Surface Science 656 (2017) 96–100

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Activation energy of thermal desorption of silicon oxide layers on silicon substrates

Yoshiharu Enta*, Shodai Osanai, Takahito Ogasawara

Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki 036-8561, Japan

ARTICLE INFO

Keywords:
Silicon oxide
Thermal desorption
Void growth
Desorption kinetics
Activation energy
Frequency factor

ABSTRACT

Thermal desorption rates of silicon oxide layers, from 20 to 120 nm in thickness, on silicon substrates in vacuum have been accurately obtained from intervals between ring structures formed inside voids on the oxide layers. From the temperature dependence of the desorption rate, the activation energy and frequency factor of the desorption reaction have been derived as a function of the oxide thickness. The obtained values are compared with the previous studies, and as a result, the activation energy is found to be almost constant (~4 eV) in a wide range of the oxide thickness. The frequency factor decreases as the inverse square of the oxide thickness. The decomposition kinetics of the oxide layer is also discussed from the obtained results.

1. Introduction

Since the characteristics of a gate insulator determines the performance of metal oxide semiconductor field-effect transistors in integrated circuits, a great number of studies on the silicon oxides (SiO_2) on silicon substrates have been both experimentally and theoretically performed to form a high-quality gate oxide. The thermal desorption as well as the growth of the SiO_2 layers has attracted many researchers' attention because of its distinctive reaction behavior [1–20]. When the SiO_2 layer is subjected to high temperatures above ~720 °C in vacuum, interfacial reaction between the SiO_2 layer and a silicon substrate occurs, generating volatile SiO species as a result of the chemical process $SiO_2+Si \rightarrow 2SiO$ followed by the desorption from the surface [21]. The desorption process of the SiO_2 layer is inhomogeneous; the desorption starts with the formation of small voids, which expose the clean silicon surface, that grow laterally while the surrounding SiO_2 retains its initial thickness [1]. The desorption reaction can be represented by the following four steps: (1) the promotion of a lattice bound silicon atom to a mobile monomer in the void, (2) the migration of the monomer to the void periphery, (3) the production of the volatile intermediate complex (SiO) by the incorporation of the monomer into the SiO_2 layer, and (4) the desorption of the SiO species from the surface [2]. The rate of the step (1) is considered to be proportional to a void area, because the mobile monomer is promoted in the void. On the other hand, the rates of the steps (3) and (4) are considered to be proportional to a perimeter of the void and thus approximately a diameter of the void, because the reactions occur at the void periphery. The step (2) is expected to be independent of the void size. Therefore, the rate-limiting step of the desorption reaction can be revealed by investigating the void growth rate as a function of the void size. In fact, many studies on the rate-limiting step have been reported. Although the void growth rate proportional to the void area was reported by one research group [2,3], most of the studies showed that the growth rate was proportional to the void diameter [4–9,22–24]. Therefore, it is generally accepted that the rate-limiting step of the desorption reaction is the step (3) or (4), that is, the reaction at the void periphery, irrespective of the oxide thickness.

Since the activation energy of the desorption reaction also gives information about the rate-limiting step, it has been investigated by many workers. However, most of the studies have paid attention to ultrathin oxides or surface etchings by oxygen [8–12,21,25–31], and thus only few studies have reported the activation energy of the desorption reaction for the oxide layers at a thickness of above 1 nm. Hibino et al. investigated the activation energy and the frequency factor for the oxide layers at a thickness between 1.0 and 2.2 nm by low-energy electron microscopy (LEEM) [7]. The obtained activation energy was approximately 4 eV, irrespective of the oxide thickness. The value of 4 eV is close to the desorption energy of SiO from a Si(100) surface, which is theoretically estimated at 3.6–3.8 eV [32], indicating that the rate-limiting step is the reaction at the void periphery. However, since the result was obtained in a narrow range of oxide thickness, it is necessary for the determination of the activation energy and the rate-limiting steps to perform the measurements in a wide thickness range.

