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Authors	Vardhan, Vaishali; Biswas, Subhajit; Ghosh, Sayantan; Tsetseris, Leonidas; Ghoshal, Tandra; Hellebust, Stig; Georgiev, Yordan M.; Holmes, Justin D.
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Pseudo Molecular Doping and Ambipolarity Tuning in Si Junctionless Nanowire Transistors Using Gaseous Nitrogen Dioxide

Vaishali Vardhan, Subhajit Biswas,* Sayantan Ghosh, Leonidas Tsetseris, Tandra Ghoshal, Stig Hellebust, Yordan M. Georgiev, and Justin D. Holmes*

Ambipolar transistors facilitate concurrent transport of both positive (holes) and negative (electrons) charge carriers in the semiconducting channel. Effective manipulation of conduction symmetry and electrical characteristics in ambipolar silicon junctionless nanowire transistors (Si-JNTs) is demonstrated using gaseous nitrogen dioxide (NO_2). This involves a dual reaction in both p - and n -type conduction, resulting in a significant decrease in the current in n -conduction mode and an increase in the p -conduction mode upon NO_2 exposure. Various Si-JNT parameters, including “on”-current (I_{on}), threshold voltage (V_{th}), and mobility (μ) exhibit dynamic changes in both the p - and n -conduction modes of the ambipolar transistor upon interaction with NO_2 (concentration between 2.5 – 50 ppm). Additionally, NO_2 exposure to Si-JNTs with different surface morphologies, that is, unpassivated Si-JNTs with a native oxide or with a thermally grown oxide (10 nm), show distinct influences on I_{on} , V_{th} , and μ , highlighting the effect of surface oxide on NO_2 -mediated charge transfer. Interaction with NO_2 alters the carrier concentration in the JNT channel, with NO_2 acting as an electron acceptor and inducing holes, as supported by Density Functional Theory (DFT) calculations, providing a pathway for charge transfer and “pseudo” molecular doping in ambipolar Si-JNTs.

1. Introduction

Semiconductor nanowires play a crucial role in integrated nanodevices and systems.^[1–4] Specifically, Si nanowires offer advantages such as ease of fabrication, compatibility with existing semiconductor technology, high carrier mobility, stable surface oxides, and excellent sensitivity to surface-adsorbed analytes.^[5–9] The precise control and tunability of electrical transport properties in Si nanowires has created numerous opportunities for creating various functional nanosystems, including photodetectors, LEDs, and 3D integrated electronics.^[10–12] The main advantage of nanowires in transistors is their superior electrostatic control and scalability, enabling smaller, faster, and more energy-efficient devices. This results from their 1D structure, which allows for better gate control and reduced short-channel effects.^[13] Among

V. Vardhan, S. Biswas, S. Hellebust, J. D. Holmes
School of Chemistry
University College Cork
Cork T12 YN60, Ireland
E-mail: s.biswas@ucc.ie; j.holmes@ucc.ie

V. Vardhan, S. Biswas, S. Hellebust, J. D. Holmes
AMBER Centre, Environmental Research Institute
University College Cork
Cork T23 XE10, Ireland

S. Ghosh, Y. M. Georgiev
Institute of Ion Beam Physics and Materials Research
Helmholtz-Zentrum Dresden Rossendorf
01328 Dresden, Germany

S. Ghosh
Technische Universität Dresden
01069 Dresden, Germany

L. Tsetseris
Department of Physics
School of Applied Mathematical and Physical Sciences
National Technical University of Athens
Athens 15780, Greece

T. Ghoshal
AMBER Research Centre and School of Chemistry
Trinity College Dublin
Dublin 2, Dublin D02AK60, Ireland

Y. M. Georgiev
Institute of Electronics at the Bulgarian Academy of Sciences
72, Tsarigradsko Chaussee Blvd., Sofia 1784, Bulgaria

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aelm.202400338>

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nanowire transistors, Si-JNTs, which do not possess gated junctions,^[14] have high surface-to-volume ratio and the ability to chemically interact with surface analytes, exhibiting extreme sensitivity to variations in the electrostatic potential on their channel surfaces.^[9,14–17]

To the best of our knowledge, most Si-JNTs exhibit unipolar behavior, demonstrating either hole-dominated *p*-type conduction or electron-dominated *n*-type conduction depending on the type of doping. However, ambipolar transistors are distinct in that they are capable of facilitating both hole (positive) and electron (negative) transport.^[18] This unique characteristic has produced interest across various fields, including complementary metal-oxide-semiconductor (CMOS) devices, light emitting transistors, memory devices, neuromorphic computing, and sensors.^[18,19] Ambipolar transistors enable the integration of both *p*- and *n*-type electrical characteristics within a single device.^[18,20,21] In applications such as ambipolar field effect transistor (FET) sensors, exposure to oxidative species induces dual responses: enhancing conductivity in the *p*-conduction regime while reducing it in the *n*-conductive mode.^[20,21] This dual behavior significantly expands the parameter space, offering greater potential for algorithm development in sensor calibration optimization.

To advance the development of nanoelectronics based on Si nanowires, such as ambipolar JNTs, precise tuning of their electrical properties is essential, a task that is still proving to be challenging. Ex situ methods are becoming increasingly attractive for achieving successful doping and manipulation in Si devices.^[22,23] Nanocrystals, especially nanowires, known for their large surface-to-bulk ratio, offer greater surface sites and the possibility of doping through the external adsorption of molecules,^[24] rather than the incorporation of substitutional impurities. The potential for adsorbed molecules to provide shallow electronic states for tuning the electrical properties of transistors has received less attention, though some promising experimental results have been reported for surface transfer doping through surface passivation of Si.^[25,26]

Changes in the electrical conductivity of Si upon adsorption of gas molecules has been reported for mesoporous Si systems,^[27–29] suggesting that molecular doping and the manipulation of electrical properties in ambipolar Si-JNTs can be accomplished through the surface adsorption of specific molecules such as nitrogen dioxide (NO₂). The interaction of NO₂ with Si is a complex adsorption process that influences the molecular coating of Si nanocrystals and noticeably alters their properties. NO₂ adsorption enhances electrical conductivity in the mesoporous Si layers.^[30] Within the porous Si layers, NO₂ molecules interact with the surface of nanocrystalline Si through a complex physicochemical process that may involve adsorption, charge transfer, the formation of donor-acceptor pairs, and chemisorption, resulting in the oxidation of Si surfaces. The passivation of dangling bonds, and the formation of adsorption-induced compounds can further increase the concentration of free charge carriers (holes) in nanocrystalline Si. Additionally, in a typical back gated Si nanowire FET design, the analyte adsorbed close to the charge carrier channel affects electronic transport through the Si nanowire.^[31–34]

