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O.S.I.**Retention and switching kinetics of protonated gate field effect transistors****R. A. B Devine\* and G. V. Herrera<sup>#</sup>****Center for High Technology Materials****University of New Mexico,****1313 Goddard SE****Albuquerque, NM 87106**

\* **On leave from France Telecom CNET, Meylan, France**

# **Sandia National Laboratories New Mexico, MS1405, PO Box 5800, Albuquerque,  
NM 87185-1405**

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**Abstract**

The switching and memory retention time has been measured in 50  $\mu\text{m}$  gatelength "pseudo"-non-volatile memory MOSFETs containing, protonated 40 nm gate oxides. Times of the order of 3.3 seconds are observed for fields of 3  $\text{MV cm}^{-1}$ . The retention time with protons placed either at the gate oxide/substrate or gate oxide/gate electrode interfaces is found to better than 96% after 5000 seconds. Measurement of the time dependence of the source-drain current during switching provides clear evidence for the presence of dispersive proton transport through the gate oxide.

## INTRODUCTION

Earlier<sup>1</sup> it was shown that the annealing of certain types of sandwiched Si/SiO<sub>2</sub>/Si structures in an atmosphere containing hydrogen at temperatures ~ 700 C resulted in the appearance of both mobile and fixed, positive charges in the oxide layer. The nature of the charge and the necessity for H<sub>2</sub> in the annealing atmosphere strongly supported the assumption that these charges (both fixed and mobile) were protons. If the mobile charges were first driven to one or another of the oxide/Si interfaces by application of a suitable electric field, they were found to be subsequently immobile at room temperature when the field was removed. Application of an opposite polarity field simply reversed the situation. Extensive testing involving cycling of the protons from one interface to another demonstrated that there was no loss of protons (for example, through the gate electrode or oxide sidewalls) and no reduction in total, mobile charge. The suggestion was made<sup>2</sup> that these mobile protons and their immobility in the absence of an electric field could be used to produce a form of non-volatile memory transistor in which the gate oxide would be protonated. With the protons at the substrate/oxide interface, an inversion channel would be developed and a source-drain current measured (logical "on mode"). Protons placed at the gate electrode/oxide interface would have no influence upon the transistor characteristic so that with suitably chosen threshold voltage, this mode would be the logic "off". Significant advantages of this type of memory device would be its simplicity, for example, compared to other memories such as EEPROMs, its low voltage (and hence low power) operation and its easy integration into standard Si microelectronics processing

Since the initial proposition to produce non-volatile memory transistors, several forms have been investigated and the feasibility has been demonstrated. These include the pseudo-MOSFET<sup>3</sup> (with gate oxide thickness ~ 400 nm), a standard transistor<sup>4</sup> with dimensions down to

2  $\mu\text{m}$  gatelength but using Unibond<sup>5</sup> buried oxide (200 nm) as the gate insulator and, most recently<sup>6</sup>, a simple MOSFET with a 40 nm thermally grown gate oxide. In the present work, though preliminary, we have extended our studies of "standard" transistors with protonated 40 nm gate oxides. In particular, we have addressed the problem of the switching of the protons in the gate oxide, of the nature of the motion of the protons in the oxide and of the retention of the protons when placed at one of the interfaces - oxide/substrate or oxide/gate electrode. These parameters are crucial in evaluating the technological interest of these devices.

## Experiment

6" Si epi wafers (p on p<sup>+</sup>) were oxidised to a thickness of 40 nm in dry oxygen at 900 C. A 200 nm thick polycrystalline Si film was then deposited on the oxide and the whole structure annealed for 25 minutes at 1050 C in flowing N<sub>2</sub>, this process creates the active sites for proton generation during a subsequent annealing step. The top Si film was then p doped to degeneracy either using a spin-on-dopant (P-8545 from Allied Signal) or by ion implantation ( $3 \times 10^{15} \text{ cm}^{-2}$  at 40 keV). In the case of the spin on dopant, drive in diffusion was carried out at 850 C for 10 minutes in an N<sub>2</sub>/O<sub>2</sub> atmosphere. Gate electrodes were defined photolithographically and the excess Si of the top layer etched away in XeF<sub>2</sub> gas. Source and drain areas were then defined photolithographically in the exposed oxide and the oxide in those areas removed using a buffered HF acid etch. The source and drain areas were subsequently implanted with P ions as for the implanted gate electrode. Activation of the gate and source/drain dopants was carried out for 10 minutes at 1000 C in flowing Ar. Subsequently, protons were introduced into the gate oxide by annealing the structures at 700 C in a mixture of N<sub>2</sub>/10%H<sub>2</sub> for 30 minutes then rapid cooling by pulling the wafer to the cold end of the furnace tube. Gatelengths of the transistors varied from 5

