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Gate-Bias Controlled Charge Trapping as a Mechanism for NO₂ Detection with Field-Effect Transistors

Anne-Marije Andringa, Juliaan R. Meijboom, Edsger C. P. Smits, Simon G. J. Mathijssen, Paul W. M. Blom, and Dago M. de Leeuw*

Detection of nitrogen dioxide, NO₂, is required to monitor the air-quality for human health and safety. Commercial sensors are typically chemiresistors, however field-effect transistors are being investigated. Although numerous investigations have been reported, the NO₂ sensing mechanism is not clear. Here, the detection mechanism using ZnO field-effect transistors is investigated. The current gradually decreases upon NO₂ exposure and application of a positive gate bias. The current decrease originates from the trapping of electrons, yielding a shift of the threshold voltage towards the applied gate bias. The shift is observed for extremely low NO₂ concentrations down to 10 ppb and can phenomenologically be described by a stretched-exponential time relaxation. NO₂ detection has been demonstrated with n-type, p-type, and ambipolar semiconductors. In all cases, the threshold voltage shifts due to gate bias induced electron trapping. The description of the NO₂ detection with field-effect transistors is generic for all semiconductors and can be used to improve future NO₂ sensors.

for air-quality monitoring has led to extensive research in the field. Many sensors are commercially available, ranging from electrochemical to optical sensors.

The most common NO₂ sensors are chemiresistors based on semiconducting metal oxides such as tin oxide (SnO₂), tungsten oxide (WO₃), or zinc oxide (ZnO).^[1–3] Porous oxide layers with high specific surface areas are used. The gas diffuses into the oxide and modulates the grain boundary resistances by the transfer of charge carriers from the semiconductor to the adsorbed surface species. Nowadays, many companies offer metal-oxide-based gas sensors. The lack of selectivity can be addressed by combining a number of sensors in an array. The sensors are selected for a specific application, such as bacteria growth^[4] or car seat foams.^[5] Challenges are reduction of the power consumption

1. Introduction

NO₂ is one of the most dangerous air pollutants affecting human health and the environment. The gas is released during the combustion of fossil fuels and plays a major role in the formation of ozone and acid rain. The control and improvement of the air quality is of great importance to modern society. The U.S. Environmental Control Agency has set the air-quality standard at a level of 53 ppb NO₂. The need for sensitive sensors

due to the high operating temperature and improvement of the sensitivity, which is typically about 1 ppm. To this end, other semiconductors, such as phthalocyanines^[6–8] and carbon nanotubes films,^[9] are being investigated in two terminal devices.

Field-effect transistors (FETs) have emerged as an alternative sensing technology. In 1975, a hydrogen sensor based on a Pd-gate FET was demonstrated.^[10] In recent years, a wide variety of semiconductors has been used in transistors to detect a wide range of gases. Examples are carbon nanotubes^[11] and organic^[12–18] and oxidic^[19] semiconductors. The key advantage of a transistor over a resistor is the reported amplified sensor response due to current modulation by the extra gate electrode.^[13] The sensitivity can be enhanced by operating the sensor in the subthreshold regime. Apart from the current modulation, changes in other transistor parameters, such as mobility and threshold voltage, could be used for sensing. The idea of exploiting FETs as multiparameter gas sensors was suggested by Torsi et al.^[20]

A wide variety of semiconductors has been investigated in transistors for NO₂ detection. A range of sensing layers, such as amorphous organic semiconductors,^[21,22] porous silicon,^[23] silicon nanowires,^[24] carbon nanotubes,^[25–33] and metal oxide nanowires,^[34] were used. In all cases changes in current upon NO₂ exposure has been demonstrated. In addition, a high sensitivity down to 10 ppb NO₂ has been reported. The detection mechanism however is not clear and several possible sensing mechanism have been suggested. The adsorbed NO₂ is a strong

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electron acceptor that can influence the charge carrier density in the channel. The change in current can then be explained by doping of the semiconductor by the oxidizing NO_2 ^[17,21,22] or by depleting the electrons from the conduction channel.^[31,34] For carbon nanotubes sensors Zhang et al.^[32] postulated that the NO_2 molecules change the metal workfunction, leading to a change in the Schottky barrier height at the carbon nanotube–metal interface. Finally, Kong et al.^[33] proposed molecular gating of the nanotubes by the polar NO_2 molecules as the sensing mechanism.

