

Low-Temperature Fabrication of Germanium-on-Insulator Using Remote Plasma Activation Bonding and Hydrogen Exfoliation

C. A. Colinge, K. Y. Byun, I. P. Ferain, R. Yu and M. Goorsky

Abstract Low-temperature germanium to silicon wafer bonding was demonstrated by in situ radical activation and bonding in vacuum. After low temperature direct bonding of Ge to Si followed by annealing at 200 and 300°C, advanced imaging techniques were used to characterize the bonded interface. The feasibility of transferring hydrogen-implanted germanium to silicon with a reduced thermal budget is also demonstrated. Germanium samples were implanted with hydrogen and a two-step anneal was performed. The first anneal performed at low temperature ($\leq 150^\circ\text{C}$ for 22 h) to enhance the nucleation of hydrogen platelets. 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.

1 Introduction

Germanium is gaining interest as a semiconductor material because bulk germanium has the highest hole mobility of all semiconductors (maximum $\mu_p = 1,900 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an electron mobility that is potentially twice that of silicon (maximum $\mu_p = 3,900 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Since germanium is a much rarer element than silicon, it is impractical (unpractical means impossible—remember that one form aa picky HS teacher...) to use bulk germanium wafers. More suitable is the formation of thin germanium layers directly deposited on silicon or on oxidized

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silicon. It is also possible to produce mixed substrates in which n-channel devices are made in a thin silicon-on-insulator (SOI) layer and germanium p-channel transistors are made in a thin germanium-on-insulator (GeOI) film [1]. GeOI can be produced by the germanium condensation technique. In this technique a $\text{Si}_{0.9}\text{Ge}_{0.1}$ layer is first epitaxially grown on SOI. Oxidation is performed to produce a SiO_2 layer and a Ge-enriched layer ($\text{Si}_{0.25}\text{Ge}_{0.75}$). Pure germanium is subsequently grown on the $\text{Si}_{0.25}\text{Ge}_{0.75}$ layer [2]. The epitaxial approach has the drawback of being carried out at a relatively high temperature ($>650^\circ\text{C}$). Since silicon and germanium have very different thermal expansion coefficients, use (or ‘the use’) of any high-temperature processing step results in the formation a high density of thermal mismatch defects in the germanium epilayer [3, 4].

2 Low-Temperature Bonding Mechanisms

Low-temperature direct wafer bonding eliminates the aforementioned problems associated with the epitaxial and condensation techniques. Low defect density is of prime importance for heterogeneous integration of dissimilar materials such as III–V on silicon. Low-temperature bonding eliminates the severe thermal stress that can be induced by high-temperature annealing [5]. Ge to Si direct wafer bonding has been studied for use in high-performance photodetectors as well as high-quality epitaxial templates for GaAs growth [6, 7].

Radical activation of the wafers is a key factor for the success of low-temperature bonding. The effects of free radical activation for Si to Si bonding have been previously reported in the literature [8]. In that study, a comparison of different surface treatments for direct Si to Si wafer bonding was made. Hydrophilic and hydrophobic Si wafers were exposed to a range of pretreatments, involving oxygen and nitrogen radical activation before in situ wafer bonding in a vacuum. After low-temperature annealing at 200 and 300°C , the formation of voids was observed by using scanning acoustic microscope inspection. A comparison of the bonding energy was conducted and analyzed as a function of the surface treatments, which demonstrated that the remote plasma pretreatment is a very suitable process for surface modification of hydrophilic and hydrophobic Si to Si direct wafer bonding.

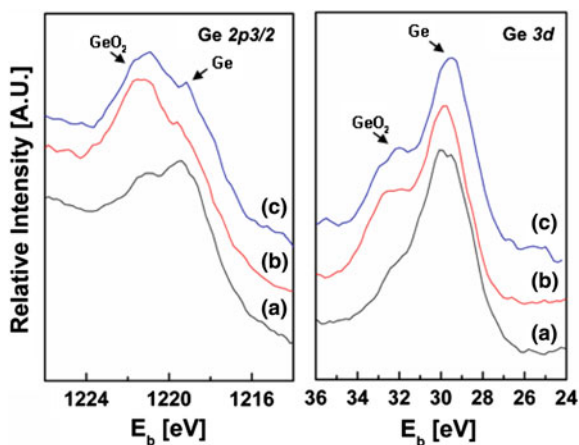
Here, we will focus on the characterization of activated Ge surfaces using oxygen and nitrogen radicals and show successful low temperature Ge to Si direct bonding using radical activation and degassing channels. The chemical species on the activated Ge surfaces were investigated using angle-resolved X-ray photoelectron spectroscopy (ARXPS), while structural analysis was performed by scanning acoustic microscopy (SAM) and high-resolution transmission electron microscopy (HR-TEM).

