

Layer transfer of semiconductors and complex oxides

by helium and/or hydrogen implantation

and wafer bonding

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Chapter 1 Introduction

The present thesis deals with the underlying physics and material science of the transfer of high-quality single crystalline layers of gallium arsenide and various complex oxides onto appropriate handling substrates by a combination of hydrogen and/or helium implantation and wafer bonding. Numerous attempts have been made for many years to develop methods of achieving high-quality thin single-crystalline layers of semiconductor or oxide materials on substrates. As an example, heteroepitaxial growth of GaAs layers on Si was intensively studied, but due to the lattice mismatch of 4.1% a high density (typically > $10^7/\text{cm}^2$) of threading dislocation could not be avoided [1, 2, 3, 4, 5, 6, 7]. In 2001 scientists from Motorola reported on supposedly device-quality GaAs epitaxial layers with low dislocation densities, close to that in bulk GaAs crystals of about $10^4/\text{cm}^2$, grown onto Si by molecular beam epitaxy (MBE) [8]. Epitaxial $SrTiO_3$ (with a 2% lattice mismatch) was used as a buffer layer in order to absorb the effects of different lattice constants between GaAs and Si based on the hotly debated and controversial concepts of a "compliant substrate" [9, 10, 11, 12, 13] which basically assumes that the intermediate layer can almost freely glide on the substrate and adapt the misfit of the subsequently grown epitaxial layer. In spite of an initial world wide publicity, Motorola has decided to stop its activity in this area. The presence of a low dislocation density in the epitaxial GaAs layers has never been independently confirmed and remains highly doubtful.

Layer transfer from a hydrogen-implanted wafer onto a desired substrate by wafer bonding and layer splitting is an attractive approach for materials integration. This approach has first been proposed by Bruel in 1995 [14] for the transfer of silicon layers and termed "smart-cut". It is now commercially used for the fabrication of silicon-on-insulator (SOI) wafers [15, 16, 17]. The substrate from which the implanted layer is split can be re-used, and a good thickness uniformity (in the 5 nm range) of the transferred layer is achieved by implantation. However, layer splitting can only be achieved if appropriate implantation conditions, specific to each material, are employed. Whereas layer splitting of silicon is now routine, and works for a relatively large range of implantation conditions, for many other materials there appears to exist only a narrow window of implantation conditions (dose, dose rate, actual implantation temperature due to beam heating) which makes it much more difficult to get reproducible results. This holds also for GaAs, one of the main materials investigated in this thesis.

A first attempt to transfer GaAs layers onto Si by layer splitting was reported by Jalaguier et al. [18], but relatively high splitting temperatures were required (e.g. 400-700 °C). The implantation temperature was not given in this publication. Tong et al. [19] reported that unbonded hydrogen-implanted GaAs wafers showed blistering of the surface after a subsequent annealing step (a prerequisite of splitting when bonded wafers are used) only if the implantation temperature was in a narrow temperature range of 160-250 °C.

When dissimilar materials are used, it is desirable that the splitting temperature is low enough to allow the bonded wafers to withstand stresses associated with the difference in thermal expansion coefficients. Recently, Gawlik et al. [20] proposed a low temperature GaAs splitting approach by two-step hydrogen implantation and wafer bonding. The two-step Himplantation consists of a high temperature (over 100 °C) implantation up to a dose of about 6×10^{16} H/cm² followed by a low temperature implantation (below 100°C) step up to the total retained dose of 2×10^{17} H/cm².

Application of the layer splitting approach for complex oxides is also an attractive alternative to fabricate thin *single-crystalline* oxide films with precise sub-micron thickness on any substrate at low temperatures [21]. Recently, crystal ion slicing (CIS) has been used to fabricate films of magnetic garnets and ferroelectric crystals [22, 23, 24]. The CIS process allows the formation of freestanding single-crystal micrometer-thick films with preserved domain structure. The technique relies on energetic (MeV) He⁺ ion implantation to generate a buried damaged sacrificial layer. This layer is found to preferentially etch upon immersion in a suitable etchant, ultimately resulting in microns-thick films separated from the parent substrate.

This dissertation consists of five chapters. Following this introductory chapter, Chapter 2 will present the concepts, key features and main advantages of the layer splitting approach. Ion implantation represents the first step of the process, therefore a review of knowledge of hydrogen and helium implantation in crystalline semiconductors is presented. Since the layer transfer approach involves wafer bonding, which is ideal for realizing material combinations, as one of its key processes, a description of the wafer bonding approach is also presented.

Chapter 3 focusses on the experimental work performed in this study. A more basic description of ion implantation technology, including implantation parameters and the heating effects of ion beams in crystalline materials is presented. Since knowledge of the exact wafer temperature during implantation is an important issue for the layer splitting process, a numerical estimate is presented. Also, the experimental procedures used in this study are described.

Chapter 4 contains the main experimental results of the dissertation. Blistering and splitting of GaAs and complex oxides will be shown. The effects of the implantation temperature are discussed, and the influence of the He+H co-implantation in reducing the splitting temperature/time of GaAs and some oxide materials is demonstrated. Low temperature layer transfer is especially desirable for layer transfer between dissimilar materials such as GaAs and oxides onto silicon. Layer transfer of thin GaAs layers onto Si substrates is demonstrated. Chapter 5 is devoted to an understanding of the blistering/splitting mechanisms. A thermodynamical model taken from the literature predicts the minimum implanted dose required for blistering/splitting. Two competing growth modes, i.e. blistering with subsequent breaking of the blisters and lateral propagation of micro-cracks are associated with the size and distribution of the platelets in as-implanted wafers and their evolution with annealing. Also, from a mechanical point of view, based on analysis of elastic deformations, the dynamics of the splitting process is described, which also explains the avalanche-like nature of the He and/or H induced layer splitting.

Chapter 2

Layer transfer by ion implantation and wafer bonding

Hydrogen implantation induced layer transfer also known as $Smart-cut^{\textcircled{B}}$, layer splitting or layer exfoliation was first introduced by Bruel in 1995 as a highly effective silicon layer transfer method for the fabrication of silicon-on-insulator (SOI) wafers. Since its first public disclosure in 1995, much effort has been spent to fully understand the basic processes of hydrogen agglomeration and micro-crack formation and overlap leading to layer splitting [25, 26, 27, 28, 29, 30, 31, 32] and to explore the potential provided by this technology. So far, besides its commercial application in fabricating SOI substrates [14, 15, 33] several attempts have been made to extend the hydrogen implantation induced layer transfer method to prepare a variety of other material combinations such as SOQ (silicon on quartz) [34, 35, 36], single-crystalline SiC on glass [37], silicon or polycrystalline SiC [38, 39], GaAs [18] or InP on silicon [40, 36, 41, 42].

2.1 General features of the layer transfer process

Layer splitting is a generic process enabling potentially any type of single crystal layer to be achieved on any type of substrate. As shown in Fig. 2.1, the first step is to implant hydrogen ions into a single-crystalline wafer frequently called device wafer. Since in applications the actual devices will be fabricated in this material this implanted wafer will give the active layer, while the host substrate onto which the layer is transferred is called handling wafer. Typical implantation doses for silicon vary from 1×10^{16} to 1×10^{17} H⁺/cm². The implanted device wafer and the handle wafer are bonded at room temperature (RT). The bonded pair is first annealed at a low temperature, to enhance the bond strength, followed by a higher temperature anneal to split the hydrogen implanted layer from the device wafer [14, 15, 36, 43].

During implantation, hydrogen ions collide with the host atoms to generate displacement damage (denoted as X in the following) in the form of vacancies and interstitials (Frenkel pairs) along with their agglomerates. In addition to generating displacement defects, the implanted hydrogen atoms can interact with defects created by previously implanted hydrogen ions to



Figure 2.1: Schematics of layer transfer by ion implantation and wafer bonding approach.

form defect-hydrogen complexes (X-H). Besides X-H complexes, platelets, which are separated, H-terminated adjacent crystalline planes over a finite area are formed along the $\{100\}$ and {111} planes [44, 45, 46]. In silicon platelets are believed to result from a supersaturation of hydrogen and hydrogen passivation of broken bonds [47]. During annealing, some trapped hydrogen dissociates from X-H complexes and diffuses into the platelets forming H₂ molecules and subsequently, leading to an increase of the internal pressure and formation of micro-cracks. It was proved that platelet generation is essential in the splitting process. Platelets are acting as nucleation sites for micro-crack formation when hydrogen atoms diffuse into the platelets to form molecular hydrogen. After annealing for a sufficiently long time, the pressure in the micro-cracks becomes sufficiently high to allow cracks to expand in lateral direction. In reality a distribution of micro-crack sizes develops. The smaller cracks containing a higher pressure will shrink and the larger ones will expand by diffusion of hydrogen from the smaller to the larger cracks in terms of a typical Ostwald ripening process [28, 46, 48, 49]. The splitting happens when the micro-cracks join together in the same plane. The hydrogen implanted layer bonded to the handle wafer splits off close to the mean hydrogen ion penetration depth (R_p) , provided the implanted hydrogen dose exceeds a critical value [29]. Another thermal annealing step at high temperatures (e.g. 1100°C for silicon) is frequently applied for further increasing of the bonding strength and for removing of residual implanted hydrogen and related defects. Because the mean surface micro-roughness of the split layer surfaces is relatively high in the range of 100 Å, a final short chemical mechanical polishing (CMP) step has to be applied to remove a

few hundred Angstroms from the top surface, resulting in a smooth surface with a mean surface micro-roughness of < 1.5 Å and with a thickness variation of ~ 50 Å[14, 50]. Alternatively, the surface smoothing can be accomplished by a high temperature process at 1100 °C in a low pressure of hydrogen which allows a high mobility of silicon surface atoms [51].

Compared to conventional layer transfer methods which employ wafer bonding and polishing/etching thinning technique, e.g., bond-and-etched back SOI (BESOI), the ion implantation induced layer splitting has many advantages. Firstly, a high thickness uniformity of the transferred layer is guaranteed by the ion implantation process which allows to control the implantation depth R_p (determining the thickness of the transferred layer) within a few percent over the whole wafer area. Thickness control is much more difficult by grinding and polishing processes. The use of an etch-stop layer also allows accurate thickness control but it requires the epitaxial growth of the etch-stop layer and subsequently of a layer of the device wafer material which is an expensive approach and involves the risk of introducing undesirable defects such as dislocations. Secondly, the device wafer can be reused for the next cycle after a short polishing step. This is of special interest for expensive materials, such as SiC for which costs, for a 3-inch wafer, in the range of several thousand US dollars are typical, since the cost can be significantly reduced by transferring many thin layers of these materials onto appropriate inexpensive substrates (in the case of SiC those inexpensive substrates could be either poly-crystalline SiC or single-crystalline Silicon) without sacrificing the original wafers, as it is always the case for methods based on polishing and etching.

2.2 Ion implantation induced layer transfer

Before the development of the Smart-Cut[®] process [14], hydrogen (H) and helium (He) in semiconductors have been studied for more than two decades. Since the middle 80's, the behavior of hydrogen in single crystalline semiconductors has attracted growing interest because it was found that hydrogen passivates the electrical activity of many impurities including dopants, impurity atoms, defects and interfaces in almost any semiconductor material [52, 53, 54, 55]. Since then, extensive experimental and theoretical work has been carried out to understand the role of H in semiconductors, especially in silicon [56, 57, 58].

Given sufficient concentration and atomic mobility, implanted He forms gas bubbles or micro-cracks in crystalline materials [59, 60, 61, 62, 63, 64]. More recently, it was shown that H and He ion implantation enhances the thermal strain relaxation of pseudomorphic $\operatorname{Si}_{1-x}\operatorname{Ge}_x/\operatorname{Si}(100)$ heterostructures grown by molecular beam epitaxy (MBE) and reduces significantly the density of threading dislocations [65, 66, 67, 68]. A narrow defect band is generated by ion implantation slightly underneath the SiGe/Si interface. The defects promote nucleation of dislocation loops which glide to the interface where they act as misfit segments and enable strain relaxation.

Some of the most prominent results that are relevant to hydrogen or helium implantation induced layer splitting process are summarized in the following.

2.2.1 Hydrogen in crystalline semiconductors

Hydrogen is usually introduced into crystalline materials by ion implantation but other techniques are also available such as electrochemical [69] and plasma [70, 71, 72, 73] hydrogenation. Hydrogen was found to have significant effects on the microstructure and electrical properties of silicon. If it is implanted in a high dose $(10^{16} - 10^{17} \text{ cm}^{-2})$ platelets-like planar defects are generated on {100} and {111} planes. Romani and Evans [44] determined the range of hydrogen dose required to induce H-containing platelets in silicon. Moreover, they estimated that only about 1/8 of the implanted H is actually contained in the platelets while most of H atoms are trapped by other defects, such as vacancy agglomerates or dislocation loops that are present in the H as-implanted silicon. Cerofolini et al. [74] found that the size of the platelets increases with the annealing temperature, while the density of the defects decreases correspondingly. Above 900^oC most of the platelets disappear except a small number of {111} platelets. Instead many gas bubbles bound by {100} and {111} planes are formed.

A number of theoretical investigations were carried out in order to study the hydrogencontaining complexes and the evolution of hydrogen-induced defects (platelets or bubbles) in H-implanted silicon. Using the pseudopotential-density-functional method, Van de Walle et al. [75] have calculated the stable sites and migration paths of hydrogen in silicon. They have pointed out that the bond-centered site (BC) is the favorable site for the neutral and positively charged H in silicon, while the tetrahedral interstitial site (Td) is preferred when H is in the negative charge state in n-type silicon. The possibility of two hydrogen atoms combining into a H_2 complex was also investigated [53]. The minimum energy for forming a molecule was achieved when two hydrogen atoms occupy two adjacent tetrahedral interstitial sites oriented in the < 100 > direction. In the silicon crystal the H₂ bond length is 0.82 Å (slightly higher than the bond length of H₂ in vacuum ~ 0.75 Å) and the binding energy is correspondingly reduced to -1.92 eV/atom compared to the values in vacuum: -2.31 eV/atom (calculated) or -2.26 eV/atom (experimental). It is further postulated that the existence of voids or vacancy clusters favors the formation of H_2 gas molecules. Diffusion from one site to another requires an energy of 0.8-1.0 eV [47]. Besides H_2 in tetrahedral position, an alternative stable configuration denoted as H_2^* was suggested by Chang et al. [53]. H_2^* contains one H that is center-bonded and the other existing in interstitial site. Even though there are controversial views in literature on many aspects of hydrogen in silicon such as the exact energy states, the diffusivity and diffusion path of hydrogen at elevated temperatures, etc., it is accepted that H may predominantly exist in the form of $H^+(BC)$, H_2^* , H_2 and B-H in boron doped p-type silicon; and in the states of $H^{-}(Td)$, H_{2}^{*} , H_{2} and P-H in phosphorus doped n-type silicon. Table 2.1 lists the energies for various interstitial configurations of atomic hydrogen, diatomic hydrogen complex, and dopanthydrogen complex in p and n-type silicon [53]. The energy states for H^+ , H^0 , and H^- at their most stable positions were calculated relative to H⁰ in vacuum.

Table 2.1: Calculated energy states for different configurations of hydrogen in silicon [53]. The energies are in units of eV per H atom *except* for H_2^* and H_2 where the energies are in eV *per diatomic complex*. The energy of a free H atom in free space is taken as the zero of energy.

| Position of H | p-type Si | n-type Si |
|-------------------------------|---------------------|---------------------|
| $H^{-}(Td)$ | -0.4 eV | -1.54 eV |
| $\mathrm{H}^{0}(\mathrm{Td})$ | -1.1 eV | -1.1 eV |
| $H^+(BC)$ | $-1.85~\mathrm{eV}$ | $-0.71~\mathrm{eV}$ |
| H_2^* | -3.4 eV | -3.4 eV |
| H_2 | -3.8 eV | -3.8 eV |
| B-H | -2.5 eV | |
| P-H | | -2.0 eV |

Hydrogen implantation into GaAs is a frequently used processing step in the fabrication of various optoelectronic devices, diodes and semiconductor lasers [76, 77, 78, 54, 47, 79]. Therefore, many studies have been performed in order to understand the nature of the defects produced by hydrogen implantation [80, 81, 82, 83, 84]. Neethling et al. [85] found that after room temperature implantation of protons with a dose of $10^{15} \div 10^{16}$ cm⁻² very little damage can be detected by cross section transmission electron microscopy in as-implanted samples. Significant damage can be observed for doses higher than 10^{17} cm⁻². However, even for lower doses damage is detected if the samples undergo post-implantation annealing. Thermal treatment at about 500^{0} C causes point defects to precipitate in the form of dislocation loops and voids that are centered around the projected range of protons (R_p). After subsequent annealing of such implanted samples {111} hydrogen platelets are formed. A similar result is obtained if hydrogen implantation is directly performed at 600^{0} C [86].

A theoretical model is also available for estimating the gas pressure in the H-filled platelets induced by H-implantation [87]. It was found that for low dose implantation $(5.0 \times 10^{15} \text{ cm}^{-2})$ approximately 1.9% of the implanted hydrogen atoms are trapped in the platelets, while the remaining implanted hydrogen diffuses to the surface and into the bulk crystal. The gas pressure in the platelets was calculated and found to be of the order of 1 GPa. The average hydrogen density in the platelets was calculated [87] to be ~ $4 \times 10^{22} \text{ cm}^{-3}$, which corresponds to between one and two hydrogen atoms per vacancy in a platelet.

2.2.2 Helium in crystalline semiconductors

Due to its low solubility, He segregates in gas-vacancy complexes and may also form bubbles depending on implantation parameters such as energy, temperature and dose [88, 89, 62, 64]. During annealing at elevated temperatures of He-implanted silicon, bubbles grow and He is released from the bubbles by gas out-diffusion leading to void formation, i.e., cavities. Recent studies have shown that these cavities can be used as very efficient trapping sites for metallic impurities [90].

It was shown that the cavity nucleation and growth phenomena in He implanted and annealed Si strongly depend on the implanted He dose (Φ_{He}) [61]. For low doses (e.g. $\Phi_{He} < 5 \times 10^{15} \text{ cm}^{-2}$) He vacancy $(He_m V_n)$ clusters are formed, but they dissociate at low temperatures (250^{0}C) preventing the formation of bubbles (He filled cavities). For high doses (> 1 × 10^{16} \text{ cm}^{-2}), cavity nucleation takes place during He implantation and, upon thermal annealing, cavity coarsening occurs simultaneously with the release of He atoms from the sample. At intermediate He doses $(5 \times 10^{15} \text{ cm}^{-2} \le \Phi_{He} \le 1 \times 10^{16} \text{ cm}^{-2})$, thermal annealing causes desorption of most of the implanted He atoms, but the remaining He forms a low density system of clusters. These clusters shows strong strain contrast in TEM images, indicating that such cavities may contain He atoms under high pressure [61].