Here, we elucidate the NO_2 detection mechanism using transistors with ZnO as a model semiconductor. ZnO was selected because it has been widely investigated in resistive sensors.^[35–37] Other semiconductors were also investigated and we argue that the detection mechanism is independent of the type of semiconductor. The charge transport upon NO_2 exposure was measured. The current decreased with time, but only in combination with a positive gate bias. The decrease is due to charge trapping mediated by NO_2 , yielding a shift in the threshold voltage. It is shown that for any positive gate bias, the threshold voltage shifts towards the applied gate bias. The dynamics of the shift under prolonged gate bias are evaluated at room temperature as a function of the NO_2 concentration and ZnO layer thickness. The kinetics of the threshold voltage shift can phenomenologically be described by a stretched-exponential time dependence. The functional dependence on the ZnO layer thickness and NO_2 concentration is discussed and a generic interpretation based on charge trapping is presented for different semiconductors.

2. Transistor Fabrication and Characterization

ZnO field-effect transistors were fabricated using spray pyrolysis in ambient atmosphere. Details on the fabrication and characterization procedures are given in the Experimental Section. A solution of zinc acetate in methanol was nebulized on prefabricated transistor substrates heated at 400 °C, as reported by, for example, Bashir et al.^[38] This simple deposition technique yields high-performance n-channel transistors with negligible hysteresis and a field-effect mobility of $0.1\text{--}2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. The current modulation exceeded 6 orders of magnitude and the threshold voltage was 0 V. The ZnO layer was characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), and atomic force microscopy (AFM). The mirror-like ZnO films exhibited a microcrystalline morphology with a surface roughness of 1 nm (root mean square (rms)). XRD measurements showed that the ZnO films exhibited a (102) textured microstructure. The film thickness was typically only 10 nm to ensure permeability for NO_2 .

To measure the current transport of the ZnO transistors in an NO_2 atmosphere, initially a closed static gas system was used. The NO_2 concentration dropped with time due to a surface reaction with the interior of the closed chamber. Therefore this setup could only be used to perform measurements at high NO_2 concentration, above 0.5 ppm, within half an hour. Reliable measurements at lower NO_2 concentrations, in the range of 0–1200 ppb, were performed in a dynamic flow cell. The gases were flushed through the chamber at a constant total flow rate of 500 sccm. After 30 min a stabilized concentration was achieved. The NO_2 concentration was calibrated in both setups.

The semiconductor parameter analyser was programmed to perform a complete measurement in less than one second. The state of the transistor was determined to be unaffected by the measurement. Because the transistors were stable when no bias was applied, the NO_2 concentration could be stabilized before starting the electrical measurements.

3. Chemiresistors Versus Transistors

In a metal-oxide-based gas sensor, the resistance is monitored as a function of the concentration of the target gas. The operation mechanism is well established.^[1,2,39,40] Conventional metal oxide sensors are operated in air, at temperatures between 200 and 400 °C. The partial oxygen pressure is fixed and therefore the amount of oxygen absorbed on the metal oxide grains is constant. At the temperature used, the oxygen thermally dissociates. Due to the large electronegativity of oxygen atoms, charge transfer occurs. Electrons are removed from the metal oxide semiconductor, the free charge carrier concentration is reduced, and a depletion layer is formed. The resistance in air is therefore larger than in vacuum. Exposure to, for instance, a reducing gas leads to the removal of the oxygen atoms, thereby reinjecting electrons into the conduction band. Both the thickness of the depletion layer and the resistance decreases. The sensitivity of the sensor depends on the size of the depletion layer relative to the thickness of the bulk semiconductor. Commercial sensors therefore typically consist of thick porous films. Schottky contacts at the grain boundaries then dominate the electrical transport.