to 70  $\mu\text{m}$  whilst the gatewidth was 100  $\mu\text{m}$ . Electrical testing of the MOSFET devices was made using an HP 4145A tester, contacts to the gate, source and drain electrodes were made using tungsten probe tips.

## Results

In Fig. 1 we show the typical source-drain current ( $I_{ds}$ ) versus gate to source voltage ( $V_G$ ) obtained using a source-drain voltage of 0.6 V, the transistor gatelength was 50  $\mu\text{m}$ . The solid curve was obtained by first polarising the gate at +12 V for 50 seconds then sweeping to negative voltages in 0.3 V steps in  $\sim$  2 seconds. The dashed curve was obtained by polarising the gate at -12V for 50 seconds then sweeping to positive voltage. The hysteresis in the curves, between the case with the protons at the oxide/substrate interface (solid line) and then at the gate electrode/oxide interface (dashed line) is  $\sim$  - 17 V. The threshold voltage of the transistor in the absence of mobile proton effects is  $\sim$  0 V whereas prior to protonation it was +1.5V. This suggests that some fixed positive charge is also present in the oxide resulting from the annealing step. Note that the full downsweep curve was not obtained because of fears that gate voltages greater in magnitude than 12 V ( $\sim$  3 MV  $\text{cm}^{-1}$  field) might either breakdown the gate oxide or induce electron injection through Fowler-Nordheim tunneling. It should further be pointed out that in both upsweep and downsweep curves there was a gate voltage independent leakage current of  $\sim$  180  $\mu\text{A}$  which was due to current flowing between the drain contact and the substrate (held at the same potential as the source contact, i.e. the earth). From the hysteresis  $\sim$  17 V we estimate the density of mobile protons in the gate oxide to be  $8.5 \times 10^{12} \text{ cm}^{-2}$ , this number is large. However, it is generally assumed that the mobile protons are bonded to O atoms in Si-O-Si inter-tetrahedral bridges and the areal density of bridging oxygens is  $\geq 100$

times the measured number of mobile protons. The number of mobile protons is therefore not so significant.

In Figs. 2a and 2b we show the results of switching tests on the 50  $\mu\text{m}$  transistors. To perform these tests the transistors were first polarised with +12 V (-12 V) for 120 seconds and then the gate voltage switched rapidly and maintained at -6, -8, -10 or -12 V (+6, +8, +10 or +12 V) whilst the source-drain current was measured with a source-drain voltage of 0.6 V. For each curve, data points were taken every 20 milliseconds. Note that the current values for the different voltages do not begin at the same value for time  $t = 0$ . The reason for this is that can be easily understood by inspecting Fig. 1. Taking the switch to negative voltage example (Fig. 2a), we see from the solid curve of Fig. 1 that when the protons are at the oxide/substrate interface where they have their full influence on the inversion channel and the applied voltage is zero, the inversion channel current is  $\sim 550 \mu\text{A}$ . Applying a negative gate voltage creates an opposite field to that created by the protons and partially counteracts it so reducing the inversion channel charge density, hence the current.

### Analysis

In the linear, small source-drain voltage regime, the source-drain current can be written as<sup>7</sup>:

$$I_{ds} = (Z/L) C_{ox} \mu_n (V_t(t) - V_G) V_{ds} \quad (1)$$

Where  $C_{ox}$  is the gate oxide capacitance per  $\text{cm}^2$ ,  $\mu_n$  is the mobility of the inversion channel carriers (here electrons),  $Z$  is the gate width,  $L$  is the gatelength and  $V_t(t)$  is the time dependent threshold voltage. The threshold voltage becomes time dependent through the proton induced threshold voltage shift.

$$V_t(t) = (\phi_{ms} - Q_f(t)/C_{ox}) + 2\psi_B + (4\epsilon_s q N_A \psi_B)^{1/2}/C_{ox} \quad (2)$$