Follstaedt et al. [91] have found that appropriate He implantation into (100)-oriented GaAs induces blistering after post-implantation annealing. Elastic recoil detection (ERD) and TEM analysis have shown that a combined dislocation-bubble microstructural feature appears responsible for breaking away of the implanted layers from the substrate. The dislocation-bubble lines are localized near the end-region of the damaged layer for room-temperature implantation, whereas they were found between the projected He range (R_p) and the back of the damaged layer for implantation at 150^oC.

Another orientation, (111)-oriented GaAs, was implanted with He and annealed for short times (180-300 s) at 250^oC or 300^oC, and then examined with plan-view TEM by Nomachi et al. [92]. These short anneals produced features interpreted to be extended He platelets ~ 1 μm in diameter and lying on {111} planes. They also observed that longer anneals induce flaking of the implanted surface.

2.3 Basics of blistering and splitting

Since long time it is known that high dose inert gas or hydrogen implantation in materials can induce visible macroscopic effects such as blistering, swelling, flaking and exfoliation during implantation [93, 94, 95, 96]. Medium-dose implantation followed by thermal annealing also induces blistering and exfoliation of the implanted material. These effects are associated with the microscopic defects created during implantation and their evolution during an annealing process.

2.3.1 Onset of blistering

Experimentally, by optical microscopy, it has been found that surface blisters in hydrogen implanted silicon wafers do not form if the annealing time has not reached a critical value. The critical time at which surface blisters are optically detectable is widely used to quantify the blistering process. Tong et al. [97, 98] found that the time required to generate optically detectable surface blisters strongly depends on annealing temperature via an Arrhenius relationship (2.1). This characteristic time was termed "on-set" or blistering time t_b :

$$1/t_b \propto exp(-E_a/kT) \tag{2.1}$$

where k is Boltzmann's constant, T the absolute temperature, and E_a the activation energy of the process.

Experimentally it was found that the time required for large area splitting, referred to as splitting time, when the surface of the implanted wafer is stiffened by any means including bonding to a handle wafer, is proportional to and about 10 times longer than the blistering time [97]. Therefore, the blistering time may be used for an estimate of the time needed for transfer of layers by splitting. Blistering and splitting processes by ion implantation and post-implantation annealing are schematically described in Fig. 2.2



Figure 2.2: Schematic description of the blistering and splitting processes.

Bruel et al. [99] studied the microstructure of hydrogen implanted silicon using high resolution cross-section TEM. After implantation of hydrogen doses in the range of a few 10^{16} H⁺/cm² up to 10^{17} H⁺/cm², no defects are present at the silicon surface, but TEM observation indicates the presence of platelets or micro-cavities confined around the maximum hydrogen concentration depth (R_p) (see Fig.2.3). They observed that the hydrogen platelets grow during thermal annealing by an Ostwald ripening mechanism. HR-TEM revealed the formation of a large crack parallel to the wafer surface with a zigzag shape which follows the paths of some big {100} and {111} oriented platelets along the hydrogen implantation peak. In the very beginning the growth is more likely a lateral propagation since the platelets themselves are



Figure 2.3: Cross section TEM image of H-platelets in silicon [99].

not yet open, but held together via van der Waals forces between the two hydrogen covered internal surfaces of the platelets. The platelets grow in a closed form up to a critical size upon which the internal pressure is high enough to overcome the surface energy γ_p associated with the interaction between the hydrogen covered surfaces of the platelets. Due to the presence of implantation-induced defects, stress concentration and the chemical reaction at the edges of micro-cracks, it can reasonably be assumed that γ_p is much lower than the surface energy γ_{Si} of the corresponding crystal planes of silicon determined by the cleavage method.

Along with the mentioned progress based on experimental work, an elegant analysis of the H-induced blistering/splitting process was given by Freund from a mechanical point of view [29]. Freund's model predicts a minimum hydrogen implantation dose for splitting of silicon, which is in reasonable agreement with many experimental observations. This model, along with other mechanical and thermodynamical work will be addressed in more detail in Chapter 5.

2.3.2 Splitting kinetics

Layer splitting is a special case of blistering which occurs when the implanted wafer is bonded to a stiffener. Aspar et al. [100] investigated the splitting kinetics of H-implanted silicon wafers. They investigated the activation energy for splitting in different temperature regimes (see Fig. 2.4). At high temperatures, a splitting activation energy of about 0.5 eV was found and it is



Figure 2.4: Logarithm of inverse time required for on-set of blistering or layer transfer (splitting) for H-implanted $(5.5 \times 10^{16} \text{ H}^+/\text{cm}^2 \text{ at } 69 \text{ keV})$ silicon as a function of inverse temperature [100].

associated with free atomic hydrogen diffusion (0.48 eV). At low temperatures, the splitting activation energy is about 2.2 eV: hydrogen diffusion is still expected to occur, but this time linked to a trapping-detrapping phenomenon due to the trap efficiency in this temperature range:

$$[H_{free}] + [X] \leftrightarrows_{k_1}^{k_2} [HX] \tag{2.2}$$

The equilibrium constant can be written as:

$$K = \frac{k_1}{k_2} = K_0 exp \left[\frac{E_{bind}}{kT}\right]$$
(2.3)

with k_1 and k_2 being respectively the [HX] complex formation and dissociation constant in the reaction, E_{bind} the binding energy of the hydrogen atom on the trap, and K_0 a constant depending on the nature of the trap. Fick's second law applied to the H diffusing species in the presence of trapping sites leads to an expression of the effective diffusion coefficient of hydrogen in silicon [47]:

$$D_{eff} = \frac{D_{H_{free}}}{1 + K[X]} = \frac{D_0 exp[-E_{H_{diff}}/kT]}{1 + [X]K_0 exp[E_{bind}/kT]}$$
(2.4)

where $D_{H_{free}}$ is the free hydrogen diffusion coefficient and [X] the concentration of unsaturated traps.

At high temperatures, this equation leads to $D_{eff} = D_{H_{free}}$. At low temperatures, considering $K[X] \gg 1$, the activation energy is found to be expressed as $E_{bind} + E_{H_{diff}}$, therefore the low temperature splitting is mostly controlled by hydrogen diffusion limited by the trapping phenomenon. The transition between high and low temperature mechanisms depends on the binding energy and the value of $K_0[X]$ (depending on the nature and concentration of non-saturated traps).

It has also been found experimentally that in order to achieve blistering/splitting, the wafer temperature during implantation must fall within a temperature window which is specific for each material [19]. The temperature window appears to be mainly associated with the conditions to form platelets and micro-cracks in the materials which require an appropriate level of damage during implantation. It is worth mentioning that many studies were performed in order to reduce the splitting temperature and/or the dose required for splitting. One of most prominent approaches to reduce the required dose or temperature is the so-called *smarter-cut* approach which is based on low dose boron implantation prior to hydrogen implantation [101]. The B + H mechanism as well as an approach based on He + H co-implantation will be discussed in the following section.

2.4 X + H co-implantation technique

X+H co-implantation, i.e. hydrogen implantation along with another element (denoted as X), is an important step beyond the original Smart-Cut[®] process, in which the only implantation species is hydrogen. The interaction between hydrogen and other implantation species may have a significant influence on atomic processes leading to surface blistering or layer splitting. Since the co-implantation approach enabled a reduction of either total implantation dose required for layer splitting or splitting temperature many studies have been performed in order to understand the mechanisms of X+H co-implantation.

2.4.1 B + H co-implantation approach

Atomic boron and hydrogen in silicon substrates form complexes even at room temperature. The B-H complex is one of the most stable forms of hydrogen at RT in hydrogenated p-type silicon [53]. Implanted boron may trap up to 12 hydrogen atoms [55]. The B-H complexes are not stable and usually dissociate at temperatures as low as 150° C. Since the energy barrier for the dissociation of a B-H complex (2.14 eV) is less than that for Si-H (3.6 eV) [75, 102, 103], the formation of B-H and its subsequent dissociation may create an energetically more favorable path to release hydrogen from these Si-H complexes. Therefore, the probability of releasing mobile hydrogen from its associated complexes is increased and more atomic hydrogen is available to form H₂ gas, leading to blistering/splitting.

It is generally accepted that the Si-H bond is weakened by the interaction between H and the present, nearby B atom, which makes it easier to release H from Si-H complexes [52, 104]. It has

also been reported that the diffusivity of hydrogen in p-type silicon is higher than in intrinsic and in n-type silicon [53]. The involvement of boron in the development of blistering could also involve a catalytic process, associated with the following chemical reaction (Eq. (2.5)). [54]:

$$H^0 + BH \longrightarrow H_2 + B^- + h^+ \tag{2.5}$$

It has also been suggested that boron leads to an increase of hydrogen detrapping and diffusion indirectly via its influence on the Fermi level [105].

Based on the previous findings that blistering and splitting are much easier in heavily boron doped p-type silicon wafers, a low dose of boron implant was introduced prior to the H implant with their projected range aligned. Experimentally, it was found that the blistering time for the co-implanted samples is significantly reduced. Another striking feature associated with B+H co-implantation is the reduced activation energy (E_a) for blistering and splitting (Fig. 2.5). The effect of different thermal pre-annealing times of B+H co-implanted silicon is also shown.



Figure 2.5: Blistering time as a function of inverse absolute temperature for B+H co-implanted (a), B+H co-implanted and pre-annealed at 250°C for 10 minutes (b) or 50 minutes (c) and H-implanted only (d) Si wafers. Hydrogen (H_2^+) was implanted at 130 keV with a dose of 5×10^{16} cm⁻² while for co-implantation experiments boron (B⁺) was implanted at 180 keV with a dose of 5×10^{14} cm⁻² prior to hydrogen implantation.

Based on the B+H co-implantation, a low temperature splitting approach was suggested for layer transfer between dissimilar materials with grossly different coefficients of thermal expansion, e.g., silicon and sapphire (SOS) or silicon and quartz (SOQ) [34]. Another feature of the B+H co-implantation technique is its effectiveness in reducing the minimum H implantation dose required for blistering/splitting. It was demonstrated that for B+H co-implantation a dose of $2.5 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ is equivalent in terms of blistering time and temperature to the case of H implantation only in which a $5 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ dose was used. In other words, approximately half of the hydrogen implant dose was saved in this case. Based on the B+H co-implantation technique, the least H₂⁺ dose that was used for a successful large area (e.g., 4-inch in diameter) layer transfer is $1.4 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ [106].

2.4.2 He + H co-implantation approach

Even though appropriate He+H co-implantation shows similar effects as B+H co-implantation in terms of reducing the hydrogen dose for layer splitting, the mechanisms behind these two co-implantation processes are very different. Unlike boron, He is a non-reactive species and it is not chemically involved in the development of blistering and splitting. It is believed that the main contribution of He is rather to serve as an alternative gas species to drive the growth of hydrogen-induced micro-cracks, which finally leads to blistering and splitting.

Agarwal et al. [107] have shown that the minimum hydrogen dose necessary to trigger blistering and exfoliation of silicon can be decreased by about one order of magnitude by helium and hydrogen co-implantation. In this case, the helium atoms provide the pressure inside the cavities more efficiently than molecular hydrogen. Moreover, they stabilize the hydrogen bonded to the cavity walls facilitating the propagation of the buried cracks [108].

Since then, much work has been done in order to understand the physical mechanisms responsible for blistering and exfoliation of He+H co-implanted crystals. Using thermal desorption spectrometry (TDS) it was found that during thermal annealing of He+H co-implanted silicon samples an explosive emission of both gases occurs [109]. The phenomenon is kinetically controlled with an effective activation energy of 1.3 ± 0.3 eV. Strict correlation between He desorption during annealing and exfoliation efficiency was experimentally observed [110]. The influence of He+H co-implantation on blistering and splitting of other materials (i.e. SiC, InP) was also shown [111, 112].

2.4.3 Two-step H implantation approach

Recently, another group reported on low-temperature (i.e. 200° C) GaAs layer splitting using a two-step hydrogen implantation [113, 20]. This process is composed of high temperature (over 100° C) implantation up to a dose of about 6×10^{16} H/cm⁻² followed by a low temperature (below 100° C) hydrogen implantation with a dose of 1.6×10^{17} cm⁻². This approach has been used to transfer a thin GaAs layer onto silicon.

2.5 Wafer direct bonding and layer transfer

In order to achieve good uniformity of the transferred layers a high quality of the bonding interface between implanted and handle wafers is required [114, 115]. Wafer direct bonding

refers to the phenomenon that mirror-polished, flat and clean wafers, when brought into contact, bond to each other at room temperature without the use of adhesives or external forces [116]. Typically, wafer direct bonding consists of three basic steps: (1) Surface treatments of the device wafer and handle wafer prior to bonding; (2) room temperature bonding, i.e., the two pre-conditioned wafers are brought into contact and bonded at room temperature; (3) bonding energy enhancement through thermal treatment after room temperature bonding. The basics of these steps are briefly described in the followings.

2.5.1 Surface treatments

Surface treatment is an essential step in wafer bonding and strongly influences the bonding probability and bonding quality. Given that the wafers (with or without intermediate layers) are sufficiently smooth, flat and properly chemically cleaned, almost any materials can be bonded to each other [117]. Surface treatments of wafers prior to bonding usually include chemomechanical polishing (CMP) [118] and chemical treatment of the wafer surfaces. CMP is used to smoothen and flatten the wafer surfaces since wafer direct bonding is based on intermolecular van der Waals attraction forces between mating surfaces of the wafers. Macroscopically, all intermolecular forces are short-ranged forces, therefore sufficient surface for bonding depends on the surface bonding species that determine the distance over which the intermolecular forces are effective. Based on analysis of elastic deformation at the bonding interface when two wafers are brought into contact, a quantitative expression for bonding criterion is given by Eq. (2.6) (see Fig. 2.9) [119]:



Figure 2.6: Schematic drawing of a gap caused by flatness non-uniformities [119]: (a) R > 2d; (b) R < 2d.

$$h^{1/2}/R < [\gamma/(1.2Ed^3)]^{1/4} \qquad for R > 2d$$
 (2.6)

$$h^2/R < 6.7\gamma/E \qquad for R < 2d \tag{2.7}$$

R represents half of the width of the gap and h is half of the gap height. E is Young's modulus and d the wafer thickness assumed to be identical for both wafers involved. γ is the specific surface energy of the interface (or energy to open the interface). Typical values of γ after room temperature bonding of silicon to silicon are about 0.1 J/m² for hydrophilic bonding and 0.01 J/m² for hydrophobic bonding. Equation 2.6 suggests that two wafers are bondable if the elastic energy required for deformation is less than the surface energy reduction by closing the interface gap. The surface roughness, which is characterized by the root-mean-square (RMS) value, of most commercially available prime grade wafers meets the bonding criteria since the RMS roughness is less than ~ 0.5 nm and therefore these wafers can directly be used for bonding without any additional polishing step. Nevertheless, for many materials which are difficult to polish, e.g. Ge, AlN, LaAlO₃, an intermediate bonding layer such as SiO₂ or Si₃N₄ can be used.

Wafer bonding requires wafers with clean surfaces which are free of particles and of organic and metallic contaminants. Particles lead to local unbonded areas, which are often referred to as interface voids or bubbles. Too many particles attached on the wafer surfaces may even result in total failure of any bonding. Lateral dimension of bubbles caused by particles in the micrometer range are typically in the order of mm and therefore can be detected easily by ultrasonic microscopy or infrared transmission. For avoiding inclusion of particles and consequent interface bubbles, room temperature wafer bonding is usually performed in a cleanroom of class 10 or better environment. Surface cleanliness has a direct effect on both the structural and electrical properties of the bonding interface. Surface contaminants can significantly reduce the surface reactivity and lower the bonding energy. Moreover, trapped interface particles can result in unbonded areas (bubbles) many orders of magnitude larger than the particles. A particle with a diameter of 2h can form an unbonded interface area with a diameter of 2R for R>2d:

$$R = \left[\frac{0.67(\frac{E}{1-\nu^2})d^3}{\gamma}\right]^{1/4} h^{1/2}$$
(2.8)

A particle of about 1 μ m diameter leads to a bubble with a diameter about 5000 times larger (0.5 cm) for typical 4-in diameter wafers with a thickness of 525 μ m. The cleaning procedures employed prior to room-temperature wafer bonding have to remove contamination on the surfaces without degrading surface smoothness.

Wet-chemistry wafer cleaning commonly used in the semiconductor industry [120] is fully applicable to wafer bonding. However, since the quality of the bonding interface is extremely sensitive to particulate and organic contamination, additional cleaning techniques may be needed. Hydrogen-peroxide-based (RCA) wet cleans are most commonly used in silicon wafer bonding. The basic cleaning steps involve two solutions: RCA1 (or SC-1, refers to Standard Clean-1) and RCA2 (or SC-2), which are used sequentially: after cleaning in RCA1, the wafers are rinsed thoroughly in DI water with a resistivity of about 18 MΩcm.

The RCA2 solution is then employed to remove metal contaminants such as Al, Fe, Mg, Au, Cu, Cr, Ni, Na, etc. Because the involved chemicals NH_4OH , HCl and H_2O_2 can deteriorate even at room temperature, the two solutions should be prepared immediately before use. Wafer

cleaning is always followed by a de-ionized (DI) water rinse. After this step, most of the metal and organic contamination on the surface has been removed. After RCA cleaning and/or additional chemical treatments, the silicon surface is typically terminated by polar hydroxyl (-OH) groups and one or more monolayers of water molecules and is referred to as hydrophilic surface. A hydrophobic silicon surface can be obtained by simply dipping the hydrophilic silicon wafer in dilute (2 to 5 % in volume) HF solution. The silicon surface is then terminated by hydrogen atoms. The hydrophilicity of wafer surfaces which underwent different pre-treatments as well as the long-term stability of a clean surface have been investigated by contact angle measurements [121, 122, 123]. The typical compositions of the RCA solutions and operating conditions are listed in Table 2.2.

