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DEFECTS IN HIGH TEMPERATURE AND HIGH PRESSURE PROCESSED Si:N REVEALED BY DEUTERIUM PLASMA TREATMENT

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Deuterium is accumulated by defects in nitrogen-implanted silicon (Si:N). This effect is investigated for Si:N processed at HT ≤ 1400 K, also under enhanced hydrostatic pressure, HP ≤ 1.1 GPa. Si:N was prepared from Czochralski grown silicon by N_2^+ implantation at E = 140 keV with nitrogen doses, $D_N = 1–1.8·10^{18}$ $cm^{–2}$. Si:N was subsequently processed in RF deuterium plasma to prepare Si:N,D. Si:N and Si:N,D were investigated by Transmission Electron Microscopy (TEM), X-ray and Secondary Ion Mass Spectrometry (SIMS) methods, also after additional annealing at 723 K. In heavily implanted Si:N ($D_N = 1.8·10^{18}$ $cm^{–2}$), plasma treatment leads to deuterium pile up to $c_{D1} = 2·10^{21}$ $cm^{–3}$ at a depth, d = 50 nm, while, at d = 80–250 nm, deuterium concentration is practically constant with $c_{D2} = 1·10^{21}$ cm^{-3}. This suggests dominating accumulation of deuterium within the bubble-containing areas. Determination of deuterium depth profiles in Si:N,D can reveal implantation- and processing-induced defects.

Keywords: Cz–Si, implantation, nitrogen, high temperature, high pressure, deuterium plasma, defect, gettering

Introduction

Silicon-on-insulator structures (SOI) prepared from nitrogen-implanted single crystalline silicon (Si:N) present usually the dislocated SiN_x/Si interface and may contain nitrogen-filled bubbles formed within the buried SiN_x layer [1].

Enhanced temperature (HT) and hydrostatic pressure (HP) applied at processing of Si:N affect its microstructure and can improve quality of the SiN_x/Si interfaces [2].

As it has been stated earlier for self-implanted silicon, the buried defect region, created by implantation, can getter hydrogen in-diffused from hydrogen plasma [3]. This effect is now investigated for the Si:N samples, preliminary processed at HT–HP. Basing on our earlier results, the treatment in deuterium (hydrogen isotope) plasma has been considered as a tool helpful in revealing the defects in such structures.

Experimental

Details concerning preparation of the Si:N structures are presented in Table.

Table

Investigated Si:N samples, prepared by N_2^+ implantation at ≤ 350 K into (001) oriented Czochralski grown silicon (Cz–Si) with interstitial oxygen concentration, $c_0 = 9 \cdot 10^{17}$ cm^{-3}

Sample	Energy E, keV	Dose D (calculated for atomic nitrogen), 10^{18} cm^{-2}	N_2^+ projected range R_p, nm
A	140	1.0	180
B	140	1.8	180

After ion implantation the Si:N samples were processed for 5 h at HT up to 1400 K under hydrostatic Ar pressure HP ≤ 1.1 GPa.

Structure of the HT–HP processed Si:N samples was determined by TEM and X-ray methods.

To introduce deuterium, the as-implanted and processed Si:N samples were subsequently treated for 2 h at 530 K in RF deuterium plasma in Plasma Enhanced Chemical Vapour Deposition (PECVD) reactor [3]. In what follows, the plasma-treated Si:N samples are labelled as Si:N,D.

SIMS was used to determine the nitrogen, deuterium and oxygen depth profiles in Si:N,D. The mentioned depth distributions were also determined after annealing the Si:N,D samples for 1 h at 723 K under 10^5 Pa.

Results and discussion

Upon annealing the amorphous (aSi) defect layers produced by implantation of N_2^+ at $D \geq 1 \cdot 10^{18}$ cm^{-2} are subjected to Solid Phase Epitaxial Re-growth (SPER). Layers or/and precipitates composed of stoichiometric (Si_3N_4) or substoichiometric (SiN_x) nitride were formed within the buried damaged areas (Fig. 1).