In this study, we present experimental findings on the adsorption of NO₂, as an oxidative gas-phase reagent, and resulting molecular transfer doping on the surface oxide-encapsulated Si

nanowires. We show the extent of the surface reaction between NO₂ and Si and its impact on the electrical properties of ambipolar Si-JNTs exhibiting different surface morphologies, for example unpassivated (referred to as P1) and with thermally grown silicon dioxide (referred to as P2 and P3). The interactions between NO₂ and Si effectively influences various electrical parameters in ambipolar Si-JNTs, resulting in a distinct dual response in both *p*- and *n*-conduction regimes to oxidative NO₂ gas. To the best of our knowledge, similar surface-transfer doping of Si nanowires leading to tuneable electrical properties and parameters in ambipolar transistors has never been previously reported. To gain deeper insights into the NO₂-Si interaction, we have employed first-principle electronic structure calculations using density functional theory (DFT) to validate the influence of physisorbed NO₂ on the Si surface in Si-JNTs.

2. Results and Discussion

Figure 1a shows a schematic of the ambipolar back-gated configured Si-JNT device with Au/Ni contact pads (a 3D schematic of the device is shown in Figure S1, Supporting Information). The scanning electron microscope (SEM) image in Figure 1b shows a representative Si-JNT, highlights a nanowire array consisting of 20 nanowires, each with a height of 20 nm and covered by a native oxide layer. All Si-JNT devices possess a channel length of 5 μm. Figure 1c,d displays transmission electron microscopy (TEM) images of cross sections of the Si-JNT device, showing the native oxide layer (device P1) and a 10 nm thick thermally grown SiO₂ layer (device P2). The TEM images reveal a crystalline nanowire core with an amorphous oxide layer at the nanowire surface.

Transfer characteristics of Si-JNTs were measured under ambient conditions. For the transfer characteristics, the back-gate voltage (V_{gs}) was swept from –30 to 30 V using a butterfly sweep (0 to 30 V, 30 to –30 V and –30 to 0 V), while the drain-to-source voltage (V_{ds}) was kept constant at 1 V. Despite the devices being nominally doped with phosphorous (*n*-type), the transfer characteristics of the Si-JNTs with different surface morphologies exhibited typical ambipolar behavior. Figure 1e shows a representative I_{ds} - V_{gs} characteristic plot of a Si-JNT with an unpassivated native oxide. The observed V-shape curve in log-linear transconductance (Figure 1e) indicates that the number of free carriers can be controlled by the externally applied V_{gs} , resulting in gate-tuneable hole and electron charge transport characteristics. The transport characteristics involve both electron (or hole) depletion and hole (or electron) accumulation. The energy band diagram for hole conduction, the off state, and the electron conduction region is presented in our previous publication on ambipolar transistor.^[35] The output characteristics (I_{ds} - V_{ds}) for a representative unpassivated Si-JNT device is shown in Figure 1f. Here, V_{ds} varies from –1 to 1 V while the back gate voltage is kept constant at 30 V. The use of Ni-based contact pads results in a clear Schottky (non-ohmic) behavior, indicating that I_{DS} is non-linearly dependent on V_{DS} (Figure 1f; Figure S2, Supporting Information).

This trend suggests that the Ni silicide Schottky junction hinders the formation of an ohmic contact for charge carriers. The Schottky barriers are modulated by the back gate, and because Schottky barrier height for holes is lower, *p*-type conductance becomes apparent, resulting in ambipolar behavior that resembles a reconfigurable field-effect transistor (RFET) rather than the