Commercial metal oxide sensors are two terminal chemiresistors. The change in resistance is due to a change in the charge carrier density. A field-effect transistor, discussed below, is a three terminal device in which an additional gate electrode modulates the charge carrier density in the semiconductor. Here, the influence of the gate field on the sensitivity is investigated.

A schematic diagram of a transistor is presented in the inset of Figure 1. A semiconductor layer is contacted by two

Figure 1. Typical transfer curve of a ZnO field-effect transistor measured with a drain bias of 2 V. In the inset, a schematic presentation of a transistor is shown. At a negative gate bias the semiconductor is depleted and the transistor is off. At a positive bias electrons are accumulated in the semiconductor at the ZnO– SiO_2 interface and current flows.

electrodes, the source and the drain. The third electrode, the gate, is electrically insulated from the semiconductor layer via an insulating oxide layer, creating a parallel plate capacitor with a capacitance per unit area, C_{ins} . By applying a gate voltage, V_G , with respect to the source electrode, charge carriers can electrostatically be accumulated or depleted in the semiconductor at the semiconductor–insulator interface. Due to this field-effect the charge carrier density in the semiconductor can be varied. Therefore, the resistivity of the semiconductor, and hence the current through the semiconductor (upon application of a source–drain field), can be varied over orders of magnitude.

A typical transfer curve of a ZnO transistor, where the current is measured as a function of gate bias at a constant drain bias, is presented in Figure 1. ZnO is an intrinsic undoped n-type semiconductor. At zero gate bias there are no charges accumulated and the current is negligible. At positive gate bias electrons are accumulated in the channel. Upon applying a source drain bias, current flows. The magnitude is proportional to the induced charge carrier density, $C_{\text{ins}}V_G$, and the field-effect mobility. At negative gate bias any electron in ZnO is depleted. Holes cannot be injected and are immobile in ZnO. Hence, as schematically depicted in the inset of Figure 1, in depletion no current flows. The transistor is measured in the linear region, where the drain bias is much smaller than the gate bias, hence the charge density is uniform throughout the channel. Figure 1 shows that the current starts to flow around zero gate bias. This onset is the pinch-off voltage, which is assumed to be equal to the threshold voltage.

The ZnO transistors were characterized in an NO_2 ambient at room temperature. The gate was grounded and there were no charges in the semiconductor. The current was low for all drain biases and did not change with NO_2 content. Large changes occurred, however, when a gate bias was applied. Figure 2a serves as an illustration. A ZnO transistor kept in vacuum was turned on by applying a positive gate bias. A small source drain bias was applied and the current was measured as a function of time. The current was stable, there was only a small drift due to residual gate bias stress.^[41] After 4 min of measuring, NO_2 gas was admitted. The current immediately dropped and within 10 min the current decreased by more than three orders of magnitude. To elucidate the origin of the current drop, the transfer curves were measured a few times during the transient current measurement. Figure 2b shows that in vacuum the transistor switches on at 0 V gate bias (red curve). After NO_2 exposure and upon continuously applying a positive gate bias, the transfer curve shifts towards the applied gate bias (green and blue). The shape however remains unaffected, implying that the field-effect mobility remains the same. The main effect of NO_2 exposure is a shift of the threshold voltage, V_{th} . At room temperature the recovery can be disregarded.

In summary, at zero gate bias the electrical transport did not change; the ZnO transistors were chemically stable in NO_2 . The transport only changed when a positive gate bias was applied in NO_2 ambient. The measurement of the transfer curve should not influence the state of the transistor. Hence it is crucial to keep the time to measure a transfer curve as short as possible.

