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.

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

In Eq. (5.1), $\Delta p$ 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, $\nu$ Poisson’s ratio and $\alpha$ a numerical factor in the order of $\sim1$ depending on the details of the calculation. The
quantity \( \gamma_p \) 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 \( \Delta p \). The plot was obtained for the following parameters: \( E=130 \) GPa, \( \nu=0.28 \), \( \gamma_p=2.13 \) Jm\(^{-2}\) (fracture energy of the \{100\} silicon surfaces [143]), \( \alpha=1 \).

![Graph](image-url)

Figure 5.1: Dependence of the \( r_{crit} \) to the implantation depth (at \( \Delta p=10 \) GPa) and to the \( \Delta p \) (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 \( \phi_m \) 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 \( \mu \) and Poisson ratio \( \nu \). 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
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Figure 5.2: Cross-sectional view of a planar circular crack in an elastic material.

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

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

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

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

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

If the surface energy density of the material is $\gamma$ the total surface energy is:

$$\Gamma(a) = 2\gamma \pi a^2$$  \hspace{1cm} (5.5)

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

$$\left( \frac{\delta}{\delta a} (\Omega + \Gamma) \right)_p = 0 \Rightarrow \frac{p}{\mu} = \sqrt{\frac{\pi \gamma}{1 - \nu a^2 \mu}}$$  \hspace{1cm} (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.
5.1 Development of blistering

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

$$pV = Nk_bT$$

(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

$$\frac{8}{3}\pi a^2\gamma = Nk_bT$$

(5.9)

This result 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 $\Phi$ 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

$$\frac{8}{3}\pi a^2\gamma = \Phi_{\min}\pi a^2k_bT$$

(5.10)

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

$$\Phi_{\min} = \frac{8}{3} \frac{\gamma}{k_bT}$$

(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 $w$: $w \approx 1000 \cdot t$.

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 micro-cracks 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 $\alpha$ 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

\[
a^4 = \frac{3Et^3h_{\text{max}}^2}{16\gamma}
\]

Figure 5.3: Schematic configuration of a surface blister.

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

\[
h_{\text{max}} = \frac{3p(m^2 - 1)}{16Em^2t^3} a^4
\]

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

\[
p^2 = Nk_bT \frac{16Em^2}{\pi(m^2 - 1)} \frac{t^3}{a^6}
\]
Substituting the Eq. (5.13) and (5.14) into Eq. (5.12) we get
\[ a^2 = \frac{27 N k_b T m^2 - 1}{256 \pi \gamma m^2} \]  
(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 \( \Phi_m \) is then given by
\[ \Phi_m \approx 19 \frac{\gamma}{a k_b T} \]  
(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 \( \Phi_m \) 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 \( \sigma_{max} \) in the layer of the blister which exceeds the fracture strength \( \sigma \) 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].
\[ \sigma_{max} = 3 a^2 p \frac{1}{4 t^2} \]  
(5.17)

Introducing \( p \) from Eq. (5.14) we get
\[ \sigma_{max} = \frac{9 N k_b T E m^2}{\pi a^2} \frac{1}{m^2 - 1} \]  
(5.18)

Assuming the conditions for fracture, \( \sigma_{max} > \sigma \) then the minimum dose \( \Phi_{m,\text{fract}} \) required for the blister to fracture is given by
\[ \Phi_{m,\text{fract}} = \frac{2 \sigma^2}{9 a k_b T E} \frac{m^2 - 1}{m^2} \frac{1}{t} \]  
(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 one-half the thickness, the middle part of the blister becomes appreciably strained and the stress
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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))

\[ \sigma_{\text{max}} = 4.40E\left(\frac{h_{\text{max}}t}{a^2}\right) + 0.47E\left(\frac{h_{\text{max}}}{a}\right)^2 \]  \hspace{1cm} (5.20)

\[ \sigma_{\text{max}} = 2.86E\left(\frac{h_{\text{max}}t}{a^2}\right) + 0.97E\left(\frac{h_{\text{max}}}{a}\right)^2 \]  \hspace{1cm} (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 \( \sim 16 \, \mu m \)) and got large area exfoliation. Since the size of their micro-cracks is similar (typically below 1 \( \mu m \)) 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 \( \Phi_m \).

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
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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 than 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 $l << d$ 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.
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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
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. SiO₂ 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 micro-cracks 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.

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

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 \(\geq 0.5\). The maximum tensile stress is located at the edge of the micro-crack, where x/t=0 and is given by

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

where N is the total number of gas-molecules in the micro-crack, \(\mu\) the shear modules of the implanted substrate and \(\nu\) Poisson’s ratio.

In a heat treatment, when more gas molecules are incorporated in the micro-crack, \(\sigma_{y,\text{max}}\) increases accordingly. If \(\sigma_{y,\text{max}}\) 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.
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 coalescence of these micro-cracks 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.