This study reports the activation energy and frequency factor of the desorption reaction for the thermal oxide layers at a thickness between

* Corresponding author.
E-mail address: enta@hirosaki-u.ac.jp (Y. Enta).

http://dx.doi.org/10.1016/j.susc.2016.10.007
Received 21 September 2016; Received in revised form 21 October 2016; Accepted 21 October 2016
Available online 22 October 2016
0039-6028/ © 2016 Elsevier B.V. All rights reserved.

20 and 120 nm. The desorption model mentioned above seems to be not appropriate for thicker oxide layers because it should be difficult for Si monomers to migrate to the upper side of the oxide layer. Therefore, it is expected that the activation energy depends on the oxide thickness. The main purpose of this study is to verify this assumption and to discuss the decomposition kinetics for thicker oxide layers on the basis of the obtained results. The void growth rate was measured by intervals between ring structures, which were recently found in the voids by our group [22–24]. The ring structures in the voids were formed by repeating annealing process and exposing the surface to a small amount of volatile organic compounds during cooling process [24]. The area surrounded by neighboring ring structures corresponds to the desorbed area during one annealing process. Since the temperature dependence of the void growth rate is measured at once without changing the sample, it can be accurately determined in a wide range of oxide thickness by scanning electron microscopic (SEM) measurements. Moreover, this method can eliminate the effect of the electron beam irradiation upon the oxide desorption [33–36], because SEM measurements are carried out after finishing the void growth.

2. Experimental

Mirror-polished, B-doped Si(100) wafers cut to a size of $20\times5\times0.5\ \mathrm{mm}^3$ were used as silicon substrates. The wafers were chemically treated by dipping in hydrofluoric acid, and then several thick oxide layers were grown on the substrates by dry oxidation with 100% oxygen gas at oxidation temperatures above 950 °C. The oxide thicknesses were measured by spectroscopic ellipsometry. After the samples were introduced into an ultrahigh vacuum (UHV) chamber at the base pressure of 2×10^{-8} Pa, they were annealed by direct resistive heating at temperatures in the range of 950–1150 °C to form void structures in the oxide layers. The sample temperatures were measured with an optical pyrometer. The annealing/cooling process was repeatedly carried out at different temperatures to investigate the activation energy of the void growth. Propanol (99.9%) vapor was introduced into the UHV chamber through a variable leak valve during cooling process to reproducibly form the ring structures. The surfaces of the samples were observed *ex situ* at room temperature by SEM using an Auger microprobe (JEOL Ltd. JAMP-9500F).

3. Results and discussion

Fig. 1 shows typical SEM images of the void-formed surface with the ring structures in a 20-nm-thick oxide layer. The process of annealing for 30 min and subsequent cooling for 5 min in vacuum was repeated eleven times. Propanol vapor was introduced at a pressure between 6.7×10^{-7} and 1.3×10^{-4} Pa for 2 min during the cooling process. Distinct ring structures are formed as can be seen in Fig. 1(b) and a region surrounded by neighboring ring structures corresponds to the area where the oxide was desorbed from the surface during the 30 min annealing process. The ring structures with even intervals clearly show that the void growth rate is proportional to the annealing time, and therefore that the rate-limiting step for the void growth is the step (3) or (4), that is, the reaction at the void periphery, as mentioned above. All samples at the oxide thickness of 20–120 nm showed the same behavior, which agrees with the previous studies [5–7].

The activation energy of the void growth rate was obtained by changing the annealing temperature systematically and measuring the intervals between the ring structures. Fig. 2 shows SEM images of the void-formed surfaces in (a) 20-nm-thick, (b) 30-nm-thick, and (c) 90-nm-thick oxide layers. The annealing/cooling durations are the same as that in Fig. 1, while the annealing temperature is systematically changed to obtain the activation energy. As the oxide layer was thicker the average of the annealing temperature was elevated, because the void growth rate became slower. The interval of the ring structures

