



Germanium substrate loss during thermal processing

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ABSTRACT

Germanium layers are very attractive for future semiconductor devices due to their high carrier mobility. To form pn-junctions in such devices, ion implantation followed by an annealing step is the most feasible way. Several previous studies reported severe surface degradation during annealing of germanium without a capping layer. The observed deteriorations are, e.g., heavy surface roughness or even loss of bulk material. To study the loss of germanium, samples with patterned silicon dioxide layer were annealed at temperatures between 500 and 600 °C in different atmospheres. The chosen atmospheres were selected to be nominally inert (N₂, Ar, or vacuum). Yet, the samples showed rates of substrate loss, e.g., up to 3 nm/min at 600 °C in Ar atmosphere. The resulting rates of substrate loss can be approximately described by Arrhenius laws with an activation energy of 2.08 ± 0.21 eV in the case of Ar. Direct evaporation of germanium or germanium dioxide can be excluded because of the low vapor pressures reported in the literature. As mechanism, we propose the evaporation of germanium monoxide formed with residual oxidants such as oxygen or water vapor in the atmosphere used for processing. Rough calculations exhibit that a desorption rate of about 10^{-8} mol GeO per min is required in our experiments to achieve the maximum rate of substrate loss in argon at 600 °C. Results for the different atmospheres will be compared.

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1. Introduction

Current predictions of the International Technology Roadmap for Semiconductors (ITRS) [1] forecast an increasing use of high-mobility semiconductors for aggressively scaled high-speed devices. Therefore, germanium is nowadays of renewed scientific interest for future highly integrated circuits.

During manufacturing processes of integrated circuits, thermal steps are common, e.g., annealing of ion implanted layers. Though, several studies reported substrate loss during thermal processing [2–4] of uncapped germanium.

Recently, Ioannou et al. [4] presented a detailed study of the dose loss and the loss of germanium substrate material during annealing in nitrogen. But there are also other processing steps at elevated temperatures like surface cleaning by evaporation of the native oxide [5] during which loss of substrate material may occur. Thus, more information about the loss of substrate material is necessary. This study deals with the influence of gases, pressure, and mass flow on the loss of substrate material.

2. Experiments

Ge wafers (orientation (100), Ga doped, resistivity approximately 0.4 Ω cm) were obtained from Umicore. The wafers were

cleaned with diluted H₂O₂ and HF, and rinsed in de-ionized (DI) water. After plasma-enhanced chemical vapor deposition (PECVD) of 100 nm silicon dioxide (SiO₂), a lithography step was performed. The wafers were etched in buffered oxide etch (BOE) to pattern the oxide. The lithography resist was removed by acetone. The wafers were scribed and broken into small rectangular pieces, rinsed again in DI water and blown dry in nitrogen.

Subsequently, the samples were annealed in nitrogen (atmospheric pressure), argon (atmospheric pressure) or vacuum ($\sim 10^{-4}$ Pa) at temperatures in the range of 500–600 °C for up to 96 h. The annealing time periods used were chosen to achieve a step height between the capped and the uncapped area of approximately 200 nm according to the equation given by Ioannou et al. [4], e.g., 120 min at a temperature of 550 °C. Additional annealing experiments were twice and tenfold longer. The gas flow was varied between 0.1 and 1 SLM (standard liter per minute) for argon and between 2 and 10 SLM for nitrogen, respectively. Two resistively heated furnaces with volumes of 12 and 86 l were used. Typical heating rates were in the range of 10 K/min. Additionally, one sample was lamp-annealed in the chamber of a Varian 350D implanter with an experimental sample holder at 1.1×10^{-3} Pa. Apart from two samples, the silicon dioxide was removed by BOE. The samples were rinsed in DI water and blown dry with nitrogen.

The samples were characterized by the use of interferometry, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Focused ion beam (FIB) processing was used for preparation of cross-sectional SEM pictures.

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Referring to published wet chemical etch rates [6], the loss of germanium material during sample preparation is negligible. Interferometry gave a step height of less than 0.5 nm between the capped and uncapped area of an unannealed control sample, which may be due to growth of a natural oxide on the uncapped germanium.

3. Results

The atmospheres used in this study are nominally inert (99.9999% N₂, 99.9999% Ar, or vacuum of $\sim 10^{-4}$ Pa). However, the samples showed loss of germanium material. Fig. 1 shows the substrate loss rate as a function of the inverse temperature. The samples of the data set of a gas flow of 10 SLM N₂ were annealed in the furnace with a volume of 86 l. All other samples were annealed in the furnace with a volume of 12 l. In contrast to Ioannou et al. [4], we used only one sample per data point in the Arrhenius plot. The periods of annealing at each temperature were identical for the different atmospheres. But the clear differences observed experimentally indicate a great influence of the atmosphere on the loss rate. Similar results were also obtained if the systems was flushed several extra times before annealing. However, the loss rates can be well described by Arrhenius laws for all atmospheres

$$R = R_0 \exp\left(-\frac{E_a}{kT}\right). \quad (1)$$

The extracted prefactors R_0 and activation energies E_a are summarized in Table 1. Tenfold longer annealing times led to a reduction of the loss rate. To illustrate the influence of annealing time, the substrate loss rates from tenfold longer annealing in argon atmosphere are given in Fig. 1.