Figure 2. a) Drain current of a ZnO field-effect transistor as a function of time using an applied gate bias of 30 V and a drain bias of 2 V. The measurement starts in vacuum and after 4 min 250 ppb NO_2 was admitted. b) Transfer characteristics corresponding to the indicated times during the measurement in (a). The red curve was measured in vacuum, the green and blue curves were measured during NO_2 exposure.

4. Threshold Voltage Dynamics

The applied gate bias dominates the threshold voltage shift. A ZnO transistor was kept in NO_2 atmosphere with all contacts grounded. At regular time intervals quick transfer curves were measured. Because the gate was grounded, the threshold voltage hardly changed. Hence doping of the ZnO semiconductor by oxidizing NO_2 can be disregarded.

To elucidate the role of a finite gate field, a continuous gate bias was applied for a longer time, with grounded source-drain electrodes. The resulting threshold voltage shift was monitored by measuring the transfer curves as a function of time. In Figure 3a, the linear transfer curves measured at a 2 V drain bias are presented as a function of stress time, the time at which the gate bias is applied. Figure 3 shows that the transfer curve shifts with stress time towards the applied gate bias, in this case 30 V. The arrows indicate transfer curves measured after 1 to 1000 s. The shape of the curves does not change. Therefore the shift in threshold voltage is similar to the shift

Figure 3. a) Transfer curves of a ZnO transistor under exposure of 320 ppb NO₂ as a function of time under continuous applied gate bias of 30 V. The arrows indicate transfer curves measured after 1 to 1000 s. b) The threshold voltage shift obtained from (a) presented as a function of time on a semilogarithmic scale. The solid line is a fit to a stretched-exponential time dependence.

in pinch-off voltage. The threshold voltage shift, with respect to the reference value measured in vacuum, is presented in Figure 3b as a function of time on a semilogarithmic scale. Initially a fast change is observed, while at longer times the threshold voltage shift saturates at the value of the applied gate bias. This rate of change resembles the temporal behavior of a stretched-exponential relaxation. Hence the threshold voltage shift was fitted to:

$$\Delta V_{th}(t) = V_0 \left\{ 1 - \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \right\} \quad (1)$$

where τ is a relaxation time, β is a dispersion parameter equal to T/T_0 , and $V_0 = V_G - V_{th0}$, where V_G is the applied gate bias and V_{th0} is the threshold voltage at the start of the experiment. Figure 3b shows that a good agreement is obtained with a characteristic relaxation time of 26 s and a dispersion parameter β of 0.25.

The shift was determined for various gate biases. **Figure 4a** shows the threshold voltage as a function of time for various gate biases of 0, +10, +20, and +30 V. When the gate is grounded,

Figure 4. a) Threshold voltage shift as a function of time for various applied gate biases. The NO₂ concentration was 300 ppb. The data points were fitted to a stretched-exponential time dependence, Equation (1), as shown by the solid lines. The inset shows the threshold voltage shifts normalized to the applied gate bias. b) Schematic representation of the charge trapping process in a transistor. With time, mobile electrons are continuously trapped until the steady-state is reached and the gate bias is completely compensated by immobile trapped charges.

the threshold voltage does not shift and the transfer curve does not change. Only when a finite positive gate bias is applied the threshold voltage shift towards the applied gate bias. The solid lines show that each measurement can be fitted with a stretched-exponential time dependence. The fit constants τ and β are independent of the gate bias as can be inferred from the inset of Figure 4a, which shows the threshold voltage shift normalized to the applied gate bias. Equation (1) describes the threshold voltage shifts for all gate biases.

