Time dependence study of hydrogen-induced defects in silicon during thermal anneals

S. Personnic, A. Tauzin, K.K. Bourdelle, F. Letertre, N. Kernevez, F. Laugier, Nikolay Cherkashin, Alain Claverie, R. Fortunier

Time Dependence Study Of Hydrogen-Induced Defects In Silicon During Thermal Anneals

S. Personnic, A. Tauzin, K. K. Bourdelle, F. Letertre, N. Kernevez, F. Laugier, N. Cherkashin, A. Claverie, and R. Fortunier

Citation: AIP Conference Proceedings **866**, 65 (2006); doi: 10.1063/1.2401463
View online: https://doi.org/10.1063/1.2401463
View Table of Contents: http://aip.scitation.org/toc/apc/866/1
Published by the American Institute of Physics

Time Dependence Study Of Hydrogen-Induced Defects In Silicon During Thermal Anneals

S. Personnic[1], A. Tauzin[2], K. K. Bourdelle[1], F. Letertre[1], N. Kernevez[2], F. Laugier[2], N. Cherkashin[3], A. Claverie[3] and R. Fortunier[4]

[1] *SOITEC, Parc technologique des Fontaines, Bernin 38926, Crolles Cedex, France.*
[2] *CEA-DRT-LETI, CEA-GRE, 17 rue des Martyrs, 38054 Grenoble cedex 9, France.*
[3] *nMat Group, CEMES/CNRS, BP 4347, F-31055 Toulouse, France.*
[4] *CMP "Georges Charpak", Avenue des Anémones, 13541 Gardanne, France.*

Abstract. Hydrogen implantation in silicon and subsequent thermal anneal result in the formation of a wide range of point and extended defects. In particular, characteristic two-dimensional extended defects, i.e. platelets, are formed. The growth of these defects during thermal anneal, related to H migration, induces the development of micro-cracks in Si. In this paper, a time dependence study of H defects during isothermal anneals is performed using SIMS, FTIR and TEM techniques. We calculate the kinetics of H_2 formation based on SIMS depth profiling and FTIR measurements. We show that the splitting is determined by H migration and rearrangement of hydrogenated defects.

Keywords: hydrogen, implantation, platelets, migration, splitting kinetics.
PACS: 6172Cc, 6172Qq, 6180-x

INTRODUCTION

The discovery of the way to fabricate silicon-on-insulator (SOI) structures with the Smart Cut™ technology [1] has significantly enhanced the scope of applications of industrial ion implantation. The Smart Cut™ is based on ion implantation and wafer bonding. The SOI substrates are in widespread use in the microelectronic industry [2], and the technology was shown to be applicable to many other materials.

It is well known that H is mobile and has a strong chemical activity in crystalline Si [3,4]. In the absence of defects, H moves rapidly through silicon. During ion implantation a large variety of H-related defects is created. The reported general form can be written as $Si\text{-}H_n$, and more specifically I_mH_n and V_mH_n where V and I are, correspondingly, a vacancy and an interstitial. In addition, two-dimensional extended defects, i.e. platelets, are formed in a region near R_p, the ion range. The growth of these defects by means of the H migration and defect rearrangement during subsequent thermal anneal, induces the formation of large gas-filled micro-cracks in the implanted Si. It has been shown that these defects undergo a ripening process in which they exchange H atoms [5]. The anneal is one of the possible technological option to obtain the layer transfer of thin films in Smart Cut™ technology in the specific case of thermal transfers. Despite significant efforts, many physical aspects of implanted H evolution in Si are still unclear.

In this paper, we present a time dependence study of the evolution of hydrogen induced defects in Si after isothermal treatment using secondary ion mass spectrometry (SIMS), Fourier transform infrared spectroscopy (FTIR) and cross section transmission electron microscopy (XTEM) experiments. In addition, splitting kinetics measurements are performed.

EXPERIMENT

The (100) p-type Czochralski (Cz) silicon substrates were H implanted at an energy of about 40 keV and a dose of a few 10^{16} H^+/cm^2, through a 140 nm thick thermally grown oxide layer. After the implantation and the hydrophilic bonding to a base substrate, the structures were cut into pieces. The samples underwent anneals at temperatures ranging from 350 to 500°C for different times ranging from 30 seconds to 50 hrs. SIMS technique was used to obtain the depth distribution of implanted H in the as-implanted and annealed samples. FTIR measurements were performed in the MIR (Multiple Internal Reflection) mode to determine the as-implanted state

CP866, *Ion Implantation Technology,*
edited by K. J. Kirkby, R. Gwilliam, A. Smith, and D. Chivers

of Si and the evolution of H-complexes during anneals. Finally, the XTEM study provided additional information about the platelet defects distribution, evolution and morphology.