In a first experiment, 100-mm, $\langle 100 \rangle$ oriented p-type Ge wafers (Ga doped with a resistivity of $0.016 \, \Omega \, \text{cm}$) were selected. The oxygen and nitrogen radical activated Ge surfaces were studied in a Vacuum Science Workshop Atomtech

ESCA system using Al $K\alpha$ radiation ($h\nu = 1,486.6$ eV). The Ge wafers were cleaned in an SC1-equivalent solution without ozone using a Semitool Spray Acid Tool (SAT) prior to surface activation. Wafers were then loaded into an Applied Microengineering Limited (AML) AW04 aligner bonder and vacuum was applied. The wafers were then exposed for 10 min to either oxygen or nitrogen free radicals at a pressure of 1 mbar and a plasma power of 100 W. The radicals were generated by a remote plasma ring. A reference sample of Ge cleaned and bonded without exposure was also prepared. Wafers were bonded under a pressure of 1 kN applied for 5 min and immediately transferred for XPS analysis. The three bonded Ge to Ge samples were then de-bonded using a razor blade, cleaved into 2×2 cm size samples and loaded into a high-vacuum sample holder of the XPS tool. The total exposure to ambient air was kept <1 min. The photoelectron peaks and chemical composition of the Ge surface were analyzed at various take-off angles.

In addition, blank Ge wafers were bonded directly to Si using the same recipe and bonder used for the Ge bonded to Ge, i.e. 10 min oxygen or nitrogen radical activation at low temperature. (100)-oriented n-type Czochralski grown prime grade bare Si wafers with a diameter of 100 mm were bonded with the Ge wafers. Prior to bonding, the Ge and Si wafers were cleaned in an SC1-equivalent solution with ozone for Si and without ozone for Ge. After loading into the AML wafers were activated and bonded in situ under a pressure of 1kN applied for 5 min at a chamber pressure ranging from 5 to 10 m bars. The wafers were annealed in situ at 100°C for 1 h with an applied pressure of 500 N in vacuum followed by an ex-situ anneal at 200°C for 24 h in order to increase bond strength. The bonded pairs were then annealed again at 300°C for 24 h. The ramp-up rate was set to $0.5^\circ\text{C}/\text{min}$ in both cases. After the anneal, Ge-Si bonded pairs remained intact despite their coefficient of thermal expansion (CTE) mismatch, owing to the slow ramp-up rate. Bonded interfaces were imaged by SAM. Then Ge was directly bonded to a patterned Si wafer with $2\text{-}\mu\text{m}$ deep channels at a pitch of $400\text{ }\mu\text{m}$ using oxygen radical activation. The bond strength of the patterned Ge-Si wafer pair was

Fig. 1 Ge 2p_{3/2} and Ge 3d photoelectron features (take-off angle = 75°): **a** reference cleaned sample **b** oxygen radical activated sample **c** nitrogen radical activated sample



measured using the crack opening method. Structural analysis of buried interfaces was studied by SAM and HR-TEM inspection.

Binding state configurations of germanium atoms at the activated surfaces were evaluated by ARXPS using the de-bonded cleaved samples. Figure 1 shows the Ge 2p_{3/2}, Ge 3d photoelectron features (take-off angle = 75°). As expected the Ge 2p_{3/2} signal shows two binding energy contributions at 1,218.5 and 1,221.0 (±0.2) eV [9]. These can be assigned to zero- and quadra-valent germanium, respectively. Zero-valent corresponds to bulk Ge while quadra-valent indicates the presence of a GeO₂ layer. The Ge 3d peaks exhibit similar information. Two features can be resolved at 29.8 and 32.5 eV that once again are attributed to zero- and quadra-valent Ge respectively [10–12]. There was no evidence in this work of the formation of detectable quantities of sub-stoichiometric oxides, which agrees with the Ge 3d signal (which is bulk sensitive) and Ge 2p signal (which is surface sensitive).

