APPLIED PHYSICS LETTERS VOLUME 74, NUMBER 7 15 FEBRUARY 1999

Onset of blistering in hydrogen-implanted silicon

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(Received 17 September 1998; accepted for publication 14 December 1998)

The onset of surface blistering in hydrogen-implanted single crystalline silicon was studied. A combination of atomic force microscopy and optical measurements shows that hydrogen-containing platelets grow laterally below silicon surface until they suddenly pop up as surface blisters due to the internal hydrogen pressure after a critical size has been reached. Experimentally and theoretically, the critical size of the onset blisters was found to increase with increasing implantation depth or top layer thickness. © *1999 American Institute of Physics.* [S0003-6951(99)01207-3]

Semiconductor layer transfer by hydrogen implantation in combination with wafer bonding technology has opened new possibilities for the fabrication of silicon-on-insulator materials such as silicon-on-oxidized silicon,[1] silicon-on-quartz,[2] or similar structures such as SiC-on-glass[3,4] or GaAs-on-silicon.[5] For the purpose of layer transfer, splitting of whole wafers parallel to the bonding interface along hydrogen-induced microcracks is required. However, for the understanding of the processes leading to these microcracks, it is much more convenient to investigate the development of surface blisters on hydrogen-implanted but unbonded wafers.

Tong *et al.*[6] studied the surface blistering process as a function of annealing temperature and annealing time in various materials by optical microscopy. As a characteristic quantity to describe the blistering process, the annealing time required for the formation of optically detectable surface blisters was used. This characteristic time which showed an Arrhenius relationship with annealing temperature was termed ''onset'' or blistering time. Of course, the question then arises whether this onset time does have a specific physical background. The question may be formulated as follows: Do hydrogen-induced microcracks pop up as surface blisters at the onset time after originally closed hydrogen-induced platelets have grown to a critical size, or is this experimentally defined onset time for blistering just a parameter associated with the resolution of optical microscopy? In the present letter we report on investigations which answer this question based on optical microscopy combined with atomic force microscopy (AFM).

4 in., (100), Czochralski, *p*-type boron doped silicon wafers covered with 150 nm SiO_2 were implanted by H_2^+ with a dose of $5\times10^{16}/cm^2$ for different implantation energies of 38, 90, and 129 keV. After implantation, the SiO_2 layer on some of the wafers was removed by wet etching to get different thicknesses of the layer over the hydrogen implantation peak. This way, we got a group of hydrogen-implanted silicon wafers with different hydrogen implantation depths as shown in Table I.

The H_2^+-implanted silicon wafers were then cut into small pieces in the size of $2\,mm\times2\,mm$ and annealed in air at different temperatures. The onset time for surface blistering at every annealing temperature was determined as the annealing time at which tiny blisters can first been observed on the sample surface at a magnification of 500 under an optical microscope with a differential-interference-contrast system. AFM was used to overcome the resolution limit of optical microscopy and, therefore, to check whether surface blistering already occurs before these blisters could be detected optically. The size of surface blisters, when present, was also determined by AFM.

By optical microscopy, we found that surface blisters do not form if the annealing time has not reached a critical value. However, upon reaching the onset or blistering time, all of a sudden, tiny blisters in the size of 1–2 μm depending on hydrogen implantation depth appear on the sample surface. With further annealing, these blisters grow and finally break.[7] In the case of bonded wafers, the blisters may merge and cause splitting over the whole area.

In order to ensure that the observed sudden appearance of small blisters is not just caused by the resolution limit of optical microscopy, we used AFM to study the surface morphology of five silicon samples which were implanted by H_2^+ (38 keV, $5\times10^{16}/cm^2$) and annealed afterwards at 350 °C for 5, 8, 12, 15, and 17 s, respectively. 17 s is the onset blistering time at 350 °C determined by optical microscopy. The size of blisters, when present, is measured more precisely by AFM and is considered zero if surface blisters are not detected

TABLE I. Experimental parameters used for hydrogen implantation.

Implantation energy H_2^+ dose: $5.0\times10^{16}/cm^2$	Top layer thickness (nm)
38 keV	80 (SiO_2 removed)
	230
90 keV	300 (SiO_2 removed)
	450
129 keV	440 (SiO_2 removed)
	590