Definitions of the standard symbols may be found in reference 7 page 841/842 and in Chapters 7 and 8. The charge,  $Q_f(t)$ , can be expressed in terms of the distribution of charges (for example, protons) throughout the gate oxide thickness,  $d_{ox}$  (measured from the gate electrode) as:

$$Q_f(t) = (1/d_{ox}) \int x \rho_p(x,t) dx \quad (3)$$

$\rho_p(x,t)$  is the spatial distribution of charges which varies with time as the protons drift in the presence of an electric field. In Figs. 2a and 2b the only time dependent parameter is  $V_t(t)$  so that it is useful to examine the derivative of equation (1) with respect to time:

$$dI_{ds}/dt = (Z/L) C_{ox} \mu_n V_{ds} dV_t(t)/dt = (Z/L) \mu_n V_{ds} dQ_f(t)/dt \quad (4)$$

The derivative of the source-drain current is then directly proportional to the derivative of the threshold voltage i.e. the derivative of the mobile charge variation with time. From equation (4) we see that a plot of  $dI_{ds}/dt$  for the different applied switching voltages,  $V_G$ , gives us some information of the variation of the proton charge distribution with time,  $dQ_f(t)/dt$ . In Fig. 3a and 3b we show plots of the variation of  $dI_{ds}/dt$  with time as a function of  $V_G$ , negative  $V_G$  in Fig. 3a, positive  $V_G$  in Fig. 3b. Note that we use an expanded timescale from 0 to 1 seconds where the maximum variation of  $dI_{ds}/dt$  with time occurs. In Fig. 4 we plot the maximum value of  $dI_{ds}/dt$  for each applied electric field,  $E$ , obtained from these curves. For simplicity we show  $|dI_{ds}/dt|$  plotted as a function of  $|E|$  to avoid a confusion of signs. Note that account must be taken of the surface potential and the work function difference of the gate electrode material and substrate materials in estimating  $E$ . It turns out that when the substrate is in inversion, the effects of surface potential and work function difference essentially cancel so that the electric field is approximately given by  $V_G/d_{ox}$ . In discussing electric fields in the following we will assume that an upper limit to the error in the value

given is  $\leq 10\%$ . The data shown in Fig. 4 was obtained from the results shown in Figs. 3a and 3b by first smoothing the curves numerically then plotting them on a log-log plot. The maximum value for  $dI_{ds}/dt$  was then deduced by extrapolation of the smoothed data points to short times. The observed behaviour is very similar whether one sweeps the protons away from the oxide/substrate interface (negative gate voltage, negative electric field - open circles of Fig. 4) or towards it (positive gate voltage, positive electric field, open squares of Fig. 4). We draw the conclusion that  $dQ_f(t)/dt$  varies with applied electric field so that the proton velocity is clearly electric field dependent.

In order to define a "switching time" for removal of the protons from one interface and their displacement to the opposite interface a criterion must be established. As a general rule one would consider the time it takes for a measurable value to vary from 10% of its initial value to 90%. Given the mode of operation of the protonated gate MOSFET memory, this requires more attention. Consider the situation in which we have first placed the protons at the oxide/substrate interface, the transistor is in the on state and with zero gate voltage a significant source-drain current is measurable (see Fig. 1 - solid curve). If we now apply a negative gate voltage of say - 20 V for the example of Fig. 1, the transistor will switch off and the current drop to zero (account taken of the forementioned leakage). However, if the protons do not move during the time of application of the negative gate voltage, its subsequent removal will result in a re-appearance of the source-drain current. In consequence, what might have appeared to be a rapid switching event, which would indeed have switched off the transistor, is not in fact a "permanent" change in state. In consequence, care must be taken in interpreting the switching observed in Figs. 2a and 2b, one must be sure that the protons have been totally removed from a given interface during the time of application of the switching voltage. From Eq. (1) we see that the  $I_{ds}$  goes to zero when  $(V_i(t) - V_G) = 0$ . In consequence, when the switching voltage  $V_G$  is large, the current will drop rapidly to zero. This phenomenon can be clearly seen in Fig. 2a in the curves for  $V_G =$