For GaAs, as a first step in typical substrate cleaning, as received GaAs wafers are exposed to a UV-generated ozone atmosphere for 10-20 minutes [124]. This procedure removes residual organics from the surface by volatilizing them. This cleaning procedure leaves a very thin oxide on the wafer surface, 0.8 to 1.5 nm, as measured by X-ray photoemission spectroscopy [125]. Different methods are used to remove the UV-ozone grown oxides: (i) thermal desorption (> 500⁰C), (ii) chemical etching and (iii) atomic-hydrogen etching. In the case of chemical oxide removal the ozone-oxidized samples are dipped in HCl or NH₄OH - based solutions and then rinsed in DI water. Atomic hydrogen surface cleaning was successfully used before GaAs wafer bonding [126].

| | Compositions | Cleaning | Cleaning | Designed | |
|----------|--|-------------------------|------------|------------------|--|
| | $\mathbf{by} \ \mathbf{volume}^a$ | temperature (0 C) | time (min) | to remove | |
| RCA1 | NH ₄ OH:H ₂ O ₂ :H ₂ O | 75 to 85 | 10-20 | Particles, or- | |
| | | | | ganic contam- | |
| | | | | inants, some | |
| | | | | metals | |
| | =1:1:5 to $1:2:7$ | | | | |
| Modified | NH ₄ OH:H ₂ O ₂ :H ₂ O | 70-85 | 5-10 | Particles, or- | |
| | | | | ganic contam- | |
| | | | | inants, some | |
| | | | | metals | |
| RCA1 | = 0.01 - 0.25 : 1:5 | | | | |
| RCA2 | $\mathrm{HCl:H_2O_2:H_2O}$ | 75-85 | 10-20 | Alkali and heavy | |
| | | | | metals | |
| | =1:1:6 to $1:2:8$ | | | | |

Table 2.2: Compositions of standard and modified RCA1 and RCA2 cleaning solutions and application conditions in Si wafer cleaning [116].

^aNote: CMOS grade, 30% H₂O₂, 29% NH₄OH, 37% HCl and DI water are used.

2.5.2 Room temperature bonding

After the first step of surface treatments, two flat and clean wafers are brought into contact and bonded at room temperature [116]. A small external force is usually needed to initiate the bonding at a local point, which can be at the center or at the edge of the contacting wafers. Driven by the van der Waals force between the two closely spaced wafer surfaces, the bonding front spreads over the whole area in a few seconds [127]. Typical physical and chemical phenomena associated with the room temperature bonding process include elastic deformation, atomic interaction between ion groups, adsorption of tiny particles at the surfaces, and possible trapping of inert gas such as N_2 , which is abundant in air. The first two processes are positive for bonding in the sense that the two wafers are compliant and attractive to each other which fundamentally makes wafer bonding possible. The last two factors, on the other hand, are detrimental to wafer bonding.

2.5.3 Bonding energy

The bonding strength is characterized by the specific surface energy acquired at the bonded interface after a bonding process. The most convenient method to measure the surface energy of bonded pairs is the crack-opening method [128], schematically shown in Fig. 2.7. The



Figure 2.7: Schematics of crack-opening method for investigating the bonding energy [128].

technique is actually based on the equilibrium of elastic forces of the bent separated part of a pair and bonding forces at the crack tip.

Table 2.3 lists the formula of surface energy in various configurations [116].

| Configuration | Formula of bonding energy |
|---------------------------------|---|
| Pair of identical wafers | $\gamma = \frac{3Et^3h^2}{32L^4}$ |
| Pair of dissimilar wafers | $(\gamma_1 + \gamma_2) = \frac{3h^2 E_1 t_1^3 E_2 t_2^3}{8L^4 (E_1 t_1^3 + E_2 t_2^3)}$ |
| Pair with very different | $3E_1t_1^3h^2$ |
| wafer thicknesses $t_2 \gg t_1$ | $\gamma = \frac{1}{16L^4}$ |

Table 2.3: Formula for surface energy in various configurations.

After room temperature bonding, the wafer pairs physically adhere to each other with a typical bonding energy γ in the range of 100 mJ/m² for hydrophilic bonding and 10-20 mJ/m² for hydrophobic bonding [127]. However, for most applications a much higher bonding energy is required. An enhanced bonding energy is usually achieved by annealing the room temperature bonded wafer pairs at elevated temperatures. The increase of the bonding energy with temperature is attributed to the chemical reactions occurring at the bonding interface during the annealing process. Typical curves of bonding energy as a function of temperature are given in Fig. 2.8.



Figure 2.8: Comparison of surface energies of bonded hydrophilic and hydrophobic Si/Si pairs as a function of annealing temperature [116].

When an already implanted wafer is bonded to another substrate it is highly desirable that the bonding energy gets high enough before the onset of blistering, because otherwise blistering may induce debonding of the wafers. A quantitative treatment was suggested by Huang et al., [129] in order to calculate the critical bonding energy required for layer splitting in the case of Si/Si wafer bonding. Assuming that one silicon wafer was implanted with hydrogen prior to bonding, the waved surface presented in Fig. 2.9 represents the situation when surface blistering occurs during thermal treatment due to insufficient bonding energy.



Figure 2.9: Schematics of blistered bonding interface. Here d refers to the thickness of the bonded wafers and t to the thickness of the delaminated layer approximately corresponding to the hydrogen implantation depth.



Figure 2.10: Calculated critical surface energy γ_c required for layer splitting for Si/Si: HB - hydrophobic bonding and HL - hydrophilic bonding [106]. The crossing points for hydrophilic and hydrophobic bonding are indicated.

The critical surface energy required for layer splitting is given by

$$\gamma_c = \frac{k}{24} \frac{R^3}{t^3} T \alpha \phi_H \tag{2.9}$$

where R represents the lateral dimension of surface blisters, t is the layer thickness, T the absolute annealing temperature, ϕ_H is the hydrogen implantation dose and α , the so-called H efficiency, represents the fraction of the implanted H which contributes to blistering or splitting [129].

The critical surface energy depends also on the implanted dose, therefore a proper implantation and a careful design of the annealing procedure are important to obtain a surface energy higher than the required value for layer splitting. The critical surface energy for layer splitting of H ($5 \times 10^{16} \text{ cm}^{-2}$) implanted silicon wafers is shown in Fig. 2.9. Experimentally it was also shown that the smoothness of the transferred layer can be improved by an enhanced bonding energy [106].

2.6 Objectives of this work

Despite substantial progress made so far, layer transfer by ion implantation and wafer bonding is far from being well established for other materials than silicon. A better understanding of the splitting mechanism and kinetics is required for further development of this promising technique. Questions concerning optimization of implantation conditions, bonding and annealing in the layer splitting process still remain. The work presented in this dissertation deals with these questions and to advance this approach. The objectives of this work are summarized as follows:

▶ Optimization of the implantation parameters in order to achieve blistering of GaAs and other compounds such as complex oxides after post-implantation annealing.

► Layer transfer of GaAs and complex oxides after bonding of as-implanted wafers to various host substrates.

 \blacktriangleright An improved understanding of the physical processes which occur in the layer transfer approach.

The goal of GaAs/Si bonding and layer transfer is to produce a material system in which a thin, bulk quality GaAs layer is monolithically integrated on a silicon substrate. In contrast to the case of epitaxial growth of GaAs on silicon, the wafer-bonding approach can avoid the generation of threading dislocations in the GaAs layer caused by the 4.1% difference in the lattice constants of silicon and GaAs. The composite has the advantage of combining the properties of Si and GaAs to realize the integration of GaAs optical devices with Si-signal processing devices on the same chip. Moreover, the GaAs film on Si substrate can be used as a buffer layer for the growth of other compound semiconductors. For comparision, some important properties of GaAs at 25^oC are listed together with those of silicon in Table 2.4.

Superior thermal and mechanical properties of Si compared to those of GaAs constitute another important advantage of the combination of Si and GaAs. GaAs devices fabricated on a Si substrate can dissipate heat more easily than those on a GaAs bulk substrate owing to the more than three times higher thermal conductivity of Si. Thinner bonded GaAs/Si wafers can achieve the same mechanical strength as thicker GaAs substrates, resulting in lower cost and weight [116]. As seen in Table 2.4, Si and GaAs crystals have different thermal expansion coefficients. This 4.2×10^{-6} K⁻¹ mismatch presents a major challenge for GaAs/Si wafer bonding because of thermal stresses induced in the bonded pair when subjected to a thermal annealing which may lead to cracking as long as the GaAs layer has not yet been split off and transferred to the silicon wafer.

A major effort has been directed towards integration of complex oxide materials into semiconductor technology. However, lattice-mismatch, incompatible growth (need for low temperature growth), complex surface chemistry and stoichiometry have presented a considerable challenge. In recent years various techniques have been used to study the deposition of complex oxides onto various substrates. Chemical vapor deposition, sol-gel processing, metalorganic decomposition, RF sputtering and pulsed-laser deposition, have been reported in the literature [130, 131, 132, 133, 134].

Lithium niobate (LiNbO₃) is an important ferroelectric material whose superior optical and dielectric single-crystal properties make it useful in a large variety of applications, ranging from optical communications to wireless and micro-mechanical systems. Strontium titanate (SrTiO₃) and lanthanum aluminate (LaAlO₃) have attracted much attention due to their structural and dielectric properties. Crystal wafers of SrTiO₃ and LaAlO₃ are well known as substrates for epitaxial growth of high temperature superconductors. Poly-crystalline lanthanum-modified lead titanate zirconate ((Pb,La)(Zr,Ti)O₃, in short PLZT) is an electro-optic (EO) material which has as major advantage over single-crystal EO materials its ease of manufacturing, low operating voltages and reduced long-range strain effects. Materials based on lead zirconatetitanate (Pb(Zr,Ti)O₃, in short PZT) or PLZT are used in electronic and electro-optic devices, such as non-volatile memories, piezoelectric SAW devices, micro-actuators, pyroelectric sensors and electro-optic modulators. Many of these applications require the miniaturization which is achieved with the use of thin films on substrate materials. Some of the important properties of the investigated oxides are summarized in Table 3.11.

| Properties | Si | GaAs |
|--|---------------------|----------------------|
| Crystal | Diamond | Zincblende |
| Polarity | Nonpolar | Polar |
| Atomic or molecular density | $5.0 	imes 10^{22}$ | 2.21×10^{22} |
| (cm^{-3}) | | |
| Lattice constant (Å) | 5.4307 | 5.6536 |
| Covalent radius (Å) | 1.17 | Ga: 1.26 |
| | | As: 1.18 |
| Band gap (eV) | 1.124 | 1.429 |
| Melting temperature (K) | 1685 | 1511 |
| Thermal conductivity (W/mK) | 156 | 58 |
| Density (g/cm^3) | 2.33 | 5.3176 |
| Bulk modulus (GPa) | 98 | 75.3 |
| [100] Young's modulus | 130 | 85 |
| (GPa) | | |
| [110] Young's modulus | 169 | 120.7 |
| (GPa) | | |
| [111] Young's modulus | 187.2 | 140.5 |
| (GPa) | | |
| Cleavage planes | {111} | $\{110\}$ |
| Thermal expansion coefficient (K^{-1}) | $2.6 	imes 10^{-6}$ | 6.8×10^{-6} |
| Dielectric constant | 11.7 | 13.1 |
| Refractive index | 3.51 | 3.3 |
| Breakdown field (V/cm) | 3×10^5 | $3.5 	imes 10^5$ |
| Electron mobility (cm^2/Vs) | 1450 | 8800 |
| Hole mobility (cm^2/Vs) | 500 | 360 |
| Poisson's ratio | 0.28 | 0.312 |
| Specific heat (J/kg K) | 710 | 327 |

Table 2.4: Some important properties of Si and GaAs at RT [135, 136].

| Material | Crystal | Density | Melting | Thermal expansion | Dielectric |
|-----------------------------|----------------------------|------------|-----------|----------------------------|-------------------------|
| | | (g/cm^3) | point (K) | coeff. $(x10^{-6} K^{-1})$ | constant (ϵ) |
| LiNbO ₃ $^{(1)}$ | hexagonal, a=5.148 Å | 4.64 | 1473 | α_{11} :15.4 | 29 |
| | c = 13.863 | | | α_{33} :7.5 | |
| LaAlO ₃ $^{(1)}$ | hexagonal, a=5.377 Å | 6.51 | 2453 | 9.2 | 20-25 |
| | c=13.22 Å | | | | |
| | cubic (> 500°C), a=3.821 Å | | | | |
| $SrTiO_3$ ⁽¹⁾ | cubic, a=3.905 Å | 5.12 | 2353 | 10.3 | 300 |
| PLZT [137] | tetragonal, a=4.076 Å | 7.854 | | $\sim \!\! 4.5$ | 3350 |
| 8/58/42 | $c{=}4.088$ Å | | | | |

Table 2.5: Materials properties of investigated complex oxides

⁽¹⁾ www.matweb.com

Chapter 3 Experimental

Ion implantation is an important step in the layer splitting process. Therefore, a short introduction of ion implantation technology is presented. The implantation parameters, such as energy, dose and temperature, used for blistering/splitting investigations of GaAs and complex oxides are given. For most common ion implanters the exact wafer temperature during implantation can not be precisely measured. Since the actual wafer temperature during implantation is an important parameter in order to achieve blistering/splitting after post-implantation annealing, an estimate of the wafer temperature during implantation is presented. The experimental procedures followed in this study are also described in this chapter.

3.1 Ion implantation

An ion implanter (see Fig. 3.1) consists of the following major components: an ion source, an extracting and ion analyzing mechanism, an accelerating column, a scanning system and an end station. The ion source is the most important component in industrial implanters and contains the species to be implanted either as solids, or as liquids or as gases and an ionizing system to ionize the species. The source produces an ion beam with very small energy spread enabling high mass resolution. Ions are extracted from the source by a small accelerating voltage and then injected into the analyzer magnet. A spacial separation of ions subjected to the Lorenz force occurs due to the differences in the mass and charge. Only the selected ions are injected into the accelerating column, the others are stopped by the presence of suitable screens. The selected ions are accelerated by a static electric field, are focussed and shaped in the column and then implanted with an energy up to 80-400 keV. The ions are scanned uniformly over a target by electrical fields varying in the x and y directions.

The depth distribution of the implanted ions depends on several parameters such as the ion mass and energy, the target mass and the beam direction with respect to the main axes or planes in the case of a single crystal target [138]. The knowledge of the total energy stopping power allows the calculation of the range distribution of implanted ions. As an energetic ion penetrates a crystalline solid, it loses energy primarily through two mechanisms. The first is



Figure 3.1: Schematic drawing of an ion implanter.

by inelastic collision with bound electrons in the solid. Energy loss is by means of ionization of the target atoms and does not involve atomic displacements. This process is termed electronic stopping and represents a kind of viscous force slowing down the incident ion. The second mechanism involves nuclear collisions with the nuclei of target atoms and produces the majority of atomic displacement during implantation. The energy of the incident ion is transferred to nuclei involved in these collisions and this loss is termed as nuclear stopping. In a specific implantation process, the relative importance of these two processes depends upon a number of physical parameters including: the mass M_1 , the atomic number Z_1 , and energy E of the incident ion; the mass M_2 , the atomic number Z_2 , and the density N of the target material; the orientation of the crystal with respect to the incident beam; and the lattice structure of the target crystal.

The two loss mechanisms are described in terms of cross sections, one for the electronic stopping S_e and another for the nuclear stopping S_n :

$$S_{e,n} = -\frac{1}{N} \frac{dE}{dX_{e,n}} eV cm^2 \tag{3.1}$$

where (dE/dX) is the energy loss per unit distance for either process. Figure 3.2 schematically shows the relative energy losses as a function of incident ion energy for implantation. For the moderate energy (100-400 keV) implants of H in the materials considered in this study, the

relevant portion of these curves is near E_3 and most of the energy loss is through electronic stopping. The cross section for this process can be expressed as:

$$S_e = k E^{1/2} (3.2)$$

where k is a function of N, M_1 and Z_1 , M_2 and Z_2 , of the incident ion and target atoms [79].



Figure 3.2: Schematics of the relative energy loss due to electronic (S_e) and nuclear (S_n) stopping processes, as a function of incident ion energy [79].

From a knowledge of S_e and S_n the total range R that the incident ion travels in the solid before it stops can be calculated. Since the direction of the incident ion changes considerably during its trajectory, especially when nuclear stopping predominates, the projection of the range R onto a normal to the surface is used. For an implantation involving a large number of incident ions, the final location of the implanted ions form a distribution of particles. Normally, this distribution is non-Gaussian and higher order statistics are required to describe the shape [79]. During ion implantation part of the projectile kinetic energy is transferred to the atoms of the target displacing them from their lattice sites. Therefore, point defects as well as other complexes are created. The knowledge of the damage created by the implanted ions is of relevance for planning of the subsequently thermal annealing required to anneal out these defects. The calculation of the range and damage distribution is a transport problem describing the motion of the ions during their slowing down to zero energies.

The Monte Carlo method, widely used to simulate the ion implantation phenomena in solids, is based on the simulation of individual particle trajectories through their successive collisions with target atoms. The most widely used program to simulate the range distribution is the


Figure 3.3: Depth distribution and projected range of H_2^+ -implantation at 160 keV calculated by using the TRIM code.

TRIM (TRansport of Ions in Matter) code [139]. An example of the projected range obtained by TRIM for H_2^+ implanted at 160 keV into different materials is shown in Fig. 3.3.

3.2 Beam heating effect

The kinetic energy of the implantation beam that hits the wafer is mostly transferred into heat and a corresponding temperature increase of the implanted wafer occurs. A standard medium current implanter develops beam currents of 1-400 μ A at an acceleration voltage of 5-400 keV. Therefore, the beam power may vary from 5 mW up to 160 W. Since the implanted ions are stopped within a damaged layer the beam energy is deposited in a layer of thickness much smaller than the wafer thickness. Therefore, one may assume a surface heating at an average power flux. The implantation dose (D (ions/cm²)) is given by Eq. (3.3)

$$D = \frac{1}{A} \int \frac{I_{beam}}{q_{ion}} dt \tag{3.3}$$

where A represents the implanted area, I_{beam} is the beam current, q_{ion} the charge of the ions implanted over the time t.

The ion implantation technology is widely used in semiconductor industry and low implant times are required from a productivity point of view. Therefore, rather high beam power densities are applied usually. The rise of temperature critically depends on the beam power density, the total accumulated dose, the thermal capacity of the implanted material, and on how the wafer is fixed onto the wafer holder. The problem is aggravated by the low thermal capacity of many substrates. GaAs is very brittle, has a relatively large thermal expansion coefficient, α = 6.8×10^{-6} K⁻¹ (for Si α = 2.6×10^{-6} K⁻¹) and a low thermal conduction coefficient (58 W/mK, while for Si it is 156 W/mK). Therefore, it is rather difficult to fix the GaAs wafer firmly directly on the implanter holder without breaking the wafer during the implantation process. Since a good thermal contact between the implanted wafer and the wafer holder is usually difficult to be achieved, the main heat loss mechanism occurs by thermal radiation and conduction through the wafer. Moreover, measurement of the wafer temperature during implantation is not trivial for most common implanters especially if the temperature is in the range of RT to a couple of hundred degrees. In collaboration with Dr. V. Popov from the Institute of Semiconductors Physic (ISP), Novosibirsk, Russia, we tried to measure the temperature of the GaAs wafers during implantation by an infrared (IR) absorbtion method near the absorbtion limit set by the band gap of GaAs. A light emitting diode (LED) was used as the IR light source and the transmitted light was obtained using a photosensitive diode.

