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# The surface blistering kinetics and the H-platelet evolution in H-implanted germanium

Fan Yang [a], Xuan Xiong Zhang [a,b,*], Tian Chun Ye [a], Song Lin Zhuang [b]

[a] Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China
[b] Shanghai Key Laboratory of Modern Optical System, University of Shanghai for Science and Technology, Shanghai 200093, China

A R T I C L E I N F O

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A B S T R A C T

The surface blistering phenomenon produced in H-implanted Ge by a series of low temperature annealing processes was investigated. The kinetic plot of the onset of blistering contains a break point that separates the straight-line plot into two parts, with two distinct slopes based on the calculated activation energy from the different temperature regions for $3\times10^{16}\,cm^{-2}$ and $5\times10^{16}\,cm^{-2}$ H-implanted doses. This plot indicates the existence of distinct, temperature dependent mechanisms, probably caused by the release of different types of H-platelets. The turning direction (from low to high temperature) of the Arrhenius plot with the break point is contrary to that of other known materials. The formation and evolution of the H-platelets under the Ge surface was revealed by TEM (transmission electron microscopy). The TEM results demonstrate that the $\langle 0\,0\,1\rangle$ platelets parallel to the sample surface are first produced by a low H implantation dose; however, the vertical $\langle 0\,1\,0\rangle$ platelets perpendicular to the sample surface form later as the H implantation dose increases. The H-platelets combine with each other, becoming micro-cracks. The {1 1 1} and {3 1 1} micro-cracks serve as interconnections between the $\langle 0\,0\,1\rangle$-oriented micro-cracks below the substrate surface. Finally, the accumulated $H_2$ pressure in the cracks deforms the surface to generate Ge surface exfoliation.


## 1. Introduction

In the recent years, there has been significant interest in germanium and III–V semiconductor integration with silicon substrates for the enhancement of carrier mobility in future transistors because the current transistor, based on bulk silicon CMOS, is reaching the physical limits of silicon. Germanium has attracted significant attention because of its higher carrier mobility compared to silicon (approximately $2\times$ for an electron and $4\times$ for a hole). Germanium technology is also compatible with the present silicon processes and bridgeable to GaAs because of the almost consistent lattice constant, which facilitates epitaxy [1–3]. Although the narrow bandgap (0.66 eV) of germanium will lead to current leakage, this effect can be suppressed by GeOI (germanium-on-insulator) structures, which are similar to SOI (silicon-on-insulator).

Smart-cut technology is a popular approach to achieve thin-layer transfer, using the combination of ion implantation and wafer bonding to produce structures like SOI [4], GeOI [5] and other heterostructures [6–9]. Therefore, the study of the surface blistering of H-implanted germanium is of primary importance for the manufacture of GeOI by Smart-cut. A 200 mm GeOI wafer with a high defect density has been obtained using Smart-cut technology [10], but there are only a few papers concerning the annealing blistering kinetics of a germanium wafer implanted by hydrogen or/and helium [5,11–14]. Ref. [15] showed that a duration of more than 20 h was required to obtain highly uniform strength from a 120 °C annealing process for Si/Si bonding, but the longest isothermal annealing in the study [5,11–14] of germanium blistering at relatively high temperature lasted less than 15 h. Heterogeneous wafer bonding should be carried out at as low a temperature as possible to avoid the blisters formed ahead of strong wafer bonding, which makes the layer transfer invalid. As a result, the blistering of the germanium surface during lower temperature annealing for longer annealing times must be explored. Better understanding of the evolution of H-platelets from their as-implanted state to the state in which they form micro-cracks is required to achieve ideal layer transfer.

In this paper, we present an experimental investigation of germanium blistering kinetics at low temperature ranges for long annealing time in H-implanted germanium wafers. First, the Arrhenius plots with a break point were produced; then, the activation energies in the high and low temperature regions for each dose were determined by a fitting calculation. The unusual turning direction of the kinetic straight-line, from low to high

* Corresponding author at: Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China. Tel.: +86 10 82995590; fax: 86 10 62021601.
*E-mail address:* xuanxiongzhang@yahoo.com.cn (X.X. Zhang).

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temperature, is opposite to that of known materials. This phenomenon is tentatively explained in terms of diverse H–Ge binding energies. The variation of H-platelet orientation with increasing H-implanted dose was observed by TEM.

## 2. Experimental

N-type 2-in. double-side polished (1 0 0) Ge wafers were implanted with H at doses of $3\times10^{16}\,cm^{-2}$ and $5\times10^{16}\,cm^{-2}$ at an energy of 60 keV. The wafers were tilted at an angle of 7° with respect to the ion beam in order to minimize the ion channeling effect during implantation. After implantation, the wafers were cut into small pieces and annealed at low temperature under ambient atmosphere. It is worth noting that the samples were loaded into the furnace at room temperature and then heated to the annealing temperature by increasing the temperature at a rate of 2 °C/min for various durations. There was a reason for using this method to mitigate the stress from the difference of thermal expansion coefficients in the future heterogeneous integration by wafer bonding. To determine the blistering onset time, one small piece was isothermally annealed for several minutes or hours at a fixed temperature, and an Olympus optical microscope was used to detect the formation of surface blisters. When the sample had been heated for the designated time and surface blisters were not found, another piece of the same material was annealed for a longer time at the same temperature, and this process was continued until surface blisters could be just optically observed. The evolution of blisters into craters after further extended annealing was characterized by optical microscopy. AFM (atomic force microscopy) tests were carried out on the surfaces of the samples to characterize the surface roughness and three dimension profiles before and after annealing. The microstructures underneath the germanium surface were characterized by cross-section transmission electron microscopy (XTEM) with a FEI Tecnai G2 F20 S-TWIN instrument. For TEM sample preparation, the pieces were polished to approximately 50 μm thickness and ion thinned for observation.