$-12$  V and  $V_G = -6$  V. In the latter case, the protons clearly move very slowly with time in the  $1.5 \text{ MV cm}^{-1}$  electric field due to the  $6\text{V}$  bias and in fact, over the measurement timescale,  $I_{ds}$  never drops to zero. In the  $-12$  V case, the current drops to zero much more rapidly but a "discontinuity" appears present. This effect is due to the fact that the charge distribution has been modified from its initial form but only enough for  $(V_t(t) - V_G) = 0$ . Since the initial value  $V_t(0)$  was  $\sim -17$  V, the charge distribution has moved only enough to reduce it to  $V_t(t = 3 \text{ seconds}) = -12$  V. If the gate voltage were removed after 3 seconds (see Fig. 2a) then the source-drain current would again grow to a level equivalent to  $V_t = -12$  V, i.e.  $\sim 325 \mu\text{A}$ , from Fig. 1. Clearly, the transistor would not be in the "off" state even though the switching voltage had reduced the source-drain current to zero at one point in time (account taken of the leakage current). This rather laborious explanation has been necessary simply to explain the difficulty in defining a switching time for the memory device. From Figs. 2a and 2b, 3a and 3b on can reasonably conclude that the protons can be moved to switch the transistor from one state to another in a time  $\leq 5$  seconds for an applied field of  $\sim 2 \text{ MV cm}^{-1}$  and that this time can be shortened by application of larger fields. From Fig. 4 we can crudely estimate that increasing the field to  $3 \text{ MV cm}^{-1}$  will enhance the switching speed by  $\sim 50\%$  i.e. the switching time would decrease to 3.3 seconds.

### Proton Motion

In order to model the time dependence of  $Q_f(t)$  it is necessary to have detailed knowledge of  $\rho_p(x,t)$  (Eq. (3)). It is known that the nature of the interaction between the proton and the  $\text{SiO}_2$  network is such that the motion in the presence of an electric field is dispersive<sup>8</sup> so that a simple analytical form of  $\rho_p(x,t)$  is not apparent. This topic has been treated in depth by McLean and

Ausman Jr<sup>8</sup> and approximate solutions to describe the motion of the protons developed. For high densities of charges one should also take into account the influence of the "self field" resulting from the Coulomb interaction between them. Protons have been generated in irradiated, thermally grown oxides<sup>9</sup>, here the densities involved were  $\leq 10^{11} \text{ cm}^{-2}$ . Analysis of the dispersive transport of these protons through the oxide suggests that the motion is in fact very dispersive so that the inter-proton interaction is "over-ridden" by the strength of the interaction between the protons and the  $\text{SiO}_2$  network.. For the proton densities with which we are dealing,  $\sim 8.5 \times 10^{12} \text{ cm}^{-2}$ , the field in the oxide outside the sheet of charge composed of the protons would be  $\sim 4 \text{ MV cm}^{-1}$ . The repulsion would clearly be extremely strong. If we consider the analogy of a space charge limited situation, however, the strong repulsive force would be expected to maintain the sheet of charge intact and minimise the effects of dispersion. In other words, high sheet charge densities might lead to less dispersive transport because the field maintaining the integrity of the sheet is stronger than the dispersive interaction with the network. In fact, the results of experiments performed<sup>4</sup> on the transport of high densities of protons in Unibond gate oxide transistors do suggest that the motion is significantly less dispersive than for the motion of lower densities of protons in irradiated oxides<sup>9</sup>. Unfortunately, in the formalism of reference 8 it is a non-negligible problem to include these two effects and fully describe the proton motion mathematically.

Given the forementioned complexities, we begin by assuming that for short times the proton motion is a classical electrostatics problem. We can to first order ignore the effects of the "self field" and treat the proton motion as that of a sheet of charge. For a sheet of charge of areal density  $\rho_p(s)$  which does not interact with the environment the rate of variation of  $Q_f(t)$  with time can be calculated simply to be:

$$dQ_f(t)/dt = -q^2 \rho_p(s) E t / (m d_{ox}) \quad (5)$$

where  $m$  is the mass of the proton,  $E$  the applied electric field and  $q$ , the elementary proton charge. We have assumed the sheet initially at the oxide/substrate interface where the inversion channel current,  $I_{ds}$  would be maximised. Clearly, Eq. (5) predicts a negative slope whose magnitude increases monotonically with time, this is exactly the contrary to what is observed experimentally (Fig. 3a). The short time/classical motion analog is clearly unacceptable.

