Oxidation Kinetics of Silicon by Inductively Coupled Oxygen Plasma

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Abstract

The low-temperature Si oxidation kinetics by inductively coupled oxygen plasma has been studied. Linear rate constants had negative values when the oxide growth rate was described by linear-parabolic growth law. The analysis of transverse-optical mode frequencies and etch rates indicated that the density of surface oxide was lower than that of bulk oxide. The oxidation kinetics could be explained qualitatively by assuming a surface layer with larger diffusion coefficient and a bulk layer with smaller diffusion coefficient.

Introduction

Even though CVD oxides are commonly employed for gate oxide in poly-Si TFTs, thermal oxidation always provides best TFT properties. But thermal oxidation, which needs elevated temperature, makes it impossible to use glass as a substrate.

Plasma oxidation is promising as a low-temperature process. High density plasmas such as electron cyclotron resonance (ECR) plasma and inductively coupled plasma (ICP) show high-oxidation rate and low damage to the oxide due to high-radical concentration and low sheath voltage [1,2]. The ECR plasma oxide on poly-Si films showed lower-leakage current and higher-breakdown field than thermal oxide [1]. ICP has advantages of large area capability, high plasma density, and low plasma potential.

Although many studies have been made on the growth kinetics for plasma oxidation [3,4,5] the kinetics is still a subject of study. In this paper, we report the oxidation rate by ICP can be explained qualitatively by adopting a surface layer with larger diffusion coefficient and a bulk layer with smaller diffusion coefficient.

Experiment

P-type (100) silicon wafers with the resistivity of 4-12 Ω cm were used as a substrate. The wafers were cleaned in $H_2SO_4 + H_2O_2$ solution and dipped in 50:1 HF to remove native oxide. The plasma oxidation was performed in an ICP system with oxygen gas. The RF power and frequency were 2 kW and 13.56 MHz, respectively. The substrate was floated electrically and no external bias was applied.

The thickness was measured using an ellipsometry. Infrared transmission was measured using a Fourier transform infrared spectrometry (FTIR). The chemical etch rate of the oxide was measured using p-etch solution (49% HF: 70%HNO_3: H_2O = 3:2:100).

Results and Discussion

Figure 1 shows the oxide thickness as a function of oxidation time at (a) 5 mtorr and (b) 10 mtorr. The kinetics of the oxide growth was well described by the linear-parabolic growth law with initial-rapid growth as the equation

$$x^2/k_P + x/k_L = t + \tau , \qquad (1)$$

where x is the oxide thickness, t is the oxidation time, k_P and k_L are the parabolic and linear rate constants, and τ is the time constant. The fitted parameters are summarized in Table 1.
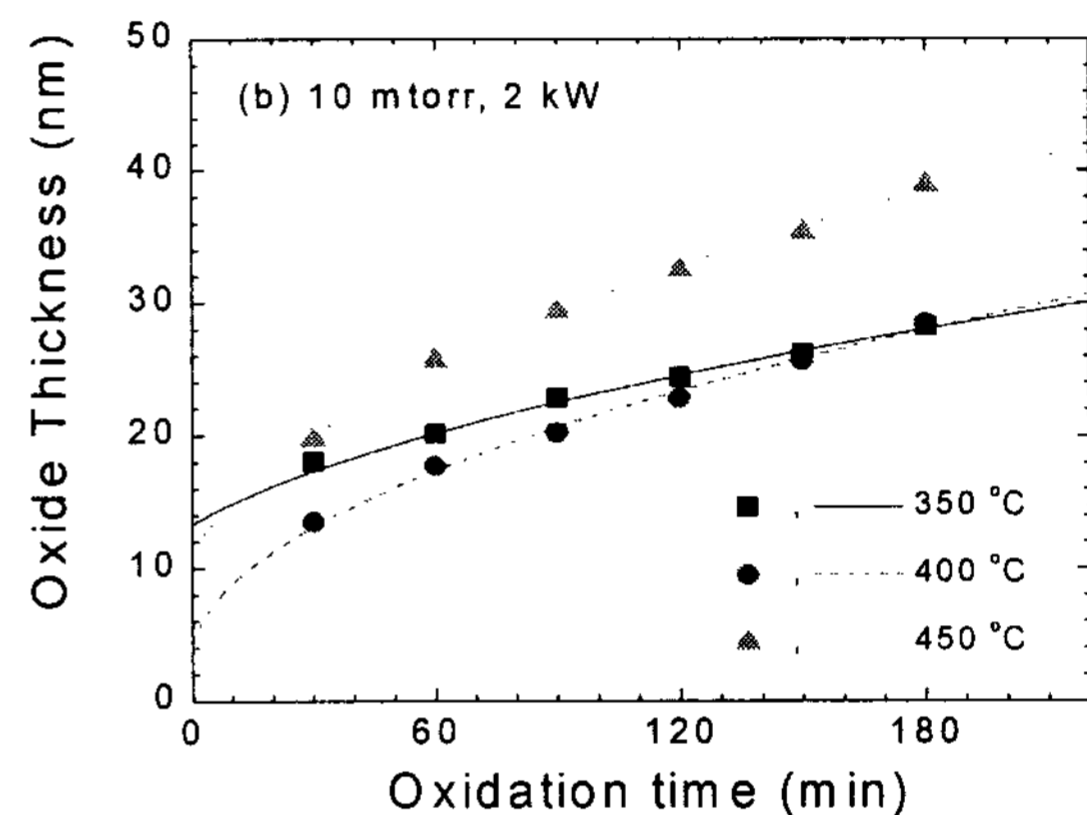

