



# Experimental investigation on oxidation kinetics of germanium by ozone



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## ABSTRACT

Oxidation kinetics of germanium surface by ozone at low temperature ( $\leq 400^\circ\text{C}$ ) is experimentally investigated. The growth process contains two regions: initial linear growth region and following parabolic growth region. The  $\text{GeO}_x$  thickness vs. oxidation time plot obeys the well-known Deal-Grove or linear parabolic model. The linear growth region contains reaction of oxygen atoms with surface bond and back bonds of outmost Ge layer. And the activation energy is experimentally estimated to be 0.06 eV. Such small activation energy indicates that the linear growth region is nearly barrier-less. The parabolic growth region starts when the oxygen atoms diffuse into back bonds of second outmost Ge layers. And the activation energy for this process is found to be 0.54 eV. Furthermore, in the ozone oxidation it is not  $\text{O}_3$  molecules but O radicals that go through the  $\text{GeO}_x$  film.

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## 1. Introduction

Germanium is a rather potential channel material to replace conventional Si [1]. This is due to its [1] high hole and electron mobility [2], process compatibility with Si technology, and [3] possible voltage scaling due to a narrow band gap [2,3]. The passivation of Ge surface is a main issue for its successful application. Several methods have been explored for Ge surface passivation such as N plasma treatment of Ge surface [4–8], Si covering on Ge [9,10], and Ge sub-oxide or dioxide ( $\text{GeO}_x$ ) passivation [1,2,7,11–19]. Of all these methods,  $\text{GeO}_x$  interlayer shows powerful vitality. This method shows excellent electrical properties such as low interface trap density and enhanced inversion mobility [20,21]. Several oxidation methods have been reported such as oxygen plasma [7,13–15], atmospheric pressure  $\text{O}_2$  oxidation at  $\sim 550^\circ\text{C}$  [11,12], high pressure  $\text{O}_2$  ( $\sim 70$  atm) at  $\sim 550^\circ\text{C}$  [16,17], high density radical oxidation [2,25], and ozone oxidation [1,18,19]. All these technologies provide favorable electrical properties. Although Ozone oxidation is an important method to grow Ge oxide and passivate Ge surface [9,19,26], the kinetics of Ge oxidation by ozone has not been comprehensively reported. Thus our paper investigates the

kinetics of Ge oxidation by ozone. The understanding of oxidation kinetics is essential to engineering the  $\text{GeO}_x$  growth and improving electrical performance of related device.

In this paper, the kinetics mechanism of Ge surface oxidation by ozone at low temperature is investigated. It is found that the  $\text{GeO}_x$  thickness vs. oxidation time plot obeys the well-known Deal-Grove or linear parabolic model [27]. The growth process contains two regions: initial linear growth region and the following parabolic growth region. The linear growth region contains the reaction of oxygen atom with surface bonds and back bonds of outmost Ge atoms. And the activation energy is experimentally estimated to be 0.06 eV, which is rather small and indicates that the linear growth region is nearly barrier-less. The parabolic growth region starts when the oxygen atom is inserted into back bonds of second outmost Ge layers. And the activation energy for this process is found to be 0.54 eV.

## 2. Experimental

The starting substrate was 2  $\mu\text{m}$  thick (100) epitaxial Ge on 8 in. (100) Si. The sample was first cleaned in diluted HF ( $\text{HF}:\text{H}_2\text{O}$ , 1:100) for 1 min at room temperature to remove the native oxide, and subsequently rinsed in deionized water for 1 min. Then the sample was immediately loaded into ultrahigh vacuum chamber within 1 min. After that, the sample surface was subjected to a flow of ozone gas to form Ge sub-oxide or dioxide ( $\text{GeO}_x$ ). Five different

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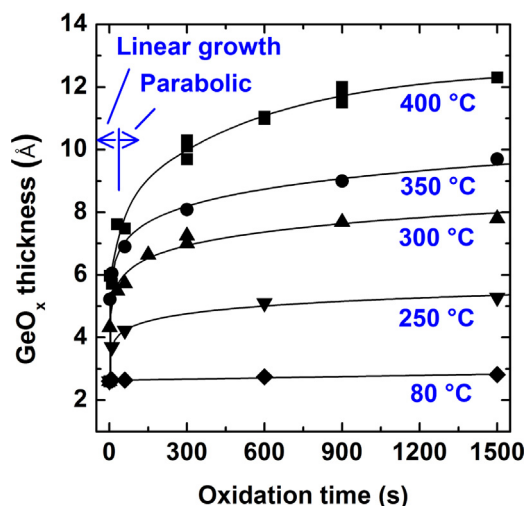


Fig. 1. GeO<sub>x</sub> thickness vs. oxidation time at temperatures from 80 °C to 400 °C.

temperatures were used in the oxidation process, i.e., 80 °C, 250 °C, 300 °C, 350 °C and 400 °C. The chamber pressure was ~2.4 Torr. The partial pressure of O<sub>3</sub> was evaluated as follows. The O<sub>3</sub> was 10 vol% in the O<sub>2</sub>/O<sub>3</sub> mixture in our experiment. Thus, similar to calculation method in review paper by Fink et al. [28] the partial pressure of O<sub>3</sub> can be calculated to be  $2.4 \times 10\% = 0.24$  Torr based on Dalton's law of partial pressures. The GeO<sub>x</sub> thickness was measured by X-ray photoelectron spectroscopy (XPS). The chemical states and atomic structure of GeO<sub>x</sub>/Ge sample were characterized by XPS. The XPS was recorded using Thermo Scientific ESCALAB 250xi equipped with a monochromatic Al K $\alpha$  radiation source. All the high resolution spectra were collected with pass energy of 15 eV.