A more representative approach may be to examine the short time behaviour during which the sheet of charge may move without significant dispersion. In this case we will assume that the sheet, again of areal density  $\rho_p(s)$ , moves via a process of hopping in which the average hop distance is  $\mu$  and the hop time,  $\tau_0$ . The derivative of  $Q_f(t)$  with time is then:

$$dQ_f(t)/dt = -q \rho_p(s) (\mu/\tau_0)/d_{ox} \quad (6)$$

From this expression we see that any electric field dependence of  $dQ_f(t)/dt$  must arise from field dependence of  $\mu$  (assuming the characteristic hopping time,  $\tau_0$ , is not a function of electric field). We cannot determine an absolute value of  $\mu$  given the fact that we do not know  $\tau_0$ . Using the data from Fig. 4 and combining Eqs. (4) and (6) we can deduce a typical value for  $\mu(E)/\tau_0$ . We find  $4.62 \times 10^{-6} \leq \mu(E = 2 \text{ MV cm}^{-1})/\tau_0 \leq 7.9 \times 10^{-6} \text{ cm s}^{-1}$  assuming  $310 \leq \mu_n \leq 530 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  from reference 6. From Fig. 4 we also determine that, within experimental error,  $\mu(E)/\tau_0$  increases linearly with field and this result is consistent with data obtained on switching in transistors manufactured using Unibond substrates with the buried oxide layer used as the gate oxide<sup>4</sup>. Finally, we have performed full simulations of charge transport in dispersive media following the model of McLean and Ausman Jr.<sup>8</sup> using their improved trial function to represent the charge density variation as a function of time (note that this neglects the space charge effect). From the calculated variation of  $\rho_p(x)$  with time for different values of  $\mu$  we have obtained the

short time "initial slope" behaviour, the results are plotted in Fig. 5. We see that for strongly dispersive transport ( $\alpha$  parameter = 0.3) and for weakly dispersive transport ( $\alpha = 0.75$ ) the initial slope behaviour is identical. Our approximation in Eq. (6) which neglected the importance of this parameter was clearly justified.

### Retention time measurements

As well as addressing the issue of switching time a second parameter of extreme importance in memory applications is retention time. We have investigated the retention of the protonated memory transistors. Previous studies<sup>1</sup> have indicated that when the protons are confined in Si/SiO<sub>2</sub>/Si structures, there is little or no loss even when cycled several million times so for the moment we have not concerned ourselves with this aspect of the problem. Our initial studies concern the amount of time protons will remain in the vicinity of one of the oxide interfaces after the removal of a gate voltage. Experiments were performed by first applying a polarisation of +6 V or -6 V to the gate for a period of 120 seconds. Immediately following this period, the gate, source and substrate contacts were shorted and the evolution of the source-drain current monitored as a function of time for periods up to 5000 seconds. The source-drain voltage, 0.2 V, was maintained throughout the 5000 second period. The measured current is plotted as a function of time in Fig. 6. for a transistor with again a 50  $\mu$ m x 100  $\mu$ m gate. The open squares corresponds to points for the case where the protons were initially placed at the oxide - substrate interface ("on mode") whilst the open circles are for the protons placed initially at the gate electrode ("off mode"). Note that the current is non-zero in the "off mode" because drain-substrate leakage mentioned previously and because the transistor is not entirely "off" when there is zero voltage on the gate (see Fig. 1). Following a small initial transient the "on" current is observed to diminish very slowly with time whilst the "off" current remains constant.

The decrease in "on" current is  $\leq 3.9\%$  of the initial value over the 5000 second period. Linear extrapolation of this result suggests that the 90% retention point of the "on" state occurs after approximately 4.2 hours. We reiterate that the experimental setup used required that the source-drain voltage be left on throughout the measurement period resulting in an electric field across the oxide in the drain region  $\sim 50 \text{ kV cm}^{-1}$ . At the present time we cannot exclude the possibility that this field induced some proton motion away from the substrate in the drain region and thereby contributed to the reduction in the "on" current with time. Any detailed study of the mechanism of loss of retention will require substantially more significant loss than we can observe with the present experimental setup.