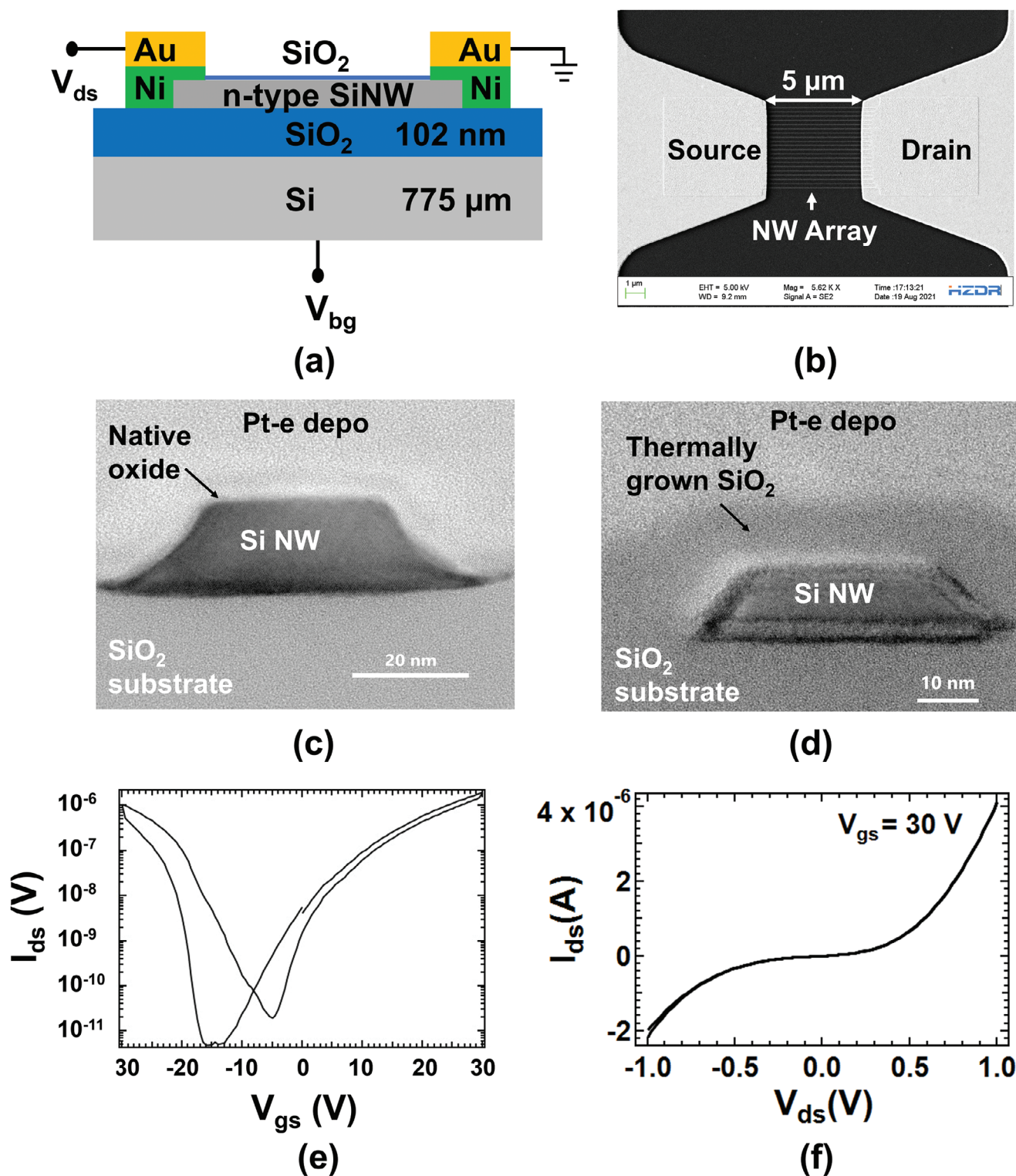


Figure 1. a) Schematic of the cross-section of the Si-JNT. b) Top-view SEM image of a Si-JNT nanowire array device. c) and d) show TEM images of the cross-section of a Si-JNT device with a native oxide (1–2 nm) and a 10 nm thermally grown oxide respectively. e) Transfer characteristics of an unpassivated ambipolar Si-JNT with a native oxide at a constant V_{sd} of 1 V. f) Output characteristics of the unpassivated ambipolar Si-JNT while sweeping V_{sd} from –1 to 1 V at $V_{\text{gs}} = 30$ V.

unipolar behavior typically observed in JNT devices. Additionally, as noted in the experimental section, the Si-JNT fabrication began with *p*-type SOI (top 20 nm layer) with a carrier concentration of $\approx 10^{16} \text{ cm}^{-3}$. During phosphorus doping (*n*-dopant) to achieve the target concentration of $\approx 10^{18} \text{ cm}^{-3}$, a recombination process occurs, resulting in a dopant concentration of $6 \times 10^{17} \text{ cm}^{-3}$ (moderate *n*-doping). This recombination likely introduced hole charge carriers in the nanowires, leading to the ambipolar behavior observed in Si-JNTs.

The SiO₂ passivated (≈ 10 nm) Si-JNT device (see, Figure S3, Supporting Information) showed improved transfer characteristics compared to unpassivated (native oxide) Si-JNT devices. The passivated devices exhibited reduced shift and hysteresis in the transfer characteristics. In unpassivated Si-JNTs, the presence of Si dangling bonds at the surfaces of the nanowires results in a high density of surface states. These states contribute to electron trapping during the forward and reverse voltage sweeps, causing a shift in the transfer curve and hysteresis. Additionally, trapped charges at the interface of the nanowires and the buried oxide further contribute to this effect. These interface-trapped charges and surface states are minimized by passivating the nanowires with a thermally grown SiO₂ shell. The “on” current observed for all Si-JNT devices with various surfaces falls within the microampere range. Additionally, it was noticeable that the “on”-current (I_{on}) for *p*- and *n*-type has different symmetries in passivated and unpassivated ambipolar devices. For example, Si-JNTs with thin (10 nm) thermally grown oxide exhibit a dominant *p*-type conduction, whereas those with a native oxide exhibit a prevalent *n*-type current (see Figure 1e; Figure S3, Supporting Information). This discrepancy could be due to the compressive radial strain induced by differently thick oxide on the Si nanowires, thereby reducing the barrier height of the electrons and holes.

We have also calculated other electrical parameters (μ and V_{th}) for ambipolar Si-JNT devices. The field-effect mobility, μ for the Si-JNT devices was determined from the following equations by considering the linear region of the transfer curve:^[36,37]

$$\mu = \frac{g_m L}{WC V_{sd}} \quad (1)$$

$$C = 2\pi\epsilon\epsilon_0 L \left[\cos h^{-1} \left(\frac{d+2h}{d} \right) \right]^{-1} \quad (2)$$

where g_m is transconductance, L and W are the length and width of nanowire, d is the diameter of the nanowire (20 nm), C is the gate capacitance for backgated nanowires ($0.349 \times 10^{-15} \text{ F}$), V_{sd} is the source-to-drain voltage (1 V), h is the thickness of the dielectric (102 nm), ϵ is the relative permittivity of SiO₂ (3.9) and ϵ_0 is the space permittivity ($8.85 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$). In ambient conditions, the typical field effect mobility calculated from the transfer characteristic curve (Figure 1e), for Si-JNTs with a native oxide range between $4\text{--}10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and between $70\text{--}120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons. The mobility range was calculated from at least five Si-JNT devices on a single chip. In contrast, under ambient condition, the mobility for Si-JNTs with thermally grown oxide (see Figure S3, Supporting Information) was between $190\text{--}222 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $215\text{--}245 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons. Notably, the calculated hole and electron mobility of unpassivated Si-JNTs is significantly lower compared to Si-JNTs with thermally

grown SiO₂ layer. The reduced mobility for unpassivated Si-JNTs can be attributed to carrier transport being hindered by scattering centers at the rough nanowire surfaces of the nanowires, compared to those passivated with SiO₂. Devices with a 10 nm thermally grown oxide exhibit significantly higher hole mobility compared to those with native oxide. This indicates a higher-quality interface in the thermally grown oxide devices, which reduces scattering and enhances hole transport. In contrast, the electron mobility (μ_e) in the native oxide devices is lower, likely due to a higher density of traps and defects at the interface, impeding electron movement.

Additionally, observed differences in mobility among devices of same type may result from fabrication inconsistencies and differing degrees of ambipolarity. For example, the native oxide device, which is predominantly *n*-type, exhibits very low *p*-type current, resulting in reduced hole mobility (device P1). In contrast, Si-JNT with a 10 nm oxide layer shows considerable *p*- and *n*-type conduction, leading to higher mobility for both conduction channels (device P2). This variability in the mobility was consistently across all the Si-JNTs studied (9 devices), both with and without NO₂ interaction (refer to Tables S1–S3, Supporting Information). The variation in ambipolar behavior and, consequently, in the device is not only due to the passivation effect but also arises from inconsistencies in the fabrication process. In particular, the nickel-silicide (NiSi) junctions play a critical role in influencing this behavior. The ambipolar behavior in silicon junction devices can be significantly affected by the quality and uniformity of these junctions, which are highly sensitive to the rapid thermal annealing (RTA) process. RTA impacts the formation and properties of the metal-semiconductor (Ni-Si) contacts, including the phase, surface roughness, and contact resistance. Variations in RTA conditions can lead to differences in Ni-Si contact properties, causing inconsistent Schottky barrier heights or doping profiles at the junction. This, in turn, alters the charge carrier injection efficiency for both electrons and holes, affecting the degree of ambipolar conduction. Therefore, the different parameter values observed for various Si-JNTs highlight the influence of fabrication precision, oxide thickness, and interface quality on carrier transport, contributing to the variations in device performance.