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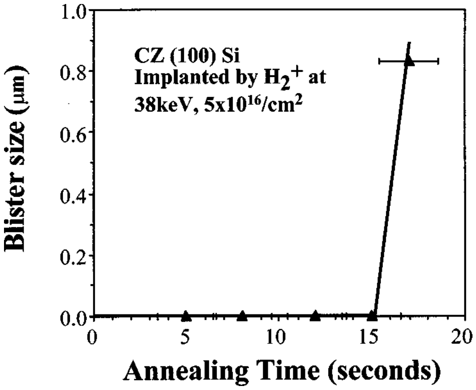
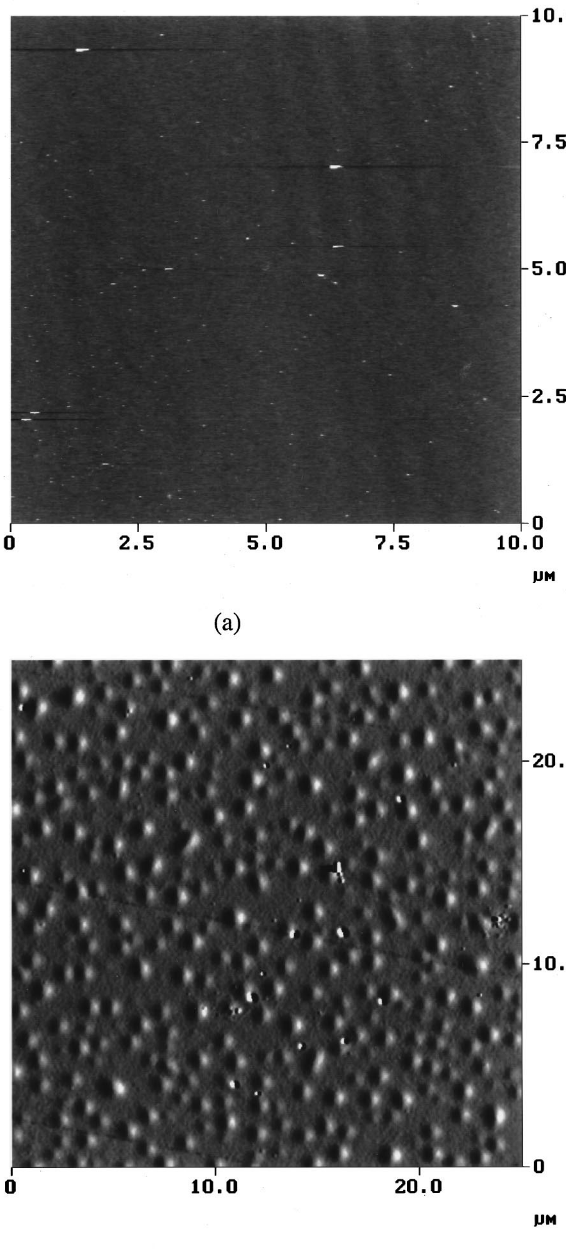


FIG. 1. Size of onset blisters as a function of annealing time as measured by AFM (annealing temperature: 350 °C).

even by AFM. The corresponding blister size versus annealing time is given in Fig. 1. The surface images obtained by AFM for the 15 s (before the onset blistering time) annealed sample and the 17 s (just after the onset time) annealed sample are shown in Fig. 2.

The AFM results above clearly show that the occurrence of these tiny blisters is more like a sudden pop-up step at a critical time and *not* a gradual growth process. The AFM results thus rule out the possibility that the onset time is just caused by the optical resolution limit and has no actual physical significance. To summarize our experimental investigations, the onset of blistering during thermal annealing in hydrogen implanted materials is schematically illustrated in Fig. 3. For the purpose of simplicity, it does not take into account the growth of larger platelets at the expense of smaller platelets, i.e., Ostwald ripening.[8]

The onset of blistering was also investigated from a theoretical point of view. Hydrogen implantation initially leads to the formation of hydrogen containing platelets on (100) or (111) planes. During annealing, the diffusing hydrogen may enter the platelets and form hydrogen molecules associated with a certain pressure which forces the platelets to grow. In the very beginning, the growth is more likely in a lateral propagation manner since the platelets themselves are not yet open, but hold together via van der Waals forces between the two hydrogen-covered internal surfaces of the platelets. The parallel extension of the pressured platelets in hydrogen-implanted silicon as well as in other materials, e.g., Ge, is evidenced by high-resolution transmission electron microscopy TEM.[6,9] Based on the TEM results in literature of the hydrogen-induced platelets/microcracks and our AFM results which show that up to the onset time the buried hydrogen agglomerates do not bulge up, we conclude that the platelets grow in a closed form up to a critical size at 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. 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 cleavage method. An expression of a critical radius derived by Mitani and Gösele,[10] for an analogous situation (the nucleation of interface bubbles formed between two bonded thin wafers) may also be used for the onset of blistering in hydrogen implanted silicon



(a)

(b)

FIG. 2. Surface morphology of hydrogen-implanted and subsequently annealed silicon wafers as measured by AFM before and after blistering time. Implantation condition: 38 keV, $5\times10^{16}/\mathrm{cm}^2$; annealing temperature: 350 °C; annealing times: (a) 15 s, (b) 17 s.