The measurements revealed that the wafer temperature initially increased linearly with dose and finally saturated at 300 °C for a dose of $1.5 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ implanted at approximately 0.25 μ A/cm². Since the implantation setup did not provide a cooling stage for the wafer holder the implantation was stopped for several hours to cool down the wafer. A diagram of some implantation experiments performed in Novosibirsk is presented in Fig. 3.4 showing the frequent breaks in implantation either to cool down the wafer or caused by external disturbances in power supply. Although the wafer temperature could be measured, after implantation of GaAs wafers no satisfactory results were obtained since the frequent interruptions of the implantations, as shown in Fig. 3.4 did not allow to work under defined conditions.

A theoretical estimate of the wafer temperature during implantation is described in the following. In general, prediction of the target temperature during implantation requires a solution of the three-dimensional, time-dependent partial differential equation of conduction of heat with nonlinear boundary conditions due to radiative cooling. The equation in an isotropic solid is given by Eq. (3.4).

$$\nabla^2 T - \frac{1}{\kappa} \frac{\partial T}{\partial t} + H = 0 \tag{3.4}$$

The constant κ is the thermal diffusivity of the substance and is given by the formulas $\kappa = K/\rho C$, where K is the thermal conductivity, ρ is the density and C is the specific heat of the solid. H represents the ion heating rate and is determined by the heating by the incident power (P_{beam}) and the heat loss. The heat is partly radiated by the implanted surface to the environment and by heat loss from the wafer to the wafer holder. The remaining part



Figure 3.4: Schematic description of the multi-step hydrogen implantations performed in Novosibirsk.

increases the wafer temperature. The energy conservation is generally described by the first law of thermodynamics. Therefore, H is given by

$$H = P_{beam} - Q_{loss} \tag{3.5}$$

with Q_{loss} being the heat loss from the wafer.

The investigated system is schematically shown in Fig. 3.5.

Because the ions actually deposit their energy into a finite region in the target, a volumetric heat generation model would be more accurate, but at the expense of increased analytical difficulties. We can reasonably assume, for the purpose of calculating thermal effects, that all of the beam energy (P_{beam}) is deposited as heat in the implanted layer neglecting the small part of the kinetic energy used for the formation of lattice defects. Equation (3.4) can be simplified to a one-dimensional case (x coordinate only) and if we consider a serial implanter, where one wafer at a time is implanted and the period of the scan system is small with respect to the thermal diffusion time through the wafer of thickness L we can assume that P_{beam} is constant with respect to a x coordinate and the differential equation for our investigated system is given by

$$\frac{\partial^2 T}{\partial^2 x} - \frac{1}{\kappa} \frac{\partial T}{\partial t} + \frac{1}{\kappa} [P_{beam} - Q_{loss}] = 0$$
(3.6)

The initial conditions (IC) and the boundary (BC) or surface conditions for the investigated system have yet to be defined. The initial temperature of the wafer is constant therefore if



Figure 3.5: Schematic drawing of the implantation process.

T=T(x,t) then T(x,0)=c. At the implanted surface (x=0) the surface condition is described by a Newman boundary condition (3.7) [140]

$$K\frac{\partial T}{\partial x} - P_{beam} + \epsilon \sigma A(T^4(0,t) - T_s^4) = 0$$
(3.7)

where the third term in the above equation represents the Stefan-Boltzmann law of thermal radiation (Eq. 3.8)

$$Q_{rad}(x=0) = \epsilon \sigma F A(T^4(0,t) - T_s^4)$$
(3.8)

where

 ϵ is the wafer emissivity,

 σ is the Stefan-Boltzmann constant,

F is the radiation factor (form factor) for radiation from the target to the implant chamber,

A is the total radiating area of the wafer,

T(0,t) is the temperature of the implanted surface,

and T_s is the temperature of the environment.

Because the wafer is enclosed in the chamber and the wafer area is much less then the chamber surface area, the factor F can be approximated to be one. At the back surface (x=L) the heat can be transferred to the wafer holder by different loss mechanisms, depending on the thermal contact between the wafer and the wafer holder, which are summarized below:

<u>Case 1.</u> If there is no thermal contact between the implanted wafer and the wafer holder then the heat is transferred by thermal radiation between the back surface of the wafer and the wafer holder. The heat loss from the back surface is then expressed as $Q_{x=L} = f(\epsilon)\sigma A(T^4(L,t) - T^4_{hold})$ where and T(L,t) represents the temperature at the back surface of the implanted wafer (L = wafer thickness). $f(\epsilon)$ is a function which considers the emissivity of the wafer (ϵ_w) and wafer holder (ϵ_h) in the net heat transfer between two bodies across a small gap, and is given by

$$f(\epsilon) = \left[\frac{1}{\epsilon_w} + \frac{1}{\epsilon_h} - 1\right]^{-1} \tag{3.9}$$

<u>Case 2.</u> If the thermal contact between the implanted wafer and the holder is rather good, then depending on the type of holder (open or solid holder) the heat from the back of the wafer is transferred to the wafer holder by conduction or convection, accordingly. For an open wafer holder the heat loss is described by the Newton's law of cooling $Q_{x=L} = hA(T - T_{hold})$, where h (W/cm²K) represents the cooling coefficient.

<u>Case 3.</u> For a solid wafer holder and a good thermal contact between the wafer and the holder we can reasonably assume that at x=L the temperature $T(L,t) = T_{hold}$.

The system of equations regarding the temperature increase during implantation with the differential conduction equation together with the required initial and boundary conditions for the studied case is given below:

$$\frac{\partial^2 T}{\partial^2 x} - \frac{1}{\kappa} \frac{\partial T}{\partial t} = 0 \tag{3.10}$$

$$IC: T(x,0) = ct = 300K \tag{3.11}$$

$$BC(x=0): k\frac{\partial T}{\partial x} - P_{beam} + \epsilon \sigma A(T^4(0,t) - T_s^4) = 0$$
(3.12)

$$BC(x = L): T(L, t) = T_{hold}$$

$$(3.13)$$

for Case 3.

Solving the general heat transfer equation is rather tedious but a few analytical solutions of the problems with different initial and boundary conditions were given [140]. Considering now constant flux of heat at x=0, F₀, the flux $f = -K\frac{\partial T}{\partial x}$ satisfies the same differential equation as T, namely

$$\kappa \frac{\partial^2 f}{\partial^2 x} = \frac{\partial f}{\partial t}, \text{ for } t > 0 \tag{3.14}$$

and the solution of f(x,t) is given by [140] as

$$f = F_0 erfc \frac{x}{2\sqrt{kt}} \tag{3.15}$$

Thus, the solution for T(x,t) is given by

$$T(x,t) = T_0 + \frac{F_0}{K} \int erfc \frac{x}{2\sqrt{kt}}$$
(3.16)

Ignoring the heat loss by conduction through the wafer thickness the target temperature is determined by the energy deposited by the implanted ions, radiative cooling from the implanted surface, heat loss from the wafer to the wafer holder and physical properties of target. The heat transfer equation becomes Eq. (3.17).

$$L \cdot C_p \cdot \rho \cdot \frac{dT}{dt} = \frac{P_{beam}}{A} - h \cdot (T - T_{hold}) - \epsilon \sigma A (T^4 - T_s^4)$$
(3.17)

Solving numerically this equation for a beam power of a few Watts per cm^2 the beam heating results in a temperature rise of several hundred degrees Celsius. For this approximation an example of the average temperature raise of a GaAs wafer during implantation at different beam power densities is shown in Fig. 3.6.



Figure 3.6: Beam heating curves for different beam current densities: a) $P_{beam} = 3 \text{ W/cm}^2$ without thermal contact between the wafer and the wafer holder, b) $P_{beam} = 20 \text{ W/cm}^2$ without thermal contact, and c) $P_{beam} = 20 \text{ W/cm}^2$ with thermal contact between the wafer and the wafer holder defined by a heat conduction coefficient of 0.5 W/K.

It can be easily seen from Fig. 3.6 that the wafer temperature may reach a relatively high steady-state value after a short time. As mentioned earlier a good thermal contact between the GaAs wafer and the holder is rather difficult to obtain. Thus, the actual situation is often rather described by case (b) of Fig. 3.6 than by (c). Nevertheless, it has been tried to ensure as good a thermal contact as possible between the implanted wafer and the holder.

3.3 Experimental procedure

Blistering and splitting after ion implantation and subsequent annealing was investigated for semi-insulating (100) and (111)-oriented, 3 and 4-inch diameter, GaAs wafers (Freiberger Compound Materials GmbH), 10 mm × 10 mm × 1 mm substrates of single-crystalline SrTiO₃, LiNbO₃, LaAlO₃ and transparent poly-crystalline (Pb,La)(Zr,Ti)O₃ (PLZT) ceramic materials. In order to minimize ion channelling implantation was performed under 7° sample tilt. H₂⁺ was implanted at 130 - 160 keV with doses ranging from 2×10^{16} to 5×10^{16} cm⁻², while He⁺ was implanted at 105 keV with 5×10^{16} cm⁻² for single ion implantation experiments. The influence of a He + H co-implantation on blistering/splitting was also investigated: a low He dose $(0.5-1\times10^{16}$ cm⁻²) was implanted first at 105 keV followed by range matched H₂⁺ (2.0 - 5.0\times10^{16} cm⁻²) implantation.

As mentioned in the previous chapter in order to achieve blistering/splitting by ion implantation and a post-implantation annealing the wafer temperature during implantation must fall within a window that is specific to each material. Unlike in the Si case, where the temperature window for H-implantation is relatively wide (RT - 450 °C), for GaAs and complex oxides the temperature window is very narrow and the optimum implantation temperatures are not yet established since measurement of the actual wafer temperature during implantation is non-trivial for most implanters. Implantation of He⁺ and/or H₂⁺ was performed at different sample holder temperatures ranging from room-temperature (RT) up to 300 °C.

After implantation oxide substrates were annealed in air at a temperature ranging from 250 up to 700 °C in order to determine the temperature and time of the on-set of blistering. For GaAs annealing at more than 350 °C was performed in hydrogen atmosphere to avoid partial oxidation of the surface. Nomarski optical microscopy, atomic force microscopy (AFM Digital instruments D5000) and scanning electron microscopy (SEM JEOL 6300F) were used to investigate surface blister formation and exfoliation.

Formation of platelet-like defects and their evolution after annealing were analyzed by cross section transmission electron microscopy (XTEM). A Philips CM 20T at primary beam energy of 200 keV was used. Specimens for XTEM were prepared (see Fig. 3.7) by gluing two 5x5 mm² implanted samples face-to-face with epoxy resign and then cut normal to the interface in slices of about 0.5 mm. Disks of about 3 mm diameter were then obtained by ultrasonic drilling of as-obtained slices. The specimens were mechanically polished with SiC (down to 100 μ m) and then dimpled down to approximately 5-10 μ m. The final step consists of ion milling which involves bombarding the thin specimen using energetic Ar ions and removal of the material by



Figure 3.7: Specimen preparation of investigated materials for XTEM investigation.

sputtering until the specimen is transparent to electrons. During ion milling the near-surface chemistry changes and a thin top layer often becomes amorphous. By careful adjusting the accelerating voltage of the Ar beam in a range of 2-4 keV and/or the angle of incidence of the beam with respect to the surface, the penetration of the ion beam is minimized.

3.4 Wafer bonding

Wafer bonding is an essential step in the layer splitting approach. In order to achieve good uniformity of the transferred layers a high quality of the bonding interface (free of voids) is required between the implanted and the handle wafer. Annealing of the as-bonded wafers has to be performed first to achieve a high bonding strength and then to transfer the layer from the implanted wafer to the handle wafer. Due to the mismatch in the thermal expansion coefficients of many materials it is desirable that annealing temperature after bonding does not exceed a critical value in order to avoid cracking or fracturing of one or both wafers.

3.4.1 GaAs on Si

For GaAs/Si wafer bonding the critical annealing temperature for typical 3" and 4" wafers of usual thickness is around 200 °C and usually the bonding energy obtained for typical GaAs/Si bonded pairs is relatively low [141]. Recently, it was shown that room temperature GaAs/Si bonding via spin-on glass (SOG) intermediate layers is a reliable approach to obtain high bonding energies after low temperature annealing [142]. Wafer bonding via an SOG intermediate layer is schematically shown in Fig. 3.8. Typically the SOG layer is deposited on the silicon layer.



Figure 3.8: Schematic flowchart of the GaAs/Si wafer bonding via SOG layer process.

The Si wafers were cleaned before bonding using the standard chemical cleaning procedure with RCA 1 (NH₄OH:H₂O₂:H₂O = 1:1:5) and RCA 2 (HCl:H₂O₂:H₂O = 1:1:5) solutions. The GaAs wafers were cleaned in 5% HCl to remove any metallic contaminants and then rinsed in deionized (DI) water. The SOG layers were deposited onto the Si wafers by a spin-on technique.

The resulting films were baked in air for 10 min on a hot plate at 180 °C to remove the chemical solvents, and then the SOG-coated wafers were bonded at RT to GaAs using the standard direct bonding procedure [142]. The surface energy of the as-bonded interface was measured by the crack-opening method [128]. A value of about 0.4 J/m² was found which is almost four times higher than the surface energy in case of Si/Si hydrophilic bonding. This relatively high surface energy can be attributed to a different chemistry at the SOG-GaAs interface compared to the usual silicon-silicon bonding. Infrared spectroscopy measurement presented in Fig. 3.9 revealed the existence of CH₃ radicals in the SOG films baked at temperatures below 200 °C.



Figure 3.9: Infrared reflection spectrum of a SOG layer annealed at 150 °C for 5 min.



Figure 3.10: Typical IR image (a) and acoustic microscopy image (b) of GaAs-Si bonding interface after bonding via a SOG intermediate layer.

Even after a baking procedure at 150 °C for 5 minutes the SOG layer still contains silanol groups, which may generate adhesion at RT due to their ability to form bonds with molecules from the other surface.

Investigation of the bonding interface revealed that a high uniformity was obtained across the wafers, as shown in Fig 3.10. An enhancement of the bonding energy, up to 2 J/m², was obtained after annealing of the as-bonded pairs (up to 200 °C) for 10-12 hours. Similar values of surface energies are obtained after annealing of bonded hydrophilic Si-Si.

3.4.2 Bonding of complex oxides

Direct wafer bonding of complex oxides was also investigated. Bonding of square-shaped (1 cm^2) oxide substrates is rather difficult since the samples are mechanically cut and some hillocks are formed at the rim after cutting. Special treatment of these substrates would be required such as etching away or polishing and rounding the edges without damaging or roughening the surface. Moreover, the as-received substrates had a relatively high micro-roughness (more than 1 nm as measured by AFM).



Figure 3.11: IR images of as-bonded 4-inch $LiNbO_3/LiNbO_3$ (a) and 30 mm diameter $SrTiO_3/SrTiO_3$ (b) wafer pairs.

For whole wafers with a low surface micro-roughness (< 0.5 nm) successful bonding of oxide wafers was accomplished (see Fig. 3.11). For the layer splitting experiments 30 mm diameter (100)-oriented SrTiO₃, 3-inch z-cut LiNbO₃ and 2-inch (100)-oriented LaAlO₃ wafers were used.

Chapter 4

Results and discussion

In this chapter the conditions for achieving blistering/splitting of GaAs as well as of complex oxides after a post-implantation annealing are investigated. The effect of the implantation temperature on blistering/splitting is highlighted. Formation of platelets in as-implanted materials after H and/or He implantation and their evolution with annealing is studied. After optimizing the implantation parameters layer transfer of investigated materials by He and/or H implantation and wafer bonding is also demonstrated. A new low-temperature layer splitting approach of GaAs based on He+H co-implantation is introduced.

4.1 Blistering and exfoliation

As mentioned in the previous chapters, heating of an unbonded He and/or H-implanted wafer leads to surface blistering instead of large area layer splitting observed in the case of bonded wafers. Therefore, to obtain the optimum conditions for splitting after post-implantation annealing it is convenient to investigate surface blistering for different implantation and annealing conditions.

4.1.1 Hydrogen implantation into GaAs

4-inch GaAs wafers, mounted directly on the wafer holder, were implanted in order to study the optimum conditions for blistering. The implantation was performed by a commercial implantation service (Implant Sciences, USA). The hydrogen implantation conditions and the corresponding blistering results are summarized in Table 4.1.

| Dose | Energy | Holder temperature | Does blistering occur? | |
|--------------------------|------------------|--------------------|------------------------|-----------------|
| (cm^{-2}) | (keV) | $(^{\circ}C)$ | As implanted | After annealing |
| $3.5 \mathrm{x} 10^{16}$ | 130 | 80 - 175 | Yes | - |
| $5x10^{16}$ | 130 | RT-175 | Yes | - |

Table 4.1: H_2^+ implantation conditions of GaAs wafers.

It can be seen from Table 4.1 that surface blisters formed directly during the implantation even when the wafer holder was kept at RT. This indicates that, due to the beam heating effect, the actual wafer temperature reaches a sufficiently high value to allow blistering. The



Figure 4.1: Surface blisters in as-implanted GaAs observed by optical microscopy (a) and AFM (b). H_2^+ implantation at 130 keV with 3.5×10^{16} cm⁻² was performed at 100 °C.

surface blisters formed directly during implantation have about 2-3 μ m in lateral size and a relatively high density over the implanted surface, about 10⁶ blisters/cm². Examples of blister observations are shown in Fig. 4.1.

A detailed XTEM investigation was performed of the as-implanted samples. The analysis revealed that the micro-cracks have a relatively large (0.1 - 0.3 μ m) lateral size and they are preferentially oriented along {111} and {100} planes. Due to the overlapping of these microcracks, surface blisters already formed in the as-implanted samples (see Fig. 4.2). The resulting crack is larger than 1 μ m in lateral size which is in agreement with the size of optically detected blisters. The cracking occurred at the peak region of the damaged layer, about 600 nm from the implanted surface as expected from the TRIM estimation. It is worth pointing out here that the already formed blisters did not grow even after further annealing at elevated temperatures (250 - 500 °C).





As estimated in the previous chapter the temperature increase of the wafer surface during implantation can be significantly reduced if the thermal contact between the implanted wafer and the holder is improved. In this study different approaches were used to minimize the beam heating effect of the wafers during implantation.

In a first approach a research implantation setup was used (Research Center Jülich, group of Prof. S. Mantl), in which a good thermal contact between the wafer and the holder was provided by using an electrostatic holder. However, the implantation experiments could be performed only at relatively low temperatures (near RT) since the wafer holder did not allow the temperature to be set over 50 °C. These experiments revealed that RT implantation of hydrogen does not induce blistering of GaAs even for relatively high doses (such as 5×10^{16} H_2^+/cm^2).

