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Effect of annealing at argon pressure up to 1.2 GPa on hydrogen-plasma-etched and hydrogen-implanted single-crystalline silicon

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Abstract

Effect of annealing at up to 1400 K under argon pressure up to 1.2 GPa on hydrogen-plasma-etched and hydrogen-implanted Czochralski or floating-zone-grown single-crystalline-silicon (FZ), were investigated by secondary ions mass spectrometry (SIMS), X-ray, transmission electron microscopy (TEM), electrical, infrared and photoluminescence (PL) methods. External stress during annealing of hydrogen-containing Si results in suppression of hydrogen out-diffusion, but in its pronounced diffusion into the sample depth. The result is also stress-stimulated creation of small bubbles, thermal donors and crystallographic defects and prevention of sample splitting. © 2001 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Properties of hydrogen-containing single-crystalline silicon (Cz–Si and FZ–Si with hydrogen introduced by etching in the hydrogen-containing plasma, HPE-Si, or by implantation, Si:H) are of considerable interest for microelectronics, because of hydrogen effect on the creation of thermal donors [1,2] and passivation of impurities or dangling bonds, but especially because of recently invented “smart-cut” processing (hydrogen-induced silicon surface cleavage [3]) for producing silicon on insulator (SOI) structures.

Annealing of Si:H, at atmospheric pressure results in the creation of hydrogen-filled microcavities and bubbles. The hydrogen pressure in microcavity can reach the Giga-Pascal (GPa) range [3]. Internal stress in Si:H is of crucial importance for “smart-cut” processing and preparation of SOI structures; and its value can be changed for the sample annealed at increased hydrostatic pressure.

The effect of external stress (exerted by high pressure (HP) of argon) on annealing related effects in Si:H is investigated in this paper. As stated earlier [4], increased pressure of the argon environment during annealing (treatment (annealing) at HP, HT–HP treatment) can influence features of hydrogen-plasma etched silicon (HPE-Si) and hydrogen-implanted silicon (Si:H). The details of HT–HP treatment are described elsewhere [5]. Such an approach proved its effectiveness also for investigation of transformation of the state of impurities and defects in Czochralski-grown single-crystalline silicon (Cz–Si), Si–Ge and other materials [6].

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Nomenclature

c_0	concentration of oxygen in interstitial positions
CVD	chemical vapour deposition
Cz–Si	Czochralski-grown single-crystalline silicon
d	distance between crystallographic planes
D	hydrogen dose in hydrogen-implanted Si:H samples
FZ–Si	floating-zone-grown single-crystalline silicon
HP	enhanced (high) hydrostatic pressure
HPE-Si	hydrogen-plasma-etched silicon
HT	enhanced (high) temperature
HT–HP	treatment (annealing) at HP
IR	infrared absorption (measurement)
PL	photoluminescence
Si:H	hydrogen-implanted silicon
SIMS	secondary ions mass spectrometry
SOI	silicon on insulator ($Si/SiO_8/Si$) structure
TEM	transmission electron microscopy

Greek letters

λ	wavelength

2. Experimental

p-type Cz–Si samples of (0 0 1) orientation with $c_0 = 8 \times 10^{17}$ cm^{-3} were subjected to high-frequency hydrogen plasma etching (HPE) for 1 h using a commercial CVD system [4]. High-frequency (110 MHz) plasma with a power of 50 W at a pressure of 250 mTorr and a hydrogen flux of 200 cm^3/min was applied. The sample temperature during plasma exposure was about 530 K.

Other Cz–Si and floating-zone-grown single-crystalline silicon (FZ–Si) wafers of (0 0 1) and (1 1 1) orientation were implanted by H_2^+ ions (hydrogen dose D up to 6×10^{16} cm^{-2}, energy 130–135 keV).

HPE-Si and Si:H samples of about 10 × 8 × 0.6 mm^3 dimension were subjected to HT–HP treatment for up to 10 h at up to 1400 K and argon HP up to 1.2 GPa [6].