$$r_{\mathrm{crit}}=\{16\gamma_p E t^3/[9\alpha(1-\nu^2)\Delta p^2]\}^{1/4}. \tag{1}$$

In Eq. (1), Δp is the difference between the pressure inside the platelets and that of the outside atmosphere, t corresponds to the hydrogen 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. It is worth pointing out here that we only use Young's modulus for silicon in our case though the top layers of some samples contain both Si and SiO_2 layers of comparable thicknesses (see Table I). Since Young's modulus of Si is about twice that of SiO_2, the simplification we used in our treatment may cause some discrepancy between experimental results and theoretical predictions which will be presented later. There-

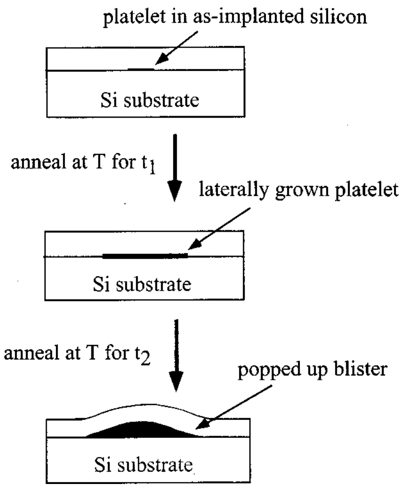


FIG. 3. Schematic of the growth of hydrogen-containing platelets into surface blisters upon annealing.

fore, we use Eq. (1) to give a qualitative rather than a fully quantitative description of the onset of blistering.

In agreement with our experimental observations that the onset blisters always come with a certain size, Eq. (1) confirms the existence of a critical size of the growing platelets before they pop up as surface blisters. If we assume $\gamma_p = 0.5\,\mathrm{J/m^2}$, $E = 1.3\times10^{11}\,\mathrm{Pa}$, $t = 500\,\mathrm{nm}$, $\alpha = 1$, $\nu = 0.3$ for silicon, $\Delta p = 10^8 - 10^9\,\mathrm{Pa}$,[11] we get r_{crit} in the range of 0.4–1 μm which is in good agreement with the onset blister size ($\sim$1 μm) determined experimentally. Equation (1) also predicts that an increased implantation depth or top layer thickness will lead to an increased critical size of the fully grown platelets (also the size of the first emerged surface blisters). The calculated results based on Eq. (1) and the AFM measurement of the layer thickness dependence of the onset blistering size are given in Fig. 4. The theoretical curve qualitatively agrees with our experimental results though the experimentally observed increase is smaller than predicted by Eq. (1). This discrepancy might be partly associated with the substantially different mechanical properties between Si and SiO_2 layers as mentioned before. It may also be caused by the fact that Eq. (1) was derived for the case of blister that is much larger than the wafer thickness *t*, whereas the actually observed onset blisters usually have the size in the order of the layer thickness *t*.

It is worth mentioning that the predominant growth of platelets in a closed form before the sudden pop up of surface blisters allows to preanneal the wafers to a time shorter than the onset time at the given preannealing temperature while keeping the wafer surface still good enough for subsequent wafer bonding. This way, the preannealed wafers can still be bonded and split even at a temperature lower than the preannealed temperature which is desirable for layer transfer between dissimilar materials with grossly different thermal expansion coefficients.[2]

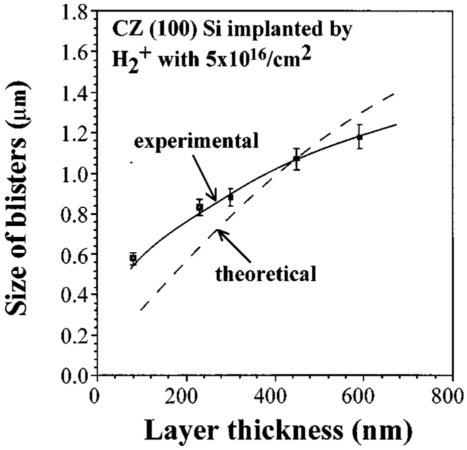


FIG. 4. Critical size of onset blisters as a function of hydrogen implantation depth.

In conclusion, we have found that the formation of surface blisters from hydrogen-containing platelets in hydrogen-implanted silicon consists of a sudden pop-up step at the onset or blistering time rather than a gradual growth. The blistering time corresponds to the annealing time at which the platelets have reached a critical size through lateral propagation during thermal annealing. At this point, the hydrogen pressure inside the platelets is sufficiently high to open up the platelets. The critical size of the onset blisters is found to increase with increasing hydrogen implantation depth or top layer thickness.

The authors are grateful to Shin-Etsu-Handotai Company and to the German Federal Ministry of Science and Technology under Contract No. 13N6758 for financial support.

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