_2/Si interface. Both v and τ_r are weak functions of temperature and incident power density (table), indicating that the acceleration of silicon oxidation by laser irradiation is not thermally activated.

(2) The oxidation under laser irradiation at 1.064 μm is close in kinetics (v and τ_r) to thermal oxidation. The slight increase in the oxidation rate [2], at the relatively low incident power density in this regime, is due to the increase in v (by a factor of 1.1–1.4 in comparison with thermal oxidation).

(3) Interestingly enough, laser irradiation at 10.6 μm reduces the rate of silicon oxidation [3, 5]. As apparent from the table, the decrease in the oxidation rate is due to a decrease in v and an increase in τ_r as compared to thermal oxidation. The variation of τ_r with temperature is nonmonotonic, presumably because τ_r has an integral character, while the effect of laser irradiation on the rate of thermal oxidation depends not only on the oxide layer thickness but also on the surface temperature in the laser spot [3]. Why laser irradiation reduces the oxidation rate is not yet fully clear. One possibility is that this effect is related to strong absorption by the SiO_2 film at 10.6 μm [6].

In conclusion, note that the above approach to describing reaction kinetics can also be applied to various chemical reactions, such as

$$\text{gas (liquid)} + \text{solid(I)} \longrightarrow \text{solid(II)}.$$

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 98-03-83157a.

REFERENCES

1. Khoviv, A.M., Nazarenko, I.N., and Malevskaya, L.A., A Model for Thermal Oxidation of Silicon with Consideration for the Self-Ogranization of the Interfacial Layer, *Neorg. Mater.*, 1997, vol. 33, no. 11, pp. 1294–1297 [*Inorg. Mater.* (Engl. Transl.), vol. 33, no. 11, pp. 1095–1097].

2. Ugai, Ya.A., Khoviv, A.M., Nazarenko, I.N., and Dubov, S.I., Laser-Enhanced Silicon Oxidation, *Zh. Fiz. Khim.*, 1986, vol. 60, no. 6, pp. 1554–1556.
3. Mittova, I.Ya., Khoviv, A.M., Nazarenko, I.N., and Dubov, S.I., The Effect of IR Laser Radiation on Formation of Silicon/Silica Heterostructures, *Neorg. Mater.*, 1995, vol. 31, no. 2, pp. 276–277 [*Inorg. Mater.* (Engl. Transl.), vol. 31, no. 2, pp. 258–259].
4. Khoviv, A.M., *Lazernyi metod formirovaniya oksidnykh plenok na poverkhnosti provodyashchikh tverdykh tel* (Laser Processing as a Means for Producing Oxide Films on Conductive Solid Surfaces), Voronezh: Voronezh. Gos. Univ., 1997.
5. Khoviv, A.M., Mittova, I.Ya., and Dubov, S.I., Nonthermal Effects of Mid- and Far-IR Laser Radiation on Silicon Oxidation, *Zh. Tekh. Fiz.*, 1996, vol. 66, no. 7, pp. 151–155.
6. Rakov, A.V., *Spektrofotometriya tonkoplenochnykh polupovodnikovykh struktur* (Spectrophotometry of Thin-Film Semiconductor Structures), Moscow: Sovetskoe Radio, 1975.