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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 5×10^{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 ($\leq$150 °C for 22 h) enhances the nucleation of hydrogen platelets significantly. The second anneal is performed at 300 °C for 5 min and is shown to complete the exfoliation process by triggering the formation of extended platelets. Two key results are highlighted: (i) in a reduced thermal budget approach, the transfer of hydrogen-implanted germanium is found to follow a mechanism similar to the transfer of hydrogen-implanted InP and GaAs, (ii) such a low thermal budget ($<$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-blister anneal at a temperature of 300 °C (40 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 ($\leq$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-

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

	RMS roughness (nm)	Scan area
As-implanted	1.5	
After 100 °C anneal—22 h	0.4	10×10 μm^2
After 130 °C anneal—22 h	1.7	
After 150 °C anneal—22 h	0.4	10×10 μm^2
After 200 °C anneal—19 h	23.9	

cal vapor deposition (PECVD) silicon dioxide was deposited and densified at 600 °C. Germanium substrates were implanted at room temperature with H_2^+ at a dose of 5×10^{16} 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 (1×1 cm^2) prior to anneal. Strain profile within as-implanted germanium samples has been assessed by high resolution x-ray diffraction (XRD) measurements. $\omega/2\theta$ diffraction patterns provide information about strain involved by the H_2^+ implant.[13,14] 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.[14]

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^+ 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 $NH_4:H_2O$ solution dispended in a spray acid tool followed by four cycles alternating 1200:1 $HF:H_2O$ and DI water cleans. Both wafers were then subjected to a megasonic clean with DI water. Their surfaces are hydrophilic

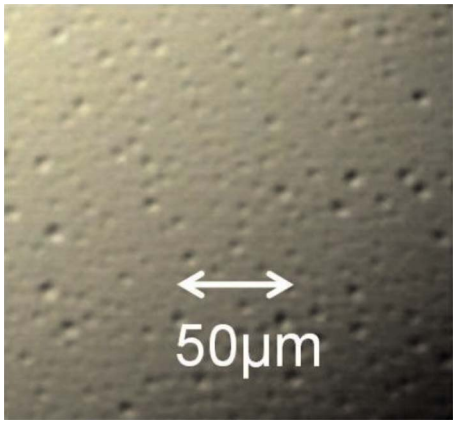

FIG. 1. (Color online) Optical graph of surface blisters in hydrogen-implanted germanium following a 22 h anneal at 130 °C and a 5 min anneal at 300 °C. Surface blisters reflect the formation of coalescing microcracks in the implanted region of bulk germanium.

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.[15] 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.[16]

