CHARGING OF SIO$_2$ ELECTRET FILM BY ION IMPLANTATION FOR MEMS BASED ENERGY HARVESTING SYSTEMS

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Abstract: This paper presents results of charging SiO$_2$ thin film electret by ion implantation. Maximum charge density of 16 mC/m^2 has been shown using 500 nm thermal oxide. Charge is reproducible and stable in time. Two types of ions were used for ion implantation: Phosphorus (P$^+$) and boron (B$^+$). It was found that charging with B$^+$ resulted in more stable surface potential than that of P$^+$. SiO$_2$ is a promising electret for energy harvesting, which can be charged in a reproducible and stable way by ion implantation. The results are used for the realization of a vibration based, capacitive energy harvester.

Key words: SiO$_2$ film electrets, Ion implantation, Charge decay, vibration energy harvesting

1. INTRODUCTION

The availability of electrets with good long-term stability, large charge density and compatibility to standard micromachining process is essential for the realization of vibration based energy harvesting systems. CYTOP [1] is a widely used organic electret in miniaturized harvester. However, SiO$_2$ electrets are also used for capacitive energy harvesting [2], because of their long charge storage stability and their ability to work in harsh environment. Other advantages are the compatibility to CMOS processing and the availability of simple structuring processes. Especially SiO$_2$ can be used as very thin film because of its high dielectric strength. However, the relative low volume resistivity of 10^{16} Ωcm might result in a fast decay of the stored charges.

Here we report our results of charging SiO$_2$ films with different dose of B$^+$ and P$^+$ ions by ion implantation instead of the common used corona charging. Especially the long-term stability and the stability at elevated temperatures have been investigated. SiO$_2$ and ion implantation are fully compatible with MEMS fabrication technique.

Charging of SiO$_2$ was reported in [3] where the destruction of integrated circuits by ion implantation due to charge effects and change of photo resist characteristic was investigated, but no data regarding the stability of this charge phenomenon were reported. In [4], charging of SiO$_2$ film electrets by corona discharge were discussed, especially the improvement of the stability of charge storage by further ion implantation with Argon.

In this paper, the electret characteristics of thermal grown SiO$_2$ charged by ion implantation are presented.

2. EXPERIMENTAL RESULTS

For all samples 10 - 15 Ωcm boron doped (100) silicon wafers were used. All samples were coated with 500 nm SiO$_2$ film using wet oxidation at 1000°C. To provide a hydrophobic surface Hexamethylcyclo-trisiloxane (HMCTS) was used. Ion implantation was performed at 30 keV in order to get shallow and narrow charge distribution. Implantation currents between 0,5 and 28 µA were used. The surface potential measurements were done with an electrostatic voltmeter (Model 541-1, TREK, USA). Measurements of the charge density started immediately after the ion implantation. To investigate the effect of long term drift, also long term measurements up to two month were performed. Samples were stored in clean room environment at a humidity of 50% rH. The reported results are the averaged values of 2D charge profiles measured on each wafer. Charge homogeneity over a wafer is typically better than $\pm$ 10%. Thermal stability was characterized by temperature loads up to 250°C.
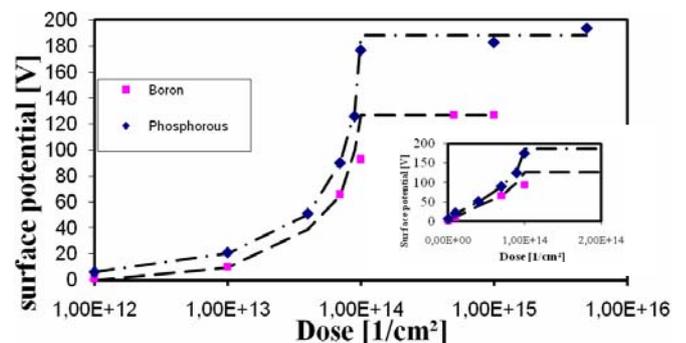

Fig. 1: Initial surface potential directly after implantation

The dependence of surface potential over implanted dose directly after ion implantation is shown in Fig. 1. At small dose (up to $7 \cdot 10^{13}$ cm^{-2}), initial surface potential increases almost linearly with dose (inlet), after a narrow transition region with a steep increase of charge density a saturation of surface charge density above an implanted dose of around $1 \cdot 10^{14}$ cm^{-2} is found. The saturation value for phosphorous is considerable larger than for charging with boron-ions. Comparing the results of different implantation currents (5 µA and 28 µA) no significant influence is observed.