## 3. Results and discussion

The Arrhenius plot of the blistering time (plotted as $\ln(1/t)$) as a function of the inverse of the absolute annealing temperature (plotted as $1/kT$, where $k$ is the Boltzmann constant) is shown in Fig. 1. The plot is fitted by linear functions in the different temperature regions, according to their distinct slopes. The kinetic straight-lines are divided into two parts, and the turning directions of the curves with respect to the different temperature intervals are opposite to those of silicon and other known materials. Hurley et al. [14] also observed a discontinuity in the Arrhenius straight-line in H and He co-implanted germanium, and they observed that the activation energy at moderate temperatures was much higher than at low temperatures. They attributed the reversed activation energy between the low and moderate temperatures to helium implantation. However, the presence of helium cannot be used to explain the phenomenon in our experiments. The literature [16] reveals the existence of analogous defects in hydrogen-implanted silicon and germanium, but the decomposition process of the defect complexes involved in blistering is different in germanium and silicon [17]. Moreover, the binding energies of Ge–H complexes are much lower than those of Si–H because of the weaker Ge–H bond [18]. The change of the activation energies from high to low temperature is reduced, from 2.08 eV to 0.69 eV for $3\times10^{16}\,cm^{-2}$H implantation and from 2.12 eV to 0.52 eV for $5\times10^{16}\,cm^{-2}$H implantation.

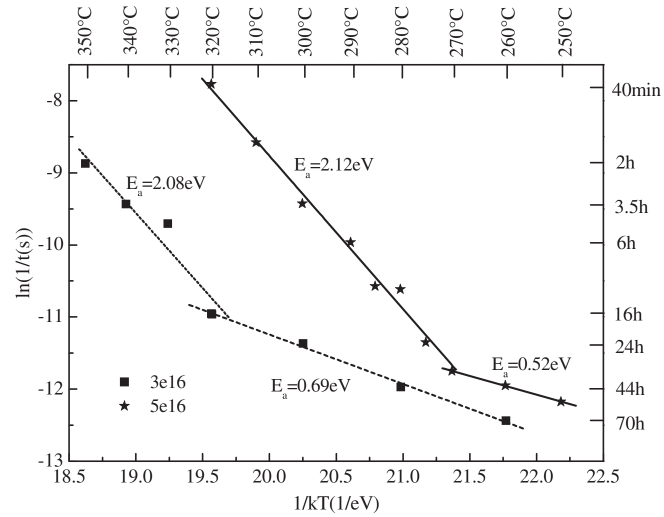


**Fig. 1.** Arrhenius plots of blistering onset (time) as a function of annealing temperature for H-implanted germanium with doses of $3\times10^{16}$ and $5\times10^{16}\,cm^{-2}$ with 60 keV energy implantation.

This change may be related to the combination of different blistering mechanisms at high and low temperatures. We infer that hydrogen should be gradually released from low to high temperature during the blistering process as a reverse reaction of the defect complexes, according to the H-platelet binding energy difference in germanium. The activation energies calculated from the least squares fit are consistent with the Ge–H complex binding energies reported in Ref. [19] (~0.5 eV for (2Ge–H) and $H_2^*$ complexes, ~2.0 eV for ($2Ge–H+2H_2$) complexes).

In addition, the formation and the evolution of the subsurface defects in low temperature ranges are also studied by TEM. Fig. 2 shows the XTEM images of the as-implanted samples at $3\times10^{16}\,cm^{-2}$ and $5\times10^{16}\,cm^{-2}$H implantation doses. A large number of extended defects, the majority of which are H-platelets originating from hydrogen implantation, form a damaged zone underneath the germanium surface. The width and defect density of the damage band increase as the H implantation dose increases, as can be seen by comparing Fig. 2a (for $3\times10^{16}\,cm^{-2}$) with Fig. 2b (for $5\times10^{16}\,cm^{-2}$) for the as-implanted state. Because more H-platelets are involved in the formation of surface blisters for a higher implanted dose, it takes shorter time for blistering to occur at the same temperature. This relationship explains the shift to the right of the kinetic plot for $3\times10^{16}\,cm^{-2}$ dose compared to the $5\times10^{16}\,cm^{-2}$ plot (see Fig. 1). Meanwhile, as can be seen in the inset pictures from the high resolution TEM in Fig. 2, most of the induced H-platelets are inclined to lie on certain crystal orientations, like {0 0 1} and {1 1 1} (not shown in the picture). It is obvious that the induced H-defects are mainly formed on the Ge (0 0 1) plane, parallel to sample surface in Fig. 2a, but many ⟨0 1 0⟩ platelets perpendicular to (0 0 1) can also be clearly seen in Fig. 2b as the H implantation dose increases. We speculate that the vertical platelets perpendicular to (0 0 1) are probably produced by location saturation of the preferential ⟨0 0 1⟩ platelets.

During isothermal annealing, the H-platelets develop by an Ostwald ripening process until the micro-crack formation due to the merger of the extended platelets with each other results in cavities (H-implanted germanium annealed at 300 °C for 24 h for $3\times10^{16}\,cm^{-2}$ dose, and 4 h for $5\times10^{16}\,cm^{-2}$ doses shown in Fig. 3a and b, respectively). The ⟨0 0 1⟩ H-platelets and the ⟨0 1 0⟩ platelets (vertical to ⟨0 0 1⟩) are combined by the interlinked micro-cracks (shown in the inset pictures from high resolution TEM in Fig. 3b) after a 300 °C annealing for 4 h. The growth of the vertical cracks produces tangles of ⟨0 0 1⟩