In a second approach the GaAs wafers were mounted onto Si handle wafers prior to implantation experiments using a thermally conductive layer, e.g. silver paste. These experiments were performed again at the previously used commercial implantation service (Implant Sciences, USA). The use of the mechanically much more robust silicon wafers allowed a different way of mechanically fixing the wafers than in the case of the very brittle GaAs wafer, which in turn allowed a much better thermal contact to the wafer holder. The hydrogen implantation conditions for this new set of samples are summarized in Table 4.2.

| Dose | Energy | Holder temperature | Does blistering occur? | |
|----------------------|------------------|--------------------|------------------------|-----------------|
| (cm^{-2}) | (keV) | $(^{\circ}C)$ | As implanted | After annealing |
| $2x10^{16}$ | 130 | 100 | No | No |
| $2x10^{16}$ | 130 | 200 | No | No |
| $2x10^{16}$ | 130 | 300 | Yes | - |
| $3x10^{16}$ | 130 | 100 | Yes | - |
| $3x10^{16}$ | 130 | 150 | Yes | - |
| $3x10^{16}$ | 130 | 200 | No | No |
| $5 x 10^{16}$ | 130 | RT | No | No |
| $5 x 10^{16}$ | 130 | 100 | Yes | _ |

Table 4.2: H_2^+ implantation conditions of GaAs wafers mounted on Si.

We can now assume that the wafer temperature is given by the holder temperature, without significant temperature increase during the implantation. Unless specified otherwise we will refer from now on to the implantation temperature as wafer temperature during implantation.

In order to achieve blistering/splitting only after a post-implantation annealing H_2^+ was implanted with different doses varying from $2x10^{16}$ up to $5x10^{16}$ cm⁻² at different temperatures. As can be seen in the above table, RT-implantation of $5x10^{16}$ cm⁻² did not induce blistering of GaAs even after post-implantation annealing up to 500 °C for 2 hours, while for the same dose implanted at 100 °C surface blistering occurs directly during implantation. Therefore, for a H_2^+ implantation at 130 keV with a dose of $5x10^{16}$ cm⁻² the optimum implantation temperature has a value between RT and 100 °C which has to be reached. Similar results are obtained for low H-implantation doses. It is worth pointing out here that surface blistering of GaAs was observed even when the implanted dose was as low as $2x10^{16}$ cm⁻².

For blistering/splitting to take place in the hydrogen implanted GaAs the implantation temperature must fall within a temperature window, specific to each selection of implantation parameters (energy and dose), as also previously reported [19]. If the wafer temperature during hydrogen implantation is within an adequate range, an appropriate amount of implant damage remains and the hydrogen mobility is just in the proper range for the formation of platelets and micro-cracks. However, if the wafer temperature is too low the density of the implantation defects becomes too high, reducing the effective diffusivity of hydrogen, hence the material may be too defective to form platelets. On the other hand, if the wafer temperature during implantation is small and the H₂ molecules may become highly mobile and can diffuse out during implantation resulting in no blistering/splitting. It is worth mentioning that Tong et al. [19] reported that the window for the implantation temperature for getting blistering only after annealing is 160-250 °C (based on the temperature of the sample holder) for doses ranging from 2.5 to 3.5×10^{16} H₂⁺/cm². This is different from our results which indicate that the temperature window should be somewhere in the range between RT and 100 °C for doses ranging from 3 to 5×10^{16} H₂⁺/cm².

The different results can be reconciled if one assumes that better thermal contact was achieved in the experiments by Tong et al. [19] and that a lower beam current density might have been used. Within this interpretation it can not be excluded that the wafer temperature in our case was actually higher by as much as 100 °C than the holder temperature.

4.1.2 Helium implantation into GaAs

In a next step it was checked whether H-implantation could be replaced by He-implantation. In order to define the optimum conditions for blistering/splitting the He-implantation was performed at different implantation temperatures, from RT up to 300 °C for GaAs pieces mounted to silicon wafers with thermally conductive silver paste. The implantation was performed at Implant Sciences, USA. Investigation of as-implanted GaAs revealed that surface blisters during implantation already occur when implantation temperatures are above 100 °C. On the other hand, for the specific parameters used (energy of 105 keV and dose of $5 \times 10^{16} \text{ He}^+/\text{cm}^2$) post-implantation annealing induces exfoliation of GaAs layer only after implantation at RT (see Table 4.3).

| Holder temperature | Does blist | ering occur? |
|--------------------|--------------|-----------------|
| $(^{\circ}C)$ | As implanted | After annealing |
| RT | No | Exfoliation |
| 100 | Yes | - |
| 200 | Yes | - |
| 300 | Yes | - |

Table 4.3: Influence of the wafer temperature during He-implantation on blistering/splitting. The implantation was performed at 105 keV with $5 \times 10^{16} \text{ He}^+/\text{cm}^2$.

XTEM investigation of as-implanted GaAs (He@105 keV with $5 \times 10^{16} \text{ cm}^{-2}$) at RT revealed the following details as partly shown in Fig. 4.3. A damaged layer of about 300 nm thickness is observed. At the end-region of the damaged zone bright linear features, about 20 nm in lateral size, mostly parallel to the sample surface and surrounded by strain fields are visible. The linear features are He-filled micro-cracks imaged at underfocus in Fresnel contrast. They are responsible for blistering and/or exfoliation. At higher magnification and under kinematical imaging conditions the whole damaged region was found decorated by spherical He-bubbles of nanometer size.

Annealing of the GaAs implanted with He at RT induces large area exfoliation instead of blistering, as shown in plan view SEM images, in Fig. 4.4. The thickness of the exfoliated layer is about 850-900 nm, which corresponds to the XTEM observation that the He-induced microcracks are distributed close to the end-region of the damaged layer. Even after low temperature annealing (i.e. 150 °C) only few areas of about 100-150 μ m² remained bound to the host sample. This experimental result is in agreement with theoretical considerations [29, 30] indicating that



Figure 4.3: Cross section TEM image of helium (105 keV, 5×10^{16} cm⁻²) as-implanted (100) GaAs at RT.



Figure 4.4: Exfoliation after 1 hour annealing at 300 °C of He implanted (100)-GaAs at RT: a) exfoliated thin layer piece and b) remaining part after exfoliation in the surroundings (implantation energy 105 keV, dose 5×10^{16} cm⁻²).

large area exfoliation and blistering are two competing processes. Size, density and orientation of the platelets (micro-cracks) induced by implantation and their evolution during annealing determine whether blistering or layer exfoliation occurs. Qualitatively, it is expected that many small micro-cracks (with diameter much smaller than the depth in which they are located) favor exfoliation and larger micro-cracks (with diameter in the range of their depth) favor blistering. Also, inclined platelets, such as (111)-oriented platelets observed in (100)-oriented substrates, may cause crack deflection and thus, breakage of the implanted surface occurs.

As can be seen from Fig. 4.5, after annealing at low temperatures the He-induced exfoliation mechanism has an activation energy of about 1.1 eV, while a value of about 0.4 eV is obtained for exfoliation at higher temperatures.

Analogous results were obtained by Aspar et. al [100] for the activation energy of blistering in H-implanted silicon. Aspar et al. [100] explained the change-over in the activation energy in



Figure 4.5: Activation energies of exfoliation for He-implanted (100)-GaAs. Implantation of He⁺ ($5x10^{16}$ cm⁻² at 105 keV) was performed at RT.

terms of trap limited H diffusion at low temperatures and free H diffusion at higher temperatures. Even though the binding mechanism of He to specific traps is expected to be different from the case of H, we can qualitatively apply the H-diffusion model in the presence of trapping sites [47] for a qualitative treatment of the exfoliation mechanism based on He diffusion. The density of intrinsic defects (vacancies+ interstitials) formed after implantation is relatively high. The trapping-detrapping phenomenon is described by the relation (4.1)

$$[He_{free}] + [X] \leftrightarrows_{k_1}^{k_2} [HeX] \tag{4.1}$$

where [X] is the concentration of unsaturated traps.

The equilibrium constant can be written as:

$$K = \frac{k_1}{k_2} = K_0 exp \left[\frac{E_{bind}}{kT}\right]$$
(4.2)

with k_1 and k_2 being respectively the [HeX] complex formation and dissociation constant in the reaction, E_{bind} the binding energy of the helium atom on the trap, and K_0 a constant depending on the nature of the trap.

Fick's second law applied to the He diffusing species in the presence of trapping sites can be written as

$$D_{eff} = \frac{D_{He_{free}}}{1 + K[X]} = \frac{D_0 exp[-E_{He_{diff}}/kT]}{1 + K_0[X]exp[E_{bind}/kT]}$$
(4.3)

where $D_{He_{free}}$ is the free helium diffusion coefficient.

At low temperatures, $K[X] \gg 1 \Rightarrow K_0[X]exp[E_{bind}/kT] \gg 1$. If we assume that [X] is constant or slowly changes with temperature then the Eq. 4.3 becomes

$$D_{eff} = \frac{D_0}{K_0[X]} exp\left[\frac{-(E_{He_{diff}} + E_{bind})}{kT}\right]$$
(4.4)

where the activation energy of the exfoliation is found to be $E_{bind} + E_{He_{diff}}$. The exfoliation in the low temperature regime is mostly controlled by the combined He diffusion and the trappingdetrapping phenomenon. At high temperatures, the trapping efficiency is considerably reduced and $D_{eff} = D_{He_{free}}$. Therefore, a lower activation energy of exfoliation is obtained based on $E_{He_{diff}}$ for annealing in the high temperatures regime.

It should be mentioned that a complete investigation of He diffusion in He-implanted GaAs is not presently available. In order to investigate if the proposed mechanism of exfoliation in the low and high temperature annealing regime is valid, a rough estimation of the diffusion coefficients of He in GaAs was performed. The diffusion coefficients were estimated from the expression of the diffusion length $l = \sqrt{D_{Hex}}$ which gives us just a rough estimation of the order of magnitude for the diffusion coefficients. If the estimated diffusion coefficients are expressed by the Arrhenius equation $D = D_0 exp(-E_a/kT)$, and considering the activation energies E_a for the exfoliation from Fig. 4.5 for the low and high temperature annealing regimes, then the frequency factor D_0 (pre-exponential factor) can be determined. The results of the estimation, for which the diffusion length, x was considered to be 100 nm, are presented in Table 4.4.

| | Annealing | Annealing | Diffusion | Pre-exponential |
|------------------|---------------|-----------|--------------------------------|--------------------------------|
| | temperature | time | coefficient | factor D_0 |
| | $(^{\circ}C)$ | (\min) | $(\mathrm{cm}^2/\mathrm{sec})$ | $(\mathrm{cm}^2/\mathrm{sec})$ |
| High temperature | 250 | 13.5 | $1.2 \mathrm{x} 10^{-13}$ | $1.1 \mathrm{x} 10^{-9}$ |
| regime | 325 | 4.5 | $3.7 \mathrm{x} 10^{-13}$ | $1.0 \mathrm{x} 10^{-9}$ |
| Low temperature | 175 | 420 | $4.0 \mathrm{x} 10^{-15}$ | $4.8 \text{x} 10^2$ |
| regime | 225 | 27.5 | $6.1 \mathrm{x} 10^{-14}$ | $1.4 x 10^2$ |

Table 4.4: Estimation of helium diffusion parameters.

As shown in Table 4.4 the determined pre-exponential coefficients (D_0) for the high temperature regime are not typical, and therefore cannot be directly correlated with a free helium diffusion. For comparison, the pre-exponential factor D_0 for hydrogen diffusion in GaAs was determined to be about 90 cm²/sec and the activation energy 1.43 eV [79]. Therefore, we speculate that the diffusion takes place more rapidly than the obtained exfoliation times at a specific temperature and therefore, the activation energy of exfoliation obtained in the high temperature regime cannot be attributed only to the free helium diffusion. A more realistic explanation has to include not only the diffusion process but also the growth process of the micro-cracks. A transition temperature (T_{tr}) between the low and high temperature regimes was obtained at about 230 °C. The value of the transition temperature is in quantitative agreement with the work of Follstaedt et al. [91] which observed by elastic recoil detection (ERD) measurements that isolated He in GaAs, located in the lattice or trapped at point defects, can be easily released at temperatures higher than 250 °C. It is worth mentioning that the exfoliation observed after annealing of He-implanted GaAs is a kind of avalanche effect because no surface modification was observed when the annealing was just a bit shorter than required for exfoliation.

Influence of the substrate orientation

In order to study the influence of the substrate orientation on blistering/exfoliation (111)oriented GaAs was implanted with He at the same parameters $(5 \times 10^{16} \text{ cm}^{-2} \text{ at } 105 \text{ keV})$ at RT. As shown in the XTEM image (Fig. 4.6) the He-platelets are oriented mostly parallel to



Figure 4.6: Cross section TEM image of as-implanted (111)-oriented GaAs. Implantation of He^+ (5x10¹⁶ cm⁻² at 105 keV) was performed at RT.

the implanted surface, as observed for (100)-oriented GaAs, but now lay on the corresponding (111) planes (parallel to the surface).

Similar to the case of (100)-oriented GaAs, the annealing of the (111)-GaAs induces large area exfoliation instead of blistering. An activation energy of about 1.52 eV is obtained for the low temperature regime, and about 0.66 eV for the high temperature regime (Fig. 4.7).

If we compare the activation energies of exfoliation for the two investigated orientations of GaAs we see that for the (111)-oriented GaAs the activation energies are about 50 % higher than for the case of (100)-oriented GaAs. For (111)-GaAs the transition temperature T_{tr} is about 280 °C. If we compare the exfoliation times for both (100) and (111)-oriented GaAs we observe that at low temperatures the exfoliation time is shorter for (100)-GaAs than for (111)-GaAs, while for the high temperature regime the (111)-GaAs shows a shorter exfoliation



Figure 4.7: Activation energies of exfoliation for He-implanted (111)-GaAs. Implantation of He⁺ ($5x10^{16}$ cm⁻² at 105 keV) was performed at RT.

time. If we assume that He diffusion is an isotropic process than we can conclude that beside the diffusion mechanism present in the exfoliation mechanism, an additional activation energy such as for platelets growth has to be considered. The surface energies of $\{100\}$ and $\{111\}$ GaAs surfaces were approximated [143] by counting the number of bonds which are broken per unit cell. They reported an energy of 2.2 Jm⁻² for the GaAs $\{100\}$ surfaces, and of 1.3 Jm⁻² for the GaAs $\{111\}$ surfaces. Thus, the fracture of GaAs is more easily obtained along $\{111\}$ than $\{100\}$ directions. Also, as shown in Table 2.4 the Young's modulus of GaAs is smaller for the $\{100\}$ planes (85 GPa) than for the $\{111\}$ planes (140.5 GPa). Difference in the exfoliation times obtained for (100) and (111)-oriented GaAs can be attributed to anisotropy of the elastic properties of GaAs, and therefore it can be concluded that surface orientation has modified the exfoliation kinetics of GaAs.

4.1.3 Helium + hydrogen co-implantation into GaAs

In the case of silicon, He+H co-implantation was shown to reduce the total required dose and/or the splitting temperature [107, 108]. We applied this approach in order to study the influence of He+H co-implantation on blistering/splitting of GaAs.

| | Dose | Energy | Holder temperature | Does blist | ering occur? |
|-------------------|--------------------------|------------------|--------------------|--------------|-----------------|
| | (cm^{-2}) | (keV) | $(^{0}\mathbf{C})$ | As implanted | After annealing |
| $\mathrm{He^{+}}$ | $1x10^{16}$ | 100 | RT | | |
| H_2^+ | $3.5 \mathrm{x} 10^{16}$ | 130 | 100 | Yes | - |
| $\mathrm{He^{+}}$ | $5x10^{15}$ | 105 | RT | | |
| H_2^+ | $2x10^{16}$ | 160 | RT | No | Yes |
| $\mathrm{He^{+}}$ | $5x10^{15}$ | 105 | RT | | |
| H_2^+ | $3x10^{16}$ | 160 | RT | No | Yes |
| $\mathrm{He^{+}}$ | $5x10^{15}$ | 105 | RT | | |
| H_2^+ | $3x10^{16}$ | 160 | 100 | Yes | - |

Table 4.5: Implantation conditions for $He^+ + H_2^+$ co-implantation.



Figure 4.8: Surface blisters observed by optical microscopy (a) and AFM (b). Co-implantation of He⁺ ($5x10^{15}$ cm⁻² at 105 keV) followed by H₂⁺ ($3x10^{16}$ cm⁻² at 160 keV) was performed at RT.

The implantation parameters together with the blistering results are summarized in Table 4.5 and the optimum conditions are indicated in bold. Surface blisters are formed after post-implantation annealing only for RT co-implanted GaAs. If either implantation temperature or the total implanted dose are higher than a maximum value blistering occurs directly during implantation, as observed for H only implanted GaAs.

It is worth mentioning that the surface blisters formed after annealing of co-implanted GaAs have relatively small lateral sizes, about 2-3 μ m, and a high area density (3.5x10x⁷ cm⁻²), as shown in Fig. 4.8. However, unlike in H-implanted GaAs, the height of the blisters obtained after annealing of co-implanted samples is smaller and further annealing induces growing of the surface blisters but does not induce their fracture even after very long time annealing. This is explained by an insufficient gas-pressure inside the micro-cracks.



Figure 4.9: Activation energies of blistering obtained on He+H co-implanted GaAs. Co-implantation of He⁺ (5x10¹⁵ cm⁻² at 105 keV) followed by a) H₂⁺ (2x10¹⁶ cm⁻² at 160 keV) and b) H₂⁺ (3x10¹⁶ cm⁻² at 160 keV) was performed at RT.

It can be seen from Fig. 4.9 that for the low dose H-implantation the blistering times are about 10 times higher than for the higher H dose. In both cases a similar activation energy is obtained, about 0.77-0.87 eV. Compared to the He only implantation into GaAs no transition temperature for the activation energy is obtained between the low temperature annealing and high temperature regimes. However, it should be pointed out here that there are not enough data available in the low temperature regime (bellow 250 °C) for a direct comparison with the results observed in the case of He-implantation.

XTEM investigations show (Fig. 4.10) that during implantation a relatively narrow damaged region (150 nm) is formed, decorated with bubbles, platelet-like defects, etc. The platelets are about 30-50 nm in lateral size and are distributed over the whole damaged region. As shown in Fig. 4.10a not only (100)-oriented platelets (parallel to the surface), but also some (111)oriented platelets are formed after He+H co-implantation. During annealing, He and/or H are released from the trapping sites and accumulate at the platelets formed during implantation.



Figure 4.10: Cross section TEM images of platelets and micro-cracks in as-implanted (a) and annealed (b) (100)-oriented GaAs. Co-implantation of He⁺ ($5x10^{15}$ cm⁻² at 105 keV) followed by H₂⁺ ($3x10^{16}$ cm⁻² at 160 keV) was performed at RT.