### 3. Results and discussion

#### 3.1. GeO<sub>x</sub> thickness vs. oxidation time

Fig. 1 shows the GeO<sub>x</sub> thickness as a function of ozone oxidation time in temperature range from 80 °C to 400 °C. The data shows an increase in the oxidation rate with higher temperature. After 25 min oxidation in ozone, the GeO<sub>x</sub> thicknesses are about 2.8, 5.28, 7.8, 9.7, and 12.3 Å at 80 °C, 250 °C, 300 °C, 350 °C, and 400 °C, respectively. Furthermore, an initial linear growth of GeO<sub>x</sub> is observed below ~10 s, and then it becomes parabolic as the oxidation time increases. The two different growth modes suggest that two physical/chemical oxidation mechanisms are involved in the oxidation process. Because similar oxidation phenomenon was observed for Si substrate which can be effectively interpreted by the Deal-Grove or linear parabolic model [27], we suppose that in the region of initial linear growth in Fig. 1, the oxidation is determined by chemical reaction occurring at the GeO<sub>x</sub>/Ge interface. While in the region of parabolic growth, the oxidation is limited by diffusion process of oxygen atoms through GeO<sub>x</sub>.

In order to accurately understand the reaction mechanisms of Ge oxidation by ozone, the Arrhenius temperature dependence of oxidation process is investigated for each oxidation growth region. Fig. 2 shows the Arrhenius plot of linear rate constant ( $B/A$ ) in the initial linear growth region. The  $B/A$  is obtained by fitting linear region in Fig. 1, based on Eq. (6.28) in Ref. [27]. The activation energy is calculated to be 0.06 eV. This rather small activation energy indicates that the initial linear growth is nearly barrier-less. And this activation energy is nearly equal to that of Si surface oxidation by ozone [28–31].

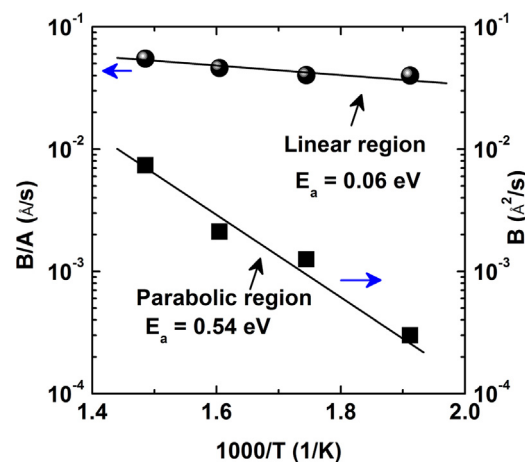


Fig. 2. Arrhenius plots for initial linear region and following parabolic region.  $E_a$  means activation energy.

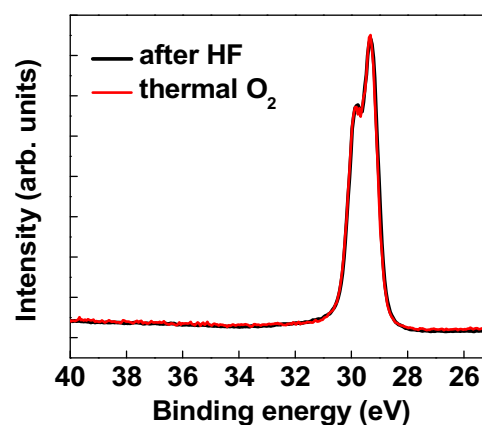


Fig. 3. Ge 3d spectra for samples after HF clean and after thermal O<sub>2</sub> at 400 °C.

Then the reaction mechanism in the parabolic growth region is investigated. The oxidation is diffusion limited and can be described as follows [27]

$$d^2 - d_0^2 = B(t - \tau) \quad (1)$$

where  $d$  is GeO<sub>x</sub> thickness.  $d_0$  is the thickness of existing GeO<sub>x</sub> at the start of parabolic growth.  $B$  is the parabolic rate constant.  $t$  is the oxidation time.  $\tau$  accounts for the time at the start of parabolic growth. Fig. 2 shows the Arrhenius plot for parameter  $B$ . The activation energy is found to be 0.54 eV, which is dramatically reduced compared to the reported value of thermal oxidation in O<sub>2</sub> [32,33]. The small activation energy in ozone oxidation is mainly due to the higher reactivity of oxygen atoms rather than oxygen molecules to diffuse through GeO<sub>x</sub>, breaking Ge–Ge bond and creating Ge–O–Ge bond. Obviously, the atomic species supplied by ozone induces a reaction pathway which is much more effective than O<sub>2</sub> species.

100% ozone cannot be obtained by using any ozone generator. Thus the ozone/O<sub>2</sub> mixture gas appears in the oxidation chamber. And the ozone proportion in ozone/O<sub>2</sub> gas is ~10% for the ozone generator in our experiment. However, we will show that only the ozone contributes to the Ge oxidation. Indeed, we have analyzed the thermal O<sub>2</sub> oxidation of Ge at 400 °C. We performed the thermal O<sub>2</sub> oxidation by closing the ozone generator, and only O<sub>2</sub> gas was introduced into the chamber. The process pressure in the oxidation chamber was 1.84 Torr. Fig. 3 shows the Ge 3d spectrum for sample in thermal O<sub>2</sub> after 10 min oxidation. It can be seen that there is no oxygen uptake, indicating that Ge cannot be oxidized in thermal O<sub>2</sub> at 400 °C in our experiment. This experimental result is consistent

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