ON THE CHARGE STORAGE AND DECAY MECHANISM IN SILICON DIOXIDE

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Abstract

In this paper, a mechanism for both the storage and the decay of charge in a charged silicon dioxide layer is proposed. The oxide layer needs neutral electron traps (NETs) to obtain stable trapped negative charge, after having been charged, resulting in an electret that can be applied in microphones.

The hydrolysis of the silanol groups, followed by charge injection, results in an electrochemical reaction with immobile SiO^- as one of the reaction products. Decay of the stable charge thus obtained, can occur by the clustering of water molecules at inner silanol groups, resulting in a conductive hydrogen bonded network, which eventually leads to the discharge of the electret.

1. Introduction

For the conventional electret microphones fluor carbon polymers, like Teflon-FEP and -PTFE form an excellent electret material. The relatively thick polymer foils form stable electrets and can relatively easy be deposited on the piece-wise manufactured microphones, having only moderately small dimensions.

The first generation of batch-processed microphones of which the backplate consists of micromachined silicon was also equipped with a polymer electret [1]. However, only after numerous tedious experiments, it was possible to attach the Teflon foil on the silicon backplate in a wafer-scale. Nevertheless, the relatively complicated batch processing of the essentially IC-incompatible polymer on the silicon wafers remained a problem.

At present, research is carried out on batch-processable microphones, manufactured completely with the standard steps of the silicon micromachining technology. This generation of microphones will no longer be equipped with polymer foil electrets: apart from the incompatibility of the deposition with standard silicon processing steps, as already mentioned, high temperature steps, not uncommon during micromachining techniques, would ruin the organic polymer. In addition, the sound sensitive diaphragm of the new generation of microphones will also no longer consist of the formerly used Mylar membrane, but will be an IC-compatible membrane, e.g., Si_3N_4 . Consequently, the

dimensions of the microphone are being redesigned, resulting in a smaller air gap width, in which the relatively thick Teflon polymer foil can no longer be used.

For the reasons mentioned above, the electret properties of some inorganic dielectrics have been investigated, such as Al_2O_3 , Ta_2O_5 , Si_3N_4 and SiO_2 . Although the results of experiments carried out with Al_2O_3 were promising, the main interest focuses on SiO_2 , because of its easy processing and compatibility with standard silicon technology as well as the fact that much is known in literature about silica concerning bulk properties (e.g., conductivity, maximum field strength) and interfacial phenomena, especially with respect to the interface with silicon.

Only a few papers report about charge retention on the SiO_2 -air interface, resulting in an external electric field [2-4]. Our previous investigations [5] led to the conclusion that an untreated SiO_2 layer is a poor electret not because of its bulk conductivity, but due to its large lateral surface conduction. It has been shown, however, that such a SiO_2 layer may be used as an excellent electret if the surface conductivity has been reduced by an appropriate chemical surface modification. This surface modification is adequately accomplished by a hydrophilic to hydrophobic conversion using hexamethyldisilazane (HMDS).

Although it is known that HMDS substitutes to a certain amount the polar silanol groups on the surface of the silica by (apolar) methyl groups [6], the exact effect this substitution has on the slow-down of the electret charge decay can only be described when a better understanding of the charge trapping and decay mechanisms focused on the role of the surface and near-surface silanol groups is at hand.

Results of charge measurements, present at the SiO_2 electrets that were prepared nearly 5 years ago, initiated investigations of the charge trapping mechanism and charge decay of SiO_2 electrets.

The results of the investigations are in agreement with the behaviour of another device, where the outer SiO_2 interface plays a major role: the Ion Sensitive Field Effect Transistor (ISFET). The drift and hysteresis behaviour of this pH sensitive device has been described using the same explanation as proposed in this paper for the charge trapping and decay of SiO_2 electrets [7].

2. Trapping and decay of charge in SiO₂ layers

2.1 Charge trapping

Permanent storage of electronic charge in the oxide layer requires initially neutral electron traps (NETs), which thus show a net negative coulombic charge of immobile nature after being filled with electrons.