Due to an increase of the inner pressure, platelets grow and overlap with each other, leading to formation of large cracks following a zigzag path (see Fig. 4.10b). Therefore a relatively high surface roughness of the transferred layer is expected after splitting. Cracking after He+H co-implantation and further annealing occurs in a depth of about 650 nm.

4.2 Blistering and exfoliation of complex oxides

Exfoliation and blistering in oxides with corundum, spinel, and rutile structures due to irradiation of gas ions including hydrogen ions with post-annealing have been studied over the last 37 years [144, 145]. Application of the layer splitting approach for complex oxides is also an attractive possibility to fabricate thin *single-crystalline* oxide films with precise sub-micron thickness on any substrate at low temperatures [21]. Also, from a scientific point of view, the study of blistering and splitting in the oxide materials may complement the understanding of the layer splitting approach in semiconductor materials.

4.2.1 SrTiO₃

Similar to the case of He-implanted GaAs, implantation of He⁺, H₂⁺, and He+H into SrTiO₃ induces large area exfoliation instead of blistering (see Fig. 4.11). However, post-annealing



Figure 4.11: SEM image of an exfoliated surface after 500 °C annealing of He+H co-implanted SrTiO₃. Co-implantation of He⁺ (5x10¹⁵ cm⁻² at 105 keV) followed by H₂⁺ (3x10¹⁶ cm⁻² at 160 keV) was performed at RT.

exfoliation occurs only if the implantation temperature falls in an adequate range specific for either He and/or H implantation.

As an example, the influence of the implantation temperature on blistering/exfoliation for the H-implanted $SrTiO_3$ is shown in Table 4.6.

| Holder temperature | Does blistering occur? | | | | |
|--------------------|------------------------|-----------------|--|--|--|
| (^{0}C) | As implanted | After annealing | | | |
| RT | No | Exfoliation | | | |
| 100 | Yes | - | | | |
| 200 | No | No | | | |
| 300 | No | No | | | |

Table 4.6: Effect of implantation temperature after H_2^+ implantation of $SrTiO_3$ (5x10¹⁶ cm⁻² at 130 keV.)

After hydrogen implantation at 100 °C blisters occur during implantation, while for implantation at temperatures higher than 200 °C no blisters are found even after 700 °C annealing. Therefore, the optimum implantation temperature of H_2^+ (5.0×10¹⁶ cm⁻² at 130 keV)-implanted SrTiO₃ is RT. In contrast to the H-implantation case, the optimum implantation temperature for He⁺-implanted (5.0×10¹⁶ cm⁻² at 100 keV) SrTiO₃ was found to be around 200 °C.

As can be seen in Fig. 4.12a a high density of H-platelets is created by H-implantation in $SrTiO_3$. The H-platelets are mostly parallel to the implanted surface and they have about 15-20 nm lateral size. The platelets and micro-cracks formed during He+H co-implantation are 2-3 times larger, as shown in Fig. 4.12b.

The activation energies of exfoliation for He and/or H implantation conditions of $SrTiO_3$ are presented in Fig. 4.13. Similar to the case of He-implanted GaAs, exfoliation of $SrTiO_3$ is associated with two activation energies depending on the temperature regime of annealing. The high temperature regime gives a low activation energy (0.18 eV for H-implanted and 0.17 eV for He+H co-implanted $SrTiO_3$), while for the low temperature regime the activation energy is higher (0.65 eV for H-implanted and 0.61 eV for He+H co-implanted $SrTiO_3$). The transition temperature (T_{tr}) between the high and low temperature regimes was found to be about 310 °C for either H-implanted or He+H co-implanted $SrTiO_3$. Within the same temperature regime exfoliation of H-implanted and of He+H co-implanted $SrTiO_3$ has similar activation energies, but the exfoliation times are about 2 times shorter for the He+H coimplanted $SrTiO_3$. Therefore, the He+H co-implantation approach can be successfully used to reduce the exfoliation/splitting time or temperature of $SrTiO_3$. This effect in reducing the exfoliation/splitting temperature is attractive for the transfer of $SrTiO_3$ layers onto substrates with different thermal expansion coefficients.

Table 4.7 lists the optimum He and/or H-implantation conditions for achieving exfoliation/splitting of $SrTiO_3$ after post-implantation annealing.



Figure 4.12: XTEM image of platelets in as-implanted SrTiO₃ (RT-implantation of 5×10^{16} H₂⁺/cm² at 160 keV (a) and RT co-implantation of 5×10^{15} He⁺/cm² at 105 keV, followed by 2×10^{16} H₂⁺/cm² at 160 keV (b)).

| Table 4.7: Optimum implantation parameters for $SrTiO_3$. | The temperature refers to the holder |
|--|--------------------------------------|
| temperature. | |

| Dose | Energy | Temperature |
|--|------------------|---------------|
| (cm^{-2}) | (keV) | $(^{\circ}C)$ |
| $5 \mathrm{x} 10^{16} \mathrm{H}_2^+$ | 130-160 | RT |
| $5 \mathrm{x} 10^{16} \mathrm{He^{+}}$ | 105 | 200 |
| $5 \mathrm{x} 10^{15} \mathrm{He^{+}}$ | 105 | RT |
| $2-5 \times 10^{16} \text{ H}_2^+$ | 160 | RT |



Figure 4.13: Activation energies of exfoliation for RT-implantation of $5 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ at 160 keV (a) and RT co-implantation of $5 \times 10^{15} \text{ He}^+/\text{cm}^2$ at 105 keV, followed by $3 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ at 160 keV (b) SrTiO₃.

4.2.2 $LaAlO_3$

Neither blistering nor exfoliation is detected immediately after He and/or H implantation. Annealing of as-implanted LaAlO₃ at 400 °C - 700 °C revealed that optical detectable blisters are observed only after H_2^+ (130 keV, $5x10^{16}$ cm⁻²) implantation at 200 °C and 300 °C. If the annealing time, for a certain temperature, is sufficiently high these surface blisters break and flaking of the implanted surface occurs, as can be seen in Fig. 4.14.

The hydrogen implantation conditions and the corresponding blistering results are summarized in Table 4.8. Again, the proper implantation conditions are indicated in bold.

| Table 4.8: | Parameters f | for H_2^+ | implantation | of | $LaAlO_3$ | $(5x10^{16})$ | cm^{-2} | at | 130 | keV) | and | the |
|-------------|------------------|-------------|--------------|----|-----------|---------------|--------------------|---------------------|-----|------|-----|-----|
| observed bl | listering result | ts. | | | | | | | | | | |

| Holder temperature | Does blist | ering occur? |
|--------------------|--------------|-----------------|
| $(^{\circ}C)$ | As implanted | After annealing |
| RT | No | No |
| 100 | No | No |
| 200 | No | Yes |
| 300 | No | Yes |



Figure 4.14: Plan-view SEM image of H-implanted (at 130 keV with H_2^+ at a dose of 5×10^{16} cm⁻²) LaAlO₃ at 200 °C after annealing at 500 °C.

Similar to previously reported results [106], blistering of LaAlO₃ could not be achieved by hydrogen implantation at room temperature, even if a high proton dose $(10^{17} \text{ cm}^{-2})$ was used. Moreover, H₂⁺ implantation at temperatures lower than 200 °C did not induce blistering of LaAlO₃ even after 2 hours of annealing at 700 °C. The fact that RT-implantation does not induce blistering/splitting of LaAlO₃ can also be explained by the vacancy concentration at the damage peak. Given the H₂⁺ dose (5x10¹⁶ cm⁻²), based on Monte Carlo simulation (TRIM 2003), the implantation-induced vacancy concentration in LaAlO₃ is about 2-3 times that in silicon. A higher vacancy concentration implies also a higher accumulated damage of the crystal lattice which prevents easy nucleation of micro-cracks even after annealing. Implantation at higher temperatures generally leads to a lower damage accumulation. It is worth mentioning that for all investigated conditions neither He implantation nor He+H co-implantation induces blistering/splitting of LaAlO₃.

H-platelets, about 20-30 nm in width, formed in as-implanted $LaAlO_3$ are identified by XTEM (Fig. 4.15). As can be seen, they are mostly oriented on (100) planes but also some (111)-oriented platelets are observed.

The blistering time for H-implanted $(5 \times 10^{16} \text{ cm}^{-2} \text{ at } 130 \text{ keV})$ LaAlO₃ at 200 °C and 300 °C is obtained in the investigated temperature range. As shown in Fig. 4.16, an activation energy of about 0.62 eV is obtained for H-implantation at 200 °C, while for 300 °C the activation energy is lower by about a factor of two. An interesting feature is that for annealing in a high temperature regime (more than 600 °C) blistering is more rapidly observed for the sample implanted at 200 °C. This result is relatively unexpected and it might be explained by the



Figure 4.15: XTEM image of H-platelets in as-implanted LaALO₃ at 300 °C ($5x10^{16}$ H₂⁺/cm² at 130 keV).

fact that the high temperature implantation results in a lower density of point defects during the implantation compared to the RT-implantation case because these implantation-induced defects recombine and annihilate due to their enhanced mobility [56].

The hydrogen-implantation induced defects, mainly point defects such as vacancies and self-interstitials, have two effects in the process of blistering/splitting. On the one hand, a certain amount of defects are needed for the nucleation of platelets (or micro-cracks), which is the starting point of blistering/splitting. On the other hand, these lattice defects, especially the vacancy clusters, can effectively trap chemically reactive atomic hydrogen and form hydrogen-containing complexes. In H-implanted Si some of these complexes, such as the two with H-stretching frequency of 2160 cm⁻¹ and 2208 cm⁻¹ which were assigned to VH₃ and VH₄ accordingly, can not be annealed out at temperatures up to 600 °C. These defects could hamper the transformation from bonded hydrogen to hydrogen molecules which is the main driving force for blistering/splitting. As a result, the probability of the implanted hydrogen getting trapped by those defects becomes lower for H-implantation at higher temperatures in which less of these vacancy agglomerates will form compared to the case of RT-implantation.



Figure 4.16: Activation energies of blistering for H-implantation at 130 keV with $5 \times 10^{16} \text{ H}_2^+/\text{cm}^2$ at 200 °C (a) and at 300 °C (b) of LaAlO₃.

4.2.3 LiNbO₃

Optical investigation of the LiNbO₃ wafers showed that neither H-implantation nor He+H coimplantation at the investigated temperature range induced blistering/exfoliation even after annealing up to 700 °C. However, surface exfoliation occurs directly after He ($5x10^{16}$ cm⁻² at 100 keV) implantation at 100 °C and 200 °C, while after RT-implantation annealing at elevated temperatures is required to achieve exfoliation (see Fig. 4.17).

Table 4.9: He⁺ implantation conditions (5x10¹⁶ cm⁻² at 130 keV) for achieving blistering/exfoliation of LiNbO₃.

| Holder temperature | Does blistering occur? | | |
|--------------------|------------------------|-----------------|--|
| (^{0}C) | As implanted | After annealing | |
| RT | No | Exfoliation | |
| 100 | Yes | - | |
| 200 | Yes | - | |
| 300 | No | No | |

A XTEM image of the He-platelets (see Fig. 4.18) formed in as-implanted $LiNbO_3$ shows that they are mostly distributed at the end region of the implanted layer.



Figure 4.17: SEM image of He-implanted (5x10¹⁶ cm⁻² at 100 keV) LiNbO₃ at RT after 1 hour annealing at 700 °C.



Figure 4.18: XTEM image of He-platelets in He-implanted (100 keV with 5×10^{16}) LiNbO₃ at RT.

The platelets are imaged at underfocus in Fresnel contrast and have smaller lateral sizes, about 15 nm, as compared to the platelets identified in $LaAlO_3$ and $SrTiO_3$ (about 20-30 nm). At higher magnification the whole damaged region is found decorated by spherical He-bubbles of a few nanometers in diameter.

4.2.4 PLZT

Similar to the LiNbO₃ case, for all given parameters of H-implantation as well as He+H coimplantation no blistering/exfoliation is observed even after annealing at elevated temperatures. Only He-implantation at 300 °C induces blistering of PLZT during implantation. The optimum implantation temperature of He (100 keV, $5x10^{16}$ cm⁻²) at which blistering is achieved after post-implantation annealing is 200 °C, as shown in Table 4.10.

Table 4.10: Implantation conditions of He⁺ ($5x10^{16}$ cm⁻² at 130 keV) for achieving blistering of PLZT.

| Holder temperature | Does blistering occur? | | |
|--------------------|------------------------|-----------------|--|
| (^{0}C) | As implanted | After annealing | |
| RT | No | No | |
| 100 | No | No | |
| 200 | No | Yes | |
| 300 | Yes | - | |

XTEM investigations were performed for PLZT, He-implanted at 200 °C. During implantation He-platelets of about 10-20 nm lateral size are formed, as seen in Fig. 4.19. The platelets are mostly surface-parallel oriented and are distributed over the whole damaged region, as shown for H-implanted LaAlO₃. Also, similar to the case of He-implanted LiNbO₃ and partly visible in Fig. 4.19 the damaged region is decorated with He-bubbles of nanometer size. The activation energy of blistering for He-implanted (130 keV, 5×10^{16} cm⁻²) at 200 °C PLZT is about 0.35 eV, as shown in Fig. 4.20.



Figure 4.19: XTEM image of He-platelets in as-implanted PLZT at 200 °C ($5x10^{16}$ He⁺/cm² at 100 keV).



Figure 4.20: Blistering time as a function of 1000/T for PLZT implanted with He at 200 °C ($5x10^{16}$ cm⁻² at 130 keV).



Figure 4.21: XTEM image showing orientation of the He-platelets in different grains within poly-crystalline PLZT implanted with He at 200 °C ($5x10^{16}$ He⁺ cm⁻² at 100 keV).

PLZT is a poly-crystalline material, with grain sizes of about several tens of μ m. Thus, one would expect different orientation of the platelets within the grains. As shown in the example of Fig. 4.21, XTEM investigation of as-implanted PLZT revealed that the He-platelets are oriented almost parallel to the surface, independent on the grain orientation. This indicates that blistering/splitting can be induced even in poly-crystalline materials under appropriate implantation conditions.

Discussion

As described in the previous section, blistering or exfoliation of investigated complex oxides can be achieved if specific implantations are performed. Moreover, hydrogen implantation was proven to be ineffective for blistering/exfoliation of some oxide materials (LiNbO₃ and PLZT) and similarly, blistering/exfoliation of LaAlO₃ cannot be achieved by helium implantation. In order to understand the differences of these results let us start describing the complex oxide formation.

The perovskites, with the general formula ABO_3 , and perovskite-related compounds, constitute a large group of oxides displaying a great diversity in physical and chemical properties. $SrTiO_3$ is a mineral perokvsite and it is often described as a typical perovskite material. Formation of the investigated complex oxides is schematically shown below

$$\begin{array}{lll} \mathrm{SrTiO_3:} & \mathrm{SrO} + \mathrm{TiO_2} \Rightarrow \mathrm{SrTiO_3} \\ \mathrm{LaAlO_3:} & \mathrm{La_2O_3} + \mathrm{Al_2O_3} \Rightarrow 2\mathrm{LaAlO_3} \\ \mathrm{LiNbO_3:} & \mathrm{Li_2O} + \mathrm{Nb_2O_5} \Rightarrow 2\mathrm{LiNbO_3} \\ \mathrm{PLZT:} & (\mathrm{Pb_{1-x}La_x})(\mathrm{Zr_yTi_{1-y}})_{1-x/4}\mathrm{O_3}, \, \mathrm{x=0.08}, \, \mathrm{y=0.58} \end{array}$$

As presented in previous sections the He-implantation is effective in achieving blistering/exfoliation of LiNbO₃ and PLZT materials, while H-implantation has to be used for the case of LaAlO₃. In contrast, for SrTiO₃ He or H-implantation, and He+H co-implantation were effective in achieving surface exfoliation. This could be attributed to a different interaction mechanism between implanted species (He and/or H) and the host materials. One possibility might be complex formation such as a O-Li-H complex in the H-implanted LiNbO₃, which may be stable at a few hundred degrees Celsius, and therefore not sufficient hydrogen atoms will remain available to diffuse into the platelets. On the other hand, He might be too diffusive in LaAlO₃ and therefore not sufficient He remains available for blistering/exfoliation.

In order to understand the formation of such O-Li-H complexes the chemical properties of the metal cations involved in ABO₃-H complex formation were compared. Table 4.11 shows some properties of the metal elements for the ABO₃ compounds.

| ABO_3 | Cation | Ionic | Covalent |
|--------------------|--------------------|-------------|-------------|
| compound | (\mathbf{M}) | radius (pm) | radius (pm) |
| | | | |
| $SrTiO_3$ | Sr^{2+} | 118 | 191 |
| | Ti^{4+} | 61 | 132 |
| $LiNbO_3$ | Li^+ | 76 | 123 |
| | Nb^{5+} | 64 | 134 |
| LaAlO ₃ | La^{3+} | 103 | 169 |
| | Al^{3+} | 54 | 125 |

Table 4.11: Properties of metal cations involved in the formation of ABO₃ compounds.

If we compare the charge differences between the involved cations within the compounds and the effect of He and/or H implantation we observe that for a large difference in the charge (LiNbO₃) blistering or exfoliation was achieved only by helium implantation. In contrast, when the difference in charge is reduced (LaAlO₃) blistering/exfoliation was achieved only by hydrogen implantation.

Another interesting feature observed in Table 4.11 is that the ABO₃ complex shows various ratios between the ionic radii of the elements A and B. For instance, $LiNbO_3$ has similar ionic radii for Li and Nb cations, while for the other perovskites (SrTiO₃ and LaAlO₃) the ionic
radius for the element A (Sr, La) is almost twice compared to the ionic ratio of the element B (Ti, Al). If we look at the possibility of A-H and B-H formation (Table 4.11), and given the ionic radius for A elements it is clear that A-H complex formation is more favorable for the elements with small ionic radius, such as Li. The electronegativity of oxygen is larger than that of hydrogen by a factor of 1.24 and the O-M bonds are ionic. The LiH bond has a small difference of electronegativity (1.2) and is almost covalent. For the elements which form B-H complexes there is no major difference in the ionic radii and a covalent B-H bond would have too large a radius.

Another possibility is Li-O-H complex formation which can be described by the local charge conservation:

$$O^{2-} + H^+ \Rightarrow OH^-$$

 $Li^+ + H^- \Rightarrow LiH$

However, the dominant charge state of H in implanted perovskites is not known. If neutral H or H_2 is stable in the perovskite material the Li-O-H complex might be formed.

Hydrogen predominantly exists in the form of H^+ in p-type silicon and in the form of H^- in n-type silicon [53]. The electronic doping of the material influences the nature of the hydrogen charge within a specific material, and therefore the hydrogen-metal complex may be more likely be formed in a material which contains an excess of conduction band electrons. On the other hand, the bandgap of the complex oxides (> 3 eV) is larger than the silicon bandgap (1.12 eV), and knowledge about hydrogen-induced energy levels in the bandgap of complex oxides is presently not available.