Figure 4 can qualitatively be understood as follows. Upon application of a positive gate bias, electrons accumulate in the channel. Some are trapped at defect sites or acceptor molecules. The trapped charges do not contribute to the current but they shift the threshold voltage. When the trapped charges

Figure 5. Drain current of a ZnO field-effect transistor under an applied gate bias of 30 V and drain bias of 2 V as a function of time. The NO_2 concentration was approximately 800 ppb. At certain time intervals the drain bias was grounded.

fully compensate the applied gate bias, there is no driving force left for charge accumulation. The threshold voltage shift saturates at the applied gate bias and a steady-state is reached. The charge trapping process is schematically depicted in Figure 4b. With time, mobile electrons are continuously trapped until the steady-state is reached where the gate bias is completely compensated by immobile trapped charges.

The threshold voltage shifts only when the gate bias is applied; the drain bias in the linear regime has no influence, in contrast with classical chemiresistors. A ZnO transistor was kept in NO_2 atmosphere and, as above, the current was measured as a function of time. At certain time intervals the drain bias was grounded. **Figure 5** shows a continuous current decrease, irrespective of the time that the drain bias was grounded, demonstrating that the drain bias can be disregarded. Implicitly it also shows that current itself is not the origin of the current decay. Therefore, contact degradation^[42] can be ruled out as the sensing mechanism.

The temporal behavior was measured for various NO_2 concentrations using a single ZnO transistor. After each series of measurements the transistor was annealed at 150 °C in vacuum for 1 h to recover the original 0 V threshold voltage. For each NO_2 concentration the threshold voltage shift was determined as a function of the stress time. **Figure 6a** shows the extracted threshold voltage shifts as a function of time and NO_2 concentration. For all concentrations, the threshold voltage shifts to the applied gate bias of 30 V. The main effect of exposing the transistor to different concentrations is the time dependence. The solid lines are a stretched-exponential fit to the data. For all concentrations a good agreement is obtained. The dispersion parameter β is almost unchanged. **Figure 6b** shows that the main change is in the characteristic relaxation time, which varies over orders of magnitude by changing the NO_2 concentration. The slope is unity; the relaxation time is inversely proportional to the NO_2 concentration. Finally it is noted that **Figure 6** shows that extremely low NO_2 concentrations, down to the ppb level, can be detected.

Experimentally, a shift of the threshold voltage is found that can phenomenologically be described. To investigate the vast

Figure 6. a) Threshold voltage shift of a ZnO transistor as a function of time upon exposure to different concentrations of NO_2 . The continuously applied gate bias was 30 V. The extracted shifts were fitted to a stretched-exponential time dependence. b) Relaxation time, τ , as a function of the NO_2 concentration. The slope of the fit is unity.

parameter space of field-effect transistors, the ZnO layer thickness was varied. For each thickness, the shift in threshold voltage was extracted and is plotted in **Figure 7** as a function of stress time. The solid lines are a fit to the data. A good agreement is obtained for all thicknesses. Again the change in dispersion parameter is negligible; the main effect is a change in relaxation time. **Figure 7b** shows that, within experimental accuracy, the relaxation time increases exponentially with layer thickness.

5. Rationalization of the Temporal Behavior

The experimental data can be summarized as follows. Without applied gate bias the transistors are stable in an NO_2 ambient. Hence doping of the ZnO semiconductor by oxidizing NO_2 can be disregarded. Only when a positive gate bias is applied in an NO_2 ambient the current drops, regardless of the applied drain bias. The origin of the current drop is a shift in the threshold voltage. The shape of the transfer curve does not change, the mobility remains constant, and hence the material properties remain unaffected. Also contact degradation can be ruled out as the sensing mechanism because the current itself is not the origin for the current decay.

Figure 7. a) Threshold voltage shift as a function of time upon exposure to 3 ppm NO_2 for different ZnO layer thicknesses. The continuously applied gate bias was 30 V. The time dependence was fitted with a stretched-exponential. b) Relaxation times, τ , as a function of ZnO layer thickness. The solid line is an exponential fit to the data points.

