

Short communication

Influence of phosphorus doping on the chemical etching rate of polycrystalline silicon films

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ABSTRACT

The chemical etching of intrinsic and n-type poly-Si with phosphorus concentration $5 \times 10^{18} \text{ cm}^{-3}$ in Cl₂ environment is investigated. It is found that phosphorus doping increases formation and desorption of SiCl₂ molecules. The activation energy of Si + Cl₂ → SiCl₂ reaction for intrinsic poly-Si is equal to (1.73±0.24) eV, and it decreases to (1.51±0.16) eV when n-type poly-Si films are used. Meanwhile, the desorption activation energy of SiCl₂ molecules for intrinsic poly-Si is equal to (1.86±0.16) eV, and it decreases to (1.54±0.16) eV when n-type poly-Si films are used. The etching-rate limiting process is determined using the calculated mean times of elementary processes.

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1. Introduction

Silicon is the most popular semiconductor in the electronics industry. Monocrystalline silicon is required for the production of integrated circuits, while polycrystalline silicon is preferred in the fabrication of solar cells. With the increase in concentration of activated carriers, the etching rate of n-type silicon increases and that of p-type silicon decreases [1,2]. The etching rate variations are more pronounced in n-type silicon. This allows one to calculate reliably the doping level induced changes in the activation energies of elementary processes. The activation energies are usually derived under steady-state conditions because the transient etching behavior of silicon is extremely sensitive to sample history and experimental parameters [3].

The activation energy variations induced by temperature and time (reaction progress) are frequently observed. Meanwhile, the influence of doping level on the activation energies of elementary processes is little investigated [4]. Variable activation energy is a multi-step process, which is described by a collective parameter linked to the activation energies of individual steps [5]. Quantitative analysis of the activation energy variations allows one to obtain activation energies of individual steps, to evaluate and predict other important parameters of the etching process.

In previous work [6], chemical etching of silicon in Br₂ environment is simulated. It is found that desorption activation energy

of SiBr₂ molecules depends on the phosphorus doping of silicon films. However, the observed difference of 0.43 eV was attributed to the heating of the reaction layer by exothermic reaction. Although the situation is theoretically possible, it is highly unlikely because:

- 1) single SiBr₂ molecule is formed after about 10⁵ collisions of Br₂ molecules with the surface;
- 2) the heat released during the reaction is transferred into the bulk of silicon film and the heat sink;
- 3) thermal desorption of Si atoms from the surface being etched is not observed. Silicon boiling temperature at standard pressure is equal to 3538 K. This yields average temperature of single Si atom 0.30 eV.

In this work, the influence of phosphorus doping on the reaction and desorption rate constants during chemical etching of poly-Si films in Cl₂ environment is investigated. In the experiment [7], chemical etching of intrinsic and n-type poly-Si (doping level $5 \times 10^{18} \text{ cm}^{-3}$) was performed in the reactor consisting of 30 cm length quartz tube with inner diameter of 25 mm. The sample section of the quartz tube was externally heated with a heating tape along 15 cm length. The thickness of intrinsic poly-Si films was 350 nm, and the thickness of n-type poly-Si films was 420 nm. The surface area of the films was in the range of (4–9) mm². The samples were mounted on 18 × 14 × 9 mm segment of silicon wafer, which was covered with a thermally grown 20-nm-thick silicon oxide layer. Glass springs were used to press the samples against this heat sink to make good thermal contact. The temperature was

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measured in the center of the silicon plate using chromel-alumel thermocouple. During the etching process the flow rate of high purity Cl_2 gas varied from 10 to 15 sccm. In order to measure the etching rates reliably, the etching process for intrinsic and n-type poly-Si is performed at different temperatures. The etching rates were measured using laser interferometer. Theoretical results, obtained by fitting the experimental data, are used to analyze the influence of phosphorus doping on the reaction and desorption activation energies.

2. Model

During silicon etching in Cl_2 environment competition between formation and desorption of SiCl_2 molecules takes place. Cl_2 molecules from the gas phase react with Si atoms on the surface



The reaction consists of two elementary steps: dissociative chemisorption of Cl_2 molecules on the surface $2\text{Si(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{SiCl(a)}$, and formation of SiCl_2 molecules as the final reaction product $2\text{SiCl(a)} \rightarrow \text{SiCl}_2(\text{a}) + \text{Si(s)}$. According to the transition state theory (TST), which is described in work [8], the reaction rate constant is equal to

$$k_r = A v_{\text{TST}} \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right), \quad (2)$$

where A is the average kinetic transmission coefficient, $v_{\text{TST}} = kT/h$ is the lattice atom oscillation frequency, h is the Planck constant, k is the Boltzmann constant, T is the temperature, ΔS is the activation entropy, and ΔH is the activation enthalpy. The reaction activation energy E_r linearly depends on the activation enthalpy [9]. Because these two physical quantities differ little, the activation enthalpy is usually referred to as the reaction activation energy. The mean reaction time is equal to

$$\tau_r = (k_r p)^{-1} \quad (3)$$

where p is the pressure of Cl_2 molecules.