Fig 1. The oxide thickness as a function of ICP oxidation time at various temperatures.

Pressure	Temperature	k_P (nm²/min)	K_L (nm/min)
10 mtorr	350 °C	2.28	-0.17
	400 °C	3.57	-0.68
	450 °C	5.88	-0.53

Table 1. The fitted parameters: parabolic rate constant k_P and linear rate constant k_L.

Note that the k_L values are negative. The negative k_L values cannot be explained by the Deal-Grove model [6]. The negative k_L was also reported by other researchers in oxidation with microwave plasma[4,5] and thermal oxidation at low pressure [7].

Figure 2 shows the transverse-optic (TO) mode frequency associated with the asymmetric stretch mode of the O in Si-O-Si intertetrahedral bridging bonds. Note that the TO mode frequency significantly decreases as the thickness is below 25 nm. Among several possibilities [8,9], the decrease of the density of oxide is considered to be the reason.
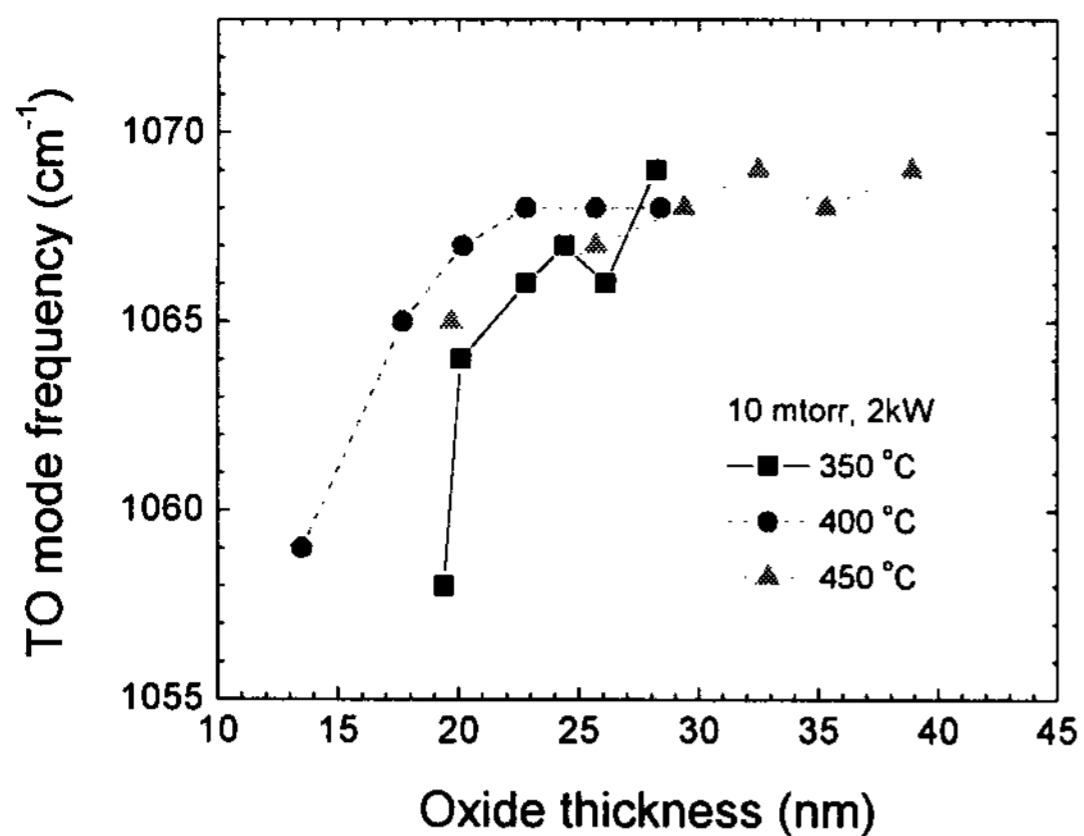
Fig. 2 TO mode frequency associated with asymmetric stretch mode of O in the Si-O-Si intratetrahedral bridging bonds as a function of oxide thickness.

