PROPERTIES OF $Si\text{-}SiO_2$ INTERFACES IN MOS STRUCTURES WITH NITROGEN-DOPED SILICON

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Summary The article presents the results of capacitance measurements on MOS structures with a silicon substrate that was doped by nitrogen during the growth of the single crystal by Czochralski's method. Attention is paid to the energy distribution of the trap density at the $Si\text{-}SiO_2$ interface. The effect of the bond of nitrogen and oxygen brought about a slight increase in the trap density with a typical distribution of energy maxima of the deep levels in the forbidden band of Si.

1. INTRODUCTION

A highly important precondition for the production of quality integrated circuits is the well mastered production of semiconductor wafers. It is imperative for the substrate wafer to contain as little defects as possible, above all in the subsurface functional region in which active elements of integrated circuits are located. Another important requirement is a small scatter of material parameters across the wafer. In effort to produce the best possible substrate with suitable parameters, numerous procedures are introduced into the process of manufacture.

Recently, much attention has been paid to the properties of nitrogen-doped silicon substrates grown by the method of Czochralski [1-3]. The presence of nitrogen in the silicon substrate has been known for several decades already. In the past, however, nitrogen in silicon was understood as an undesired impurity causing a large amount of defects. As a result, the generation-recombination parameters of the silicon substrate are worsened. In the case of substrates with large diameters there is a possibility to utilize Si wafers containing nitrogen in the production of integrated circuits, particularly thanks to the good mechanical and electrophysical properties of silicon. Motivation for further research is the expected improvement in reliability and production yield of devices based on nitrogen-doped silicon.

In quest to create the best subsurface region with a low concentration of electrically active defects (of the so-called denuded zone), it is inevitable to remove from it primarily metallic impurities that give rise to deep levels in the forbidden band of the semiconductor. One of the ways how to create a high-quality denuded zone is intrinsic gettering by means of oxygen precipitates [4]. These behave like gettering centres for metallic impurities. Oxygen is introduced into silicon during the Czochralski growth. In the course of the multi-stage process of thermal treatment, oxygen precipitates are created in the bulk of the semiconducting substrate, whereas in the subsurface region oxygen diffuses to the interface and contributes to the creation of SiO_2. In this way, metallic impurities are drawn into the bulk of Si, where they are bonded to precipitates. Nitrogen, even in small amounts, possesses the ability to support precipitation of oxygen and hereby to improve the process of intrinsic gettering. Precipitates created in the nitrogen doped Czochralski-grown substrate (NCZ) have smaller dimensions and a higher density than in an undoped Czochralski-grown (CZ) structure. In the case of a standard CZ silicon structure, the use of intrinsic gettering by means of oxygen precipitates can only be considered for silicon wafers of small diameters. In the case of larger diameters, a decrease in the creation of precipitates occurs in peripheral regions. This decreases the gettering efficacy and, as a result, a big scatter in parameters occurs across the wafer. In an NCZ structure, nitrogen supports creation of precipitates also in the peripheral regions and improves the radial uniformity of the denuded zone [5,6]. Nitrogen allows locking of dislocations resulting in an improvement of the mechanical strength of semiconducting wafers, which is another advantage of nitrogen doping of silicon substrates.

2. EXPERIMENT

Measurements were performed on four samples of a Si MOS structure: nitrogen-doped (NCZ) and reference (CZ) of *n* and *p* types. The substrate was prepared by Czochralski's method using phosphorus to get *n*-type, and boron for *p*-type of doping. In order to intentionally contaminate the silicon wafer by nitrogen, silicon wafers were inserted into the melt with 1 μm thick layers of Si_3N_4 deposited on both sides of the wafer by LP CVD. The nitrogen doped and reference wafers had the same resistivity 2 to 5 Ωcm and depth 500 μm. The SiO_2 gate oxides (thickness 100 nm for *n* type, and 80 nm for *p* type) were formed by thermic oxidation in O_2+H_2O atmosphere at 1050°C. The initial concentration of nitrogen for the NCZ substrate was 1.6×10^{15} cm^{-3}.

The MOS capacitors were characterized by capacitance and current methods. High-frequency *C-V* and non-equilibrium *C-t* measurement were performed using a 4280 1 MHz C Meter/C-V Plotter Hewlett-Packard [7]. Quasistatic *C-V* measurements were performed using a Keithley 595 Quasistatic C-V Meter [8].

3. RESULTS AND DISCUSSION

Figures 1a and 1b show low- and high-frequency *C-V* characteristics of MOS structures with *n* and *p* types of substrate doped by nitrogen.

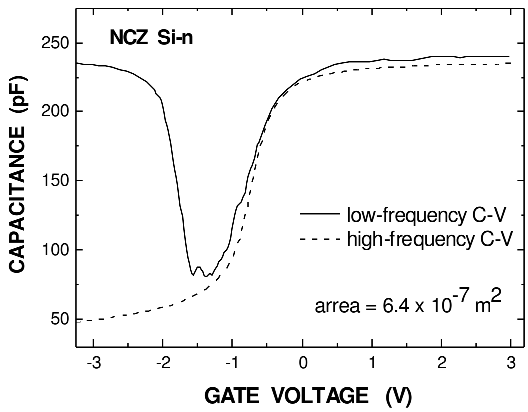

Fig. 1a Low-frequency and depleted C-V curve of the MOS structure with an n-type silicon substrate doped by nitrogen.