Quantitative relative contributions of the oxygen and germanium features are found by curve-fitting the XPS data. These data are reported in Table 1 as peak area ratios and are used to derive stoichiometric amounts using known sensitivity factors. The data collected at 75° are the most accurate representation of the actual stoichiometry close to the Ge surfaces. Curve fitting reveals a peak indicating the presence of OH⁻ which is located at a binding energy which is higher than the binding energy of GeO₂ [17]. This data is shown in the first column of Table 1 where the ratio of OH⁻ to GeO₂ (labeled O⁻/O²⁻) is represented. In the second column we have derived the O/Ge ratio which is the total O 1 s peak area divided by total Ge 2p_{3/2} peak area. From the second column of Table 1, it is clear that exposure of hydrophilic cleaned Ge substrates to free radicals produces some oxidation.

For samples exposed to either nitrogen or oxygen radicals, the quantification shown in Table 1 shows higher values of O/Ge ratio, which is more likely due to a

Table 1 ARXPS peak area ratio

Sample/take-off angle		O ⁻ /O ²⁻	O/Ge total
Reference substrate	0°	0.34	0.04
	25°	0.24	0.04
	50°	0.09	0.08
	75°	0.00	0.25
Post oxygen radical	0°	0.11	0.06
	25°	0.11	0.07
	50°	0.02	0.12
	75°	0.00	0.40
Post nitrogen radical	0°	0.07	0.05
	25°	0.09	0.06
	50°	0.06	0.11
	75°	0.00	0.35

O⁻ /O²⁻ is the O⁻ signal area divided by O²⁻ signal area in O 1 s spectra. O/Ge is the total O 1 s peak area divided by total Ge 2p_{3/2} peak area

thicker oxide film compared to the reference Ge sample. The nitrogen radical exposed Ge also shows a significant GeO_2 formation; this is similar to previous studies where Ge exposed to nitrogen plasma resulted in a more hydrophilic surface signifying formation of an oxide [13]. These quantifiable XPS data were used to estimate the film thickness as 0.39, 0.58 and 0.72 nm for the reference, nitrogen radical activated and oxygen radical activated samples, respectively.

Most extensive hydroxylation, which is indicated in the first column (O^-/O^{2-}) of Table 1, was observed for the reference samples. Nitrogen radical activated samples gave the lowest $-\text{OH}$ concentration and oxygen radical activated samples an intermediate value. The presence of hydroxyl species is important because increased hydroxyl groups can give rise to more hydrophilic reactions at bonded interfaces, which can then induce intrinsic void generation due to trapped reaction by-product. The signal due to O^- (OH^-) decreases towards grazing emission for all samples, which is due to a sub-surface hydroxide or sub-stoichiometric GeO_x .

The buried interfaces of bonded pairs were inspected using SAM after annealing at 200°C 24 h and additionally at 300°C for 24 h. Figure 2 shows scanning acoustic microscope images of bonded pairs: (a) pre-cleaned by SC1-equivalent solution, (b) post oxygen radical exposure, and (c) post nitrogen radical exposure. The hydrophilic reaction at the interfaces can be described the following equations:

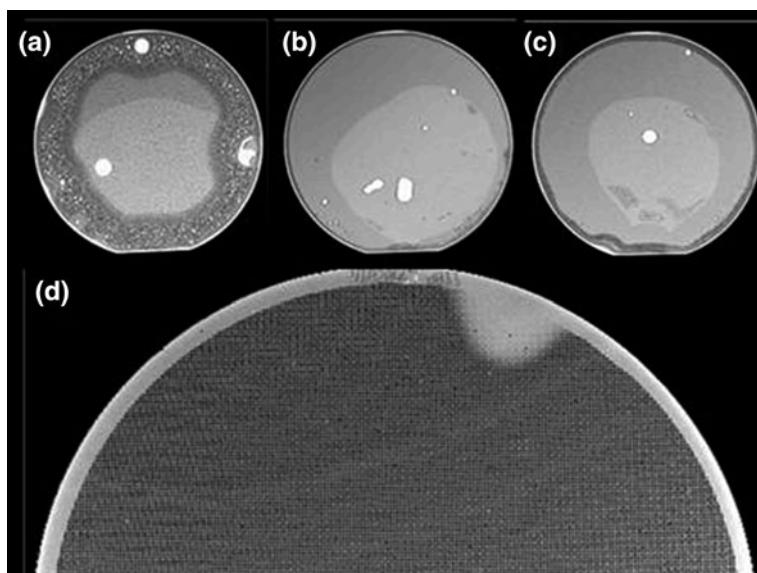


Fig. 2 Scanning acoustic images of Ge/Si bonded wafer pairs after annealing at 200°C for 24 h, and additionally at 300°C for 24 h: **a** cleaned in an SC1-equivalent solution, followed by **b** O_2 radical 10 min exposure, **c** N_2 radical 10 min exposure, and **d** formed 2 μm depth channel in Si wafer prior to oxygen radical activated (10 min) bonding creates an exhaust path for trapped gas

