

Molecular Control of the Drain Current in a Buried Channel MOSFET

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ABSTRACT

We present results from a buried channel MOSFET with a molecular monolayer deposited on the surface. After attachment of the monolayer, the threshold voltage of the device shifts by approximately -4.5 V. We explain this result in terms of an increase in the concentration of fixed positive charge at the upper Si:SiO₂ interface due to protonation of the surface by the molecular monolayer. Numerical simulations of the device show that the observed shift in threshold voltage can be explained by an increase of 2.5×10^{11} cm⁻² in the positive charge density located at the surface of the MOSFET.

Keywords: SOI; electron transport; molecular electronics

1 INTRODUCTION

It is often tacitly assumed that in any future applications of molecular electronics the molecules themselves support the flow of current, with semiconductor or metallic nanoelectrodes providing the input and output connections. An alternative, and less studied approach, is to use a molecular system to control the current flowing predominantly in a semiconductor device. Examples include using the dipole field of molecular layers to control the work function of Au-GaAs Schottky diodes [1] as well as the protonation of NH₂ groups that deplete hole charge in the underlying silicon nanowires [2]. In this approach, although the molecular systems do not carry significant current, their functional properties can be exploited for a variety of switching and/or sensing applications.

We have developed a novel silicon-on-insulator (SOI) MOSFET in which a buried channel electron inversion layer can be formed by the application of a substrate bias. The inversion layer is less than 40 nm from the exposed silicon surface and is sensitive to the presence of a molecular layer attached to the surface. In the experiments described below a shift in threshold voltage of -4.5 V is observed after a spiropyran monolayer is attached to the surface via carboxylic acid bonding. By means of numerical simulation we can accurately reproduce the measured data before and after application of the monolayer, simply by increasing the fixed oxide charge density at the upper Si:SiO₂ interface. We explain this result in terms of an increase in the protonation of the native oxide due to the presence of the monolayer.

2 DEVICE FABRICATION

The buried channel MOSFET is fabricated from an SOI substrate and a schematic cross-section of the finished device is shown in Figure 1. The SOI layer was formed by a SIMOX process and consists of a 200 nm silicon surface layer above a 400 nm buried oxide (BOX). The silicon layer is thinned to 40 nm by a wet oxidation at 1000° C. Device isolation is achieved by a mesa etch down to the BOX layer and n-type source and drain contacts are formed using spin-on-dopants followed by rapid thermal annealing. An aluminum metal layer is then deposited to make electrical contacts to the source, drain and substrate regions.

The top surface of the MOSFET is free of any insulating layers apart from a thin native oxide that forms on exposure to air. The buried inversion layer is less than 40 nm away from the exposed surface, and the threshold voltage of the device, V_{th} , is strongly influenced by the surface potential. The molecular monolayer is attached to the surface of the MOSFET via carboxylic acid bonding to the native oxide. The charge configuration of the molecular layer changes the surface potential of the MOSFET, resulting in large shifts in the threshold voltage as described below.

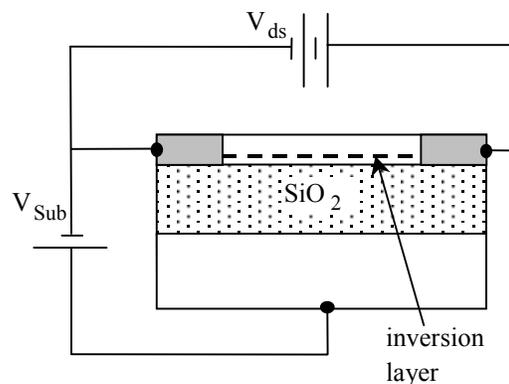


Figure 1: Schematic cross-section through the buried channel MOSFET. The distance between the source and drain contacts of the device is $37 \mu m$ and the channel is $20 \mu m$ wide

3 ELECTRICAL CHARACTERIZATION

Unlike a conventional MOSFET we use a substrate voltage, V_{Sub} , to invert the lower Si:SiO₂ interface, creating a buried channel electron inversion layer [4]. The turn-on characteristic of the device (i.e. drain current vs. substrate voltage for $V_{\text{ds}}=10$ mV) before the application of the molecular monolayer is shown in Figure 2. The error bars indicate the variation in the drain current for measurements made on nominally identical devices.