We disregarded in the results reported in Fig. 1 the natural oxide on germanium as well as ramp-up and cooling-down of the system. During ramp-up and cooling-down, substrate loss should also occur. Consequently, the calculated rates are overestimated. In the case of annealing for 30 min in argon at 600 °C, the thermal etch rate can be estimated to be up to 30% too high. In general, the overestimation of the loss rate is largest for high temperatures and short process times. However, for the longer time periods used at lower temperatures, this problem is of minor

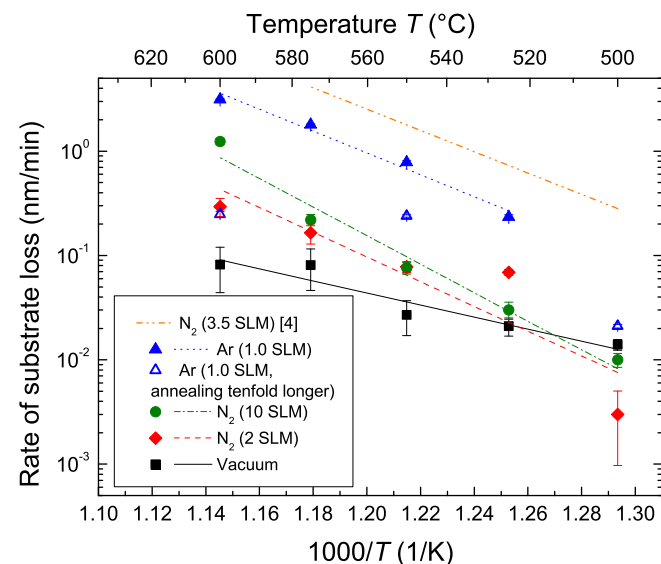


Fig. 1. Arrhenius plots of germanium substrate loss rate measured by interferometry. The results of Ioannou et al. [4] is given for comparison.

Table 1

Overview of obtained values for the Arrhenius law of germanium substrate loss in different atmospheres.

	Prefactor R_0 (nm/min)	Activation energy E_a (eV)
Vacuum ($\sim 10^{-4}$ Pa)	3.69×10^5	1.15 ± 0.20
2 SLM N ₂	1.62×10^{13}	2.35 ± 0.63
10 SLM N ₂	4.00×10^{15}	2.71 ± 0.24
1.0 SLM Ar	3.62×10^{12}	2.08 ± 0.21
3.5 SLM N ₂ [4]	4.75×10^{12}	2.03

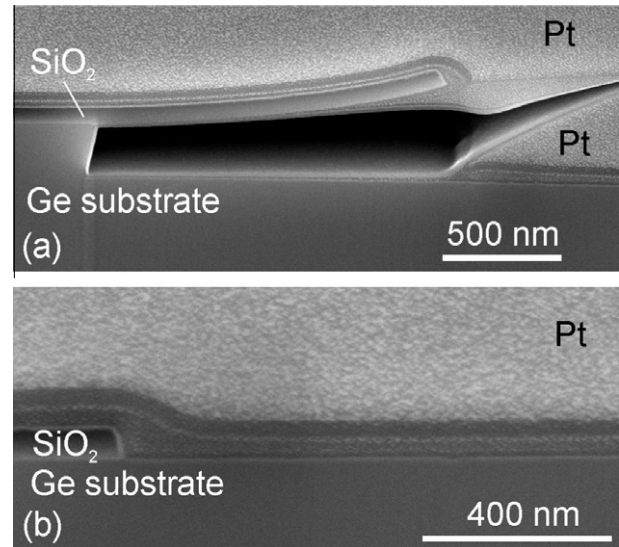


Fig. 2. Cross-sectional SEM picture of samples with patterned SiO₂ capping layer annealed (a) at 550 °C for 240 min in Ar and (b) at 550 °C for 120 min in vacuum of 4×10^{-3} Pa.

importance. Yet, the calculation of more precise steady-state rates will not be addressed in this paper.

In Fig. 2, two cross-sectional pictures are given. The sample of Fig. 2(a) has been annealed for 4 h at 550 °C in argon. The germanium below the SiO₂ mask shows significant lateral etching which exceeds the vertical etching by far. The use of SiO₂ as a masking layer for thermal processes is therefore disadvantageous in this case because of lateral thermal etching. However, this phenomenon cannot originate directly from outgassing of oxygen from the SiO₂ layer. Fig. 2(b) shows a sample annealed at 550 °C for 120 min in vacuum of 4×10^{-3} Pa with a patterned SiO₂ layer. Interferometry gave a step height of less than 1 nm in this case. As a consequence, we assume that substrate loss is caused by the atmosphere.

We also observed the formation of etch pits, which have the geometry of four-sided pyramids. These pits may also form at the rim of a SiO₂ mask as shown in Fig. 3. The respective sample was annealed in vacuum at 1.1×10^{-3} Pa for 60 min at 600 °C. The step height measured by AFM was as low as 1.5 nm. Yet, the pyramids had a depth of almost 200 nm. Etch pits formed also during annealing in argon or nitrogen at atmospheric pressure. However, pit formation or its relation to substrate loss is not addressed in this study.

4. Discussion

In this section, we discuss first possible origins of substrate loss. For severe substrate loss rates, we can neglect simple evaporation of the native oxide. For the thickness of the native oxide, values between 1 and 5 nm were reported, depending on prior treatments of

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