In order to obtain an electret microphone with sufficient sensitivity, the potential over the shallow air gap (typically 20-50 μm) between the electret and the diaphragm, which is induced by the fixed electret charge, must typically be -100 to -300 Volt. It is assumed, that the negative charge is trapped at the immediate proximity of the oxide-air interface. This assumption is based both on the discussion to follow and on the fact that SiO₂ electrets of 1.1 μm thickness have been charged to an equivalent electret voltage of ca. -700 V, which results in an electric field near the maximum field strength of 7 MV/cm found by others [8], only if the charge is considered as a sheet or thin layer of charge very near to the SiO₂-air interface. In that case, the relation between the electret surface charge density σ_e and the resulting equivalent electret potential V_e is given by

$$V_e = \frac{\sigma_e d_{ox}}{\epsilon_0 \epsilon_r} \quad (1)$$

Typical values for a 1.1 μm SiO₂ layer ($\epsilon_r=3.9$) are $V_e = -150$ V and, correspondingly, $\sigma_e = 0.5 \mu\text{C}/\text{cm}^2$ or ca. $3 \cdot 10^{12}$ e/cm².

The basic classification of charges and traps in SiO₂ layers as posed for metal-SiO₂-Si (MOS) devices consists of 4 types [9]:

(1) Si-SiO₂ interface trapped charges Q_{it} , due to the interruption of the periodic lattice structure. Q_{it} can exchange charges with silicon in a short time and can be as low as 10^{10} /cm².

(2) Immobile fixed oxide charge near the Si-SiO₂ interface Q_f , which can not be charged or discharged easily. Q_f depends mainly on the processing conditions and the orientation of the silicon. This charge is thought to be caused by excess (trivalent) silicon or the loss of an electron from excess oxygen centers.

(3) Mobile ionic charge Q_m , a space charge largely caused by alkali ions such as sodium. This oxide charge has its maximum concentration at the Si-SiO₂ interface and is mobile under bias-temperature aging conditions.

(4) Oxide trapped space charges Q_{ot} , which can be created by radiation or electron injection and is considered to be associated with defects in the SiO₂. Q_{ot} consists of usually electrically neutral traps, which can be charged by introducing electrons (or holes) into the oxide.

Of the four mentioned types of charge and traps, the first three are supposed to be unable to cause a stable electret, either because of the mobile nature of the charge and the position of the charge with respect to the SiO₂-air interface or because of the fact that these charges do not form NETs but appear as (mostly positively) charged centers instead of traps. Therefore, it may be possible that the charge, making up a stable electret, consists of filled NETs of type Q_{ot} . It should be mentioned that Q_{ot} is still a collection of traps of different cause and nature. Results of detailed investigations, described in literature, are, however, rather confusing: it is on the one hand reported, that annealing in O₂ removes electron traps, which suggests oxygen deficiency as the cause of the trap centers [10], whereas on the other hand it is reported, that NETs are generated by oxygen ion implantation [11]. The number of NETs/cm² is in that case, however, too small to explain the electret behaviour of SiO₂.

Nicollian and co-workers assume a quite different origin of NETs [12]. They suggest Q_{ot} to be caused by the diffusion of water (at low temperature, < 200 °C) into the SiO₂, resulting in NETs formed by water related impurities, which can capture an electron. This capturing mechanism, essentially an electrochemical reaction in which the NET is consumed, is accompanied by the evolution of neutral hydrogen. The result is a stable negatively charged center, which no longer traps charge. In the same paper, the authors also compared experimentally the spatial distribution of the negative charge with the water diffusion kinetics. It was found that both the charge and the water related centers were distributed over the first 400 Å of the oxide.

The following chain of reactions is proposed, resulting in stable trapped negative charge [12,13].

Formation of silanol groups, during or shortly after processing of the oxide:

The second reaction, at much lower temperatures ($<200^\circ\text{C}$) involves the hydrolysis of the silanol groups by water:

Clearly, the hydrolyzed silanol groups and the protonized water will form a closely adjacent pair. It is assumed, that an incoming electron can be captured by one of the fragments of this pair:

This electrochemical reaction results in a stable negative charge with a negligible probability of being emitted after capturing; the trap is consumed and coulombic repulsion keeps off other electrons.