It is noteworthy that the complex oxides changed their color after He and/or H implantation. This can be explained by the defect formation during implantation, most probably oxygen vacancies. The oxygen vacancies are charged by $2e^{-}$. The position of V^{2-} within the bandgap is not known and an electronic doping would require a electronic state close to the conduction band.

4.3 Layer Splitting

4.3.1 GaAs layers on Si substrates

In order to investigate whether the exfoliation mechanism presented in the previous section can be used for transferring a thin GaAs layer onto a silicon wafer, room-temperature bonding of a He-implanted (@105 keV with 5x10¹⁶ cm⁻² at RT) GaAs wafer with a Si wafer was performed. Prior to bonding the silicon wafer was coated with a 400 nm spin-on glass (SOG) layer. After annealing of the bonded pair at 200 °C for 14.5 hours the GaAs layer was partly transferred onto Si, as shown in Fig. 4.22. Several defects are present at the bonding interface (i.e. voids) which are responsible for the non-uniformity of the transferred layer. AFM measurements indicate a





micro-roughness (RMS value) of about 9 nm of the GaAs layer after splitting, therefore a final soft chemical mechanical polishing step is needed before further processing. Similar values of the micro-roughness are obtained after silicon splitting [116]. In order to enhance the uniformity as well as the quality of the transferred layer an improvement of the bonding interface is required.

Bonding of He+H co-implanted GaAs wafers to Si was also performed in a similar way. The bonded pairs were annealed at 200-225°C for 10-15 hours to achieve splitting. Uniform transfer of the GaAs layer onto Si was successfully obtained, and as can be seen in Fig. 4.23 a high quality of the bonding interface is obtained.

The micro-roughness of the transferred layer measured by AFM in contact mode indicates a RMS value (see Fig. 4.24) of about 17 - 20 nm, 2 times higher than the value obtained for He-implanted GaAs transfer on Si. As mentioned earlier, the micro-roughness of the transferred layer is basically induced by the overlapping of micro-cracks along the fracture plane. The difference in surface roughness of the transferred layers is correlated to He+H co-implantation and to He only implantation. Hydrogen implantation produces inclined platelets, (111)-oriented, that are deflecting the crack propagation up and down.



Figure 4.23: Cross section TEM image of the bonding interface showing a thin GaAs layer transferred onto a SOG/Si wafer after annealing at 225 °C for 14 hours. The GaAs wafer was co-implantation with $\text{He}^+(5 \times 10^{15} \text{ cm}^{-2} \text{ at } 105 \text{ keV})$ and $\text{H}_2^+(3 \times 10^{16} \text{ cm}^{-2} \text{ at } 160 \text{ keV})$ at RT.





Figure 4.24: AFM roughness measurement of the transferred GaAs layer onto Si via a SOG intermediate layer (implantation and annealing conditions as described in Fig. 4.23).

4.3.2 Transfer of complex oxide layers onto different substrates

Layer transfer of complex oxides onto various substrates was also attempted. Initially RT-direct bonding of oxide substrates (square-shaped) to Si wafers was tried but due to a nonhomogeneous bonding interface the bonding failed. The micro-roughness of the as-received oxide substrates was relatively high (more than 1 nm for the RMS value). Therefore, various intermediate layers,



Figure 4.25: SEM image of a shattered $SrTiO_3$ layer transferred onto a Si substrate. Inset shows magnified feature including an area in which layer transfer was not successful.

such as SOG, were used to improve bonding between the oxides and Si. After annealing in the range of 200-300 °C of the as-bonded substrates small areas of oxide layers were successfully transferred (see Fig. 4.25). The shattering of the transferred layer occurred due to thermal stress at the bonded interface induced by different thermal properties of the oxides and silicon. When materials with a better thermal match were used uniform transfer of the implanted layer was observed, as shown in Fig. 4.26 for the transfer of a $SrTiO_3$ layer onto a $SrTiO_3$ substrate.



Figure 4.26: Cross section TEM image of a thin $SrTiO_3$ layer transferred onto a $SrTiO_3$ substrate (implantation conditions: $5x10^{16}$ H₂⁺/cm² at 130 keV implanted at RT, annealing: 4 hours at 200 °C).

The $SrTiO_3$ layer which was transferred by implantation, bonding and further annealing remains single-crystalline as seen from the diffraction image inserted in the Fig. 4.26. Similar to the case of GaAs layer transfer, the micro-roughness after splitting is relatively high and in the order of some tens of nanometers.

4.4 Summary

Blistering of GaAs and complex oxides induced by hydrogen and/or helium implantation and subsequent annealing was demonstrated. In order to achieve blistering/splitting the wafer temperature during implantation must fall within a temperature window, specific to each material. Comparing to Si, where the temperature window is rather large, from about RT to 400 °C, for GaAs as well as several complex oxides the temperature window is narrower, and less than 100 °C. This observation explains the difficulty of getting the proper implantation conditions for blistering/splitting and the limited use of hydrogen/helium-induced splitting and layer transfer of other materials than silicon. For LaAlO₃ and PLZT oxides a high temperature implantation is required. The effects of high-temperature implantation are associated with the fact that part of the implantation-induced defects can be annealed out during implantation.

The implantation conditions were optimized in order to achieve blistering/splitting only after a post-implantation annealing. Formation of platelets and micro-cracks in as-implanted materials and their evolution with annealing was investigated. The initial distribution of platelets and micro-cracks formed in He and/or H-implanted materials is responsible for the development of the splitting at the damaged layer. Large area exfoliation instead of blistering was observed after annealing of He-implanted GaAs, He-implanted LiNbO₃ as well as for He and/or H-implanted SrTiO₃. The effect of large area exfoliation corresponds to a narrow distribution of the platelets within the damaged region after implantation.

Layer transfer of GaAs and complex oxides was demonstrated. By He+H co-implantation the total required dose for blistering/splitting is reduced. Moreover, the splitting temperature can also be decreased using the He+H co-implantation approach. This approach can be used for transferring thin layers onto appropriate substrates and was successfully applied for transferring GaAs layers onto Si substrates.

GaAs-on-Si structures have been obtained by He implantation and also by He+H coimplantation and wafer bonding. A high quality bonding interface was obtained. Due to poor bonding between the oxide substrates and the Si host substrates no uniform transfer of He and/or H-implanted oxides was obtained. Bonding of square-shape substrates is always problematic due to non-homogeneity induced by the cutting-edges. Nevertheless, small areas $(100 \ \mu m^2)$ of oxide layers were transferred onto various substrates.

Chapter 5 Blistering and splitting mechanisms

The layer splitting approach by He and/or H implantation and wafer bonding has not only found a variety of important applications in microelectronic industry, but has also stimulated great interest in the scientific community. The experimental results presented in the previous chapters will be discussed in terms of several theoretical models for blistering and/or splitting phenomena presented in the literature. The physical process by which large scale splitting is achieved is complex.

The temperature plays a crucial role in controlling diffusive transport of hydrogen or helium, in nucleating sites for micro-crack formation, and in increasing the pressure in the expanding crack via incorporation of hydrogen/helium. A detailed and self-consistent description and modelling of all these effects is presently not available. Several theoretical investigations dealing with blistering and/or splitting were presented in the literature [98, 29, 30, 32].

Based on the experimental results presented in previous chapters, a qualitative model of the development of blistering and splitting will be presented. Also the newly observed effect of large area exfoliation instead of blistering after annealing of samples implanted under certain implantation conditions will be discussed.

It was shown that the platelets formed after He and/or H implantation will develop into surface blisters in an unbonded sample during a thermal treatment provided the amount of He and/or H is sufficient. Experimentally it has been found that surface blisters do not form if the annealing time has not reached a critical value, called on-set time of blistering. As mentioned in the previous chapters, up to the on-set time the platelets grow in a closed form up to a critical size upon which the internal pressure is high enough to open up the crack. An expression of the critical radius derived by Mitani and Gösele [146], for an analogous situation (the nucleation of interface bubbles formed between two bonded thin wafers) may also be used for the on-set of blistering.

$$r_{crit} = \left\{ \frac{16\gamma_p E t^3}{9\alpha (1 - \nu^2) \Delta p^2} \right\}^{1/4}$$
(5.1)

In Eq. (5.1), Δp is the difference between the pressure inside the platelets and that of the outside atmosphere, t corresponds to the implantation depth, E is Young's modulus, ν Poisson's ratio and α a numerical factor in the order of ~1 depending on the details of the calculation. The quantity γ_p is the specific interface energy at the bonding interface in the original treatment and the specific fracture energy in the case of H/He implantation which will be modified by the presence of implantation damage. Fig. 5.1 shows the evolution of r_{crit} with the implantation depth as well as with Δp . The plot was obtained for the following parameters: E=130 GPa, ν =0.28, γ_p =2.13 Jm⁻²(fracture energy of the {100} silicon surfaces [143]), α =1.



Figure 5.1: Dependence of the r_{crit} to the implantation depth (at $\Delta p=10$ GPa) and to the Δp (at typical implantation depth of 500 nm).

It is worth pointing out here that Eq. (5.1) was derived for the case of blisters with a lateral dimension much larger than the wafer thickness t, whereas for certain implantation conditions the on-set blisters have a lateral size in the order of the layer thickness, therefore this equation is used to give a qualitative rather than quantitative description of the platelet nucleation.

5.1 Development of blistering

Freund [29] developed a model which allowed to calculate the minimum hydrogen dose ϕ_m required to induce splitting. He considered a single crack in a nominally elastic and brittle material (i.e. no plastic deformation is taken into account) with shear modulus μ and Poisson ratio ν . In the absence of internal pressure in the crack cavity, the crack is completely closed and the material is unstressed. The crack edge is taken to be circular of radius a, as indicated in Fig. 5.2.

The deformation is axially symmetric in the cylindrical r, z coordinates and a crack face opening displacement $u_z(z = \pm 0, r)$ is defined. u_z must be linear in p and must have the



Figure 5.2: Cross-sectional view of a planar circular crack in an elastic material.

physical dimension of length, so it must be proportional to $\frac{ap}{\mu}$. The opening profile is given by the Eq. (5.2).

$$u_z(z=\pm 0,r) = \pm a \frac{p}{\mu} \frac{2(1-\nu)}{\pi} \sqrt{1-r^2/a^2}$$
(5.2)

Integration of Eq. (5.2) over the crack area gives the volume of the cavity for a given pressure and crack size:

$$V(p,a) = \frac{8}{3}(1-\nu)\frac{a^3p}{\mu}$$
(5.3)

The criterion for crack growth is taken to be the Griffith energy condition, whereby a crack in a brittle solid is at the stage of incipient advance if the reduction in total mechanical energy of the system associated with a slight virtual crack extension equals the surface energy of the additional fracture surface created by that virtual extension. The total mechanical energy for a given level of pressure ($\Omega(p, a)$) is given by the elastic strain energy of the material plus the external potential energy of the applied pressure loading on the crack faces. This total potential energy can be expressed in terms of the pressure p working through the crack face displacement (Eq. 5.2), and the result of the integration over the crack surface area is then

$$\Omega = -\frac{4}{3}(1-\nu)\frac{p^2a^3}{\mu}$$
(5.4)

If the surface energy density of the material is γ the total surface energy is:

$$\Gamma(a) = 2\gamma \pi a^2 \tag{5.5}$$

Application of the Griffith criterion yields, as a necessary condition for crack growth, to the Eq. (5.6).

$$\left(\frac{\delta}{\delta a}(\Omega+\Gamma)\right)_p = 0 \Rightarrow \frac{p}{\mu} = \sqrt{\frac{\pi}{1-\nu}\frac{\gamma}{a\mu}}$$
(5.6)

To determine if the crack growth criterion is actually satisfied an equation of state relating p and V for the gas is required. The equation of state for a volume V of an ideal gas consisting in N atoms (or molecules) at macroscopic pressure p and absolute temperature T is

$$pV = Nk_bT \tag{5.7}$$

where k_b is the Boltzmann's constant. If we suppose that the gas in the evolving crack is governed by this equation of state and if the volume V is substituted from the Eq. (5.3), a second relationship between p and a emerges

$$\frac{8}{3}(1-\nu)\frac{p^2}{\mu^2} = \frac{Nk_bT}{\mu a^3}$$
(5.8)

Elimination of the pressure p from between (5.6) and (5.8) yields

$$\frac{8}{3}\pi a^2 \gamma = Nk_b T \tag{5.9}$$

This results provides an equilibrium crack size for a fixed amount of gas in the crack, as represented by N, and other system characteristics. If the amount of gas within the cavity is fixed, then crack growth is limited. Let us suppose that the implantation process introduces Φ atoms per unit area through the surface of the wafer. It follows immediately that there is splitting if the number N of hydrogen molecules in a circular area $A = \pi R^2$, given by $N_{H_2} = 1/2\Phi\pi R^2$ leads to critical radius a=R since all the circular micro-cracks overlap. This leads to the relationship

$$\frac{8}{3}\pi a^2 \gamma = \Phi_{min}\pi a^2 k_b T \tag{5.10}$$

in which the size a of the cracks cancels and an expression for the minimum hydrogen dose Φ_{min} is obtained as originally derived by Freund [29]

$$\Phi_{min} = \frac{8}{3} \frac{\gamma}{k_b T} \tag{5.11}$$

In his model, Freund uses the assumption of a symmetrical opening profile u_z . Actually, the opening profile is asymmetrical, the asymmetry depending on the ratio of crack diameter to layer thickness. Moreover, the model was developed for a single crack in an infinite solid whereas the actual solution has to consider the asymmetry given by the ratio between the layer thickness t (implanted depth) and wafer thickness w: $w \approx 1000$ ·t.

It is worth mentioning that Freund assumed that the radius a of the micro-cracks (or blisters) is small compared to the thickness t of the layer above the micro-cracks. The required dose for blistering is independent of layer thickness t. The expression for the minimum hydrogen implantation dose is not only independent of layer thickness t (for a \ll t) but also independent of the size of the micro-cracks. Therefore, this treatment does not give any indication whether a higher density of smaller micro-cracks or a lower density of larger micro-cracks (which could

possibly be influenced by the detailed implantation and annealing conditions) would be more desirable for the splitting process.

To complement the previous theoretical work presented above, Huang et al. [106] investigated the blistering/splitting model for a >> t. Moreover, not all the implanted atoms contribute to the growing of the platelets, as mentioned in chapter 2. A certain percentage of hydrogen/helium will either be strongly trapped and not available for diffusion to the microcracks or will have diffused out of the layer in which the micro-cracks develop. Therefore, the value of N can be calculated by $N = 1/2\alpha\pi a^2 \Phi_m$ [147], where $\alpha < 1$ is a parameter accounting for the fact that only a part of the implanted atoms are incorporated in the platelets to drive blistering/splitting. As an example, for H-implanted silicon it was reported that α is about 0.3 as measured by mass spectrometry [27].

A schematic configuration of a surface blister in this model is presented in Fig. 5.3. Under this assumption, the edges of the blister are fixed and the internal load (pressure) is uniformly distributed over the entire surface. According to the theory of elastic deformation of a thin plate the geometrical factors of the blister have the following relationship



Figure 5.3: Schematic configuration of a surface blister.

$$a^{4} = \frac{3Et^{3}h_{max}^{2}}{16\gamma}$$
(5.12)

where a is the radius of the platelet, t the top layer thickness, E Young's modulus, and γ is the specific surface energy, similar to γ_p from the Eq. (5.1). h_{max} is the central displacement of blisters caused by the internal pressure p and can be calculated by [148]

$$h_{max} = \frac{3p(m^2 - 1)}{16Em^2t^3}a^4 \tag{5.13}$$

where m is the reciprocal of Poisson's ratio. The internal pressure in the platelet, depending on the annealing temperature T, can be calculated by

$$p^{2} = Nk_{b}T \frac{16Em^{2}}{\pi(m^{2}-1)} \frac{t^{3}}{a^{6}}$$
(5.14)

Substituting the Eq. (5.13) and (5.14) into Eq. (5.12) we get

$$a^{2} = \frac{27}{256} \frac{Nk_{b}T}{\pi\gamma} \frac{m^{2} - 1}{m^{2}}$$
(5.15)

As mentioned earlier, N can be expressed as $N = 1/2\alpha\pi a^2 \Phi_m$. By introducing in Eq. (5.15) the minimum dose Φ_m is then given by

$$\Phi_m \approx 19 \frac{\gamma}{\alpha k_b T} \tag{5.16}$$

Even though the layer thickness t is considered in this theoretical description, the required dose for blistering is again independent of t and the blister radius a, which is basically the same outcome as in Freund's prediction in the case of a << t. For an implanted dose below Φ_m surface blistering can potentially occur but splitting will not be possible.

As observed in blistering experiments, lateral expansion of blisters is frequently interrupted by the breakage of the top layer. Breaking of the surface blisters is directly related to the maximum stress σ_{max} in the layer of the blister which exceeds the fracture strength σ of the material. For the model presented here (see Fig. 5.3) and for an isotropic material the formulas for the maximum stress were given [149]. Assuming that the central displacement of the blister, h_{max} , is smaller than about one-half the thickness t, then the maximum stress occurs at the edge of the blister and is given by the component along the y-direction [149].

$$\sigma_{max} = \frac{3a^2p}{4t^2} \tag{5.17}$$

Introducing p from Eq. (5.14) we get

$$\sigma_{max} = \frac{9Nk_b TE}{\pi a^2} \frac{m^2}{m^2 - 1} \frac{1}{t}$$
(5.18)

Assuming the conditions for fracture, $\sigma_{max} > \sigma$ then the minimum dose $\Phi_{m,fract}$ required for the blister to fracture is given by

$$\Phi_{m,fract} = \frac{2\sigma^2}{9\alpha k_b T E} \frac{m^2 - 1}{m^2} t$$
(5.19)

where now the minimum dose for fracture of blisters is proportional to the thickness of the implanted layer, i.e. the thicker the top layer, the higher an implantation dose is required for the fracture of blisters.

However, when the central displacement of the blister, h_{max} , becomes larger than about onehalf the thickness, the middle part of the blister becomes appreciably strained and the stress in it cannot be ignored [150]. Formulas for the maximum stress when middle part stresses are taken into account are given below (same loading case as taken in Eq. (5.17))

At edge:
$$\sigma_{max} = 4.40E(\frac{h_{max}t}{a^2}) + 0.47E(\frac{h_{max}}{a})^2$$
(5.20)

At center:
$$\sigma_{max} = 2.86E(\frac{h_{max}t}{a^2}) + 0.97E(\frac{h_{max}}{a})^2$$
(5.21)

From equations (5.20) and (5.21) it is obvious that there is a critical central displacement for which the breakage of the surface blister occurs at the central part and not at the edge. Also, since the central displacement is directly related to the increase of the pressure inside the blister we can conclude that there is a critical pressure for which breaking of the surface blister may be shifted from the edge to the central part.