Annealing under 10^5 Pa as well as the HT–HP treatment of Si:N at up to 1400 K do not result in complete SPER, so processed Si:N is composed of the areas with different microstructure. As confirmed also by X-ray measurements, nitrogen-filled bubbles are present near R_p after processing ([4], Fig. 1). The plasma treatment leads, first of all, to accumulation of deuterium near the sample surface. In the case of as-implanted BSi:N samples, the near-surface deuterium peak has been detected at a depth, d = 50 nm with $c_{D1} = 2 \cdot 10^{21}$ cm^{-3}, while, at d = 80–250 nm the deuterium content remains almost constant, with $c_{D2} = 1 \cdot 10^{21}$ cm^{-3} (compare [2]).

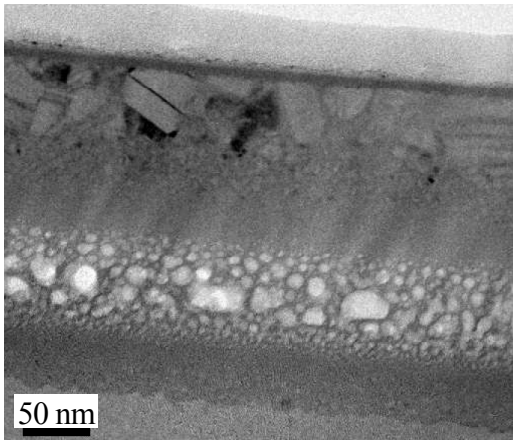
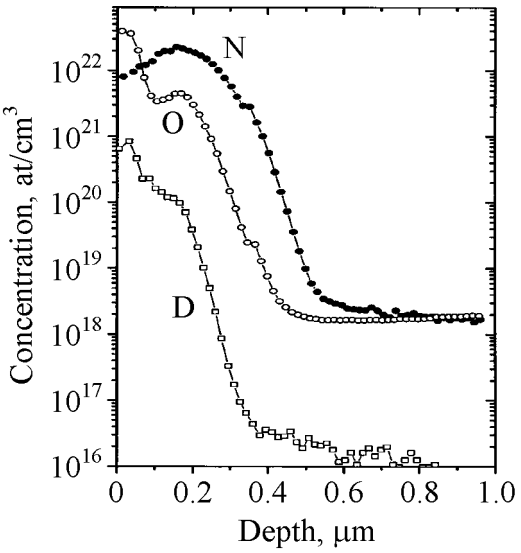


Fig. 1. Cross-sectional TEM image of ASi:N processed at 1400 K under 1.1 GPa. Si:N consists of sub-layers of different microstructure. Very top layer is amorphous with mosaic-like polycrystallites just below it. Big pores (bubbles) are observed near R_p. aSi layers containing Si nanocrystallites are visible on both sides

Processing of ASi:N at 1070 K results in the formation of N-enriched zone near R_p. Interstitial oxygen atoms always present in Cz-Si are also gettered at this defect-containing area. As follows from the oxygen depth profile (Fig. 2), substantial part of oxygen in-diffused from the sample surface covered by thin SiO_2 film is produced at the plasma treatment. The strongest deuterium accumulation is observed just within this near-surface area, at about 20 nm depth. Just this area contains numerous defects introduced by plasma etching itself.

Processing of ASi:N at 1270 K resulted in the formation of N-enriched plateau at d = 100–300 nm, containing about 20 at.% of nitrogen. This suggests almost uniform distribution of implanted nitrogen, in the form of sub-stoichiometric Si_3N_x. Deuterium introduced by the plasma treatment is accumulated mainly at the bottom Si_3N_x/Si boundary thus suggesting strong affinity of deuterium just to defects created at this place (Fig. 3).