By experiments, carried out with SiO_2 hydrolyzed with tritiated water, it was shown, that indeed hydrogen evolution (eqn. 4) occurs when an electron current flows through the hydrated SiO_2 ; the amount of hydrogen lost, was found to have about a one-to-one correspondence to the amount of negative charge injected. From experiments both to create NETs in an H_2 ambient and to discharge samples by annealing them in an H_2 ambient, it was concluded that atomic hydrogen is the immediate product of the capturing reaction rather than molecular hydrogen. This conclusion is in accordance with eqn. 4.

The given explanation of charge trapping, mainly based on one paper [12], is supported by a later paper by DiMaria et al. [14], who also states that NETs are associated with the presence of water related impurities: the deep trap sites are caused by H_2O and OH bounded to Si.

2.2 Charge decay

From the results of experiments, described in our previous paper concerning SiO_2 electrets, it was concluded that the cancellation of lateral surface conduction would result in prolonged charge retention [5]. Because the silanol groups at a SiO_2 surface were reported either to be the cause of the conductivity due to mobile protons of those groups or to attract, by their polar nature, physically absorbable water molecules, it was thought and shown that substitution of these surface groups sufficiently reduced the surface conductivity, according to the following mechanism.

Water reacts with the residual valences of the initially hydrophobic siloxane (SiOSi) surface, so that at ordinary temperature the surface becomes covered with hydrophilic silanol (SiOH) groups:

This process is called the chemisorption of water at the silica surface. These polar silanol groups may attract and bind water by physisorption:

By substitution of the silanol groups with apolar methyl groups of HMDS, neither the possible proton conduction of the silanol groups alone nor the formation of a monolayer of conductive water can occur:

This silylation process might indeed adequately reduce the number of surface silanol groups, but will not reduce the number of inner, possibly even hydrated silanol groups, which fact forms a serious threat to the long term charge stability, especially in humid environments.

It is reported that crystalline silica (quartz) gets 'coated' with a film of amorphous hydrolyzed silica with a thickness of even a few hundreds Ångström [15]. This film can be etched with HF, but reappears in ambient relative humidity. Even if this layer of inner silanol groups itself might not cause conduction by internal protons, then there is still the problem of molecular water, physisorbed to the inner SiOH groups. The origin of this water can be

twofold: first, the water molecules might diffuse into the already hydrolyzed silica film and react there, according to eqn. 6, and secondly, the water might be the product of the reported process of condensation [15] of the inner silanol groups, being eqn. 5 in the opposite direction:

These internal water molecules can form a conductive hydrogen bonded network, which might spread out in clusters, because energetically, these hydrogen bonded clusters of H_2O molecules may be formed even before all the SiOH groups have adsorbed H_2O molecules to form an uniform layer of $\text{SiOH}:\text{OH}_2$ groups [15].

Other experimental proof of the buried OH sites, which might either condense to water according to eqn. 8 or may physically bind diffused water according to eqn. 6, is reported in a paper by Bousse and Bergveld [7]. Beside the fast response of an ISFET, being a pure surface effect, the authors propose that the slow response of an ISFET to a pH step is due to the presence of a large number of OH sites buried beneath the surface. In addition, this slow response causes the observed hysteresis effect of the ISFET to a pH-scan as well as the decreased sensitivity for higher pH values.

In conclusion, it is assumed that not only the conductivity of the surface but also that of the few hundreds Ångström right under the silica-air interface, both caused by possibly hydrated silanol groups, play a decisive role in lateral conduction, causing charge decay of charged SiO_2 electrets.

3. Experimental

SiO_2 samples have been prepared from 2-inch, $\langle 100 \rangle$ p-Si, 5-10 $\Omega\cdot\text{cm}$, previously cleaned Si wafers by wet thermal oxidation at 1150 $^\circ\text{C}$ for 4 hours, resulting in a ca. 1.1 μm thick SiO_2 layer. The oxide at the reverse side of the wafer was removed by chemical etching in order to allow to contact the samples during charging and measuring. The samples of which results are reported in this paper have been charged by the liquid-contact method. Other experiments, carried out with corona-charged samples show, however, similar results. The equivalent electret voltage V_e has been measured by the vibrating reed electrostatic voltmeter (Monroe isoprobe 244). The samples, quarters of the 2-inch wafers, have been stored in small plastic boxes at 18 to 24 $^\circ\text{C}$ and

40 to 70 % RH.