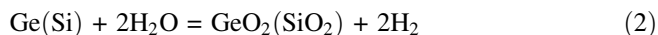
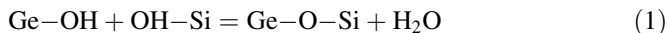


Figure 2 shows that hydrophilic reactions (Eqs. 1 and 2) at the interfaces may create trapped gas like water vapor or hydrogen following the hydrophilic chemical reaction, which appears as a different contrast in the SAM images. Some of the water molecules resulting in covalent bonding of Ge–O–Si of oxygen and nitrogen exposed samples can diffuse through the nanometer range oxide layer and react with the bulk germanium and silicon to form dioxide and hydrogen. In Fig. 2a, however, the buried oxide is so thin that the reactants and by-products cannot diffuse through the interface. Radical activated samples in Fig. 2b, c, shows minimal intrinsic voids formed due to ability of the relatively thick oxide interface, which enhances by-product diffusion. For nitrogen radical activated sample in Fig. 2c, which has a thinner oxide than Fig. 2b, we can clearly see the initiation of void generation of by-products near the wafer edge area. The formation of interface voids during low temperature anneal depends on the thickness of the stoichiometric oxide film, which is coincident with silicon wafer bonding [14]. Thus, the SAM result agrees with the oxide thickness extracted from ARXPS.

In Fig. 2d, we can clearly see that the 2 μm -deep channels formed at the surface of the Si wafer prior to oxygen radical activated bonding and anneal creates an escape path for trapped gas or moisture allowing high bond strength to be achieved. Additionally, the SAM image does show a uniformly colored SAM image indicative of a well bonded sample. The SAM image suggests that hydrophilic reaction at interface generate gas phase by-product, which can be diffused out by the channel which is similar to the result of Ge bonded to sapphire with patterned channels [15].

In Fig. 3, after low temperature anneal at 200 and 300°C, the bonding energy is so high that insertion of a razor blade results in bulk fracture of the germanium, which is consistent with the respective fracture stress of single crystal Si (62 MPa)

Fig. 3 Optical microscope observation of razor blade tested sample after annealing at 200°C for 24 h and additional 300°C for 24 h. After crack opening test, bulk of the germanium crack (no de-bonding), revealing pieces of germanium strongly bonded to the thin buried oxide

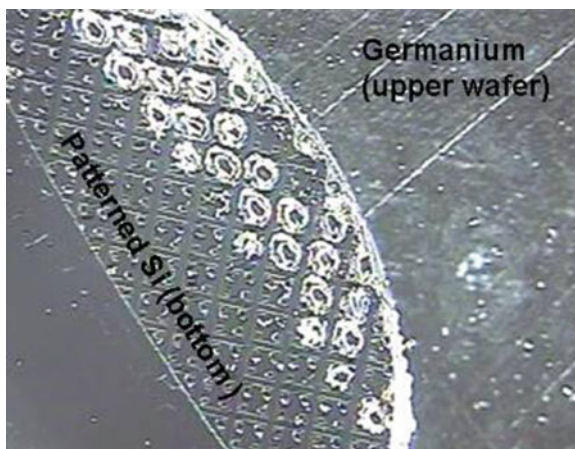
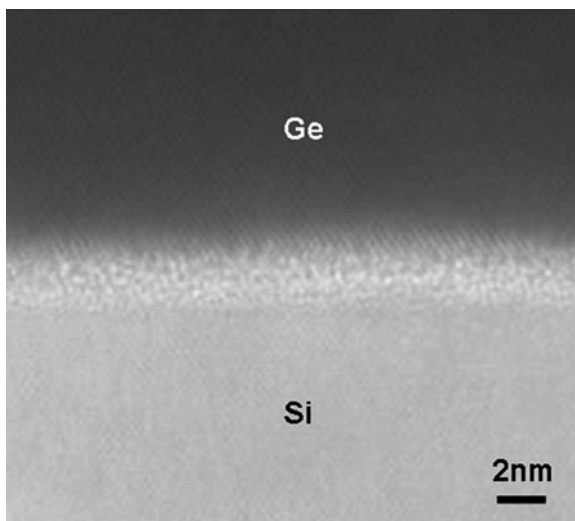


Fig. 4 HR-TEM observation of buried interfaces after annealing at 200°C for 24 h and additional 300°C for 24 h



and Ge (49 MPa) [16]. The full bond strength is attributed to the oxygen radical activation.