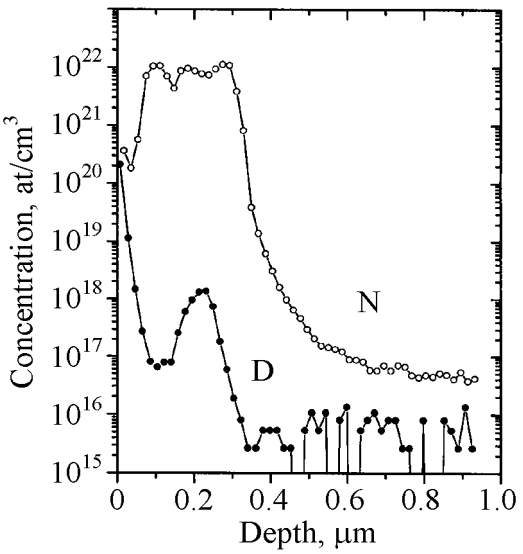


Fig. 2. SIMS depth profiles of nitrogen, oxygen and deuterium in ASi:N,D, prepared from ASi:N ($D_N = 10^{18}$ cm^{-2}) processed for 5 h at 1070 K under 1.1 GPa

Fig. 3. SIMS depth profiles of nitrogen and deuterium in ASi:N,D, prepared from ASi:N processed for 5 h at 1270 K under 1.1 GPa

Deuterium accumulation in BSi:N,D is more pronounced than that in ASi:N,D.

The deuterium profiles in the near-surface area of BSi:N,D prepared from BSi:N processed at 1270 K are similar to these in BSi:N,D prepared from the as-implanted BSi:N sample but c_{D2} decreased to $4 \cdot 10^{20}$ and $3 \cdot 10^{20}$ cm^{-3} after processing under 10^5 Pa and 1.1 GPa, respectively [2].

The BSi:N,D samples prepared from BSi:N processed at 1400 K indicate a lowered D accumulation. Deuterium concentration exhibits minimum near R_p and the maximum at a $d \approx 250$ nm (compare Fig. 4).

A lot of deuterium is still retained, especially in the BSi:N,D samples, after their subsequent annealing at 723 K under 10^5 Pa (Fig. 4).

And so the BSi:N,D sample, prepared from as-implanted BSi:N, and annealed at 723 K, still indicates $c_{D1} = 6 \cdot 10^{20}$ cm^{-3} at $d = 50$ nm, while, at $d = 150$ nm, c_{D2} equals to about $7 \cdot 10^{20}$ cm^{-3} (Fig. 4).

Accumulated deuterium is strongly bonded to defects also in the BSi:N,D samples prepared from Si:N processed at higher temperatures and finally annealed at 723 K (Fig. 5).