Extraction of threshold voltages (V_{th}) was carried out using the transconductance derivative methodology at low drain voltages ($V_{ds} = 1 \text{ V}$). The mean threshold voltage (V_{th}) for the Si-JNTs with native oxide is -21.6 V for the *p*-channel and 19.7 V for the *n*-channel conduction (and -20.0 V for the *p*-channel and 23.9 V for *n*-channel for Si-JNT with 10 nm oxide).

2.1. Interaction Between NO₂ and Si-JNTs

Electrical tests were undertaken to examine the adsorption and interaction of gas molecules with Si-JNTs. The potential to adjust the electrical conduction of Si-JNTs in both *p*- and *n*-type conduction was systematically investigated by analyzing the transport characteristics of ambipolar Si nanowires in an oxidizing environment. This investigation included an analysis of changes in the effective transistor parameters (I_{on} , μ , and V_{th}) upon NO₂ interaction.

In the ambipolar Si-JNTs, significant changes in electrical characteristics were observed in both *p*- and *n*-channel conduction

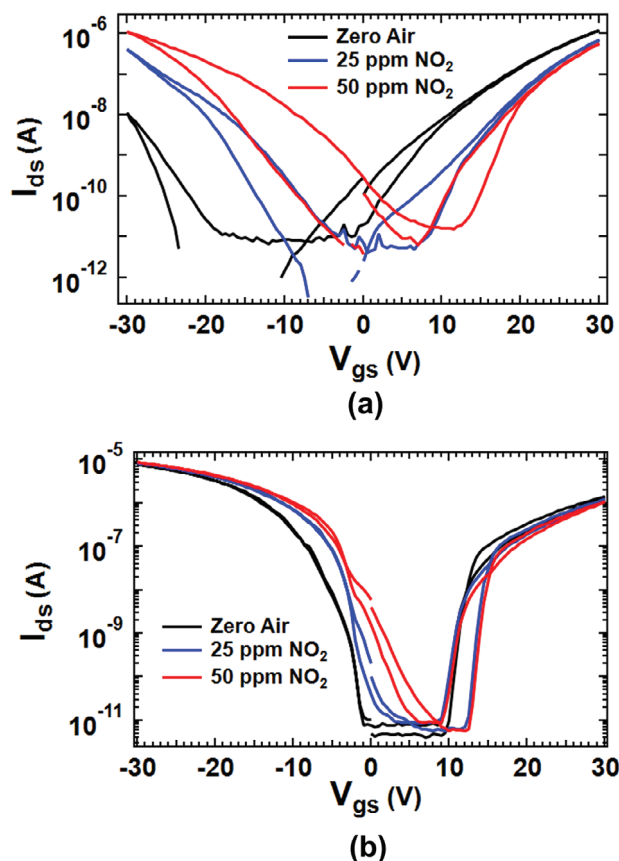


Figure 2. Transfer characteristics of Si-JNTs with a) a native oxide (P1) and b) a thermally grown oxide (10 nm, P2) under various NO₂ concentrations.

upon exposure to 25 and 50 ppm NO₂ (Figure 2). Despite exposure to NO₂ (30 min at each concentration), the transfer characteristics of all the devices retained their ambipolar nature, as evidenced by typical U-shape configuration of the I - V curves indicating both p -channel-dominated and n -channel-dominated operation. However, the current in both p - and n -conduction channels (left: p -type, right: n -type) shifted in opposite directions with NO₂ exposure. An increase in the drain current was observed with increasing concentrations of NO₂ (from 25 to 50 ppm) in the p -side, whereas a decrease in the n -type current was observed with the same concentrations of NO₂ exposure. This phenomenon is classified as a “dual interaction”. All the Si-JNT samples showed a similar change in the current with NO₂ interaction. The increase and decrease in the p - and n -current upon exposure to NO₂ exposure provides an opportunity to manipulate the symmetry and extent of ambipolarity in Si-JNTs. For example, an unpassivated ambipolar Si-JNT with n -channel dominated transport transitioned to an ambipolar device with p -channel dominated transport upon exposure to 25 and 50 ppm NO₂ (Figure 2a). Whereas upon NO₂ exposure, SiO₂ (10 nm) passivated ambipolar Si-JNT becomes more p -channel dominant with a decrease in n -channel current (Figure 2b). Significantly, a hole-mediated current can also be induced in the unipolar Si-JNT device with adsorption of 25 and 50 ppm NO₂ (see Figure S4, Supporting Information) on Si nanowire surface. Surface adsorption of NO₂ can also inject holes as charge carriers in

Si-JNTs, inducing ambipolarity in an n -doped unipolar device. Additionally, it was also observed that NO₂ interaction with Si-JNTs further increases hysteresis in both passivated and unpassivated devices (Figure 2). This hysteresis effect occurs because NO₂ adsorption on Si-JNT surface can create the electron trapping states during forward and reverse voltage sweeps. Similarly, different subthreshold swings observed for Si-JNTs with native oxide and 10 nm oxide (see Figure 2) can be attributed to the lower quality of the native oxide layer. Native oxide, or unpassivated oxide, has a higher density of oxide traps and interface states compared to thermally grown oxide, particularly at the interface with nanowire junction. These defects degrade the capacitive coupling between the gate and the nanowire channel, resulting in a poorer subthreshold swing and increased hysteresis.

Figure 3 depicts the changes in “on” drain current (I_{on}) at 30 V for each mode of the ambipolar Si-JNTs. Figure 3a,b, shows comparisons of I_{on} for ambipolar Si-JNT devices with and without a passivating layer for p -mode and n -mode, respectively. In the p -mode, I_{on} shows an increase with increasing NO₂ concentration (25 and 50 ppm), whereas a decrease in the “on” current is observed in the n -mode of the device. A more pronounced change in the “on” current for both p - and n -mode of the ambipolar devices was observed for Si-JNTs with native oxide, whereas Si-JNTs with a 10 nm thermally grown SiO₂ layer exhibited a less noticeable change in I_{on} compared to unpassivated devices. The gradual increase in the “on” current with increased exposure of the Si nanowires surfaces in the JNTs to NO₂ is attributed to the hole-donating and electron-trapping nature of NO₂.^[38] The surface interaction of NO₂ with Si is a combination of both chemisorption and physisorption. Thus, a larger number of physisorbed NO₂ sites on the Si surfaces could result in a more significant charge transfer and alteration in the conduction in Si-JNTs. As SiO₂ on the Si surfaces can impede charge transfer from the Si conductive channel, Si-JNTs with a thicker thermally grown oxide exhibit a less pronounced change in the “on” current compared to those with native oxide. For JNTs with a native oxide, the conduction channel is more substantially influenced by surface interaction with NO₂. A detailed exploration of possible charge transfer pathways due to NO₂ interaction with the oxidized surfaces of Si-JNTs has been conducted using DFT calculations.