However, for practical use, the long term charge density is important. A typical time dependence of the surface potential is shown in Fig. 2: After an exponential short term decay with decay times of about 24 h, an almost linear long term decay is observed. To compare the different samples the data defined in Fig. 2 are use: T (90%) is the time after charging, at which the surface potential decays to 90% of the initial value. U_{lin} is the potential at which the decay transfers from exponential to linear.

The 10%-decay time shows a strong dependence on the initial surface potential and thus on the initial surface charge density. For very low potentials the time for a 10% decay is as large as 60-70 days and drops down to typically 0.5-1 day at larger surface potential. The change from long to short decay times occurs for boron at around 100V whereas for phosphorus between 20 and 50 V (Fig. 3).

The decay of surface potential within the first few hours has been investigated in more detail. Wafers implanted with doses resulting in surface potential below breakdown field of oxide ($1 \cdot 10^{13}$ cm^{-2}) show even a small increase of surface potential in the first hour after implantation before the charge decreases. This increase is not observed for wafers implanted above saturation dose ($1 \cdot 10^{15}$ cm^{-2}, Fig. 1).

As criteria for the long term charge decay the voltage drop after 50 days has been evaluated and is shown in Fig. 4. The relative long term potential drop after 50 days depends only slightly on the initial surface potential and increases from about 10% (< 20 V) to about 30% at large surface potential. Only for the highest observed surface potential (200 V) the relative drop of surface potential is larger (50%). The relative slope of the long term decay (normalized to the initial long term surface potential U_{lin}) ranges from 10^{-3}/day to $3.5 \cdot 10^{-3}$/day. No significant dependence on U_{lin} is observed.

Similar to the behaviour of the initial surface potential (Fig.1) also the long-term value of the surface potential (charge density) depends strongly on the implanted dose. After a steep increase between $1 \cdot 10^{13}$ cm^{-2} and $1 \cdot 10^{14}$ cm^{-2}, also the long term voltage shows

a saturation like behaviour. This holds for both: Boron and phosphorous implantation. But in contrast to the initial potential (Fig. 1), the long term surface potential is almost the same for boron and phosphorous implantation (about 110 V).

The thermal stability of the charge in the SiO$_2$ electrect was investigated. In one type of experiments temperature treatment was performed on a wafer implanted with a phosphorus dose of $1 \cdot 10^{15}$ cm^{-2} after 57 days initial charging of the SiO$_2$, when potential was quite stabilized. For cumulative temperature treatment the same sample was hold in an oven for 30 minutes at each temperature and then measured. From Fig. 5 (top) we can see that surface potential starts to decrease by annealing above 75 °C. However, even after temperatures of 250 °C and after several hours of cumulative temperature treatment more than 60% of the initial charge is still in place. It should be noted, that for a temperature treatment in an oven, the slow adjustment of the wafer temperature to the oven temperature might influence the observed stability. To prove the time dependence of the surface charge for different temperatures, a further set of experiments for boron charged oxide (implanted dose: $1 \cdot 10^{14}$cm^{-2}) were done. Heat treatment was performed 18 days after
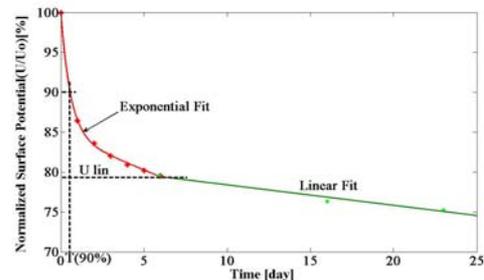

Fig. 2: Typical decay of SiO$_2$ charged by ion implant-ation (9 $\cdot 10^{13}$cm^{-2} P, initial surface potential 126 V)
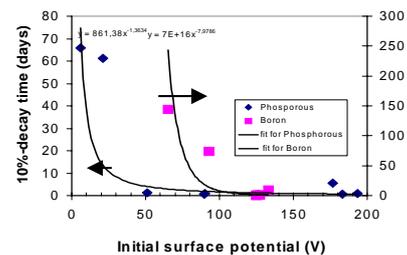

Fig. 3: Short term decay time T(90%) as function of initial surface potential for P and B implantation.
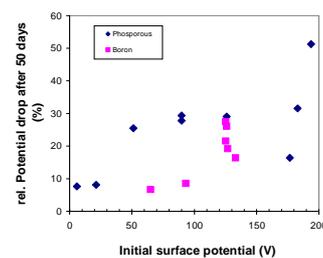