The HT–HP-treated samples were investigated by secondary ions mass spectrometry (SIMS, Cameca IMS 6F), transmission electron microscopy (TEM, Philips CM30, 300 keV), X-ray (reciprocal space mapping), electrical, photoluminescence (PL, argon laser excitation, $\lambda = 488$ nm, at 14 K) and infrared absorption (IR, dispersive-type spectrometer, room temperature) methods.

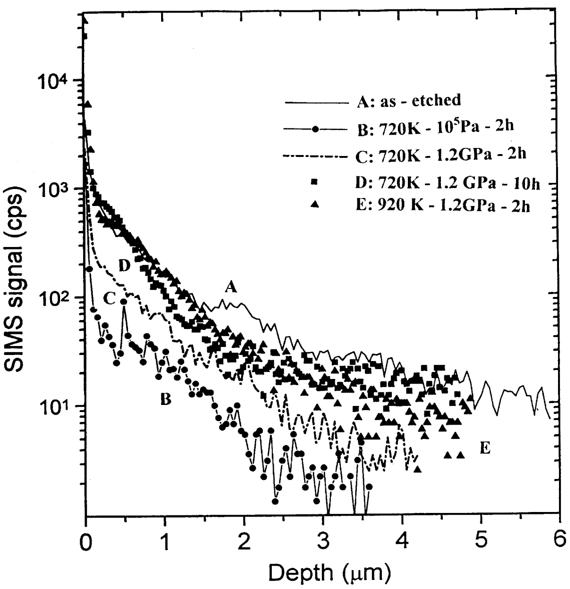

Fig. 1. Depth profiles of hydrogen in HPE-Cz–Si samples: (A) after plasma-etching; (B) annealed at 720 K–10^5 Pa for 2 h; (C) treated at 720 K–1.2 GPa for 2 h; (D) treated at 720 K–1.2 GPa for 10 h; (E) treated at 920 K–1.2 GPa for 2 h. Sputtering by Cs^+ ions.

3. Results

3.1. Effect of HT–HP on HPE-Si samples

The effect of HT–HP on the hydrogen profile in HPE-Si samples is presented in Fig. 1. In the case of non-treated HPE-Si samples, the hydrogen distribution tail reaches deeply into sample bulk, up to above 6 µm (Fig. 1A). Annealing at 720 K for 2 h at atmospheric pressure results in almost complete out-diffusion of hydrogen (Fig. 1B), whereas the treatments at 720 K–1.2 GPa (Fig. 1C and D) or the treatment at 920 K–1.2 GPa–2 h still resulted in the SIMS-detectable presence of hydrogen in the Cz–Si surface layer (Fig. 1E).

The as-etched (non-treated) HPE-Cz sample indicates pronounced X-ray diffuse scattering (Fig. 2A). The same happens for sample treated at 720 K–1.2 GPa–2 h (Fig. 2C), whereas annealing at 720 K–10^5Pa for 2 h (Fig. 2B) and the HT–HP treatment at 920 K–1.2 GPa for 2 h (Fig. 2D) resulted in decreased intensity of X-ray diffuse scattering.

The HP–HT treatment of HPE-Cz–Si samples at 720 K resulted in the HP-stimulated creation of thermal donors (Table 1, see also [4]).

3.2. Effect of HT–HP on Si:H samples

The effect of HT–HP on the hydrogen profile in some Si:H samples is presented in Fig. 3. HT–HP treatment at 720 K