The threshold voltage shift is due to charge trapping mediated by the NO_2 . The threshold voltage in a transistor is set by the flat band voltage, the difference in work function between the electrodes and the semiconductor. When a ZnO transistor is turned on electrons are accumulated. Some of them are trapped; the trapped charge themselves do not contribute to the current but are still part of the electrostatic charge that shield the gate voltage. The threshold voltage shifts by eQ_f/C_{ox} where e is the elementary charge, C_{ox} is the gate dielectric capacitance, and Q_f are the fixed charges.^[43,44] A shift of the threshold voltage with time is due to an increase of the fixed charges, Q_f . With time the effective gate field decreases and the threshold voltage saturates at the applied gate bias; no current flows and a steady-state is reached. It is tempting to assign the microscopic nature of the charged trap state directly to oxidized NO_2 , but this requires further investigation and is irrelevant for the forthcoming description.

Experimentally it was determined that the threshold voltage shift as a function of time and partial NO_2 pressure can phenomenologically be described by a stretched-exponential time dependence. This stretched-exponential decay, called William–Watts or Kohlrausch relaxation, is observed in a wide class of disordered systems, such as relaxation of glasses toward

equilibrium, dielectric relaxation in a charge density wave system, and dispersive transport in photoconductors.^[45] It holds for all dispersive transport processes in an exponential distribution of trap states.^[46]

The measurement protocol used to determine the threshold voltage shift resembles that to determine the operational stability of amorphous semiconductors due to gate bias stress.^[47,48] When a transistor is turned on for a long time, the threshold voltage shifts to the applied gate bias according to a stretched-exponential time dependence. Without NO_2 , the ZnO transistor shift is small; the operational stability does not hinder the experiment. With NO_2 however, a dramatic shift of the threshold voltage was observed. The shift was orders of magnitude faster, but the functional dependence was the same. The microscopic mechanism for the operational stability in amorphous semiconductors is heavily debated, the origin could, for instance, be due to hydrogen diffusion.^[49] That microscopic origin obviously does not apply here; hydrogen is absent. However, the formalism developed to describe the threshold voltage instability is generic and independent of the nature of the trap site. Here it is applied for NO_2 detection.

Hydrogenated amorphous silicon contains metastable defect sites with a density, N_s . Upon stressing, metastable states are transformed into charged defects. The rate of defect formation is proportional to the rate of hydrogen diffusion. The conversion from metastable to charged defect states is large at the beginning of the experiment and zero at infinite time, $t \rightarrow \infty$. Consequently the change in defect density from equilibrium, ΔN_s , is given by:

$$\frac{d\Delta N_s}{dt} = -AD(t)\Delta N_s \quad (2)$$

where A is a proportionality constant and $D(t)$ is a time-dependent diffusion constant. Diffusion by trapping and detrapping of hydrogen atoms is usually modeled by a dispersive diffusion coefficient given by^[49]

$$D(t) = D_{00}(\omega t)^{-\alpha} \quad (3)$$

in which D_{00} is the microscopic diffusion constant, α is the temperature dependent dispersion parameter given by $\alpha = 1 - \beta$, and $\omega = 1/\tau$ is an attempt frequency. Solving Equation (2) with the boundary condition that the threshold voltage at infinite time is equal to the applied gate bias yields a stretched-exponential time relaxation for the threshold voltage shift in amorphous silicon transistors similar to Equation (1).

