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Low temperature exfoliation process in hydrogen-implanted germanium layers

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The feasibility of transferring hydrogen-implanted germanium to silicon with a reduced thermal budget is demonstrated. Germanium samples were implanted with a splitting dose of $5 \times 10^{16}$ H$_2$ cm$^{-2}$ at 180 keV and a two-step anneal was performed. Surface roughness and x-ray diffraction pattern measurements, combined with cross-sectional TEM analysis of hydrogen-implanted germanium samples were carried out in order to understand the exfoliation mechanism as a function of the thermal budget. It is shown that the first anneal performed at low temperature ($\approx$150 °C for 22 h) enhances the nucleation of hydrogen platelets significantly. The second anneal is performed at 300 °C for 5 min and is shown to complete the exfoliation process by triggering the formation of extended platelets. Two key results are highlighted: (i) in a reduced thermal budget approach, the transfer of hydrogen-implanted germanium is found to follow a mechanism similar to the transfer of hydrogen-implanted InP and GaAs, (ii) such a low thermal budget ($<$300 °C) is found to be suitable for directly bonded heterogeneous substrates, such as germanium bonded to silicon, where different thermal expansion coefficients are involved. © 2010 American Institute of Physics. [doi:10.1063/1.3326942]

I. INTRODUCTION

Transfer of thin semiconductor layers by exfoliation has received a lot of attention since its first implementation for silicon-on-insulator (SOI) fabrication.1 The implantation of hydrogen or inert gas into single crystalline semiconductor substrates leads to formation of a defective region below the surface. Under high temperature treatment, usually in the range of 400 to 500 °C, hydrogen molecules tend to be trapped in these defects and form pockets of gas at the projected range, commonly referred to as ‘blisters’. As temperature and/or anneal time increase, the internal pressure inside the blisters increases and results in the formation of microcracks which triggers the splitting of a thin semiconductor layer.2,3 The mechanisms which govern defect formation in H-implanted semiconductors and the creation of microcracks has already been extensively characterized in silicon, germanium,4 and III–V compounds.5 It is often addressed from a wafer bonding perspective and targets a range of applications varying from the fabrication of low defective substrates for complementary metal-oxide-semiconductor compatible applications [SOI and germanium-on-insulator substrates “GeOI” (Ref. 6)] to advanced photonic devices like avalanche photodiodes and solar cells.7,8 The thermal budget required to generate microcracks is a sensitive matter for direct wafer bonding. The temperature range that is commonly considered lies above 400 °C. However, such a high temperature is expected to induce significant modification of the bonded interface in heterogeneous substrates due to thermal expansion mismatch. This may result in poor bond strength and in degraded quality of the bonded interface.8,9

In the present work, the feasibility of transferring hydrogen-implanted germanium to silicon with a reduced thermal budget is investigated. Recently, co-implantation of hydrogen and helium for low temperature (300 °C) exfoliation of germanium has been successfully demonstrated.10 This approach presents a relatively long time-to-blisters anneal at a temperature of 300 °C (60 min). In this paper, an exfoliation process which does not require any helium co-implant is investigated which significantly reduces the time required for exfoliation at temperatures near 300 °C. This process is based on a long defect nucleation step at low temperature (≤150 °C), followed by a very short time anneal (STA) at higher temperature (300 °C). With this technique, complete exfoliation has been successfully demonstrated for hydrogen-implanted III–V materials such as InP and InAs.11,12 The benefits expected from this two-step process for direct wafer bonding are twofold, the low defect nucleation anneal enhances bond strength without degrading the bonded interface morphology, and the STA induces minimum strain within bonded materials with dissimilar thermal expansion coefficients.