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

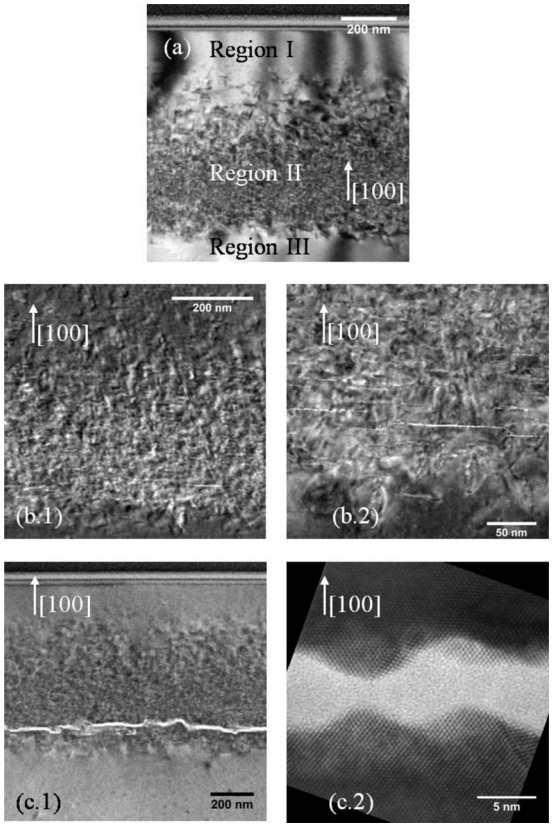

FIG. 2. (a) Low magnification X-TEM of the defective region created by H_2^+ implant, in as-implanted germanium. A 5×10^{16} cm^{-2} H_2^+ dose implanted at 180 keV generates a 600 nm thick implant-damaged region (region II) below a damage-free 150 nm thick region under the germanium surface (region I). Below the damaged region, dark cavities are observed (region III) which are of lesser interest in our study. (b1) low magnification X-TEM of hydrogen-implanted germanium following a 22 h anneal at 150 °C showing the formation of nanocracks at a depth close to the projected range, (b2) high magnification TEM of nanocracks parallel to the substrate surface (same implant and anneal conditions as b1); (c1) low magnification TEM of hydrogen-implanted germanium following a 22 h anneal at 150 °C and a 5 min anneal at 300 °C showing the transformation of nanocracks in an almost continuous and thick microcrack line at 645 nm below the germanium surface; (c2) high magnification TEM of a microcrack illustrating its creation by formation of spherical gas pockets (same implant and anneal conditions as c1).

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.[4,16] 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

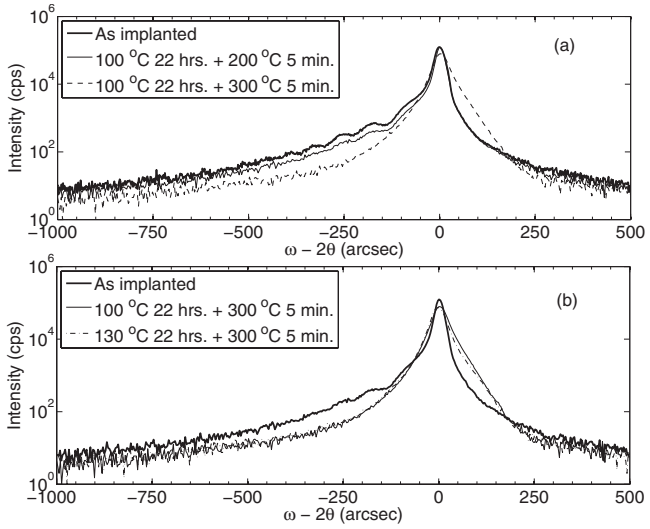

FIG. 3. XRD (ω-2θ) patterns: (a) impact of STA on strain relaxation in hydrogen implanted germanium after long anneals at 100 °C; (b) impact of thermal budget during the nucleation process on implant-induced strain after STA at 300 °C.

previously reported time-to-blister for H_2^+-implanted germanium samples (implant energy and dose are 160 keV and 5×10^{16} cm^{-2}, respectively), at a temperature equal to 200 °C, the time-to-blister is estimated at 12 h.[2]

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, ω-2θ 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

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 50×50 μm^2 unless specified.

	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	10×10 μm^2
After 130 °C anneal—22 h, followed by 300 °C anneal—5 min	14.6	
After 150 °C anneal—22 h, followed by 300 °C anneal—5 min	28.1	

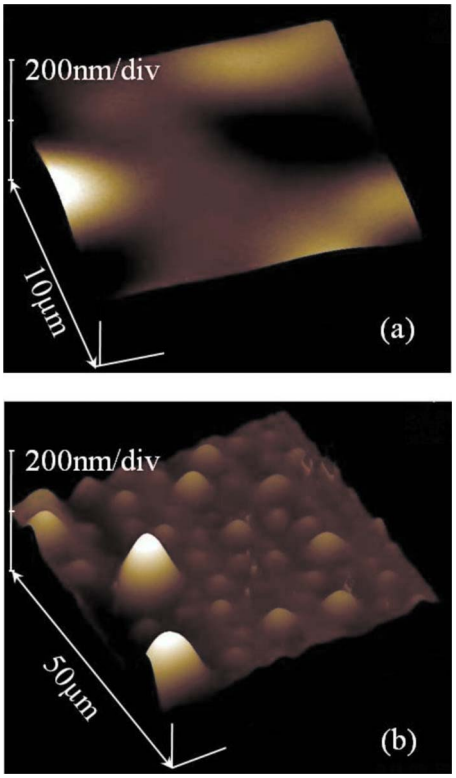

FIG. 4. (Color online) AFM scans of implanted and annealed germanium, (a) following an anneal at 100 °C for 22 h and a short anneal at 300 °C for 5 min (10×10 μm^2 scan area); (b) following an anneal at 150 °C for 22 h and a short anneal at 300 °C for 5 min (50×50 μm^2 scan area).