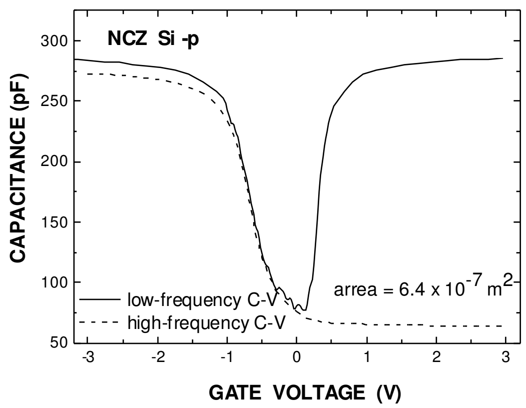

Fig. 1b Low-frequency and depleted C-V curve of the MOS structure with a p-type silicon substrate doped by nitrogen.

In Fig. 2, one can see the energy distributions of the density of traps, D_{it}. In this figure one can see the influence of oxygen upon the Si-SiO_2 interface, where it forms levels with activation energy given by the position on the energy *x*-axis. The data obtained from *C-V* and *C-t* measurements are summarized in Tab. 1.

The magnitude of D_{it} is evaluated as a mean value ±0.1 eV around the midgap and is higher by about half an order of magnitude for both *n* and *p* types of NCZ substrate than for CZ substrate. For the *n* type of CZ substrate the value of D_{it} is about 10^9 cm^{-2}eV^{-1}, which is below the sensitivity limit of the quasistatic method. The increase in D_{it} in the case of NCZ wafers is clearly due to extrinsic traps present at the Si-SiO_2 interface, whose origin can be attributed to defects containing N- and/or O-N-, such as 2N or 2NO complexes [9].

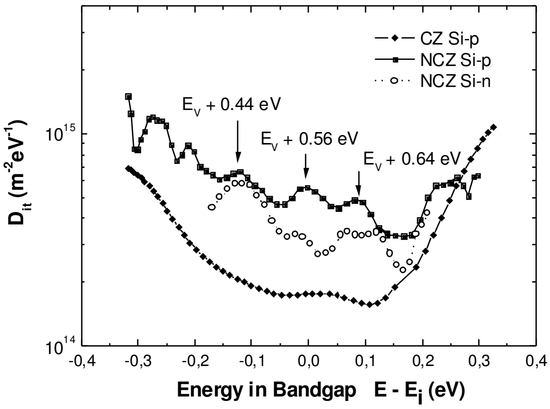

Fig. 2 Energy distribution D_{it} of MOS structures with p-type CZ and n-type NCZ silicon substrates.

Tab. 1 Parameters of structures with nitrogen-doped substrates.

Sample	V_{FB} (V)	N_{eff} (m^{-2}) $\times 10^{15}$	t_r (s)	τ_g (μs)	D_{it} (cm^{-2}eV^{-1})
CZ *n*-Si	–0.7	1.5	550	1316	~ 10^9
NCZ *n*-Si	–0.8	1.7	150	80	3.4×10^{10}
CZ *p*-Si	–0.8	2.1	125	51	1.8×10^{10}
NCZ *p*-Si	–0.8	1.7	150	80	5×10^{10}

The values of the flat band voltage V_{FB} are the same for all samples and, hereby, also the total defect charge density N_{eff}. In the case of NCZ MOS structure of *n*-type (Tab. 1) we observed a marked decrease in the relaxation time, t_r, as well as in the generation life-time of minority charge carriers, τ_g.

This decrease is caused, to a certain extent, by a large amount of defects created by the presence of nitrogen and oxygen [9,10]. In NCZ sample, their content is higher. Since precipitates behave like efficient generation-recombination centres, they have a strong contribution to the observed decrease in t_r and τ_g. On the other hand, nitrogen doping contributes to overall homogenization of the parameters across the wafer, as proved by the standard deviation of t_r. In NCZ sample we have a standard deviation of 14%, which is a marked decrease in comparison with 50% scattering for sample CZ. In *p*-type NCZ sample we surprisingly observed a rise in generation parameters (Tab. 1), which can be explained by the presence of boron impurity atoms. Nitrogen preferably forms the

B-O-N bond, which has a shallow level in the forbidden band and therefore it does not affect the generation parameters of the structure. In addition, this bond contains an atom of oxygen. The content of free oxygen atoms capable of creating defects that lower the generation parameters of the structure is therefore lower. The lower values of t_r and τ_g observed for CZ sample are caused by the presence of a larger amount of boron and oxygen related defects.

4. CONCLUSION

From quasistatic C-V measurements, we have retrieved the energy distribution of the density of traps at the Si-SiO_2 interface, and calculated the flat band voltage V_{FB}. Nitrogen-doped (NCZ) as well as reference (CZ) samples had a negative flat band voltage V_{FB} and, hence, a positive total defect charge.

On *n*-type samples, the effect of nitrogen introduced intentionally during the Czochralski growth of the Si crystal could be observed on the energy distribution D_{it} by the existence of deep levels and by a slightly increased value of D_{it}. The origin of traps at the Si-SiO_2 interface is related to the bond of nitrogen with oxygen in Si containing nitrogen species, such 2N or 2NO complexes.

NCZ samples with *p*-type substrate had a better homogeneity of D_{it} across the sample. Comparison of the energy distribution D_{it} in NCZ and CZ samples revealed the positive effect of nitrogen upon creation of oxygen precipitates due to the atoms of boron (in *p*-type Si), namely the absence of two local maxima.

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