Effect of heat treatment at enhanced pressure on electrical and structural properties of silicon surface layer co-implanted with hydrogen and helium ions

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Electrical and structural properties of silicon surface layer created by high pressure annealing of hydrogen and helium co-implanted silicon were investigated by current and capacitance measurements of Schottky barrier junction Hg-Si (mercury probe), cross-sectional transmission electron microscopy and SIMS analysis. The most striking result is finding that hydrogen and helium co-implantation leads to shallow donors generation and changes in the type of conductivity even for low concentration of oxygen in silicon. High pressure thermal anneals result in additional donor formation in the implanted silicon surface layer.

Keywords: silicon, hydrogen and helium implantation, SOI, smart-cut process.

1. Introduction

Implantation of hydrogen and helium is widely used in microelectronics especially in silicon on insulator technology (SOI) for so-called smart-cut processing [1]. According to work of Agarwal et al., smart-cut process can be in large extent improved by helium and hydrogen co-implantation [2]. It has been reported that enhanced hydrostatic pressure (HP) of ambient gas at annealing (HT-HP treatment) of Czochralski silicon (Cz-Si) implanted with hydrogen and helium exerts pronounced effect on microstructure as well as on gettering processes within the implantation damaged areas [3-5]. It is well known that in Cz-Si oxygen-related centres are responsible for thermal donors formation. The concentration of thermal donors is stress dependent what was observed after application of increased hydrostatic pressure of argon atmosphere during heat treatment of Cz-Si [6-7]. Large stress is present during smart-cut processing and its influence on electrical and structural properties of surface implanted layer is important from a point of view of semiconductor devices properties.

2. Experimental

Boron doped (resistivity 4–6 Ω cm), p-type (100) oriented Cz-Si wafers with initial interstitial oxygen concentrations, $c_o \approx 8 \times 10^{17}$ cm⁻³ and $\leq 4 \times 10^{17}$ cm⁻³ were used as the initial crystals. Hydrogen, H₂⁺ and helium, He⁺ ions with the doses of $D_{\rm H,He}$ = 5×10¹⁶ cm⁻² were co-implanted at $T_i \leq$ 350 K into Cz-Si to prepare two kinds of samples. In the case of Cz-Si with lower oxygen concentration, He⁺ ions were im-

planted at the energy $E_{\text{He}} = 50 \text{ keV}$ with the projected range $R_{p\text{H}} \approx 420 \text{ nm}$, lower then the projected range $R_{p\text{H}} \approx 580 \text{ nm}$ of H_2^+ implanted at the energy $E_{\text{H}} = 135 \text{ keV}$. The samples of other kind with higher oxygen concentration were prepared by implantation of Cz-Si with He⁺ ions at the energy of $E_{\text{He}} = 150 \text{ keV}$ (projected range $R_{p\text{He}} \approx 880 \text{ nm}$), higher than the projected range $R_{p\text{H}} \approx 580 \text{ nm}$ of H_2^+ implanted at 135 keV. These two kinds of samples were marked as Si:He,H and Si:H,He, respectively. For comparison, H_2^+ ions were implanted at the energy $E_{\text{H}} = 135 \text{ keV}$ (projected range $R_{p\text{He}} \approx 580 \text{ nm}$) into Cz-Si with the lower oxygen concentration and they were marked as Si:H.

The implanted samples were annealed at 720 K and 920 K under the atmospheric pressure or HP up to 1.1 GPa.

The implanted and annealed samples were studied by cross-sectional transmission electron microscopy (XTEM, JEOL 200CX), SIMS analysis performed with a Cameca IMS 6F instrument using Cs⁺ primary ions at an energy of 15 kV and by measurements and numerical analysis of current-voltage I-V and capacitance-voltage C-V characteristics of Schottky barrier junction Hg-Si (mercury probe) using the measurement setup shown in Fig. 1.

The measuring system was controlled via GPIB bus by PC with TestPoint environment and consisted of QuadTech 7600 admittance meter and Keithley 237 and 238 source measurement units. The QuadTech 7600 Precision LCR meter can measure capacitance in the wide band of test signal frequencies from 10 Hz to 2 MHz. Keithley 237 and 238 source measurement units provided bias voltage during the measurements of I-V and C-V characteristics. Electrical measurements of Si:He,H Si:H,He and Si:H samples were done both on the top (implanted) surface and on the back (non-implanted) one.

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Fig. 1. Block diagram of electrical measurements setup.

3. Results and discussion

The implantation-damaged buried spongy-like layers containing numerous H₂ and He-filled cavities and other structural defects are created in the samples co-implanted with hydrogen and helium if annealed at below 780 K under atmospheric pressure [8]. These samples subjected to the HP treatment at higher temperature 920 K indicate the presence of strongly dislocated areas near R_{pHe} and R_{pH} , respectively as shown in Fig. 2.