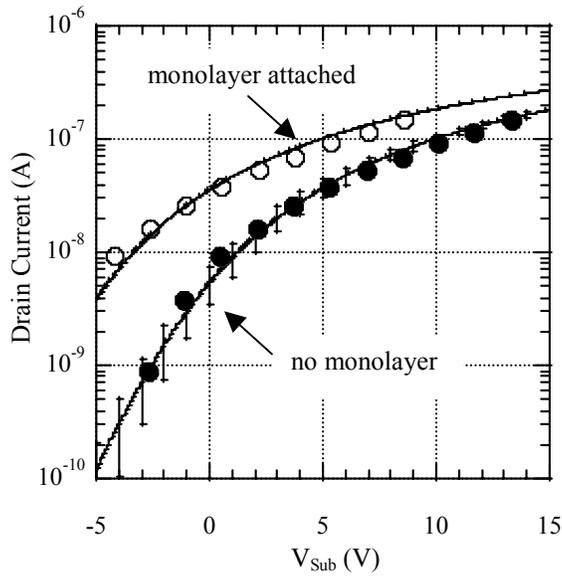


Figure 2: The turn-on characteristics of the buried channel MOSFET with and without an attached monolayer. The drain voltage in both cases is $V_{\text{ds}} = 10$ mV. The error bars indicate the random variation in current for nominally identical devices before application of the molecular layer. We attribute this variation to different concentrations of impurities attached to the surface of the different devices. The solid circles are the currents derived from a numerical simulation of the MOSFET. The current observed after the monolayer is attached can be adequately reproduced simply by increasing the concentration of fixed oxide charge at the upper Si:SiO₂ interface (open circles).

The measurement of the turn-on characteristic is repeated after a molecular monolayer is attached to the surface. For demonstration purposes we have used the spiropyran-based molecule shown in Figure 3 [5]. A single monolayer of the spiropyran is attached as follows. The MOSFET is immersed in a solution of the molecule dissolved in methanol. It is then removed, rinsed in de-ionized water and dried under a jet of nitrogen gas. The molecules attach to the native oxide on the exposed surface of the MOSFET via carboxylic acid bonding. Once attached to the MOSFET the molecular monolayer is stable but can be removed by immersing the entire device in a dilute acid.

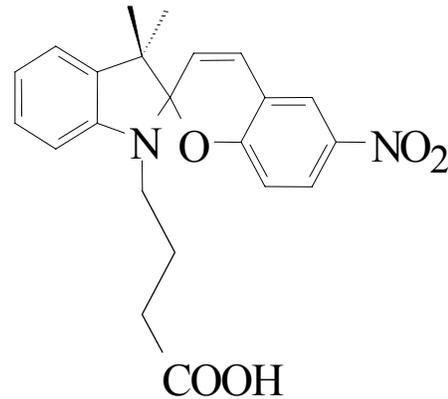


Figure 3: The spiropyran molecule attached to the surface of the buried channel MOSFET.

The results in Figure 2 also show the variation of drain current with substrate voltage after attachment of the monolayer. The shift in drain current is significantly larger than the random variation indicated by the error bars. If the molecular layer is removed by immersion in a dilute acid the original I_d - V_{Sub} curve is recovered, at least to within the measured uncertainty. This confirms that the hybrid device is sensitive to the presence of the molecular monolayer. The shift in the turn-on characteristics shown in Figure 2 correspond to a change in threshold voltage, ΔV_{th} , of approximately -4.5 V. In a conventional n-channel MOSFET an increase in the concentration of fixed, positive oxide charge would cause such a shift in V_{th} towards more negative values. Our numerical simulations of the device, described below, indicate that a similar mechanism is responsible for the shift we observe after attaching the molecular monolayer.