Another noteworthy observation is the greater change in I_{on} for the hole conduction channel compared to the electron conduction channel in the ambipolar Si-JNTs. For instance, a 60% and 120% increase in the “on” current was observed in the p -channel of the unpassivated ambipolar device (Figure 3a) with the introduction of 25 to 50 ppm of NO₂, respectively. However, a decrease in current (53% and 57%) was observed in the n -channel of the same device when the NO₂ concentrations was increased from 25 to 50 ppm. We have further validated NO₂-induced conduction change in Si-JNTs using three additional unpassivated devices (Figure S5 and Table S1, Supporting Information) and two more 10 nm SiO₂ passivation (Figure S6 and Table S2, Supporting Information). All devices showed an increase in p -type current and a decrease in n -type current. Si-JNTs with an intermediate oxide barrier height (3 nm) also showed a similar trend in conduction upon NO₂ interaction (Figure S7 and Table S3, Supporting Information). However, more profound effect of NO₂ on device parameters was observed for JNT with a thinner oxide layer (Figures

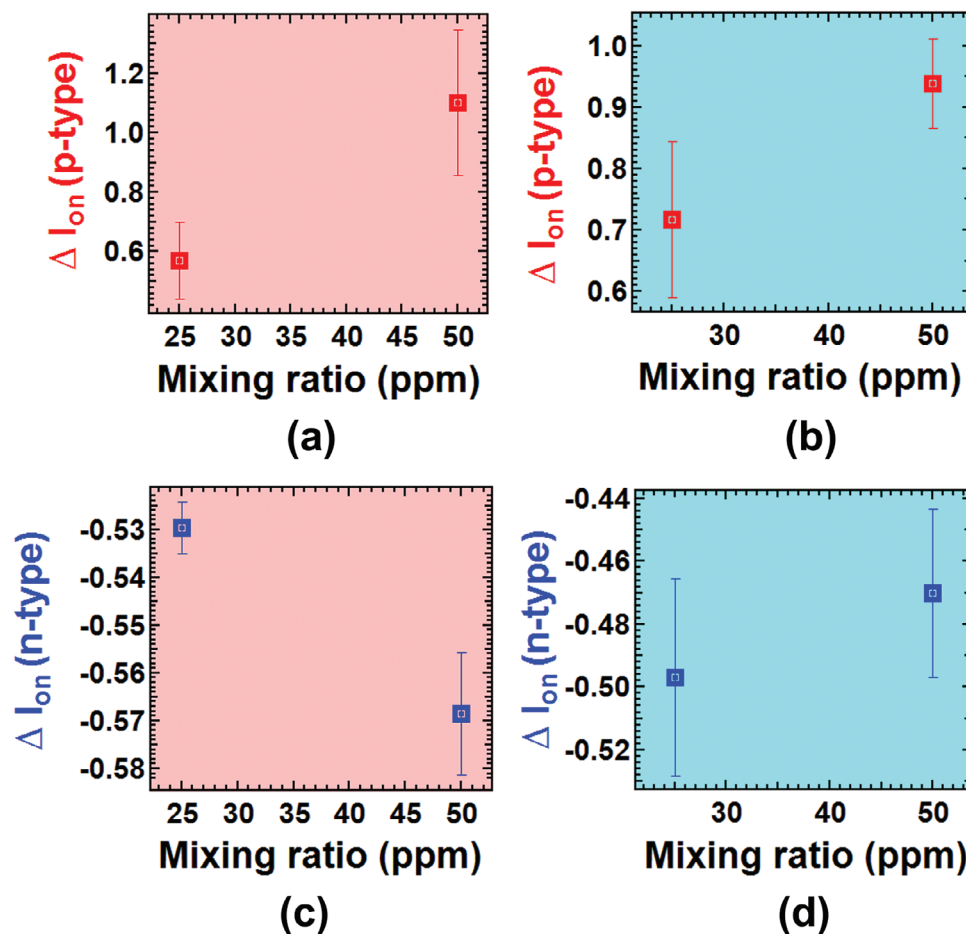


Figure 3. Comparison of ΔI_{on} upon exposure to 25 and 50 ppm NO_2 for various types of Si-JNTs, including JNT with native oxide (P1, shown in light red) for a) *p*-type and c) *n*-type conduction, and Si-JNTs with a 10 nm thermally grown oxide layer (P2, shown in sky blue) for b) *p*-type and d) *n*-type conduction.

S8 and S12c, Supporting Information), such as those with native oxide. This is because the barrier height for charge tunneling after NO_2 adsorption on the surface is proportional to the thickness of the oxide layer on the Silicon nanowire. Under NO_2 exposure, electrons are captured by the gas adsorption, potentially causing a shift of energy bands. This shift in energy levels results in a larger number of hole carriers being injected and relatively less electron carriers are injected, leading to a prominent change in *p*-type operation. Remarkably, after purging the NO_2 gas and replacing it with pure ZA at 5 SLPM, the conductance and electrical transport properties of the Si-JNTs recovered within ≈ 4 h to nearly their original values (see Figure S9, Supporting Information).

These observations demonstrate how NO_2 , as an adsorbed molecular layer, can adjust both *p*- and *n*-current in an ambipolar device, thereby tuning the device characteristics “ex situ”. As depicted in Figures 2 and 3, upon exposure to NO_2 , I_{on} in the negative V_{gs} region exhibits a noticeable increasing trend, while I_{on} in the positive V_{gs} region shows a decreasing trend. The transition voltage (V_T), corresponding to the transition points of the U-shaped transfer curve in an ambipolar device (when depletion-dominated transport shifts to accumulation-dominated trans-

port) shifts with the extent of NO_2 exposure (see Figure S10, Supporting Information). For all the devices, V_T in hole-channel conduction shifts to the positive side (decreases), whereas it shifts to the negative direction in electron-channel conduction upon NO_2 exposure. Since NO_2 acts as electron acceptor, during V_G sweeps from +30 V to V_T (electron depletion), the electron density decreases, resulting in reduced current. Conversely, from V_T to -30 V (hole accumulation), hole density increases, thus increasing current when NO_2 molecules interact with the ambipolar Si-JNT. A similar shift in V_T has been observed for the 10 nm thermally grown oxide devices, but to a lesser extent as compared to the unpassivated devices (see Figure S11, Supporting Information). The entirety of the results indicates that the symmetry in the hole and electron-dominated conduction in the ambipolar Si-JNTs can be reversibly tuned by adsorption and desorption of NO_2 gas molecules, even at relatively low concentration of 25 and 50 ppm. Enhanced *p*-type (*n*-type) and reduced *n*-type (*p*-type) conductivity can be achieved by exposing the Si-JNT surfaces to NO_2 . Significantly, a similar manipulation of ambipolar characteristics of Si-JNTs can also be achieved with a much lower NO_2 concentration of 2.5 ppm (see Figure S8, Supporting Information). A clear change in drain current is observed on both