II. EXPERIMENTS

4 in. ⟨100⟩-orientated n-type germanium wafers (Sb doped, 0.03 Ω cm) were used for this experiment. Prior to H-implant, a 100 nm thick layer of plasma-enhanced chemi-
Prior to direct bonding, 100 nm of PECVD SiO$_2$ was wafer to a single side polished 4 in. p-type/Ge substrates were implanted at room temperature with H$_2$ and densified at 600 °C. Germanium substrates were implanted with hydrogen due to lack of wafer cooling during gasonic clean with DI water. Their surfaces are hydrophilic DI water cleans. Both wafers were then subjected to a mechanical clean followed by four cycles alternating 1200:1 HF:H$_2$O and DI water cleans. Both wafers were then subjected to a megasonic clean with DI water. Their surfaces are hydrophilic.

Following XRD measurements, a set of different anneal conditions was then considered in order to estimate the optimum thermal process to induce exfoliation. Implanted samples were encapsulated and sequentially annealed according to conditions described in Table I. The onset of blistering was determined by tapping mode atomic force microscopy (AFM) and by optical microscopy. Prior to surface morphology characterization, samples were cleaned in deionized (DI) water. Cross-sectional transmission electron microscopy (X-TEM) was performed to characterize the evolution of cracks created by hydrogen implant, as a function of thermal budget.

In addition to blister tests, germanium exfoliation was tested after direct bonding of an H$_2$$_2$ implanted germanium wafer to a single side polished 4 in. p-type (100) silicon wafer. Prior to direct bonding, 100 nm of PECVD SiO$_2$ was deposited on the silicon wafer. After oxide densification, 2 µm-deep channels were patterned through the oxide and the silicon in order to facilitate the release of by-products generated during wafer bonding and annealing. The Si wafer was cleaned in a standard clean 1-equivalent solution. The germanium wafer involved in the direct bonding experiment was implanted with implant conditions comparable to those used for blister tests. The implanted germanium wafer was cleaned in a 1:1 NH$_4$$_2$H$_2$O solution dispensed in a spray acid tool followed by four cycles alternating 1200:1 HF:H$_2$O and DI water cleans. Both wafers were then subjected to a megasonic clean with DI water. Their surfaces are hydrophilic prior to the bonding. Wafers were loaded in an Applied Microengineering Ltd. (United Kingdom) bonding chamber which was pumped down to 10$^{-5}$ mbar. The wafers were exposed for 10 min to free oxygen radicals generated by a plasma ring. Wafers were bonded under a pressure of 1000 N applied for 5 min. The wafers were annealed in situ at 100 °C for 1 h with an applied pressure of 500 N followed by an ex situ anneal at 130 °C for 24 h in order to enhance bond strength and induce hydrogen platelet nucleation. The ramp-up rate was set to 0.5 °C/min in both cases in order to minimize the formation of thermally generated voids at the bonded interface.

The exfoliation was triggered by a 5 min STA at 300 °C.

### III. RESULTS AND DISCUSSION

#### A. Low temperature hydrogen diffusion

Defect nucleation, hydrogen coalescence in implant-generated defects, i.e., leads to the formation of hydrogen platelets and cracks in the bulk of the implanted semiconductor (Si, Ge, SiC, InP...). Such hydrogen-filled cavities have been reported to be located at a depth between the hydrogen projected range$^4$ and the germanium vacancy range below the germanium surface. Lattice deformation induced by these cavities generates surface blisters which are optically visible (Fig. 1). The evolution of the nucleation process can thus be monitored using AFM.

Significant hydrogen coalescence in III–V materials such as InP and GaAs has already been reported after long anneals at 150 °C.$^{11,12}$ In addition, dependence between the lowest temperature required to trigger the nucleation process and the melting point of the implanted material has also been highlighted in previous work.$^5$ As the melting point of germanium (937 °C) is close to the melting point of InP (1060 °C), defect nucleation would be expected to occur at 150 °C or below in hydrogen-implanted germanium. To study this effect, surface roughness measurements after long (22 h) anneal at 100, 130, or 150 °C have been performed. Root mean square (RMS) roughness values are detailed in Table I. As compared to as implanted germanium, these long anneals at 100, 130, and 150 °C do not modify surface

#### Table I. Germanium surface roughness, as measured by AFM, following long time anneals at low temperature ($\leq$200 °C). Scan area is 50 µm × 50 µm unless specified.