The analysis presented above can be applied to detection of NO_2 with ZnO transistors. Experimentally it was determined that the temporal behavior of the threshold voltage as a function of partial NO_2 pressure can phenomenologically be described by a stretched-exponential decay as well. The characteristic relaxation time, τ , is inversely proportional to the partial NO_2 pressure and scales exponentially with the ZnO layer thickness. We can rationalize both dependences by assuming that the NO_2 mechanism relies on charge trapping with an anomalously wide distribution of trapping times due to a time-dependent diffusion coefficient. We conjecture that the dispersive diffusion coefficient is dominated by the density of NO_2 at the gate dielectric–ZnO interface. The partial NO_2 pressures

are low (in the ppb range). Assuming a Langmuir isotherm for the NO₂ absorption, the density of absorbed NO₂ is then proportional to the partial vapor pressure. Simultaneously the density of absorbed NO₂ decreases exponentially with the ZnO layer thickness, with a decay constant determined by the morphology.^[35] These realistic assumptions are sufficient to explain the experimentally observed dependences of the characteristic time scale, τ on pressure and layer thickness, i.e., $\tau \approx 1/p(\text{NO}_2)$ and $\tau \approx \exp d_{\text{ZnO}}$.

Experimentally we observe a constant dispersion parameter, β , that is given by T/T_0 , in which T is the temperature and T_0 the isokinetic temperature characterizing the width of the density of trap states. The constant value of β might indicate that a single species is responsible for the charge trapping. The derivation above predicts an exponential dependence of τ on temperature and a linear dependence of β on T . Preliminary experimental results show, however, nearly temperature-independent parameters. This might be due to two competing thermally activated processes that cannot be disentangled, i.e., absorption or desorption of NO₂ and trapping or detrapping of charge carriers. The former has a negative temperature coefficient, which can compensate for the temperature dependence of the latter process.

6. Extension to Organic Semiconductors

The shift of the transfer curve for the ZnO field-effect transistors is towards the positive applied gate bias. ZnO is an n-type semiconductor. The shift originates from trapping of the majority charge carriers, i.e., electrons, and therefore allows for a quantitative description of the trapping dynamics. To eliminate the possibility of a specific interaction between the NO₂ and ZnO as the sensing mechanism the semiconductor was varied. For completeness, air-stable n-type (perylene),^[50] p-type (polytriarylamine),^[51] and ambipolar (NiDT)^[52] organic semiconductors were studied. The shift of the transfer curves, as measured for the n-type and ambipolar semiconductors, shows that electrons are trapped. The temporal behavior is again in good agreement with a stretched-exponential decay, indicating that the same microscopic mechanism operates. For the p-type semiconductor the threshold voltage shifts to positive gate biases as well. Consequently the current at a fixed gate bias increases upon measuring in an NO₂ ambient. The shift in threshold voltage is again due to trapping of electrons and not due to chemical doping. However, in a p-type semiconductor electrons are the minority carriers,^[53] which hampers a quantitative interpretation of trapping dynamics.

Numerous investigations on the use of transistors with a large variety of semiconductors as potential NO₂ sensors have been reported. In all cases changes in current upon NO₂ exposure have been demonstrated, i.e., a decrease for n-type semiconductors and an increase for p-type semiconductors. Many detection mechanisms have been reported, such as chemical doping of the bulk semiconductor, modulating the injection by varying the contact barrier, and depleting electrons from the charge transport layer. A detailed study of the dynamics of the threshold voltage shift has not yet been reported. The insights presented here rationalize previous results, yielding a generic

description of the NO₂ detection mechanism in transistors. Furthermore, the detection mechanism and the derived measurement protocol can be used as a guideline to improve future NO₂ sensors.

The cross-sensitivity has not yet been investigated. The charge trapping is expected to depend on both the electronegativity of the analyte and the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO and LUMO) energies of the semiconductor. Experimental verification is a topic for ongoing research.

7. Summary and Conclusion

NO₂ sensors are required to monitor and control the air-quality standards. Commercial sensors are typically chemiresistors, which monitor change in grain boundary resistances. In recent years, field-effect transistors have been suggested as an alternative sensing technology. In order to elucidate the NO₂ sensing mechanism, transistors with ZnO as a semiconductor were used. The electrical transport does not change when the transistor is exposed to NO₂. The transport only changes when in an NO₂ ambient a positive gate bias is applied. The current drops with time.