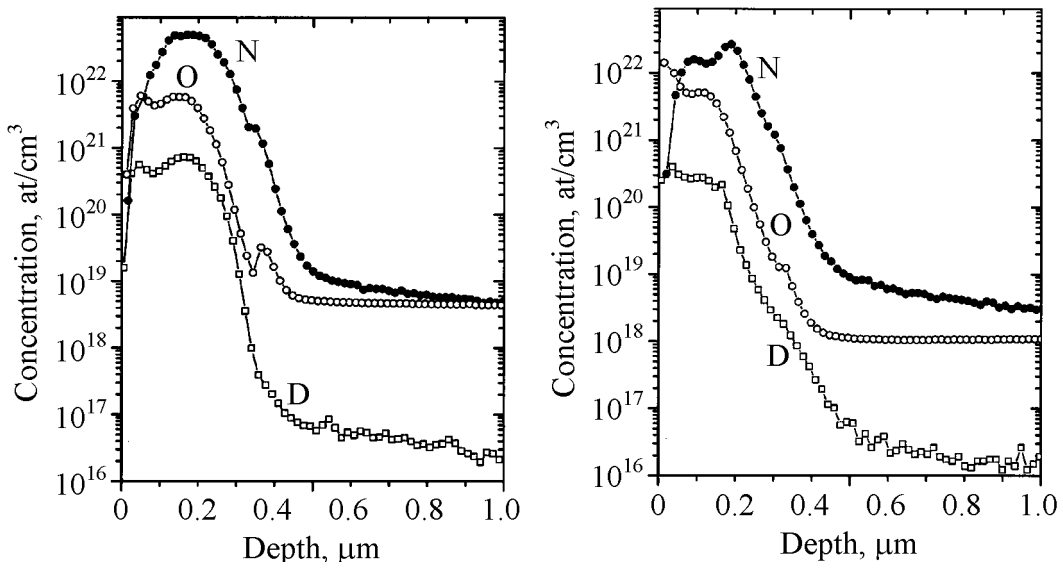


Fig. 4. SIMS depth profiles of nitrogen, oxygen and deuterium in BSi:N,D, prepared from as-implanted BSi:N ($D_N = 1.8 \cdot 10^{18}$ cm^{-2}) and finally annealed at 723 K

Fig. 5. SIMS depth profiles of nitrogen, oxygen and deuterium in BSi:N,D, prepared from BSi:N processed for 5 h at 1270 K under 10^5 Pa and finally annealed at 723 K

Also the BSi:N,D sample prepared from BSi:N processed for 5 h at 1400 K under 10^5 Pa, indicated, after annealing at 723 K, high deuterium concentration at the very sample surface ($c_D \approx 2 \cdot 10^{21}$ cm^{-3}). At $d = 100$–200 nm this concentration is equal to about $3 \cdot 10^{20}$ cm^{-3}.

As seen in TEM patterns, the very top layer of Si:N is composed of the polycrystalline-like material (compare Fig. 1). In effect of its presence, one can observe sometimes a specific artefact: massive in-diffusion of deuterium as well

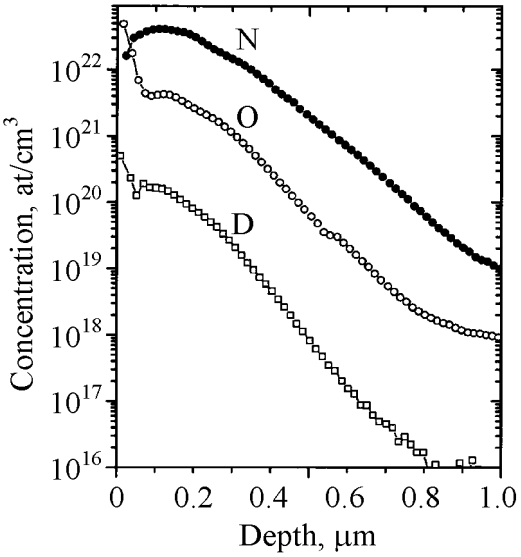


Fig. 6. SIMS depth profiles of nitrogen, oxygen and deuterium in BSi:N,D, prepared from BSi:N processed for 5 h at 1270 K under 1.1 GPa and finally annealed at 723 K

as in-diffusion and re-distribution of other admixing atoms, especially in the case of BSi:N prepared by heavy nitrogen implantation (Fig. 6).

In the case of Si:N structures prepared by ion implantation, the formation of aSi area takes place near R_p. Most of implanted nitrogen atoms are contained within this area. Upon annealing, nitrogen-containing aSi is subjected to SPER.

The processed Si:N samples indicate the presence of buried SiN_x layer containing numerous nitrogen-filled bubbles. The deuterium plasma treatment of Si:N with different microstructure induced by specific HT–HP processing, results in hydrogen accumulation at the surface and within the buried defect layers.

Deuterium concentration is the highest at the near-surface areas of the Si:N,D samples, especially in the ones prepared from as-implanted or relatively low-temperature-processed Si:N. This means that plasma deuterization itself introduces a lot of defects within the near-surface sample areas. In spite of relatively low temperature ($T \approx 530$ K) and short time of plasma treatment (2 h), a remarkable in-diffusion and subsequent gettering of deuterium within the deeper placed damaged layers has been observed.

In the case of BSi:N,D, prepared by heavy nitrogen implantation, the deuterium concentration profiles correspond roughly to these of nitrogen, suggesting a special role of N_2-filled bubbles (Fig. 1) in deuterium accumulation. A release of about 50% of deuterium after annealing of Si:N,D (prepared from as-implanted Si:N) at 723 K may suggest some D–N bonding.