Fig. 4: Relative long term charge drop as function of initial surface potential.
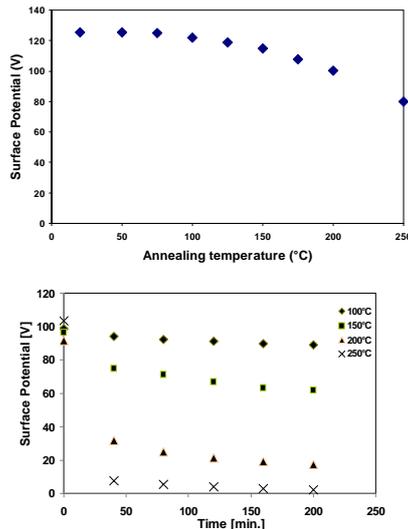
Fig. 5: Temperature stability of surface potential. Top: cumulative anneal for 30 minute at each temperature; bottom: Each wafer heated only at one temperature for different annealing times.

initial charging of the SiO_2, when potential was not well stabilized. Each sample was heated only at one temperature (no cumulative heating). The samples were treated in a preheated oven for intervals of 40 minutes. The 40 minutes intervals have been chosen so that the time that the wafer needs in the oven to reach the oven´s temperature can be neglected. From Fig. 5 (bottom) we can see that surface potential starts to decrease at annealing temperatures of about 100 °C. However, even after temperatures of 150 °C and after several hours of temperature treatment more than 60% of the initial charge is still in place. Different to the cumulative temperature treatment of the sample in Fig. 5 (top) (treatment 57 days after charging) a pronounced decrease of charge density is observed above 200°C. Further experiments are needed to distinguish the different mechanisms which might be responsible for the observed behavior. However, temperatures above 250°C destroy the charge.

Tests showed that HMCTS has no effect on charge stability when the wafers are stored with approximately 50% air humidity, as we did. However, more experiments should be done in this direction with storage in high humidity.

After long time measurements, a wafer implanted with $1 \cdot 10^{13}$ cm^{-2} P$^+$ was put into deionized water for 5 minutes. Then it was taken out, dried with nitrogen and measured again. The deionized water destroyed the surface potential till zero volts.

3. CONCEPT OF ENERGY HARVESTER

The SiO_2 electret is used for a capacitive vibration energy harvester system. A 2 wafer concept is applied. The realization is based on SOI-technology for the first wafer to provide in plane movable micromechanical structures in a simple process. The second wafer is a standard wafer coated locally with SiO_2 that is charged by ion implantation. The electrical energy is stored in a comb-like capacitor. To transfer the surface load in the SiO_2 electret to the comb electrodes in a parallel plane, a set-up similar to that proposed by [5] is used. The surface mirror charges (located in a xy-plane) are transferred to a yz-plane in order to extract energy out of a planar set-up. A schematic sketch is shown in Fig. 6.
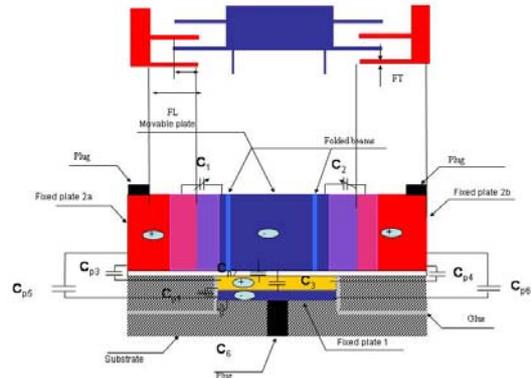

Fig. 6: Schematic set-up of vibratic energy harvester with SiO_2 electret with transformation of the planar charge to a vertical charge distribution by using the influence principle. (top: top view on comb drives, bottom: cross section)

4. DISCUSSION

The charge density σ is calculated from the measured surface potential U by equation (1)

$$\sigma = \varepsilon_0 \cdot \varepsilon_{el} \cdot U / t_{el} \qquad (1)$$

(t_{el}, ε_{el}: thickness and dielectric constant of the electret). Therefore, the initial charge density is 16 mC/m²=10^{13} e/cm² (elementary charge e=$1.602 \cdot 10^{-19}$ C) for Phosphorous and 11 mC/m²=$6.9 \cdot 10^{12}$ e/cm² for boron implantation, respectively. Therefore, even before saturations occurs only 10% of the implanted dose contribute to charges in SiO_2 even for the initial situation.