For each annealing temperature we measured the critical splitting time, denoted $t_s(T)$, needed to obtain the layer transfer. The corresponding data depicted in Fig. 1 show an Arrhenius-type dependence with an activation energy (E_a) of (2.3 ± 0.1) eV. In this study, the splitting kinetics results are used to establish the "effective" thermal budget for different annealing temperatures.

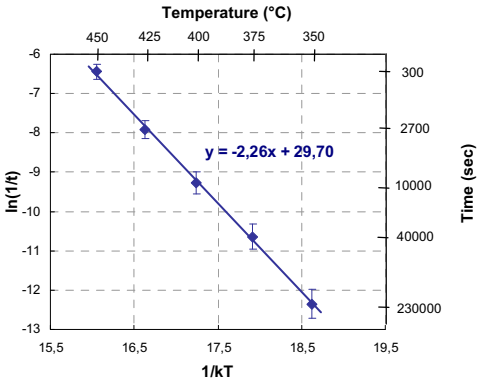

FIGURE 1. Splitting kinetics of Si implanted with an energy in the range of 40 keV and a few 10^{16} H^+/cm^2.

RESULTS AND DISCUSSION

Time-Dependence Evolution Of H Implanted Si

We determined the kinetics of evolution of hydrogen profiles from SIMS measurements. For this purpose the samples underwent isothermal anneals at three different temperatures: 350, 400 and 450°C. As an example, figure 2 shows the H-profiles obtained after annealing at 450°C for different times. It is seen that the measured H-concentration decreases with increasing annealing time. This implies that under thermal treatment, the implanted H migrates and evolves in such a manner that it becomes no longer detectable by SIMS, e.g. by forming H_2.

Figure 3 shows the time-evolution of the H-dose measured by SIMS during isothermal anneals at the three investigated temperatures. A strong time dependence during annealing, with two specific domains, is observed. Most of hydrogen SIMS dose loss occurs during the first 10% of the $t_s(T)$ at each temperature. For the time intervals corresponding from 10-30% to 100% of the $t_s(T)$, SIMS measurements show a weak time dependence.

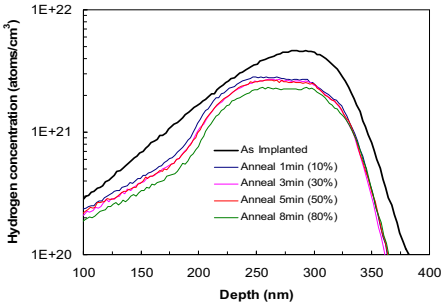

FIGURE 2. Comparison of SIMS profiles from Si implanted with H-ions, before and after isothermal anneals at 450°C.

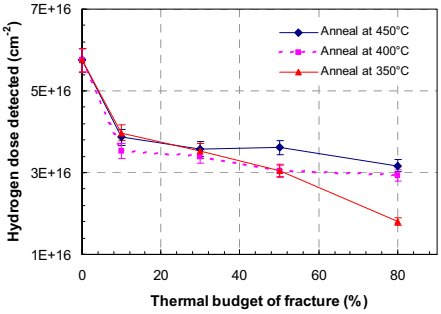

FIGURE 3. Time-evolution of hydrogen dose measured by SIMS after isothermal anneals at 350, 400 and 450°C as a function of the thermal budget of fracture.

A similar time dependence is observed using FTIR-MIR technique where a fast rearrangement of H-induced defects occurs during initial stages of anneal, the first 10% of the $t_s(450°C)$, with slow evolution from 30% of the $t_s(450°C)$ (Figure 4). The total amount of hydrogen observed by FTIR decreases with the annealing time. Indeed, the attenuation of the spectrum integrated intensity reaches ~50% after a long annealing at 450°C. We believe this is due to conversion of trapped hydrogen to an unbound form, i.e. either atomic H or H_2. The net conversion of Si-H_n into H_2 is more likely since the existence of isolated H atoms is highly improbable (unstable state) [3]. For the three investigated temperatures, we observe the same behavior with a "fast-rate" decrease domain for annealing < 10% of the splitting time at the related temperature, and a "slow-rate" decrease domain in the interval 10-30 to 80%.

The "fast-rate" decrease domain is associated with the fast dissociation of some specific hydrogenated defects. The attenuation of the pair of modes observed at 1833 and 2049 cm^{-1} in the as-implanted sample, assigned to the H_2^* defect, and the weakening multivacancy signature (i.e. the major part of the Si-H_n related features in the sub-2050 cm^{-1}, Figure 4) confirm this assumption. We believe that the dissociation of these defects results in the formation of

H_2 that is not directly detectable by SIMS or FTIR, which will fill the microcracks located close to the R_p region. The "slow-rate" decrease domain seems to correspond to another phenomenon with a slower rate of H_2 formation.