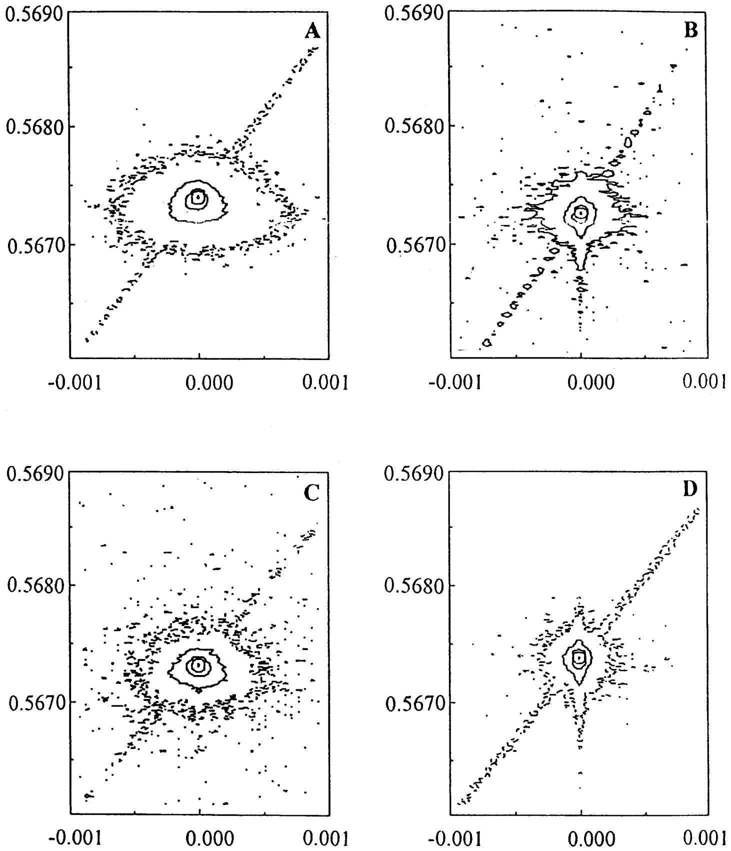

Fig. 2. Reciprocal space Bragg maps recorded near 0 0 4 reciprocal lattice point for HPE-Cz–Si samples: (A) after plasma-etching; (B) annealed at 720 K–10^5 Pa for 2 h; (C) treated at 720 K–1.2 GPa for 2 h; (D) treated at 920 K–1.2 GPa for 2 h. Axes are marked in $\lambda/2d$ units.

Table 1
Carrier concentration N_n ($\times 10^{15}$ cm^{-3}) in initially p-type HPE-Cz–Si samples with initial $N_p = 2 \times 10^{15}$ cm^{-3} and $c_0 = 8 \times 10^{17}$ cm^{-3}, after annealing/HT–HP treatment at 720 K for 2 and 10 h. Measurements were performed at the sample surface subjected to HPE

720 K/HP (Pa)	1×10^5/2 h	1.2×10^9/2 h	1×10^5/10 h	1×10^7/10 h	1.2×10^9/10 h
Type	p	n	p	n	n
N_n	0.91	2.9	0.13	0.93	8.8

results in a higher hydrogen content (as compared to that in the samples annealed at 720 K at atmospheric pressure). The treatment at 920 K–HP resulted also in the hydrogen shift to the deeper sample areas (Fig. 3C). In the case of samples treated at higher temperatures hydrogen disappeared almost completely (Fig. 3D).

The "deeper shoulder" on the depth profile for the as-implanted sample and for that annealed at 720 K –1.2 GPa was caused by the presence of single-atomic H^+ in implanting H_2^+ beam.

TEM images of the 1 1 1-oriented FZ–Si:H samples ($D = 6 \times 10^{16}$ cm^{-2}, 135 keV) were obtained for the as-implanted samples, annealed at 920 K–10^5 Pa and treated at 920 K–1.2 GPa (Fig. 4).

Annealing of the Si:H samples at 10^5 Pa resulted in the creation of numerous bubbles and indications of splitting (Fig. 4B), whereas increased pressure at annealing resulted in the suppression of splitting but in the creation of small cluster-like defects, also in the near-surface silicon layer (Fig. 4C).

X-ray diffuse scattering from the same FZ–Si:H samples ($D = 6 \times 10^{16}$ cm^{-2}, energy 135 keV), as-implanted and HT–HP treated, is presented in Fig. 5. The HT–HP treatment resulted in increased X-ray diffuse scattering, especially for