conduction sides of the ambipolar devices (Figure S12a, Supporting Information) even at this low concentration of 2.5 ppm of NO₂. Additionally, a hole mediated current can also be induced to implant ambipolarity into a *n*-type unipolar Si-JNT device (Figure S12b, Supporting Information). However, unpassivated ambipolar Si-JNT devices showed the highest change in on current, especially for the *p*-type conduction, upon exposure to 2.5 ppm NO₂ compared to *n*-type unpassivated Si-JNTs and ambipolar Si-JNT with thermally grown oxide, as observed for high NO₂ exposure (Figures S8 and S12c, Supporting Information).

2.2. Interaction Mechanism of NO₂ on Si-JNTs

NO₂, an oxidizing gas, acts as an acceptor of electron due to its high electronegativity and molecular structure. The presence of oxygen atoms, which are highly electronegative, gives NO₂ a strong affinity for electrons, making it an effective electron acceptor. Additionally, the NO₂ is a radical species with an unpaired electron, leading to electron deficiency. This deficiency drives the molecule to seek out electrons to achieve a more stable electronic configuration. Consequently, NO₂ can directly adsorb to the Si surface in JNTs devices, either trapping electrons or interacting with chemisorbed oxygen species.^[27,30] This adsorption process facilitates charge transfer, resulting in the removal of additional electrons from the bulk, specifically from the conduction band of Si. Also, the adsorption of NO₂ molecules, which captures free electrons at the surface, leads to the release of trapped holes into the valence band of Si, thereby increasing conductivity (on the *p*-side). Such changes in electrical conductivity subsequently affect the electrical characteristics of the Si-JNTs.

DFT studies have shown that NO₂ adsorption on Si leads to the formation of various surface nitrogen-containing molecular groups and the passivation of dangling bonds on the surface.^[39,40] This interaction subsequently influences the electrical conductivity of Si.^[22,38–40] For example, surface transfer doping and the resulting changes in electrical properties have been observed in Si nanowires transistors with high surface to volume ratio^[26,41,42] (diameters ≈70–200 nm). Guo et al.^[43] reported that partial electron transfer from Si silicon core to the surface is negligible for bulk Si but significant for surface-dominated Si nanowires. They calculated an incorporation of ≈10¹⁹ cm^{−3} positive charges for an additional 0.06 electron charges at each surface hydrogen atom in a 100 nm nanowire. Similarly, we have also observed a considerable change in conduction (e.g., a 100 fold increase in *p*-type conduction for *n*-dominant ambipolar Si-JNTs, see Table S1, Supporting Information) in oxide-encapsulated Si nanowires with a width of 20 nm. We also provide DFT calculations supporting physisorption of NO₂ on O-terminated Si surfaces and resulting charge transfer. Until now, the majority of calculations and predictions on NO₂-mediated charge transfer in Si are based on the postulation of a H-terminated Si surface, contrary to the Si-O surface of Si-JNT channels. To identify potential atomic-scale configurations and mechanisms governing the interaction between NO₂ and Si-JNTs, resulting in NO₂-induced molecular doping and changes in Si-JNT conduction, we performed systematic DFT calculations. These calculations focused on the interactions between NO₂ molecules and SiO₂ layer on the surface facets of the Si-JNT channels. Of significance is the inter-

action of NO₂ with the SiO₂ layers, given that all the Si nanowires are capped by either a thermal oxide layer or a native oxide. We explored several possible configurations of NO₂ molecules above a SiO₂ surface, modeled as alpha quartz with a supercell slab comprising of a total of 119 atoms. The most stable configuration observed involves physisorption of the NO₂ molecule, as shown in Figure 4a. Figure 4b illustrates the calculated electronic density of states (DOS) for the physisorbed configuration.

The illustrated DOS reveals that physisorbed NO₂ molecules generate several states within the energy bandgap of SiO₂. Specifically, four NO₂-related gap states are identified, with two (labeled as (1) and (2) in Figure 4b) are occupied and two are unoccupied (labeled as states (3) and (4) in the DOS, Figure 4b). The presence of these NO₂-induced states is consistent with experimental observations, indicating the electron-accepting nature of NO₂ molecules. While the exact positions of the unoccupied gap states, (3) and (4), may be uncertain due to the known gap underestimation by DFT, their calculated energies, relative to the bandgap of SiO₂, are proportionally comparable with the experimentally determined alignment^[44] of the Si bandgap within the SiO₂ gap. If states (3) and (4) reside within the bandgap of an underlying Si substrate, they can indeed trap electrons from the conduction band of the Si substrate via tunneling, as observed experimentally. A schematic of the proposed mechanism for NO₂-induced electron withdrawal from the Si conduction band (CB) to an NO₂-related gap state (indicated on the left with a small horizontal line) is shown in Figure 4c. An electron initially located in the CB of the Si substrate tunnels through (illustrated as a dotted line) the SiO₂ layer and becomes trapped by the physisorbed NO₂ molecule on the SiO₂ surface.

Figure 3 illustrates that as the thickness of the SiO₂ layer coating increases from 1–2 nm (for native oxide) to 10 nm, there is a decrease in the impact of NO₂ on current conduction. This effect can be attributed to the thick SiO₂ layer on the sidewalls of the nanowires, which prevents the exchange or transfer of charges from the adsorbed NO₂ gas molecules to the Si nanowire channels. Consequently, this impedes the manipulation of electrical parameters in the ambipolar Si-JNTs. Additionally, this observation serves as compelling evidence that the charge-transfer process and the subsequent molecular gating effect are pivotal mechanisms underlying the highly sensitive manipulation of the field-effect properties of Si nanowires with NO₂. To validate the significance of NO₂ adsorbed states within the SiO₂ energy bandgap in electron trapping from Si conduction band via tunneling, we have tested Si-JNT device with an Al₂O₃ top-layer on Si nanowire channel (Figure S13a, Supporting Information). This Si-JNT device was subjected to 25 ppm NO₂ exposure. As depicted in the transfer curve (Figure S13b, Supporting Information), no significant changes in the *p*- or *n*-current were observed upon exposure to NO₂. This outcome suggests role of energy gap alignment, as disclosed from DFT calculation, in the selective role of Si-SiO₂ system for characteristics manipulation of Si-JNTs via NO₂ interaction.