A series of eight samples has been charged with different potentials, ranging from -200 to -700 V. The samples have been charged after the SiO_2 surface had been treated with HMDS by liquid spinning, 4000 rpm at 90 °C. Subsequently, the charged samples have been given a heat treatment for 50 min. at 200 °C. This aging of the electrets prior to use, during which unstable traps are considered to be emptied, is a well-known pretreatment.

4. Results

The series of 8 samples, prepared as mentioned in section 3, has been charged ca. 5 years ago. Their equivalent electret potential V_e has been measured from time to time and the intermediate measurement results have been reported earlier [5]. The results of the most recent measurements are included in fig. 1.

figure 1 Normalized charge decay at ambient laboratory conditions of some liquid contact charged 1.1 μm thick SiO_2 electrets for different charge levels.

The potentials V_e are normalized to their initial potential V_{init} right after the thermal treatment, as mentioned in section 3. The conclusions of our earlier paper [5] are consolidated by the recent measurements. The electric field of the electret, charged up to 663 V amounts to 6 MV/cm, which is very close to the reported theoretical maximum field strength of 7 MV/cm [8]. The life time of an electret is assumed to be equal to the time constant of the charge decay, i.e., the period in which the electret charge has decayed to 63 % of its initial value [16]. In that case, the lower limit for the electret life time of the 663 V electret can be fixed at 40 years instead of 20 years, formerly estimated [5]. The charge decay shows a weak dependence on the charge level and thus on the electric field in the oxide.

Apart from these positive results, there were some disturbing symptoms in relation to the homogeneity of the charged samples of several years old. Originally, the electrets have been very homogeneously charged (± 2 V) by the liquid contact method over an area of more than 2 cm². Recently, some of these samples show unexpected 'holes' in the charge of a few mm², in which the charge sharply drops to ca. 50-70 % of the original value.

This behaviour, supported by other measurement results, which will be reported in a later paper, was the motive for the investigation of the decay mechanism, as discussed in section 2.2. It is assumed that in these electrets island-wise discharge occurs around water molecules, bound at internal SiOH groups, forming a local conductive hydrogen bonded network. The gradual spreading of these internal water molecules might eventually cause the total discharge of the electret.

The number of electrons, necessary for a typical application in a microphone, has been calculated in section 2.1 and is ca. $3 \cdot 10^{12}$ e/cm². The reported number [15] of silanol groups at the SiO₂ surface, however, is $5 \cdot 10^{14}$ SiOH/cm². Therefore, if the number of electrons per silanol group is restricted to the surface groups, then only one electron per 167 silanol groups is needed to obtain the necessary amount of charge in the 1.1 μ m thick electret.

It is, however, reported [6], that only ca. 95% of the surface silanol groups is substituted by methyl groups after an HMDS treatment. Therefore, it is concluded that even after the HMDS treatment, the remaining number of uncharged surface silanol groups may either cause discharge of the relatively small number of electrons or form paths for the diffusing H₂O molecules to the internal OH groups, causing cluster formation of water. As soon as the clusters

contact each other, this may lead to the discharge of the electret.

5. Conclusions

Comparing sections 2.1 and 2.2 concerning the trapping of charge and the decay of charge due to local conduction, respectively, in relation to the experimental results, it has to be stated that a dilemma shows up: silanol groups are considered to be necessary for the stable trapping of charge, whereas silanol groups also may cause, eventually, the unexpected end to the electret-life. The charge traps are, however, assumed to be generated during the oxidation process and are possibly located deeper into the oxide than the conductive sites, which may appear additionally at a later point of time. It will be obvious that if later formation of surface and buried sites under the influence of ambient water molecules should be prevented, a more definite covering of the oxide will be necessary. Therefore, new silylating agents, which might effectively close the surface of the SiO_2 for water molecules are now being tested.

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