Another noteworthy feature of this treatment is that the probability of surface blisters to break decreases with increasing implantation depth. Therefore, at high implantation energy (thicker top layer) lateral propagation of blisters is preferred and splitting instead of blistering is favored. This treatment is supported by the experimental observation of Weldon et al. [27], who used 1 MeV implantation energy for hydrogen implanted Si (layer thickness ~ 16 μ m) and got large area exfoliation. Since the size of their micro-cracks is similar (typically below 1 μ m) to the case of lower implantation energies this observation gives also a first indication that exfoliation might be favored if the size of the micro-cracks is much smaller than the layer thickness.

5.2 Blistering versus exfoliation

As observed experimentally, specific implantation parameters induce large area exfoliation instead of blistering after annealing of unbonded wafers. This is not only related to the implantation depth (layer thickness t), as described in the previous section and observed by Weldon et al. [27], but also to the distribution of the platelets and micro-cracks within the implanted region. In the theoretical treatment of Freund [29] and all the subsequent treatments it has always been assumed that all the micro-cracks are more or less on one plane (parallel to the surface) and that splitting occurs if sufficient hydrogen/helium has diffused into the micro-cracks to fulfill the conditions of the number of available gas atoms/molecules in the micro-cracks exceeds that corresponding to the minimum dose Φ_m .

A closer microscopic look at the development of micro-cracks with time shows that the integrated number of gas atoms/molecules in the micro-cracks does not change anymore after a certain initial period but that larger micro-cracks grow at the expense of smaller micro-cracks as shown in Fig. 5.4 for hydrogen implanted silicon [48].

These are the typical features of an Ostwald ripening process [151, 152, 153]. Since obviously in this case the total integrated number of gas atoms does remain constant (and higher than



Figure 5.4: Evolution of the size and density of the micro-cracks during post-implantation annealing of hydrogen-implanted silicon[48].

corresponding to the minimum dose required for splitting) the conclusion can only be that we do not simply deal with an Ostwald ripening process in a plane but rather with a depth redistribution of hydrogen/helium from a distribution of micro-cracks over depth. One could easily imagine that two micro-cracks are located at the same lateral position but at slightly different depths. Then each of these micro-cracks could contain less atoms then corresponding to the minimum dose required for splitting (say one has $0.8 \ \Phi_m$ and the other one has $0.6 \ \Phi_m$), but both micro-cracks together contain more than the minimum dose (say $1.4 \ \Phi_m$ in the example given). Only after a Ostwald ripening process involving a depth redistribution of the hydrogen/helium the condition of splitting is reached in one plane. We can therefore expect that the depth distribution of cracks will also have an influence on the splitting/exfoliation process. It is likely that a more narrow distribution of platelets favors reaching the condition of splitting at a smaller size of the micro-cracks which in turn favors exfoliation as compared to blistering.

During implantation a high density of platelets is formed which are distributed over a region of depth extension l. For the case when l is comparable with the damaged region induced by implantation (d) surface blistering was experimentally observed after annealing, while for the case $l \ll d$ large area exfoliation instead of blistering occurred. As examples, platelet distributions in He-implanted (Ia and b) and He+H co-implanted (IIa and b) GaAs and their evolution with annealing are shown in Fig. 5.5.

It is known that during thermal treatment a vertical rearrangement of the platelets occurs, following an Ostwald ripening mechanism, leading to formation of micro-cracks in a narrow layer, where cracking would occur. It is therefore obvious that for a narrow initial distribution of the platelets the vertical rearrangement is much easier than for a broad initial distribution.



Figure 5.5: XTEM images of platelets in as-implanted (Ia and IIa) and annealed (Ib and IIb) GaAs. For the case I annealing induces large area exfoliation, while for case II surface blisters occur after post-implantation annealing.

As discussed in chapter 2, the Ostwald ripening is not the only mechanism which occurs during annealing of as-implanted wafers. The platelets are efficient traps for either H or He. Therefore, the platelets grow as long as the inner pressure is high enough. When (111)-oriented platelets are present after implantation into a (100)-oriented wafer the growth of the (100)oriented micro-cracks is deflected from its original path (parallel to the surface) leading to an overall zig-zag path, as seen in Fig. 5.5IIb. If these two effects are combined the results are schematically shown in Fig. 5.6. Therefore, it is suggested that if a narrow distribution of the platelets is formed during implantation, a more likely lateral propagation of the micro-cracks occurs and large area exfoliation instead of blistering of the implanted surface is observed. This observation is in agreement with the XTEM investigation of as-implanted and annealed samples, as shown in Fig. 5.5.

Another effect which could certainly also influence the blistering/exfoliation process is the difference in the chemical interaction of He or H with the crystal lattice. Helium is chemically inert and thus will favor mostly the micro-crack planes which are favored by geometrically induced mechanical energy consideration, which means micro-cracks mostly parallel to the implanted surface. Also, experimentally it was observed that He-bubbles of nanometer size are created within the damaged layer during He-implantation. These bubbles are highly pressurized and they represent a reservoir for the diffusion of helium during post-implantation annealing. In contrast, hydrogen chemically bonds to crystal lattice atoms and favors certain lattice planes for forming micro-cracks such as {111} planes in silicon in hydrogen plasma-treated wafers [70]. For H-implanted (100)-silicon wafers a mixture of (111) and (100)-oriented micro-cracks forms which in turn does not favor exfoliation because cracks may have a tendency to move inclined and not parallel to the surface. It is worth mentioning that no hydrogen-bubbles were observed within the H-implanted materials. Exfoliation may be induced if the mechanical stress favoring development and propagation of surface parallel micro-cracks is increased, e.g. by an additional



Figure 5.6: Schematic description of a broad (a) and a narrow distribution (b) of platelets in asimplanted wafers. The He is trapped in small bubbles (b) at a position with lower concentration. The He-platelets are observed at a position with maximum concentration.

implantation increasing appropriate mechanical stresses, as was shown in the case of large area exfoliation of H-implanted SiC after an additional Si-implantation [111].

Exfoliation instead of blistering appears to be favored by the following circumstances:

i) The size of the micro-cracks (as the time for critical number of atoms/molecules is reached in one plane) is much smaller than the thickness of the layer above the micro-cracks. This also corresponds to the case of normal splitting of bonded wafers in which the thickness of the wafers has to be considered instead of the implantation depth.

ii) A narrow depth distribution of micro-cracks.

iii) Preferential orientation of micro-cracks parallel to the implanted surface which is more likely to occur for He than for H. Additional mechanical stress (e.g. by an amorphous layer inducing extra stress by a corresponding volume change going from a crystalline to an amorphous phase) may also influence the formation of surface parallel micro-cracks.

Presently, it has not systematically been checked whether the size of micro-cracks may be controlled by appropriate implantation and nucleation conditions as this is routinely done for controlling the size and density of precipitates (e.g. SiO_2 precipitates in silicon [154, 155, 156]).

5.3 Dynamics of layer splitting

It is generally accepted that splitting of the implanted wafers is the result of overlapping of a number of grown micro-cracks. It was found experimentally that the gas-containing microcracks gradually grow during heat treatment until at some point they suddenly overlap with the nearest micro-cracks in an avalanche-like mode and splitting over the whole implanted area occurs. Based on the stress analysis of each micro-crack and the interaction of stress fields associated with neighboring micro-cracks the dynamics of the layer splitting process was investigated [106].

Considering a two micro-cracks system, as illustrated in Fig. 5.7, the normal stress at each point (in the x=0 plane) ahead of each micro-crack is given by Eq. (5.22), and it is plotted as a function of x/t in Fig. 5.8, where x is the distance to the edge of the micro-crack and t the thickness of the implanted layer.



Figure 5.7: Schematic of two adjacent platelets in an implanted wafer.

$$\sigma_y(x,0) = \frac{3Eht}{8\pi a^2} \left(2\theta - \frac{1}{2}\sin 4\theta - 4\sin^2 \theta \sin 2\theta\right)$$
(5.22)

where $\cot \theta = x/t$, E is the Young's modulus, h is the central displacement of the micro-crack, and y the vertical displacement from the x=0 plane.

The stress right ahead of the crack tip is tensile but becomes compressive in further regions, e.g. when $x/t \ge 0.5$. The maximum tensile stress is located at the edge of the micro-crack, where x/t=0 and is given by

$$\sigma_{y,max} = \frac{Et}{4} \sqrt{\frac{(1-\nu)Nk_bT}{\mu a}}$$
(5.23)

where N is the total number of gas-molecules in the micro-crack, μ the shear modules of the implanted substrate and ν Poisson's ratio.

In a heat treatment, when more gas molecules are incorporated in the micro-crack, $\sigma_{y,max}$ increases accordingly. If $\sigma_{y,max}$ is beyond a critical value, which is associated with the fracture strength of the substrate, the crack opens up further and extends to a larger lateral size. It is worth pointing out here that the critical value of the maximum stress may be even smaller due to the lattice damage of the substrate material caused by implantation.



Figure 5.8: Stress field associated with a gas-filled micro-crack [106].

The combined stress field between these micro-cracks is obtained by the superposition of two single stress fields. The strong tensile stress at the edge of each gas-containing micro-crack drives the lateral propagation. If the micro-cracks are fairly close to each other there is an enhanced compressive stress existing in the middle of the gap. This compressive stress becomes more significant when the two micro-cracks approaches further at the driving force of the inner pressure. The existence of this compressive stress obviously hinders the lateral propagation of each micro-crack. Therefore, if the pressure inside the micro-cracks is not sufficiently high to overcome this barrier, the splitting process can be effectively prevented. However, this barrier disappears when these two micro-cracks come so close that the compressive stress is cancelled out by the presence of a much higher tensile stress. As a result, an exclusive tensile component of the stress field is present in the remaining implanted region. With an increase of the inner pressure of each micro-crack during annealing, this tensile stress may be beyond the critical value mentioned before, and therefore causes the avalanche coalesce of these microcracks leading to large area splitting.

A detailed quantitative treatment of the avalanche type behavior during the splitting process is presently not available. Based on the discussion concerning exfoliation in the previous section it may be speculated that the dynamics of splitting might also strongly be influenced by the depth distribution of micro-cracks, which might require a numerical treatment of crack propagation for cracks not being located on one common plane. Numerical simulations of the crack propagation with various depth distribution of the micro-cracks are currently performed in collaboration with the Fraunhofer Institute for Mechanics of Materials (Halle) and are still under progress.

Chapter 6 Conclusions and outlook

Helium and/or hydrogen implantation induced blistering, exfoliation and layer splitting of compound semiconductors, such as GaAs, and of various complex oxides, such as LiNbO₃, SrTiO₃, LaAlO₃ and PLZT, was investigated in this study. The availability of layer splitting of singlecrystalline oxide materials opens up the possibility of designing and fabricating new materials combinations such as superconductors on semiconductors or ferroelectric materials on semiconductors. Beyond the original Smart-cut[®] procedure, a new He+H co-implantation approach was developed for low temperature splitting of single-crystalline GaAs and SrTiO₃. Low temperature splitting is of importance for layer transfer between dissimilar materials with very different thermal expansion coefficients as well as for processed wafers containing temperaturesensitive devices.

Blistering/exfoliation and splitting of investigated materials was demonstrated and the optimum implantation and annealing conditions for achieving layer splitting after post-implantation annealing were obtained. It was found that the temperature window for GaAs as well as for the investigated oxides is rather narrow as compared to the temperature window for Si (room temperature - 400 °C). Therefore, close attention has to be paid to the implantation stage, where due to the beam heating effect the wafer temperature may raise up to several hundred degrees Celsius.

He and/or H implantation induces formation of platelets which undergo an evolution kinetics (size and density) which is dependent on the implantation conditions (temperature, dose, energy) and on the whole thermal treatment of the implanted wafer, starting at the very beginning of the implantation step up to the occurrence of splitting. During annealing helium and hydrogen diffuse out of the implanted region and accumulate in the platelets giving rise to a pressure increase, leading to blistering and splitting. It was found that in the high temperature regime, the blistering mechanism is rather controlled by atomic diffusion of either He or H whereas in the low temperature regime a more complex mechanism exists involving diffusion and trapping mechanisms, depending on the experimental conditions. For GaAs, the order of magnitude for the diffusion coefficient of helium was estimated to be about 10^{-13} cm²/s in the high temperature annealing regime (250 - 350 °C) and about 10^{-15} - 10^{-14} cm²/s in the low temperature regime (150 - 225 °C).

Comparing various perovskite oxides it was observed that for LiNbO₃ blistering or exfoliation is achieved only by helium implantation. In contrast, for LaAlO₃ blistering/exfoliation is achieved only by hydrogen implantation. This could be attributed to a different interaction mechanism between implanted species (He and/or H) and the host materials. One possibility might be complex-formation such as a O-Li-H complex in the H-implanted LiNbO₃, which may be stable at a few hundred degrees Celsius, and therefore not sufficient hydrogen atoms will remain available to diffuse into the platelets. On the other hand, He might be too diffusive in LaAlO₃ and therefore not sufficient He remains available for blistering/exfoliation. A high temperature implantation approach is required for blistering/splitting of some oxide materials, such as single-crystalline LaAlO₃ and poly-crystalline PLZT. This approach reduces the density of detrimental implantation-induced defects by dynamic annealing. It was also shown that layer splitting can be achieved even in poly-crystalline materials, such as PLZT, under appropriate implantation conditions.

Specific implantation conditions induce large area exfoliation instead of blistering after annealing of unbonded wafers. This effect observed for the first time for GaAs and complex oxides corresponds to a narrow distribution of the platelets in as-implanted materials. Blistering and exfoliation are two competing processes and the implantation parameters play an important role in determining whether blistering or exfoliation occurs.

The difference in the chemical interaction of He or H with the crystal lattice may influence the blistering/exfoliation processes. Helium is chemically inert and thus will favor mostly the micro-crack planes which are favored by geometrically induced mechanical energy consideration, which means micro-cracks mostly parallel to the implanted surface. Also, experimentally it was observed that He-bubbles of the nanometer size are created within the damaged layer during He-implantation. These bubbles are highly pressurized and they represent a reservoir for the diffusion of helium during post-implantation annealing. In contrast, hydrogen chemically bonds to crystal lattice atoms and favors certain lattice planes for forming micro-cracks such as {111} planes. For H-implanted (100)-wafers a mixture of (111) and (100)-oriented micro-cracks forms which in turn does not favor exfoliation because cracks may have a tendency to move inclined and not parallel to the surface. It is worth mentioning that no hydrogen-bubble features were observed within the H-implanted materials. Exfoliation instead of blistering appears to be favored by the following circumstances:

i) The size of the micro-cracks (as the time for critical number of atoms/molecules is reached in one plane) is much smaller than the thickness of the layer above the micro-cracks. This also corresponds to the case of normal splitting of bonded wafers in which the thickness of the wafers has to be considered instead of the implantation depth.

ii) A narrow depth distribution of micro-cracks.

iii) Preferential orientation of micro-cracks parallel to the implanted surface which is more likely to occur after He-implantation than after H-implantation.

Layer splitting is a special case of blistering when a mostly lateral propagation of gas-filled micro-cracks induces cracking over the wafer area as a result of the tensile stress between adjacent micro-cracks. The activation energies of exfoliation is almost two times higher for GaAs comparing with $SrTiO_3$ under the same implantation and annealing conditions. This is related to a different diffusion or detrapping activation energy of either He or H in the implanted materials.

After optimizing the implantation and annealing conditions for blistering, layer transfer of the investigated materials by wafer bonding and layer splitting was demonstrated. To achieve high-quality layer transfer, the bonding interface is critical. Special attention should be paid to the wafer bonding procedure to obtain a void-free interface and a sufficiently high bonding strength. Thin layers of GaAs on Si were obtained using the layer splitting approach and also thin $SrTiO_3$ layers were transferred by this method. It was shown that after splitting, by implantation, bonding and further thermal treatments, the transferred layer remained singlecrystalline.

In spite of an improved understanding of the physical mechanisms underlying the layer transfer process further investigations are highly desirable in the areas indicated in the following:

As shown in chapter 4, wafer bonding of complex oxides is non-trivial. Several aspects such as surface micro-roughness and proper surface cleaning have to be considered. Roomtemperature bonding of complex oxides was demonstrated, but nevertheless for materials for which it is difficult to obtain a smooth surface, e.g., LaAlO₃, proper intermediate layers might have to be deposited and subsequently polished for the improvement of bonding surfaces.

The possibility of transferring other materials, not investigated in this thesis, such as $BaTiO_3$ and AlN may open the door to further applications in the area of high power devices, mobile communications, random access memories, etc. It should also be mentioned that in principle also device layers may be transferred by wafer bonding and H and/or He-implantation induced splitting processes provided the bonding and splitting temperatures are low enough to avoid damage to the devices and that H and/or He implantation damage is restricted to a depth beyond the device layer.

A detailed quantitative treatment of the avalanche type behavior during the splitting process is presently not available. Based on the discussion concerning exfoliation it may be speculated that the dynamics of splitting might also strongly be influenced by the depth distribution of micro-cracks, which might require a numerical treatment of crack propagation for cracks not being located on one common plane. Moreover, for a complete understanding of the blistering/exfoliation numerical simulation of the crack growth has to include not only the diffusion mechanism of hydrogen and helium in the materials but also Ostwald ripening processes for micro-cracks with a certain depth distribution.

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Eidesstattliche Erklrung

Ich erkläre, dass ich keine anderen als die von mir angegebenen Quellen und Hilfsmittel zur Erstellung meiner Dissertation verwendet habe. Den benutzten Werken wörtlich oder inhaltlich entnommene Stellen sind als solche gekennzeichnet.

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Publication list

1. I. Radu, I. Szafraniak, R. Scholz, M. Alexe, and U. Gösele, *GaAs on Si heterostructures obtained by He and/or H implantation and direct wafer bonding*, In press: J. Appl. Phys. (2003).

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National and international conferences

1.I. Radu, I. Szafraniak, R. Scholz, M. Alexe, and U. Gösele, *Transfer of thin flexible layers* by *He and/or H implantation and wafer bonding*, Flexilec workshop - Flexible Electronics: Materials, Characterization and Applications, Halle (Saale) Germany, 2-3 June, 2003 (poster)

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7. V. Dragoi, M. Alexe, M. Reiche, I. Radu, E. Thallner, C. Schaefer, and P. Lindner, *Si/GaAs heterostructures fabricated by direct wafer bonding*, Wafer Bonding and Thinning Techniques for Materials Integration, Mat. Res. Soc., San Francisco CA, 2001 (poster).

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