Figure 4 shows cross-sectional HR-TEM image of buried interfaces using oxygen radical activation after 200°C and an additional 300°C 24 h anneal. The 2 nm-thick buried interface appears defect-free and a smooth bonded interface is visible. It corresponds with the calculated thickness (0.7 nm) by ARXPS of Ge exposed to oxygen and our previous TEM result which showed 1 nm-thick SiO₂ on oxygen radical activated Si. Additionally, compared to the Ge condensation technique [2], the TEM image shows no over oxidation or stacking faults generated during the low thermal budget ($\leq 300^\circ\text{C}$) anneal. This low temperature process using oxygen radical activation is the way to achieve high quality interfaces without generating stacking fault or inducing surface damage by direct plasma activation.

Chemical and structural analyses show that remote plasma treatment using oxygen and nitrogen radical facilitates oxidation on Ge surface to increase chemical reaction. Thus radical activation can enhance the bonding reaction allowing strong bond strength at low temperature while preserving the crystalline quality of the Ge. The radical activated bonding process is very suitable for a low temperature process as needed for thermally mismatched materials such as those used for photonic devices.

3 Low-Temperature Exfoliation of Germanium Layers

Transfer of thin semiconductor layers by exfoliation has received a lot of attention since its first use for the fabrication of Silicon-on-Insulator (SOI) substrates [17].

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 400–500°C, hydrogen molecules tend to be trapped in these defects and form pockets of gas at the projected range, commonly referred to as ‘bubbles’. As temperature and/or anneal time increase, the internal pressure inside the bubbles increases and results in the formation of micro-cracks which triggers the splitting of a thin semiconductor layer [18, 19]. The mechanisms which govern defect formation in H-implanted semiconductors and the creation of micro-cracks has already been extensively characterized in silicon, germanium [20] and III–V compounds [21]. It is often addressed from a wafer bonding perspective and targets a range of applications varying from the fabrication of low defective substrates for CMOS compatible applications (SOI and Germanium on Insulator substrates ‘GeOI’). The thermal budget required to generate micro-cracks 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 [6, 22].

Here, we investigate the feasibility of transferring hydrogen-implanted germanium to silicon with a reduced thermal budget. Recently, co-implantation of hydrogen and helium for low-temperature (300°C) exfoliation of germanium has been successfully demonstrated [23]. That approach presents a relatively long time-to-blister anneal (40 min) at a temperature of 300°C. 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 ($\leq 150^\circ\text{C}$), 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 [24, 25]. 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 minimizes the impact of the dissimilar thermal expansion coefficients between the bonded pair.

$\langle 100 \rangle$ -orientated n-type germanium wafers with a diameter of 100 mm (Sb doped, 0.03 $\Omega\text{ cm}$) were used for this experiment. Prior to hydrogen implant, a 100 nm thick layer of PECVD silicon dioxide was deposited and densified at 600°C. Germanium substrates were implanted at room temperature with H_2^+ at a dose of $5 \times 10^{16}\text{ cm}^{-2}$ at 180 keV without active chuck cooling. The projected ion and germanium vacancy ranges that are expected are 650 and 590 nm below the germanium surface, respectively. Following the implant, the silicon dioxide layer was completely removed in a dilute HF solution. One of the implanted substrate was diced in small samples (1 cm \times 1 cm) prior to anneal. Strain profile within as-implanted germanium samples has been assessed by high resolution X-ray Diffraction (XRD) measurements. The $\omega/2\theta$ diffraction patterns provide

information about strain introduced by the H_2^+ implant [26, 27]. Negligible strain profile variation was observed across the wafer, which suggests excellent implant uniformity among the 1 cm^2 samples. In addition, XRD measurements suggest that nucleation is already initialized during hydrogen implantation due to lack of wafer cooling during hydrogen implantation [27].

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 2. The onset of blistering was determined by tapping mode atomic force microscopy (AFM) and by optical microscopy. Prior to surface morphology characterisation, samples were cleaned in de-ionized (DI) water. Cross-sectional Transmission Electron Microscopy (X-TEM) was performed to characterise 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^+ implanted germanium wafer to a single side polished 100-mm 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 $NH_4:H_2O$ solution dispensed in a Spray Acid tool followed by four cycles alternating 1,200:1 $HF:H_2O$ 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 AML bonding chamber which was pumped down to 10^{-5} mbars. The wafers were exposed for 10 min to free oxygen radicals generated by a plasma ring [8]. Wafers were bonded under a pressure of 1,000 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 $0.5^\circ\text{C}/\text{min}$ in both cases in order to minimize the formation of thermally generated voids at the bonded interface [28]. The exfoliation was triggered by a 5 min STA at 300°C .