Figure 3 shows etch rate of the oxide with p-etch solution as a function of the depth from the oxide surface showed that the etch rate increases as the depth decreases below 10 nm. This indicates that the density of the oxide near the surface is lower than that of the bulk.
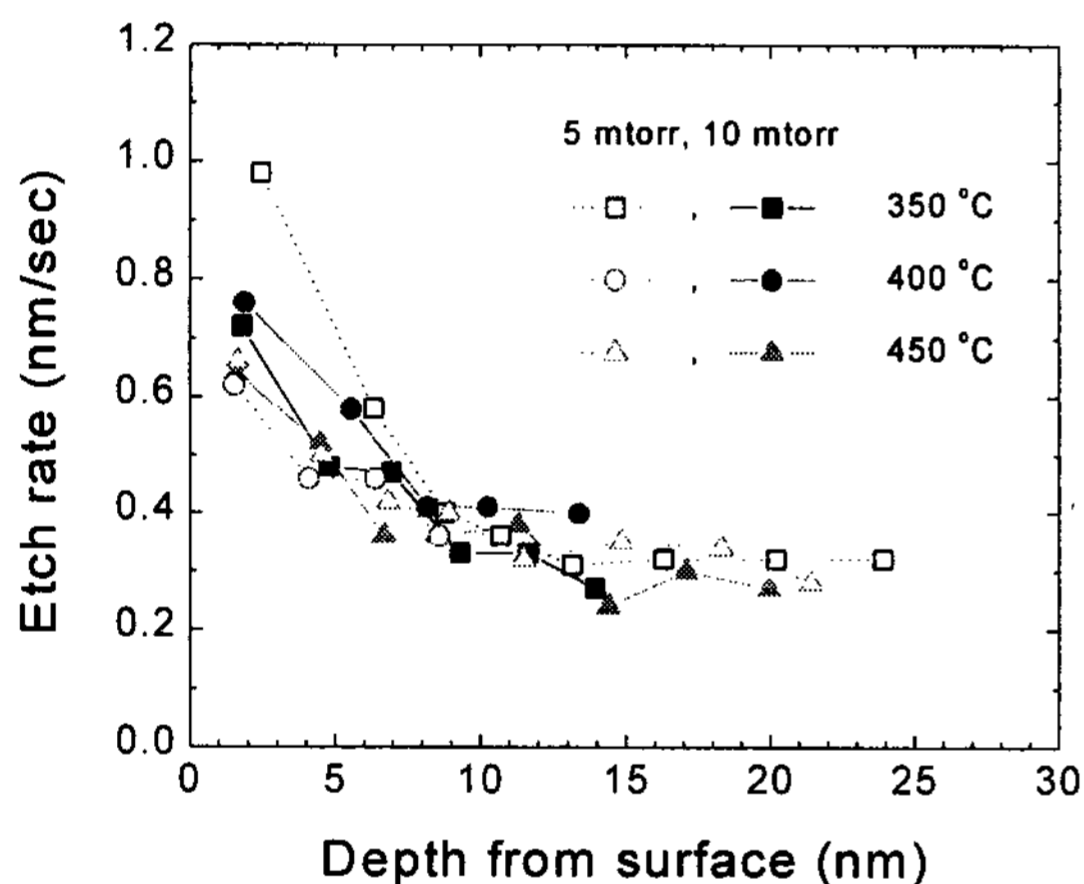

Fig. 3 Etch rate of the plasma oxide in p-etch solution (49%HF: 70%HNO$_3$: H$_2$O= 3:2:100) as a function of depth from oxide surface.

So, to simplify the oxide growth kinetics, we can model the oxide as two layers: surface layer with low density and bulk layer with high density. Assume that the recombination of oxidants only limits the oxidation rate and the exchange with Si-O network does not occur. In steady state, the oxide growth rate is expressed as

$$dx/dt = D_b C_0 \Omega / \{x - x_s(1 - D_b/D_s)\} , \qquad (2)$$

where C_0 is the concentration of the oxidants at the oxide surface and Ω is the volume grown by the unit oxidant. D_s is the diffusion coefficient in the surface layer and D_b is that in the bulk. The parabolic-rate constant k_P and linear-rate constant k_L in Eq.(1) can be expressed as follows.

$$k_P = 2 D_b C_0 \Omega$$
$$k_L = -k_P /\{2 x_s (1 - D_b/D_s)\} , \qquad (3)$$

We can see that the k_L is affected by the properties of the surface layer as well as by those of the bulk layer, while the k_P is affected only by the properties of the bulk. Note that the k_L is negative if D_s is larger than D_b.

The oxygen diffusion coefficient of the surface oxide is expected to be larger than that in the bulk layer because the density of the surface layer is lower. Therefore the k_L is expected to be negative and the fitted k_L values in Fig. 1 are negative.

Conclusion

The oxidation kinetics of silicon wafers in inductively-coupled oxygen plasma was described by the linear-parabolic growth law with a rapid initial growth.

The density of oxide near the surface was lower than that of bulk. The negative linear-rate constants (k_L), and thickness reversal could be explained qualitatively by assuming the surface layer with larger diffusion coefficient and bulk layer with smaller diffusion coefficient.

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