2.3. The Impact of NO₂ on Different JNT Parameters

To test the proposed NO₂-mediated charge-transfer mechanism's ambipolar conduction variability and its potential to adjust

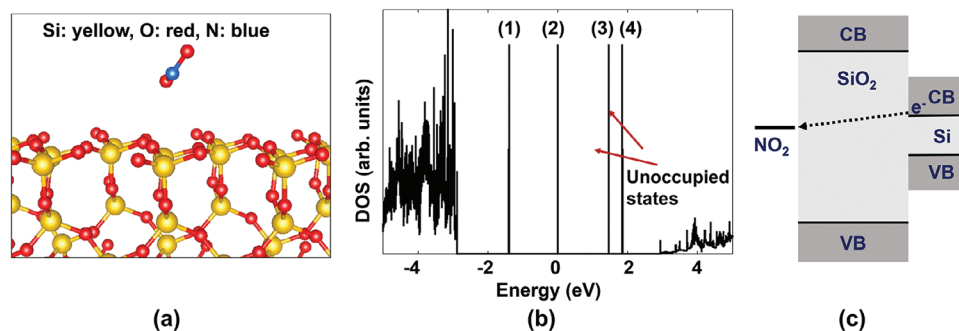


Figure 4. a) A physisorbed NO₂ molecule above a SiO₂ surface (Si: yellow, O: red, N: blue spheres). b) Electronic DOS corresponding to the configuration shown in (a), where VB (CB) denotes the valence (conduction) band of the material, and states (1)–(4) are located within the energy bandgap, with the energy of the highest occupied state set to zero. c) A schematic showing a possible pathway for charge transfer.

the electrical properties of Si-JNTs, we performed a systematic analysis of the transport characteristics and associated transistor parameters in various NO₂ environments. Si-JNTs were assessed in a controlled chamber exposed to flowing NO₂ at two different concentrations: 25 and 50 ppm. Various transistor parameters, such as threshold voltage and carrier mobility, were calculated and compared across different Si-JNT configurations.

The threshold voltage serves as a fundamental metric for characterizing JNTs. In JNTs, it represents the gate voltage required to fully deplete the device layer, that is, an “off” state sim-

ilar to an accumulation-mode device, in contrast to MOSFET where it is defined at the onset of inversion. Both the threshold and flat band voltages play critical roles, defining a device’s operating range. Upon exposure to increased NO₂ concentrations, the threshold voltage for hole-channel formation (hole accumulation) shifts positively (decreases), while that for electron-channel transport (electron accumulation) increases (Figure 5). These shifts can be attributed to the electron-trapping effect of NO₂. The most significant threshold voltage change for hole accumulation was observed in samples with native oxide (Figure 5a),

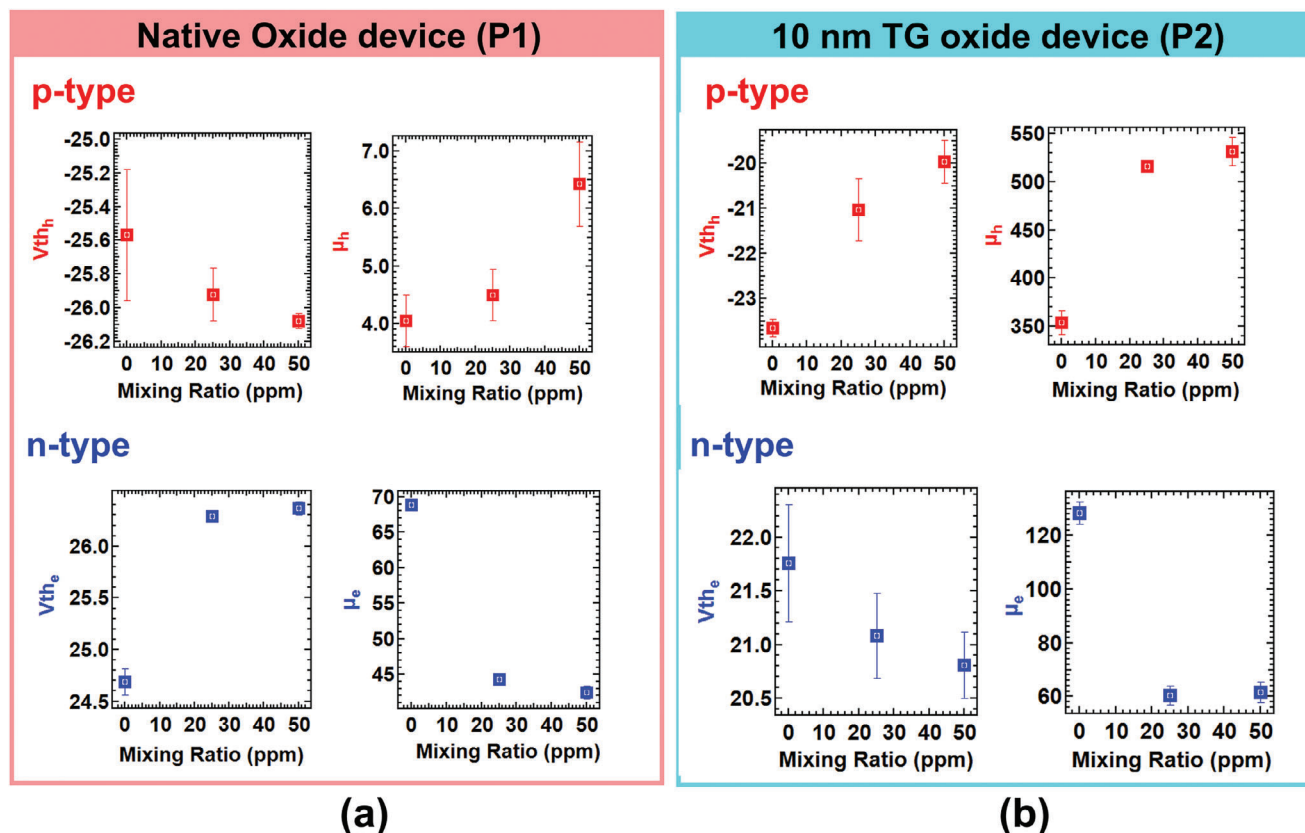


Figure 5. Impact of exposure to 25 and 50 ppm of NO₂ on the mobility (μ) and threshold Voltage (V_{th}) in ambipolar Si-JNT devices with a) native oxide (P1) and b) thermally grown oxide (P2) devices for p-type (top panel; red) and n-type (bottom panel; blue) conduction.