Table 2 Germanium surface roughness, as measured by Atomic Force Microscopy, following long-time anneals at low temperature ($\leq 200^\circ\text{C}$)

	RMS roughness (nm)	Scan area
As implanted	1.5	$50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$
After 100°C anneal—22 h	0.4	$10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$
After 130°C anneal—22 h	1.7	$50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$
After 150°C anneal—22 h	0.4	$10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$

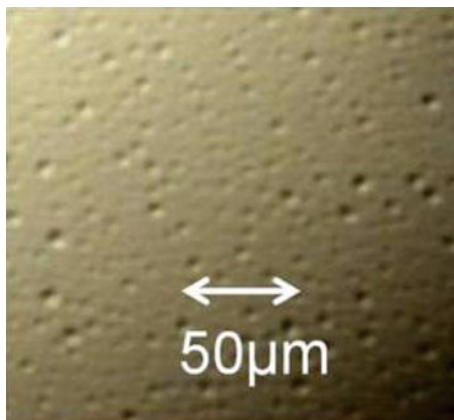
3.1 Defect Nucleation and Oswald Ripening Mechanism

Defect nucleation and hydrogen coalescence in implant-generated defects lead to the formation of hydrogen platelets and cracks in the bulk of the implanted semiconductor. These hydrogen-filled cavities have been reported to be located at a depth between the hydrogen projected range and the germanium vacancy range below the germanium surface [20]. Lattice deformation induced by these cavities generates surface blisters which are clearly visible (Fig. 5). The evolution of the nucleation process can thus be monitored using Atomic Force Microscopy or optical microscopy (image shows an optical micrograph).

Significant hydrogen coalescence in III-V materials such as InP and GaAs has already been reported after long anneals at 150°C [24, 25]. 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 [21]. Since the melting point of germanium (937°C) is close to the melting point of InP (1,060°C), defect nucleation would be expected to occur in hydrogen-implanted germanium at 150°C or below the nucleation temperature in InP.

To study this effect, surface roughness measurements after long (22 h) anneal at 100, 130 or 150°C have been performed. RMS roughness values are detailed in Table 2. As compared to as implanted germanium, these long anneals at 100, 130 and 150°C do not modify surface 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 nano-cracks are parallel to the substrate surface and are located close to the implant projected range (Fig. 6). The formation of these nano-cracks 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. 5 Optical micrograph showing the formation of blisters

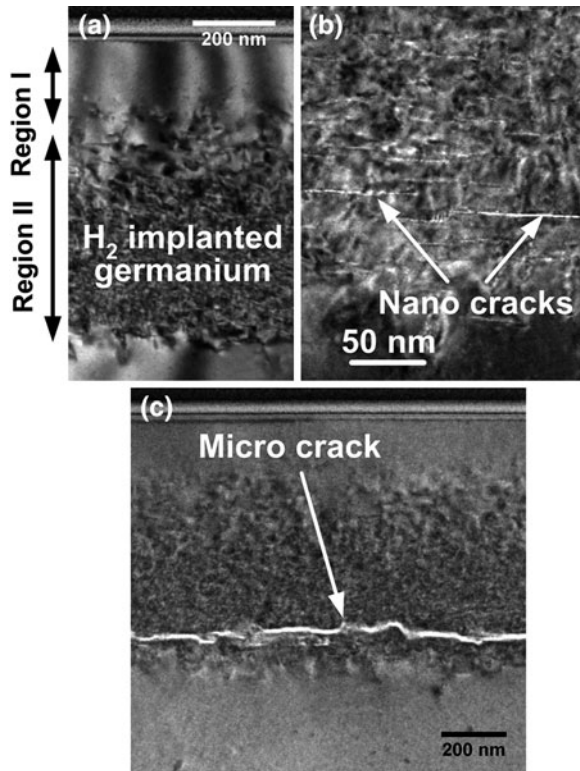


Consequently, these nano-cracks do not modify the surface morphology significantly, as compared to as implanted germanium. It must be noted that this result does not hold for implanted germanium annealed at 200°C for 19 h suggesting that the minimum thermal budget needed to trigger germanium exfoliation 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 $5 \times 10^{16} \text{ cm}^{-2}$, respectively): at a temperature equal to 200°C, the time-to-blister is estimated at 12 h [18].