## Conclusions

We have investigated the switching characteristics and retention time of "pseudo"-non-volatile memories produced by introducing mobile, positive charges (which we assume to be protons) into the 40 nm gate oxide of a standard MOSFET. Though the concept of switching is a little hard to define because of the dispersive nature of the transport of protons in  $\text{SiO}_2$ , we estimate a time  $\sim 3.3$  seconds for an applied electric field  $\sim 3 \text{ MV cm}^{-1}$  taking a criterion of current variation from 90% of its maximum value to 10%. Since there is no data presently available on transistors manufactured in the same way but having different oxide thicknesses, we cannot establish the relationship between gate oxide thickness and switching time. In the simplest case of linearity, assumption of an ultimate gate oxide thickness of 10 nm sets an upper limit on the switching time  $\sim 800$  milliseconds. Though this time may appear long, no experiments have been yet performed which enable us to say how we can correlate the switching time with the physical nature of the gate oxide. A significant reduction in the switching time by

“oxide engineering” cannot be ruled out and an in-depth study in this area is required to optimise processing.

Retention measurements demonstrate that at room temperature, “data loss” due to drift of the protons away from the interfaces is less than 4% in a 5000 second period. More detailed measurements are clearly needed to ascertain the potential effect of parameters such as temperature on this. Experiments are also necessary to ascertain whether or not part of the observed data loss was due to the application of the source-drain potential during the whole experiment. Whilst some memories may require data retention over a period of years, this is certainly not the case for all applications. The memories integrated into flat panel displays, for example, are refreshed on the scale of tens of milliseconds so extended retention is not required. Memories in satellite systems which must store information during power downs whilst passing through radiation belts or showers may require retention of the order of minutes to hours. The retention time presently observed in the protonated gate transistors may, then, already be adequate for certain applications.

We have begun the process of qualifying a novel technology exploiting proton generation and transport in sandwiched Si/SiO<sub>2</sub>/Si structures. At the moment essentially nothing is known about the proton generation mechanism or how this, and the transport and retention can be optimised. Though one can reasonably claim that these early results are promising, further, extensive work is clearly required

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## Figure Captions

**Figure 1.** Source-drain current versus gate voltage curve for a 50  $\mu\text{m}$  gatelength by 100  $\mu\text{m}$  gatewidth MOSFET with protonated gate oxide. Solid curve - polarised for 50 seconds at 12 volts prior to sweeping down to - 12 V in 2 seconds. Dashed curve - polarised at - 12 V for 50 seconds before sweeping up to + 12 V in 2 seconds.

**Figure 2.** Switching in the same transistor as in Fig. 1. a) The gate voltage was held at + 12 V for 120 seconds then switched to and held at - 6 V, - 8 V, -10 V or - 12 V. The source-drain current was measured with a source-drain voltage of 0.6 V b) gate voltage held at - 12 V for 120 seconds then switched to and held at + 6 V, + 8 V, + 10 V or + 12 V.

**Figure 3.** Derivative of the source-drain current as a function of time ( $dI_{ds}/dt$ ) following switching as described in Fig. 2 a) derivative of data in Fig. 2a, b) derivative of data in Fig. 2b.

**Figure 4.** Maximum value of  $dI_{ds}/dt$  obtained from the plots of Figs. 3a and 3b plotted as a function of the electric field across the oxide. For simplicity we plot the absolute value of  $dI_{ds}/dt$  versus the absolute value of the applied electric field.

**Figure 5.** A plot of the initial variation of the weighted proton density in the oxide,  $Q_f(t)$ , with time as a function of the parameter  $\mu$  related to the average displacement per hop in the dispersive transport model for proton motion in  $\text{SiO}_2$ . The units for  $dQ_f(t)/dt|_{t \rightarrow 0}$  are arbitrary whilst  $\mu$  is in cm. The oxide thickness was assumed to be 40 nm. The two sets of points are for

strong dispersion ( $\alpha = 0.3$ ) and weak dispersion ( $\alpha = 0.75$ ). The closeness of the points confirms the hypothesis that the initial behaviour may be treated as independent of the presence of dispersion.

**Figure 6.** Measured source-drain current as a function of time in a 50  $\mu\text{m}$  gatelength protonated transistor for a source-drain voltage of 0.2 V. The transistor was first polarised for 120 seconds at + 6 V (open squares) or - 6 V (open circles) then the source/gate and substrate contacts shorted electrically. A drain-substrate leakage current ( $\sim 90 \mu\text{A}$ ) is present in all of the curves.