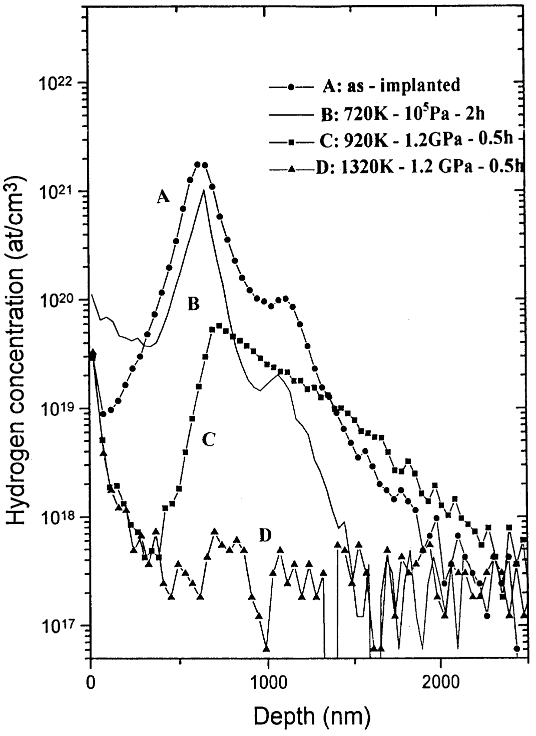

Fig. 3. Depth profiles of hydrogen in Cz–Si:H samples ($D = 4 \times 10^{16}$ cm^{-2}, 130 keV): (A) as-implanted; (B) annealed at 720 K–10^5 Pa for 2 h; (C) treated at 920 K–1.2 GPa for 0.5 h; (D) treated at 1320 K–1.2 GPa for 0.5 h. Sputtering by Cs$^+$ ions.

the samples treated at 920 K–0.6 GPa and 1400 K–1.2 GPa (Fig. 5B and 5D).

Enhanced HP during treatment of FZ–Si:H samples at 920 K resulted in much higher PL intensity at about 0.79 eV, with that at 1.01 eV markedly decreased (Fig. 6). PL related to the band-to-band transition was not detected.

The Si:H samples submitted to the HT–HP treatment at 920 K indicate the presence of additional absorption lines at IR related to localised vibrational modes of defects. For example, the sample treated at 920 K–0.6 GPa for 10 h indicates the presence of peaks at 2092, 2127, 2353 and 2597 cm^{-1}, which can be attributed to hydrogen-related bonds.

4. Discussion

Our results concerning the HT–HP treatments effects on hydrogen-containing (non-equilibrium) silicon samples obtained by HPE or hydrogen implantation are between the first results hitherto reported (see also [4]).

There is clear similarity of the HPE-Si and Si:H samples with respect to the HP-induced effects, so their features after treatment at HT–HP will be discussed jointly.

At enhanced temperature (e.g. at 720–920 K), under atmospheric pressure the hydrogen atoms escape from the silicon matrix (see Figs. 1 and 3), creating in-between numerous hydrogen-filled bubbles or even causing splitting of silicon (Fig. 4B). Treatment of the samples at an increased pressure of argon ambient at the same temperatures resulted in:

- decreased hydrogen out-diffusion, but its pronounced diffusion into the sample depth (Figs. 1 and 3),
- prevention of splitting with creation of small defects just near the sample surface (Fig. 4C),
- HP-dependent creation of microdefects and dislocations, as evidenced by X-ray reciprocal space mapping (Figs. 2 and 5),
- strongly HP-stimulated creation of thermal donors in hydrogen-doped Cz–Si samples (Table 1). This effect is obviously related to the presence of interstitial oxygen in Cz–Si, and can be considered as the proof of stress-stimulated creation of thermal donors, representing small oxygen/silicon clusters [4],
- the presence of hydrogen-related Si–H bonds [7] in the HT–HP-treated oxygen-containing Cz–Si:H samples. The presence of oxygen should stabilise hydrogen bonds in the samples; some of the IR absorption lines can be also related to H–O complexes,
- enhanced intensity of the PL line peaking at about 0.8 eV (Fig. 6).

In the case of HT–HP-treated hydrogen-containing silicon the hydrogen out-diffusion to the sample surface seems to be much diminished with retarded final escape/removal of hydrogen. Retarded hydrogen out-diffusion creates conditions for its diffusion into the sample depth.