The different maximum potentials for implantation B$^+$ and P$^+$ (Fig. 1) can be explained by the different penetration depths of implanted ions in SiO_2, resulting in different effective isolating oxide thickness. The penetration depth of the implanted ions at 30 keV can be calculated by the projected range (95,4 nm for boron, 29,2 nm for phosphorus) and the projected standard deviation (34,2 nm for boron and 11,9 nm for phosphorus), thus resulting in an effective oxide thickness for isolation of 370,4 nm (B) and 458,9 nm (P). With the reported dielectric strength of 500 kV/mm a breakdown voltage of 229 V (P) and 185 V

(B) can be calculated. This difference is close to the measured difference of initial surface potential (P: 190 V, B: 130 V). However, the absolute values are smaller than the literature values for breakdown voltage in thermally grown SiO_2, due to degradation of the oxide by ion implantation. On the other hand, the long term surface potential for B and P doped samples is similar (110 V) and corresponds to a charge density of $4,7 \cdot 10^{12}$ e/cm² (Fig 7). Therefore, the long term potential is not determined by breakdown and long term charge density is 7.5 mC/m².

It is obvious, that a simple leakage current from the mirror charges at the Si-SiO_2 interface to the immobile ions through the SiO_2-electrets in the electrical field provided by the charge potential can not explain the good long term stability of SiO_2-electrets. Assuming an Ohmic behavior and taking the volume resistivity of SiO_2 (10^{16} Ωcm) the resulting current density in an internal electric field within the electret of 200 kV/mm is about $2 \cdot 10^{-10}$ A/cm² corresponding to $1.25 \cdot 10^9$ e/(s cm²). Therefore, a surface charge of 16 mC/m²= 10^{13} e/cm²) would disappear after some minutes. In [6], a model is proposed which explains the large long term stability of electrets. Here the high field electrical conductivity of charged planar dielectrics has been simulated to depend strongly on time: After a characteristic time τ_d

$$\tau_d = \frac{1 - y^2}{1 + y^2} \cdot \frac{t_{el}}{E\mu} \approx \frac{t_{el}}{E\mu} \qquad (2)$$

(t_{el}: thickness of the electret, E the electric field caused by the charge on the surface of the electret and μ the (electron) mobility; y is parameter which denotes the ratio of free charges in the beginning (t = 0) and at long times after charging (t→∞), the approximation holds for small y) the resistivity increases up to several orders of magnitude. After several thousands of years, the resistivity returns to its initial value (low electric field resistivity). In this model, the charge density decreases first exponentially with a time constant τ_d and than linearly (long term decay) which is observed in our experiments (Fig. 2). Further on, assuming a RC-like discharging behavior and taking a typical exponential short term decay of 24 h with $\tau_d = R \cdot C \cdot = \varepsilon_0 \cdot \varepsilon_{el} \cdot \rho_{el}$. ($\varepsilon_{el}$, ρ_{el}; dielectric constant, respectively specific resistivity of electret) we get for
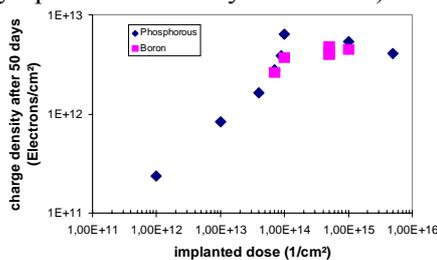
the charged SiO_2 electret an effective (high field) resistivity of $2,5 \cdot 10^{17}$ Ωcm which is in fact considerably larger than the low field resistivity of SiO_2 as proposed in the model presented in [6]. However, it should be noted that using this model and the approximation (2) the derived effective high field mobility of charged SiO_2 would be about $3 \cdot 10^{-16}$ cm²/Vs from the experimental exponential decay time of ion charged SiO_2 of about 24 h, which is many orders of magnitude smaller than experimental data of about 20 cm²/Vs [7]. This mismatch might be partially related to the creation of deep traps in SiO_2 by ion implantation and to a larger carrier generation coefficient for which y in eq. (2) cannot be neglected.

From the values of the linear long term decay (Fig. 4) we can conclude that charges in SiO_2 electrets charge by ion implantation are stable at least for about 1 (phosphorous) to 2 (boron) years.

5. CONCLUSION

Charging of thermally grown SiO_2 on Si by ion implantation has been investigated. The surface charge density can be controlled by the implantation dose. At saturation value of about 7.5 mC/m² and a charge stability of 1-2 years is achieved. A good thermal stability up to 150°C has been measured. Special temperature treatment can enhance the thermal stability up to about 250°C. The results of charge decay can be explained by a model assuming a time dependent resistivity model in the case of high electric field in charged dielectrics.

6. ACKNOWLEDGEMENT

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Fig. 7: Long term surface potential