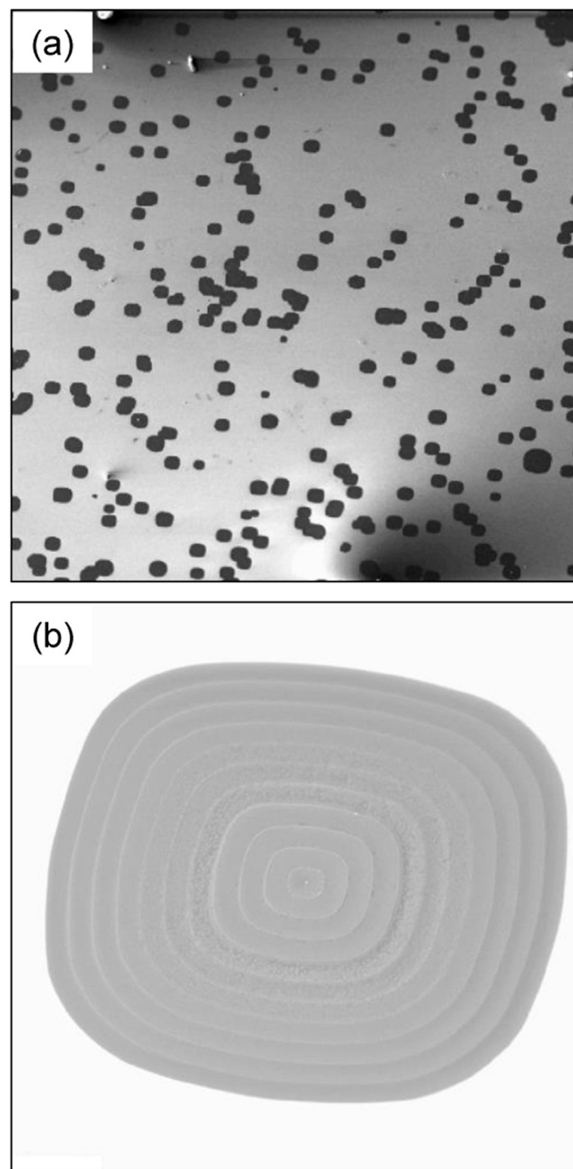

Fig. 1. Typical SEM images of void-formed surface with ring structures in a 20-nm-thick oxide layer. To form the ring structures, the process of annealing for 30 min and subsequent cooling for 5 min in vacuum is repeated eleven times. Propanol vapor is introduced at a pressure between 6.7×10^{-7} and 1.3×10^{-4} Pa for 2 min during the cooling process. The fields of view are (a) $1036\times1036\ \mu\mathrm{m}^2$ and (b) $36\times36\ \mu\mathrm{m}^2$.

becomes wider as the temperature increases. We can also observe the different shapes of the ring structures: the ring structures in the 20-nm-thick oxide layer are squares, whereas the ring structures in the 90-nm-thick oxide layer are circles. This is due to the difference in the annealing temperature. Although the void shape is basically dominated by the surface symmetry of the Si(100) substrate, it becomes isotropic by a thermal effect at higher temperatures [23]. Fig. 3 shows Arrhenius plots of the void growth rates obtained by the intervals of the ring structures. The data were fitted by a least-squares procedure, as shown by solid lines in Fig. 3. The activation energies (E_a) and frequency factors (A) obtained from fitting lines are summarized in Table 1. The activation energy is 4.06 ± 0.17 eV in a wide thickness range of 20–120 nm, and therefore seems to be independent of the oxide thickness. On the other hand, the frequency factor varies by more than two orders of magnitude, showing a strong dependence on the oxide thickness.

Hibino et al. reported the activation energy obtained by LEEM in a thickness range of 1.4–2.2 nm [7]. The values of the 1.4-, 1.8-, and 2.2-nm-thick oxide layers are 3.9, 4.1, and 4.2 eV, respectively, and thus

Download English Version:

https://daneshyari.com/en/article/5421360

Download Persian Version:

https://daneshyari.com/article/5421360

Daneshyari.com