PL spectra of HT–HP-treated Si:H samples indicated the presence of rather strong PL peaking at about 0.8 eV. The origin of the observed PL is not known. PL at about 0.8 eV corresponds to that detected for H$^+$ split silicon-on-insulator wafers [8]; however, in this case its explanation as an effect related to the creation of oxygen precipitates seems to be highly improbable because our PL spectra were taken on FZ-Si:H samples with low ($< 2 \times 10^{16}$ cm^{-3}) oxygen content (Fig. 6). One can assume that the observed PL is related rather to HP-stimulated creation of specific point-like defects [9]. Stress-stimulated creation of thermal donors (related in turn to pressure-induced transformation of oxygen present in the samples) in low concentration, but still exerting an effect on PL (compare Table 1) cannot be excluded [9,10].

Explanation of uniform stress effect at annealing on features of HPE-Si and Si:H demands more quantitative analysis. As already mentioned, some HP-induced effects seem to be related to decreased diffusivity of hydrogen at HP, and to stress-stimulated creation of nucleation centres for oxygen precipitation and of extended oxygen-related and other defects (in HPE-Cz–Si and Cz–Si:H), whereas the dimensions

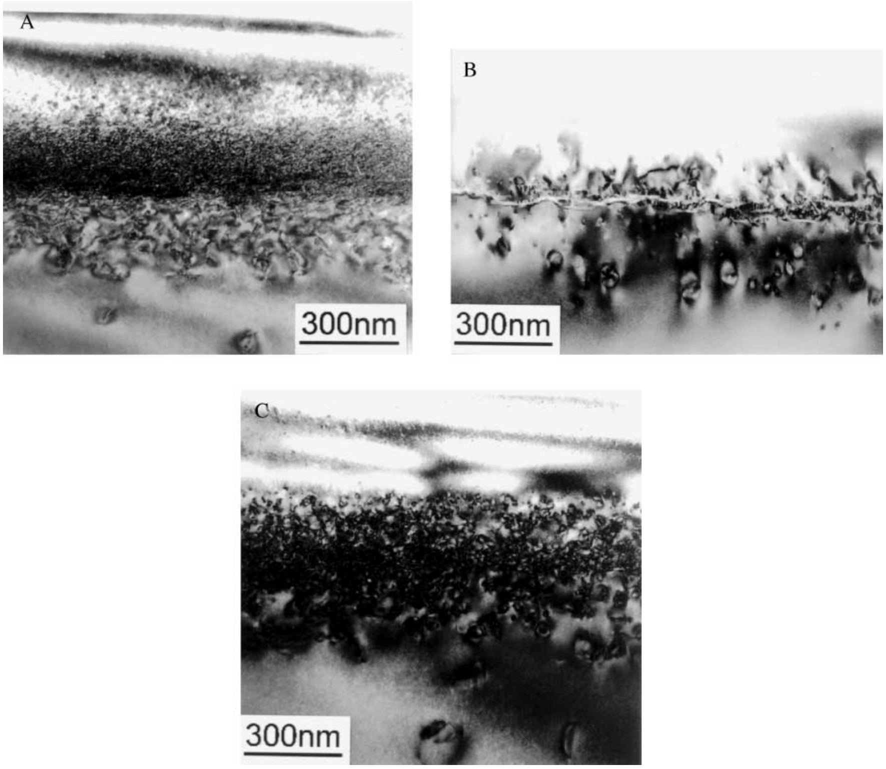

Fig. 4. TEM images of FZ–Si:H samples: (A) as-implanted ($D = 6 \times 10^{16}$ cm^{-2}, 135 keV); (B) annealed at 920 K–10^5 Pa for 10 h; (C) treated at 920 K–1.2 GPa for 10 h.