SiCl_2 molecules diffuse in the adsorbed layer until eventually desorb. First-order molecular desorption is described by desorption rate constant

$$\omega = v_{\text{TST}} \exp(-E_d/kT), \quad (4)$$

where E_d is the desorption activation energy. The mean desorption time is equal to

$$\tau_d = \omega^{-1}. \quad (5)$$

The mean time of the etching process is equal to the sum of mean times of elementary processes

$$\tau = \tau_r + \tau_d. \quad (6)$$

The chemical etching rate of silicon in Cl_2 environment is calculated using the expression

$$V = \tau^{-1}, \quad (7)$$

where the etching rate is measured in monolayer/s. The monolayer thickness is estimated using the following expression

$$h_0 = (M_{\text{Si}}/\rho_{\text{Si}}N_A)^{1/3}, \quad (8)$$

where M_{Si} is the molar mass of silicon, ρ_{Si} is the density of poly-Si film, N_A is the Avogadro constant.

3. Results and discussion

The experimental dependences of intrinsic and n-type poly-Si etching rate on pressure of Cl_2 molecules are used to determine the influence of phosphorus doping on the reaction and desorption rate constants. The fitted experimental dependences are shown in Fig. 1. It is observed that n-type doping of poly-Si films increases chemical etching rate. The reaction rate constants, found by fitting the experimental data, are subsequently analyzed using TST. The obtained theoretical results are presented in Table 1. The reaction activation energy for intrinsic poly-Si is equal to $E_{r1} \pm \Delta E_{r1} = (1.73 \pm 0.24)$ eV, and it decreases to $E_{r2} \pm \Delta E_{r2} = (1.51 \pm 0.16)$ eV when n-type poly-Si films are used. The reaction process consists of two elementary steps: dissociative chemisorption of Cl_2 molecules on the surface, and formation of SiCl_2 molecules as the final reaction product. The activation energy of dissociative chemisorption is much lower than the activation energy of SiCl_2 formation [10,11]. This indicates that n-type doping of poly-Si films increases the dissociative chemisorption of Cl_2 molecules on the surface.

The desorption rate constants, found by fitting the experimental

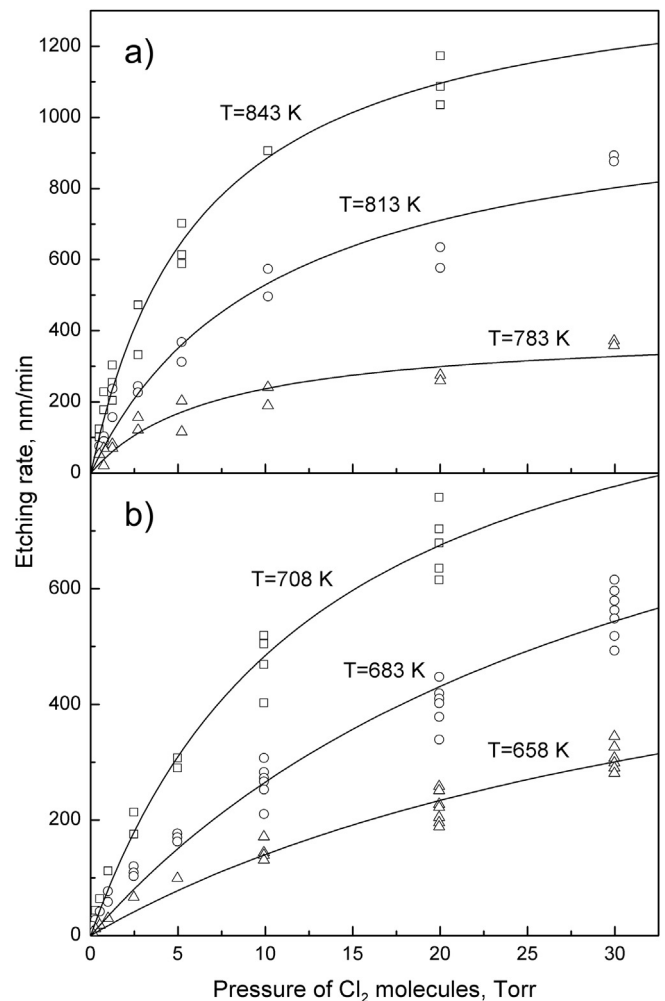


Fig. 1. Experimental [7] (symbols) and theoretical (curves) dependences of silicon etching rate on pressure of Cl_2 molecules at different temperatures: a) intrinsic poly-Si; b) n-type poly-Si. Squares, circles, and triangles represent different temperatures.

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