<table>
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<tr>
<th>Condition</th>
<th>RMS roughness (nm)</th>
<th>Scan area</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-implanted</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>After 100 °C anneal—22 h</td>
<td>0.4</td>
<td>10×10 µm$^2$</td>
</tr>
<tr>
<td>After 130 °C anneal—22 h</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>After 150 °C anneal—22 h</td>
<td>0.4</td>
<td>10×10 µm$^2$</td>
</tr>
<tr>
<td>After 200 °C anneal—19 h</td>
<td>23.9</td>
<td></td>
</tr>
</tbody>
</table>
roughness significantly. However these anneals promote some migration of the hydrogen, as shown by cross-sectional TEM and XRD.

X-TEM micrographs confirm that low temperature annealing promotes the nucleation of small platelet defects. These nanocracks are parallel to the substrate surface and are located close to the implant projected range (region II) [Figs. 2(a) and 2(b)(1)]. The formation of these nanocracks is known to be limited by the breaking of Ge–H lattice bonds and by hydrogen diffusion. The length of most of these cracks does not exceed 50 nm and their propagation causes minor lattice deformation [Fig. 2(b)(2)]. Consequently, these nanocracks do not modify the surface morphology significantly, as compared to as implanted germanium. It must be noted that this result does not hold for implanted germanium annealed at 200 °C for 19 h suggesting that the minimum thermal budget needed to trigger germanium exfoliation lies between 150 and 200 °C. This result is in agreement with previously reported time-to-blister for H$_2$ implanted germanium samples (implant energy and dose are 160 keV and 5 x 10$^{16}$ cm$^{-2}$, respectively), at a temperature equal to 200 °C, the time-to-blister is estimated at 12 h.

The sample subjected to the long temperature anneal at 100 °C was subsequently annealed at 200 °C for 5 min. RMS roughness of this sample is not impacted by this STA. Consistently, $\omega$-2$\theta$ diffraction patterns measured on this sample indicates very little relaxation of the strain created by the hydrogen implant (minor reduction of diffraction fringes), as compared to as-implanted germanium [Fig. 3(a)]. This result points toward a limited hydrogen diffusion in the implanted region and insufficiently high temperature to trigger the blistering.

B. Low temperature germanium exfoliation

Additional samples annealed at 100, 130, and 150 °C for 22 h were subjected to a STA at 300 °C for 5 min. Surface roughness measurements suggest the formation of large hydrogen-filled cavities along the cracks and subsequent germanium exfoliation (Table II). It should be noted that the height of surface blisters correlates well with thermal

![Image](image_url)

**FIG. 3.** XRD ($\omega$-2$\theta$) patterns: (a) impact of STA on strain relaxation in hydrogen implanted germanium after long anneals at 100 °C; (b) impact of thermal budget during the nucleation process on implant-induced strain after STA at 300 °C.

**TABLE II.** Germanium surface roughness, as measured by AFM, following long time anneals at low temperature (≤200 °C) and STA at 200 or 300 °C. Scan area is 50 x 50 µm$^2$ unless specified.