budget of the defect nucleation process: the higher the nucleation temperature, the larger the blisters [Figs. 4(a) and 4(b). ω-2θ 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 ω-2θ diffraction patterns prior to STA at 300 °C [Fig. 3(b)]. 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 STA at 300 °C. In addition, the broadening of the germanium feature on triple-axis ω diffraction patterns suggests an increase of local deformation [Fig. 5(a)]. The full width at 0.001 height (FW0.001M) increases from 240 arc sec in as-implanted germanium to 600 arc sec after a long time anneal at 100 °C and a STA at 300 °C. It is attributed to local lattice deformations due to hydrogen gathering.[14] The latter is observed after the STA at 300 °C, irrespective of the anneal temperature considered for completing the defect nucleation [Fig. 5(b)]. 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.[2,10]

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

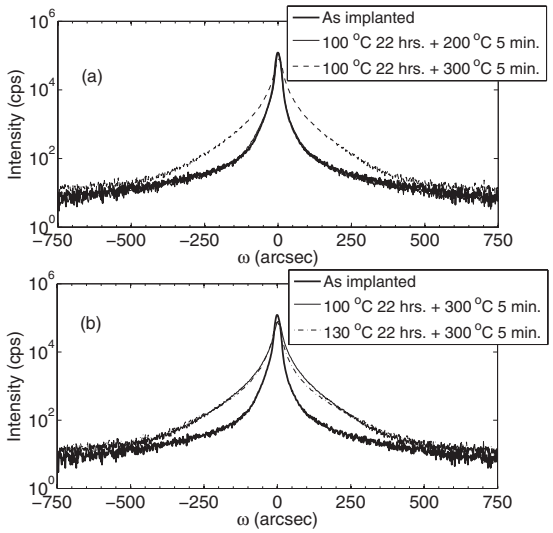

FIG. 5. XRD (ω) patterns: (a) impact of STA on lattice deformation in hydrogen implanted germanium after long time anneals at 100 °C; (b) impact of thermal budget during the nucleation process on the lattice deformation caused by the STA at 300 °C.

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.[16,17] The internal pressure in large gas pockets increases and leads to the extension of small cracks into microcracks.

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 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. The suitability of such thermal treatment for the fabrication of GeOI substrates at low temperature is illustrated in Fig. 6(a). 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(b)]. 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 II).

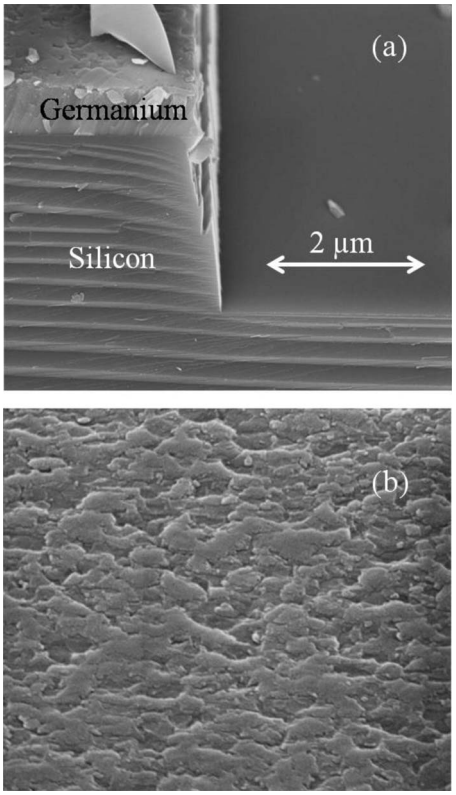

FIG. 6. Scanning electron microscopy graphs of the GeOI sample resulting from an exfoliation carried out after a 24 h long anneal at 130 °C and a STA at 300 °C for 5 min: (a) cross-sectional view of the germanium/SiO_2/silicon patterned structure. A 680 nm thick germanium layer is transferred for the donor germanium wafer to the host silicon wafer (b) top-down tilted view of the germanium surface exposed after complete exfoliation.

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 (a few minutes) 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.

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