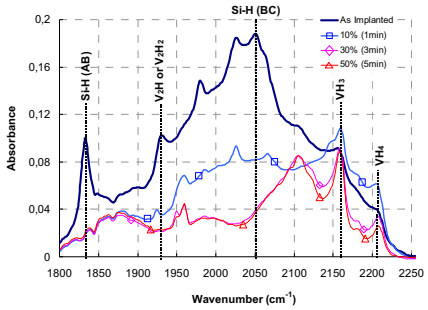

FIGURE 4. FTIR spectra of the Si-H stretching modes of H implanted Si, before and after isothermal anneals at 450°C.

Platelets Nucleation And Growth

A XTEM study was performed for the same samples and provided additional information about the platelets distribution, evolution and morphology. The damage zone is located in the region 170-370 nm. Two types of platelet habit planes are detected: a (001) plane parallel to the wafer surface and a (111) plane. (111) platelets are mostly concentrated in the deeper region of the damage zone in negligible density as compared to (001) platelets.

The platelet nucleation process is finished at the initial stage of annealing, at 5-10% of the $t_s(T)$. To illustrate this phenomenon, figure 5(b) shows the evolution of the platelet volume fraction per unit area as a function of the annealing time, which slightly increases during the first 5-10% of the $t_s(T)$. A signature of this nucleation can be seen with the FTIR experiments. Indeed, during the first minute of annealing at 450°C, a slight increase of the modes assigned to hydrogenated monovacancy defects (VH_n) appears between 2120 cm^{-1} and 2220 cm^{-1} (Figure 4). According to the authors [3, 4, 6], the VH_n defects are supposed to be the precursors of the H-extended defects. The increasing contribution of VH_n in the FTIR spectra and the platelet volume fraction (Figure 5b) measured by TEM are additional evidence that tends to confirm the VH_n precursors theory. Thus, during the first stages of annealing, there is a strong formation of H_2, associated with the end of platelet nucleation (end of VH_n creation).

The following decrease of the VH_n contribution in the FTIR spectra (from 10-30% of the thermal budget of fracture, Figure 4) indicates that the nucleation is finished. This is confirmed by the TEM study showing a stagnation of the platelet volume fraction. This behavior is also seen in FTIR spectra where the intensity of the stretching modes assigned to hydrogen passivating the internal surfaces around 2100 cm^{-1} becomes constant. So, while the duration of annealing increases (from 10% of the $t_s(T)$) the mean diameter of the platelets increases, their density decreases and the volume fraction per unit area occupied by platelets stays constant. These are the typical characteristics of a conservative Ostwald ripening mechanism [5]. This ripening mechanism seems to begin after fast H_2 formation and the slight VH_n creation show up before which takes place during the initial stages of annealing.

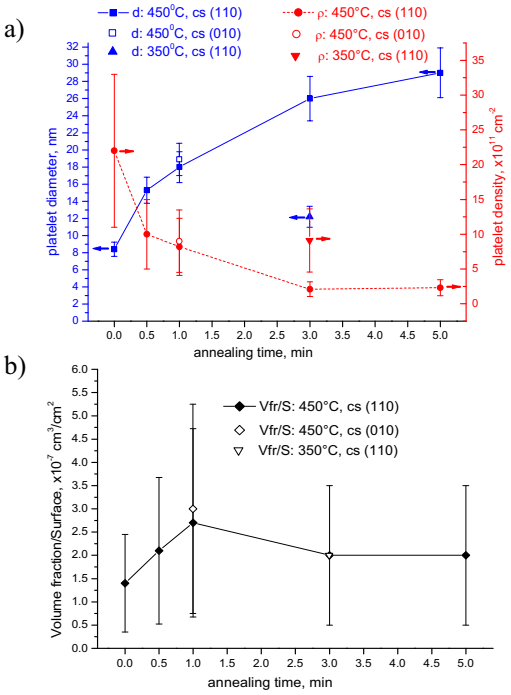

FIGURE 5. Evolution of a) mean platelet diameter and surface density and b) platelet volume fraction per square unit as a function of annealing condition.

Finally, based on the platelets volume fraction per unit area of annealed samples, the dose of H within platelets was found to be in a close agreement with the SIMS dose. That confirms that there is little out-diffusion of H from the damage zone during thermal anneals used in this study.