4 NUMERICAL SIMULATIONS

We have used the numerical device simulator Atlas from Silvaco to model the buried channel MOSFET. For the simulations, we have assumed a native oxide thickness of 3 nm, but all other dimensions are based on measured values. The mobility model takes account of acoustic and optical phonon scattering as well as interface roughness scattering. For the case when no monolayer is present the density of fixed oxide charge at each Si:SiO₂ interface, Φ_F , is assumed to be 10^{11} cm⁻², a reasonable value for SOI wafers [6]. To obtain the fits shown in figure 2 we have used the concentration of interface traps, N_{it} , as variable parameters. We required three trap states at energy levels of 0.23, 0.32 and 0.4 eV below the conduction band edge to fit the data. The traps were assumed to be acceptor-like as expected for trap states in the upper-half of the silicon band gap. The density of traps increases closer to the conduction band and we used values of 5×10^{11} , 1.5×10^{11} and 1×10^{10} cm⁻² for the respective energies given above. Although the assignment of trap energies and densities is somewhat arbitrary, they do follow the general functional form expected for N_{it} [7].

Once an adequate fit to the data from the bare device was obtained, the data with the monolayer present could be reproduced simply by increasing the concentration of positive oxide charge at the upper Si:SiO₂ interface. The open circles in Figure 2 are for an increase of $\Delta\Phi_F = 2.5 \times 10^{11}$ cm⁻², *all the other variables remain the same*. The presence of the molecular monolayer apparently increases the fixed oxide charge in the native oxide i.e. it protonates the surface.

The shift in threshold voltage after molecular attachment can be accounted for by an increase in the (positive) fixed oxide charge density, with all of the other parameters remaining constant. The charge distribution at the native oxide will be changed by the presence of the molecular layer, depending on the relative magnitudes of the dissociation constant, pKa. The pKa is a measure of acidity of a material, similar to pH. For bulk SiO₂ the value of pKa is 6.8 while that of the carboxylic binding group on the spiropyran is ~ 4.9 . Because the carboxylic acid is a substantially stronger acid than the native oxide, attaching the molecular layer to the MOSFET results in the protonation of the SiO₂ surface, i.e. more positive charge is present.

5 DISCUSSION AND CONCLUSION

To confirm the protonation mechanism it will be important to repeat the measurements using molecular monolayers with different pKa values. A suitable class of molecule is the benzoic acid derivative shown in Figure 4. The pKa value of the acid can be varied systematically by substituting different species such as NO₂, Cl, H, CH₃, etc for the group indicated as 'X'. We are currently repeating the measurements described above using the benzoic acid derivatives and will report on the results at the meeting. However, the preliminary results described here show that the threshold voltage of an n-channel inversion layer can be controlled by the properties of a molecular layer attached to the surface.

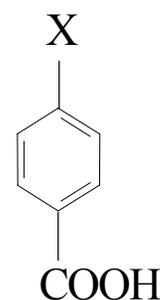


Figure 5: A benzoic acid derivative with pKa value dependent upon the species used for the group marked 'X'.

If the protonation mechanism is confirmed, the buried channel MOSFET described above has the potential for measuring changes in the surface charge distribution with very high resolution. The data in Figure 2 shows a shift in threshold voltage of 4.5 V for an increase in positive surface charge of 2.5×10^{11} cm⁻². With careful control of the surface conditions it will be possible to resolve shifts in V_{th} of 100 mV or even smaller, corresponding to $\Delta\Phi_F < 5.6 \times 10^9$ cm⁻². For an active MOSFET area of 100×100 nm², a change in protonic/electronic charge density of 5×10^9 cm⁻² corresponds to removing/adding half an electron from the surface of the device. The ability to resolve fractional changes in the electron distribution at the surface of the MOSFET suggests that experiments studying, for example, the redox chemistry of single molecules may be possible.

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