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. 7a). This result points towards a limited hydrogen diffusion in the implanted region and insufficiently high temperature to trigger the blistering.

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 3).

Fig. 6 **a** TEM picture of the defective region created by H_2^+ implant, in as-implanted germanium. A $5 \times 10^{16} \text{ cm}^{-2}$ H_2^+ dose implanted at 180 keV generates a 600 nm thick implant-damaged region (region II) below a damage-free 150 nm thick region under the germanium surface (region I). **b** TEM picture of hydrogen-implanted germanium following a 22 h-anneal at 150°C 0°C showing the formation of nano-cracks at a depth close to the projected range, parallel to the substrate surface. **c** TEM picture of hydrogen-implanted germanium following a 22 h-anneal at 150°C 0°C and a 5 min anneal at 300°C 0°C showing the transformation of nano-cracks in an almost continuous and thick micro-crack line at 645 nm below the germanium surface



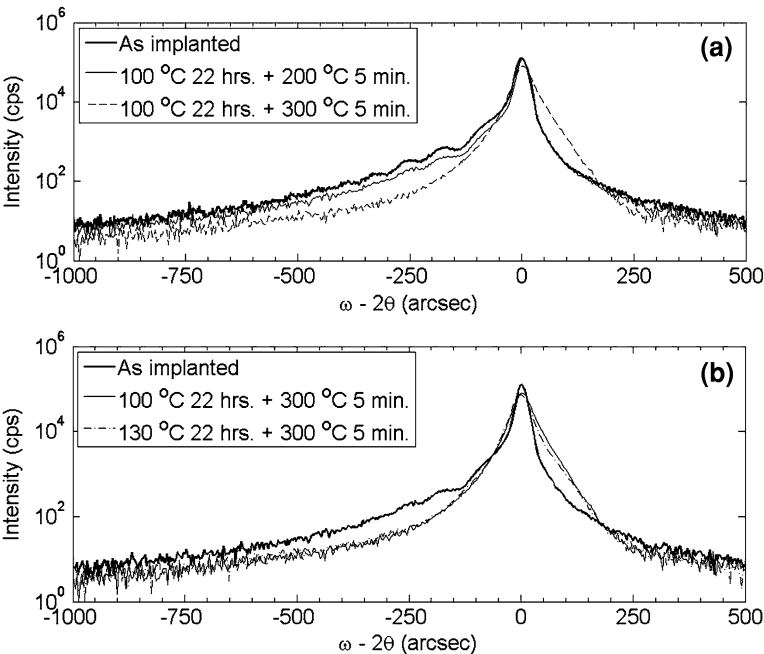


Fig. 7 X-ray diffraction (ω - 2θ) patterns: **a** impact of STA on strain relaxation in hydrogen implanted germanium after long anneals at 100°C; **b** impact of thermal budget during the nucleation process on implant-induced strain after STA at 300°C

Table 3 Germanium surface roughness, as measured by Atomic Force Microscopy, following long time anneals at low temperature ($\leq 200^\circ\text{C}$) and STA at 200 or 300°C

Anneal sequence	RMS roughness (nm)	Scan area
After 100°C anneal—22 h, followed by 200°C anneal—5 min	0.4	
After 100°C anneal—22 h, followed by 300°C anneal—5 min	7.6	10 μm \times 10 μm
After 130°C anneal—22 h, followed by 300°C anneal—5 min	14.6	50 μm \times 50 μm
After 150°C anneal—22 h, followed by 300°C anneal—5 min	28.1	50 μm \times 50 μm

Scan area is 50 μm \times 50 μm unless specified

It should be noted that the height of surface blisters correlates well with thermal budget of the defect nucleation process: the higher the nucleation temperature, the larger the blisters. $\omega - 2\theta$ diffraction patterns for these samples confirm this enhanced hydrogen diffusion after completion of such two-step anneals, as most of the diffraction fringes induced by the hydrogen implant are strongly reduced as compared to $\omega - 2\theta$ diffraction patterns prior to STA at 300°C (Fig. 7b). Such

modification of the diffraction pattern suggests that significant hydrogen diffusion occurs after a combined long time anneal at a temperature as low as 100°C and a short time anneal at 300°C.