Kinetics Of H_2 Formation

In order to investigate the rate-limiting mechanism related to the splitting phenomenon occurring during the thermal treatment, we calculated for each temperature the rate of bonded-H decrease, during the entire anneal from as-implanted state until layer transfer. This rate was calculated based on the SIMS profiles (figure 2) and is maximum around 300nm i.e.

in the area where the fracture occurs (presumably due to the formation of H_2 within the microcracks). Hydrogen after implantation exists in the form of Si-H_n defects. The formation of H_2 in a microcrack can be divided in three mechanisms : the dissociation of the Si-H_n complexes, the migration of H towards microcracks and the spontaneous formation of H_2 by association of two H atoms. Thus, we can consider the following general chemical reaction [7]:

$$2\ \text{Si-H}_n \longleftrightarrow 2\ \text{Si} + n\text{H}_2$$

The kinetics of reaction can be written after development,

$$v = -\frac{1}{2}\frac{d[N_H]}{dt} = \frac{d[N_{H_2}]}{dt} = K_0 \exp\left(-\frac{E_a}{kT}\right) N_H^{\alpha} \quad (1)$$

Where N_H is the number of H atoms in the Si-H_n form, N_{H2} is the number of molecules formed, α is the order of reaction and K_0 the rate constant (sec^{-1}) mainly defined by the implantation conditions, the experimental procedures and the substrate nature. The order of reaction represents the empirical dependence of the kinetics of reaction in comparison with the reagents concentrations. For our particular case, it is not equal to zero because the rate of H-measured decrease is not constant during the entire anneal. Figure 6 shows the rate-temperature data obtained, plotted as ln(v) as a function of 1/kT, with v the rate of bonded-H decrease and T the annealing temperature. The function is written below as equation (2).

$$\ln\left(\frac{1}{N_H^{\alpha}}\frac{d[N_H]}{dt}\right) = \ln\left(K'_0\right) - \frac{E_a}{kT} \quad (2)$$

To compare efficiently this function corresponding to the formation of H_2 with the splitting kinetics reference (figure 1), the calculation was made on the entire thermal treatment, from 0 to 100% of the t_s(T). The comparison is shown on figure 6. We fixed the order of reaction equal at 1. Indeed, the kinetics of reaction is dependent to the concentration of hydrogen in the Si-H_n form (two rate decrease domains).

The two types of kinetics coincide very well. The critical fracture time given by the splitting kinetics matches the H_2 formation rate found for the investigated depths near the R_p of implantation. We obtained the same activation energy. The E_a of (2.3 ± 0.1) eV found with the classical splitting kinetics is generally related to H-migration in the presence of gettering centers [8], or, according to some results [9], the rupture of the remaining Si-Si bonds in the implanted region. Our results tend to prove that H migration towards microcraks is the rate limiting step in the splitting kinetics.

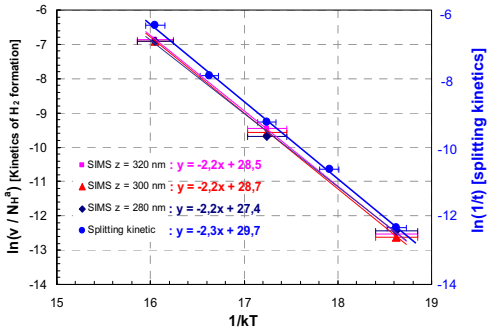

FIGURE 6. Comparison between the splitting kinetics reference and the calculated kinetics of H_2 formation (i.e. decrease of H-measured by SIMS) during the entire thermal treatments.

CONCLUSION

The migration behavior of H obtained from SIMS measurements shows strong time dependence during anneals. Most of H dose loss measured by SIMS occurs during the first 10% of the critical splitting time at a given temperature. SIMS results are in a good correlation with FTIR data where fast rearrangement of H-induced defects has been also observed in the same time. This first stage corresponds also with the end of the platelet nucleation, FTIR results indicating the major role of monovacancy defects in the platelet nucleation and growth. The typical characteristics of Ostwald ripening mechanism were found by TEM after a rapid initial formation of H_2 and the end of the platelet nucleation. For the time intervals corresponding from 10-30% to 100% of the t_s(T), SIMS and FTIR measurements show only slight evolution of the hydrogen-induced defects. Kinetics of H_2 formation indicate that the fracture phenomenon is limited by the H-migration in the presence of gettering centers. Further studies are in progress to identify the thermo-mechanical phenomena occurring at the later stages of microcrack formation and interactions.

REFERENCES

1. M. Bruel, *Electron. Lett.* **31**, 1201 (1995).
2. A. J. Auberton-Hervé, M. Bruel *et al.*., *IEICE Trans. Electron.* **E80-C**, 358 (1999).
3. M. K. Weldon *et al*., *J. Vac. Sci. Technol.* **B 15(4)**, 1065 (1997).
4. M. K. Weldon *et al*., *Appl. Phys. Lett.* **73**, 3721 (1998).
5. J. Grisolia *et al., Appl. Phys. Lett.* **76**, 852-854 (2000).
6. F. A. Reboredo and S. T. Pantelides, *Sol. State Phen.* **69-70**, 83-92 (1999).
7. A. Tauzin, *Internal CEA Report.*
8. B. Aspar *et al.*, *Microelectronic Engineering* **36**, 233 (1997).
9. Q.-Y. Tong *et al*., *Appl. Phys. Lett.* **70**, 1390 (1997).