The current decrease of the transistor originates from a gradual shift of the threshold voltage. The temporal behavior can phenomenologically be described by a stretched-exponential time relaxation. The characteristic relaxation time is inversely proportional to the partial NO₂ pressure and scales exponentially with the ZnO layer thickness. NO₂ absorption is assumed to follow a Langmuir isotherm. A trapping and detrapping process of electrons can explain the stretched-exponential decay and the dependences on ZnO layer thickness and NO₂ concentration. NO₂ detection has been demonstrated with n-type, p-type, and ambipolar semiconductors. In all cases, a shift of the threshold voltage is obtained that is due to trapping of electrons. Hence, the description of the NO₂ detection in field-effect transistors is generic and can be used to improve future NO₂ sensors.

Experimental Section

Field-effect transistors test substrates were fabricated from heavily doped n-type Si wafers acting as a common gate electrode. A 200-nm thermally oxidized SiO₂ layer was used as bottom gate dielectric. Gold source and drain electrodes were patterned using conventional photolithography, resulting in finger transistors with a channel length and width of 10 and 10,000 μm , respectively. A 10-nm titanium layer was used as an adhesion layer for the gold on SiO₂. Prior to semiconductor deposition, the SiO₂ surface was passivated with the primer hexamethyldisilazane (HMDS). Zinc oxide thin-films were deposited on transistor test substrates at 400 °C by spray pyrolysis of 0.1 M zinc acetate (Sigma Aldrich, Germany, 99.99%) in methanol under ambient atmosphere. The layer thickness was varied by the spray time, the standard layer thickness was 10 nm as measured with XRF. XRF measurements are performed on the PW-2400 XRF-spectrometer (Panalytical, The Netherlands), equipped with a Cr-anode X-ray tube. A collimator mask of $\varnothing$ 10 mm was used. Measured is the Zn K-alpha fluorescence line (wavelength, $\lambda = 1.436$ Å; energy, $E = 8.63$ KeV). Calculation of the layer thickness is done using the software program FP-Multi (Panalytical). Calibration was done with the pure bulk metal Zn. Specular XRD scans were made using a Panalytical X'Pert MPD pro diffractometer equipped with a Cu-X-ray tube and an X'Celerator

detector. An omega offset of 3° was used to suppress diffraction signals from the silicon substrate. AFM measurements were performed with a Veeco Dimension 3100 scanning probe microscope, using a Si probe in tapping mode. Prior to use, the ZnO transistors were annealed in vacuum or air at 150°C in order to make the pinch-off voltage 0 V. As the pinch-off voltage, the gate bias at which the source drain current is 1 nA was taken. In addition to ZnO, various organic semiconductors were investigated. Layers were spin-coated on transistors test substrates. The n-type ActivInkN1400 (PDIR-CN2) was obtained from Polyera Corporation (USA), p-type polytriarylamine, Lisicon S1124, was received from Merck Chemicals Ltd. (UK) and ambipolar nickel dithiolen (bis[4-dimethylaminodithiobenzyl]-nickel) was obtained from Sensient GmbH (Germany). Electrical measurements were performed using an Agilent 4155B semiconductor parameter analyzer. All electrical characterization was done at 40°C .

The sensor response in NO_2 atmosphere was tested in a stationary and a flow system equipped with feed-throughs for electrical contacting. Cylinders containing 3 ppm NO_2 in N_2 as a carrier gas and pure N_2 were supplied by Praxair (Belgium). The NO_2 concentration was calibrated in both setups using the Eco Physics (Switzerland) CLD 88p NO sensor based on chemiluminescence. A gas converter of M&C TechGroup (Germany, series CG) was used to convert NO_2 catalytically to NO at 330°C with a carbon molybdenum mixture. Two mass flow controllers were used to produce NO_2 concentrations in the range of 0–1200 ppb. Electrical measurements were performed in a stabilized concentration that is reached after 30 min flow.

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