Enhanced pressure applied during preparation of the Si:N samples affects strongly their microstructure and thus in-diffusion and depth profiles of deuterium after plasma treatment. The deuterium depth distribution depends crucially on the implanted nitrogen dose (Figs 3 and 5).

Conclusions

New data concerning the formation of buried defect-containing layers in silicon implanted with nitrogen and subjected to the post-implantation high temperature (pressure) processing are reported. Such structures absorb deuterium from deuterium plasma; the deuterium accumulation and distribution within the samples are dependent on the sample microstructure.

Specific character of SPER and of deuterium interaction with defects in as-implanted and processed Si:N has been confirmed. Determination of the deuterium depth

profiles in Si:N,D, also subjected to additional anneals, can contribute to revealing the implantation-induced and other structural defects in the SOI-like and similar structures prepared from Si:N.

This means that the deuterium plasma treatment with subsequent determination of depth concentration profiles of deuterium may be helpful in evaluating the Si:N sample microstructure, especially in view of potential applicability for SOI technology.

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ДЕФЕКТИ В Si:N, ОБРОБЛЕНОМУ ПРИ ВИСОКИХ ТЕМПЕРАТУРАХ І ТИСКАХ, ЩО ВИЯВЛЯЮТЬСЯ ВНАСЛІДОК ТРАВЛЕННЯ В ДЕЙТЕРІЄВІЙ ПЛАЗМІ

У роботі розглянуто ефекти впливу обробки температурним відпалом (до 1400 K) і гідростатичним тиском (до 1.1 GPa) на дефектний склад SOI-структур (silicon-on-insulator) на основі зразків Si:N – матеріалу, широко використовуваного в напівпровідникових технологіях. Було отримано нові дані, що свідчать про утворення прихованих дефектовміщуючих шарів в зразках кремнію, імплантованого азотом, підданих обробці високими температурами та тиском. Такі структури стають центрами абсорбції дейтерію з плазми – його накопичення і розподіл усередині зразка залежать від мікроструктури матеріалу. Таким чином, показано, що обробка в дейтерієвій плазмі з подальшим визначенням концентраційних профілів по глибині зразка може бути корисною для оцінки мікроструктури Si:N-зразка, особливо зважаючи на потенційну застосовність в SOI-технологіях.

Ключові слова: Cz–Si, імплантація, азот, висока температура, високий тиск, дейтерієва плазма, дефект, газопоглинання

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ДЕФЕКТЫ В Si:N, ОБРАБОТАННОМ ПРИ ВЫСОКИХ ТЕМПЕРАТУРАХ И ДАВЛЕНИЯХ, ПРОЯВЛЯЮЩИЕСЯ В РЕЗУЛЬТАТЕ ТРАВЛЕНИЯ В ДЕЙТЕРИЕВОЙ ПЛАЗМЕ

В работе рассмотрены эффекты влияния обработки температурным отжигом (до 1400 K) и гидростатическим давлением (до 1.1 GPa) на дефектный состав SOI-

структур (silicon-on-insulator) на основе образцов Si:N – материала, широко используемого в полупроводниковых технологиях. Были получены новые данные, свидетельствующие об образовании скрытых дефектосодержащих слоев в образцах кремния, имплантированного азотом, и подвергнутых обработке высокими температурами и давлениями. Такие структуры становятся центрами абсорбции дейтерия из плазмы – его накопление и распределение внутри образца зависят от микроструктуры материала. Таким образом, показано, что обработка в дейтериевой плазме с дальнейшим определением концентрационных профилей по глубине образца может быть полезной для оценки микроструктуры Si:N-образца, особенно ввиду потенциальной применимости в SOI-технологиях.

Ключевые слова: Cz–Si, имплантация, азот, высокая температура, высокое давление, дейтериевая плазма, дефект, газопоглощение