In addition, the broadening of the germanium feature on triple-axis ω diffraction patterns suggests an increase of local deformation (Fig. 8a). The Full Width at 0.001 Height (FW0.001 M) increases from 240 arcsec. in as-implanted germanium to 600 arcsec. After a long time anneal at 100°C and a short time anneal at 300°C. This increase is attributed to local lattice deformations due to hydrogen Oswald ripening [27]. The latter is observed after the STA at 300°C, irrespective of the anneal temperature considered for completing the defect nucleation (Fig. 8b). This is a key result since it shows that a long time anneal at a temperature as low as 100°C reduces significantly the time-to-blister at 300°C, as compared to state-of-the-art data [18, 23].

Roughness measurements show evidence of blistering, which is confirmed by X-TEM analysis and suggested by X-ray diffraction patterns. On the sample annealed at 150°C for 22 h and subsequently annealed at 300°C for 5 min, the formation of micro-cracks is observed. The latter result from the merger of nano-cracks created at low temperature, which form longer cracks and cause germanium exfoliation (Fig. 6c). The formation of these micro-cracks proceeds in a similar way to silicon: during STA, hydrogen diffuses along the defect lines and forms large gas pockets (diameter > 5 nm) at the expense of smaller ones [28]. The internal pressure in large gas pockets increases and ultimately leads to the extension of small cracks into micro-cracks.

Fig. 8 X-ray diffraction (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

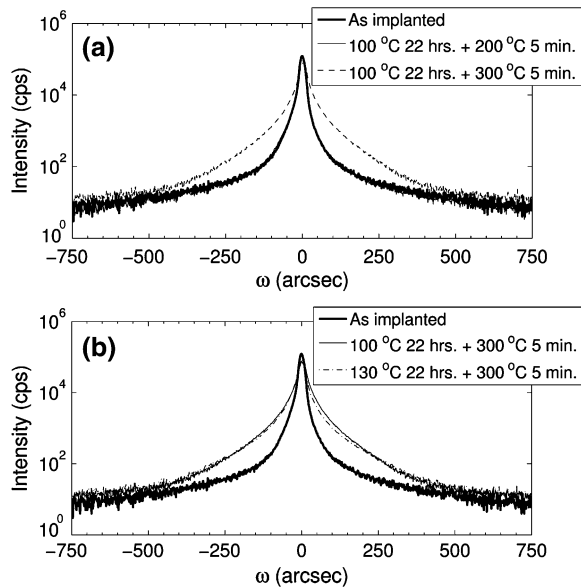
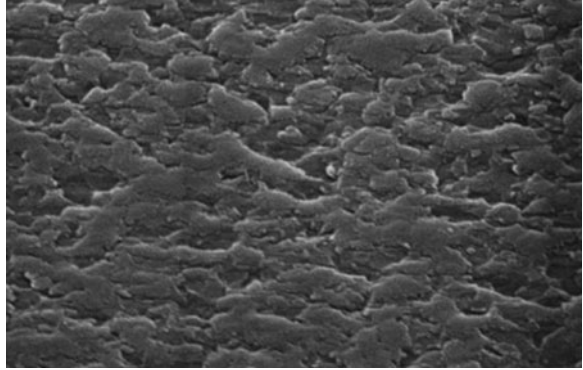


Fig. 9 Scanning electron microscopy *graphs* of the Germanium-on-insulator sample resulting from an exfoliation carried out after a 24 h-long anneal at 130°C and a short time anneal at 300°C for 5 min: *top-down* tilted view of the germanium surface exposed after complete exfoliation



3.2 Low-Temperature Formation of Ge-on-Insulator

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 twofold: 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. A 680 nm-thick layer of germanium was transferred onto 100 nm of SiO₂ deposited on the host silicon 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. 9). This value is consistent with the surface roughness value (14.6 nm) measured on bare implanted germanium after 22 h long anneal at 130°C (Table 3).

4 Conclusion

A low-temperature process for bonding and exfoliation of germanium has been developed using hydrogen-implanted germanium layers and surface plasma activation prior to bonding. It has been demonstrated proper engineering of the annealing sequence can promote hydrogen platelet formation and allow for bonding and complete germanium exfoliation after annealing at temperatures no higher than 300°C. Our results 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 hetero-junctions -like GeOI or bonded III-V material for photonics- is the main benefit expected from such low temperature exfoliation process.

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Nanoelectronics Applications

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Gamiz, F.; Lysenko, V.S. (Eds.)

2011, IX, 447 p., Hardcover

ISBN: 978-3-642-15867-4