The surface layer and the region near R_{pHe} of Si:He,H sample contains much more large defects comparing to Si:H,He sample resulting in different electrical properties.

Hydrogen and oxygen oxygen distributions obtained from SIMS analysis in sample Si:He,H annealed for 10 hours at 720 K are shown in Figs. 3 and 4.

The peak of hydrogen distribution is located at the distance of about 0.6 µm and after annealing at 720 K for 10 hours under the hydrostatic pressure of 0.1 MPa and 1.1 GPa maximum hydrogen concentration is decreasing. Oxygen distribution indicates that spongy-like buried layer and surface layer have gettering properties because oxygen concentration in the initial Si:He,H sample is rather low ($\leq 4 \times 10^{17}$ cm⁻³).

From the point of view of electrical measurements, the measured structure is rather complicated, because under the surface layer of a thickness of co-implanted ions projected



Fig. 2. XTEM images of Si:He,H (left) and Si:H,He (right) annealed for 1 hour at 920 K under pressure of 1.1 GPa.



Fig. 3. Hydrogen distribution in Si:He,H sample annealed for 10 hours at 720 K.

range, there is a strongly defected spongy-like buried layer. In this case, all the electrical measurements were performed on the surface layer taking into account existence of the buried spongy-like layer. The resistance of spongylike buried layer calculated from I-V characteristics was needed to choose the proper frequency of a test signal dur-



Fig. 4. Oxygen distribution in Si:He,H sample annealed for 10 hours at 720 K.



Fig. 5. Carrier concentration dependence on heat treatment under hydrostatic pressure for Si:He,H sample (solid points – electron concentration, open points – hole concentration).

ing the measurements of C-V characteristics. The conductivity type have been determined from I-V and C-V characteristics and carrier concentration profiles have been calculated from C-V characteristics [9–10].

Electrical measurements of surface implanted layer as well as the samples back sides summarized in Figs. 5 and 6 have provided interesting information.

We have observed from I-V and C-V characteristics of Schottky barrier for Si:He,H samples, that for the as implanted sample the type of conductivity of the surface layer



Fig. 6. Carrier concentration dependence on heat treatment under hydrostatic pressure for Si:He,H sample (solid points – electron concentration, open points – hole concentration).

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has been changed from the initial p-type (still detected at the sample back side) to n-type. The same effect has been observed for Si:H sample. As the helium projected range is smaller than the hydrogen one for this Si:He,H sample, it means that the helium implantation results in the increased generation of donor - like defect centres even for low initial oxygen concentration in Cz-Si ($c_o \leq 4 \times 10^{17} \text{ cm}^{-3}$). This is caused by high oxygen concentration at the sample surface due to gettering process. This is not the case for Si:H,He where the helium projected range is larger than that of hydrogen, though the oxygen concentration is higher ($c_o \approx 8 \times 10^{17} \text{ cm}^{-3}$). It results from the calculations of the carrier concentration for the Si:He,H sample that the concentration of donor-like defects is rather high (about 2×10^{17} cm⁻³) for as-implanted sample and decreases to the level of 3×10^{16} cm⁻³ after sample annealing at 720 K for 10 h at atmospheric pressure. This means that some implantation induced defects, not related to the presence of oxygen, were annihilated. Annealing at 920 K for 10 h under atmospheric pressure results in annihilating of all donor centres not related to oxygen and the surface layer recovers its initial p-type of conductivity, but with much higher level of hole concentration which means that acceptor - like defect centres are also generated during the implantation process. The concentration of these defects is increased after heat treatment at 920 K and HP =1.1 GPa for 10 h. We have observed that application of increased hydrostatic pressure of argon atmosphere during heat treatment at 720 K for 10 h of Si:He,H samples, resulted in stress-induced creation of TDs because of high oxygen concentration in the implanted volume. There is no such an effect for Si:He,H sample back side due to low oxygen concentration as shown in Fig. 4. Contrary to this, for the Si:H,He samples with higher oxygen concentration the change of conductivity type and stress-induced creation of TD was observed very distinctly on back sides of samples as shown in Fig. 6.

4. Conclusions

Formation of surface layer in Cz-Si subjected to implantation and high temperature-pressure treatment is accompanied by creation of the structural and electrically active defects such as oxygen related thermodonors, donor-like, and acceptor-like. Electrical properties of sponge-like silicon surface structures formed by high pressure annealing of hydrogen and helium co-implanted silicon are dependent on the implantation and annealing conditions. It is possible to form p-n junctions and to obtain various carrier concentration levels influencing the semiconductor devices properties by changing the projected range of implanted ions, oxygen concentration, and the conditions of temperature high-pressure treatment.

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