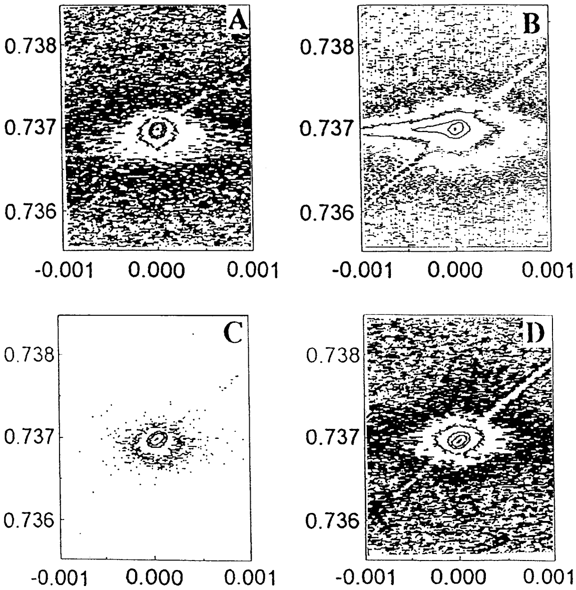

Fig. 5. Reciprocal space Bragg maps recorded near 3 3 3 reciprocal lattice point for FZ–Si:H samples ($D = 6 \times 10^{16}$ cm^{-2}, 135 keV): (A) as-implanted; (B) treated at 920 K–0.6 GPa for 10 h; (C) treated at 920 K–1.2 GPa for 10 h; (D) treated at 1400 K–1.2 GPa for 5 h. Axes are marked in $\lambda/2d$ units.

of originally hydrogen-filled bubbles seem to be suppressed at HT–HP.

5. Conclusions

The stress introduced by increased hydrostatic pressure of ambient during annealing of HPE-Si and Si:H samples exerts a pronounced effect on the hydrogen out- and in-diffusion, on the creation of crystallographic defects (e.g. bubbles), of thermal donors and on the “smart-cut” effect. Further investigations are important in order to understand the phenomena taking place during high pressure–high temperature treatment of hydrogen-containing silicon, important for microelectronics, e.g. in the preparation of SOI structures.

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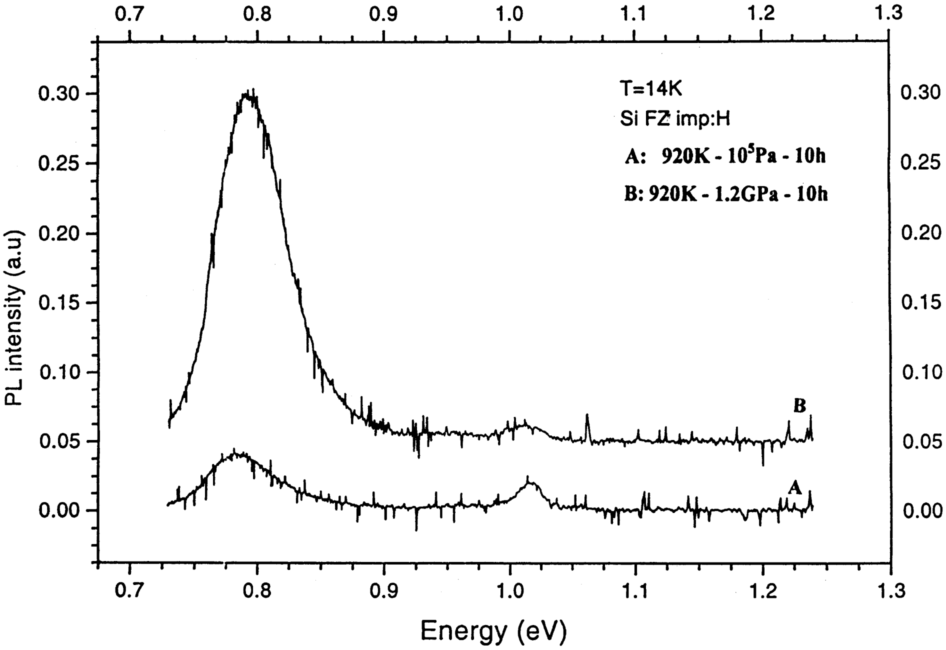

Fig. 6. PL spectra of FZ–Si:H ($D = 6 \times 10^{16}$ cm^{-2}, 135 keV) samples excited by argon laser, $\lambda = 488$ nm, at 14 K: (A) annealed at 920 K–10^5 Pa for 10 h; (B) treated at 920 K–1.2 GPa for 10 h.

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