<table>
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<tr>
<th>Conditions</th>
<th>RMS roughness (nm)</th>
<th>Scan area</th>
</tr>
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<tbody>
<tr>
<td>After 100 °C anneal—22 h, followed by 200 °C anneal—5 min</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>After 100 °C anneal—22 h, followed by 300 °C anneal—5 min</td>
<td>7.6</td>
<td>10 x 10 µm$^2$</td>
</tr>
<tr>
<td>After 130 °C anneal—22 h, followed by 300 °C anneal—5 min</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>After 150 °C anneal—22 h, followed by 300 °C anneal—5 min</td>
<td>28.1</td>
<td></td>
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A 680 nm thick layer of germanium was transferred onto 100 nm of SiO$_2$ deposited on the silicon host wafer. High bond strength was achieved, as suggested by the fact that the transferred germanium layer follows closely the pattern printed in the oxide layer prior to bonding. The germanium surface roughness as measured by AFM is 15 nm [germanium surface roughness after exfoliation is illustrated in Fig. 6(a)]. High magnification X-TEM micrographs show that the formation of these microcracks follows a path similar to the silicon case [Fig. 2(c)(2)], during STA, hydrogen diffuses along the defect lines and forms large gas pockets (diameter > 5 nm) at the expense of smaller ones. The internal pressure in large gas pockets increases and leads to the extension of small cracks into microcracks. 

\[ R_{\text{roughness}} = 15 \text{ nm} \]

C. Application to the GeOI case

A bonded sample made of a hydrogen-implanted germanium wafer directly bonded to a silicon wafer was processed in order to demonstrate the feasibility of transferring a thin germanium layer at low temperature. The thermal treatment which was considered starts with a long (24 h) anneal at 130 °C and ends with a 5 min anneal at 300 °C. The purpose of the initial long time, low temperature anneal is two-fold, it strengthens the bonds created at the germanium/oxide interface during the bonding operation; and promotes hydrogen platelet nucleation within the germanium substrate without modifying its morphology at the bonded interface. The suitability of such thermal treatment for the fabrication of GeOI substrates at low temperature is illustrated in Fig. 6(a).

Roughness measurements show evidence of blistering, which is confirmed by X-TEM analysis and suggested by XRD patterns. On the sample annealed at 150 °C for 22 h and subsequently annealed at 300 °C for 5 min, the formation of microcracks is observed. The latter result from the merger of nanocracks created at low temperature, which form longer cracks and cause germanium exfoliation [Fig. 2(c)(1)]. High magnification X-TEM micrographs show that the formation of these microcracks follows a path similar to the silicon case [Fig. 2(c)(2)], during STA, hydrogen diffuses along the defect lines and forms large gas pockets (diameter > 5 nm) at the expense of smaller ones. The internal pressure in large gas pockets increases and leads to the extension of small cracks into microcracks.

![AFM scans of implanted and annealed germanium](image)

**FIG. 4.** (Color online) AFM scans of implanted and annealed germanium, (a) following an anneal at 100 °C for 22 h and a short anneal at 300 °C for 5 min (10 x 10 μm$^2$ scan area); (b) following an anneal at 150 °C for 22 h and a short anneal at 300 °C for 5 min (50 x 50 μm$^2$ scan area).

![XRD patterns](image)

**FIG. 5.** XRD (ω) patterns: (a) impact of STA on lattice deformation in hydrogen implanted germanium after long time anneals at 100 °C; (b) impact of thermal budget during the nucleation process on the lattice deformation caused by the STA at 300 °C.
IV. CONCLUSIONS

A low temperature germanium exfoliation experiment has been conducted in hydrogen-implanted germanium layers. It has been demonstrated that a long-time anneal at a temperature as low as 100 °C can promote hydrogen platelet formation and allow a complete germanium exfoliation after a short time anneal at higher temperature (300 °C). This experiment demonstrates also that the lowest thermal budget required for defect nucleation is similar for germanium and III–V materials such as InP. Enhanced bond strength in directly bonded heterojunctions—like GeOI or bonded III–V material for photonics—is the main benefit expected from such low temperature exfoliation process.

ACKNOWLEDGMENTS

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FIG. 6. Scanning electron microscopy graphs of the GeOI sample resulting from an exfoliation carried out after a 24 h long anneal at 130 °C and a STA at 300 °C for 5 min: (a) cross-sectional view of the germanium/SiO2/silicon patterned structure. A 680 nm thick germanium layer is transferred for the donor germanium wafer to the host silicon wafer (b) top-down tilted view of the germanium surface exposed after complete exfoliation.