changing from -27 V (ZA) to -24.8 V (25 ppm NO_2) and to -21.4 V (50 ppm NO_2), with thermal oxide (Figure 5b) samples exhibiting a less pronounced change compared to the Si-JNTs with native oxide. DFT calculations show that NO_2 molecular adsorption on ambipolar Si-JNT surfaces, trapping electrons from the Si nanowire channels and leaving negative charges on the sidewalls. This induces an additional negative gating effect on the Si-JNTs, causing a positive shift in the transfer curve for p -conduction and negative shift in the n -conduction of the ambipolar device. This shift toward more positive threshold voltage values correspond to p -type doping by the deposited NO_2 molecules, introducing additional mobile charges into the semiconductor and shifting the Fermi level toward the highest occupied energy level of the semiconductor. Additionally, the observed positive shift in the threshold voltage suggests the generation of free charge carriers (hole) alongside increased conductivity. We have observed that the threshold (turn-on) voltage shifts to the right with NO_2 exposure (Figure 2). As all measurements were conducted at the same scan rate, this indicates that, with NO_2 interaction, the switch-on time for the n -conduction increases, while it decreases for the p -type conduction. However, the switch-on speed is also influenced by the exposure time and concentration of NO_2 .

In addition to the dual response of current and the shift of threshold (turn-on) voltage, the interaction with NO_2 also requires charge mobility to be considered as another parameter. Figure 5 compares the evolution of charge mobility for both holes and electrons when exposed to 25 and 50 ppm NO_2 . The impact of NO_2 exposure is most pronounced for hole mobility, which increases from a mean value of 4 to 4.5 and $6.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the native oxide, while electron charge mobility decreases from 68.9 to 44.3 and $42.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with 25 and 50 ppm of NO_2 (Figure 5a). The increased mobility (p -type) with NO_2 indicates enhanced hole transport in the Si channel. For devices passivated with thermally grown oxide, mean hole mobility increases from 353.7 to 516.2 and $531.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and electron mobility decreases from 128.3 to 60.5 and $61.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with 25 and 50 ppm of NO_2 (Figure 5b). Differences in the initial mobility values may arise from variations in the passivation of Si-JNTs, inconsistencies in fabrication and differing degrees of ambipolarity among the devices. This decrease in mobility indicates an increased density of shallow trap states at interfaces, which can lead to a lower measured (effective) mobility.^[45] Si-JNTs possesses a high concentration of charge trapping sites, thereby limiting electron mobility through trapped charge scattering. Conversely, the enhanced mobility in p -type conduction could result from the passivation of intrinsic shallow trap states by certain impurity ionized charge carriers, facilitating conductivity through the film. The substantial increase in hole concentration fills the trapping sites effectively and screens the trapped charges, thereby significantly increasing hole mobility with NO_2 concentration. We observed consistent changes in the JNT parameters across all devices: four Si-JNTs with native oxide, three with 10 nm thermally grown SiO_2 and two with 3 nm thermally grown SiO_2 . Specifically, we noted an increase in the threshold voltage for p -type conduction, a decrease in n -type conduction an increase in hole mobility and decrease in electron mobility (see Figures S5–S7 and Tables S1–S3, Supporting Information). Of note, although we used 30 min as the standard exposure time to demonstrate

the effects of NO_2 on Si-JNT parameters, changes were also after just 5 min of exposure (see Figure S14 and Table S4, Supporting Information). A clear, gradual time-dependent change in the Si-JNT parameters was observed with 25 ppm NO_2 exposure.

The number of charge carriers has been calculated for the native oxide based on output characteristics using the equation below:

$$n = \frac{I_{ds}L}{q\mu V_{ds}A} \quad (3)$$

where I_{ds} is the drain to source current, V_{ds} is the drain to source voltage (set at 1 V), L and A are the length and surface area of nanowire (Si JNT channel) respectively, q is the elementary charge and μ is the carrier's mobility. Upon exposure to 25 ppm NO_2 , unpassivated ambipolar Si-JNTs exhibit an increase in the number of holes has from 1.7×10^{18} to 3.5×10^{18} , accompanied by a decrease in the number of electrons from 5.5×10^{18} to 3.6×10^{18} . This implies a "pseudo" molecular doping instigated by the gas phase NO_2 . Conversely, for ambipolar Si-JNTs with a 10 nm grown oxide layer, the number of holes show a tiny increase from 1.7×10^{19} to 1.9×10^{19} , while the number of electrons remains unaffected upon exposure to 25 ppm NO_2 . In summary, the carrier concentration approximately doubles for holes and decreases by approximately half for electrons in unpassivated Si-JNTs, whereas there is no discernible change in carrier concentration for Si-JNTs with a 10 nm grown oxide layer. This phenomenon may be attributed to the presence of a thick oxide layer (≈ 10 nm) for thermally grown oxide passivated Si-JNT, which potentially inhibits charge transfer processes.

3. Conclusion

In summary, we have demonstrated the potential of molecular doping and tuning of ambipolar Si-JNTs characteristics in both electron and hole conduction mode with the physisorption of gaseous NO_2 . Various characteristics of the Si-JNT, including I_{on} , V_{th} , and μ , have demonstrated dynamic changes in both the p - and n -transport channels of the ambipolar JNT when exposed to NO_2 . Notably, I_{on} at the negative V_g region displays an increasing trend while I_{on} at the positive V_g region displays a decreasing trend upon exposure to NO_2 . Significantly, an ambipolarity could be induced in a unipolar Si-JNT by the molecular adsorption of NO_2 on the Si surface. The impact of NO_2 exposure (25 and 50 ppm) is significant for both hole mobility and electron mobility which rises and decreases by 1.6 times respectively with 50 ppm NO_2 interaction. Additionally, the threshold voltage decreases for p -channel transport and increases for n -channel transport in response to NO_2 exposures. These observed response behaviors are attributed to the hole-donating and electron-trapping nature of NO_2 , as demonstrated by the increase in hole carrier concentration in Si-JNTs with adsorbed NO_2 . Encouragingly, these devices can be bought back to its initial electronic state by withdrawing the NO_2 exposure to the Si-JNTs.

This study illustrates that an oxidizing gas (such as NO_2), when adsorbed as molecular layers, can effectively adjust both p - and n -currents in an ambipolar device, thereby fine-tuning its device characteristics "ex situ". These observations suggest that NO_2 can be used as an active p -type dopant for thin Si nanowires. This

gas-phase doping approach offers a scalable solution for doping large scale device. For designing and fabricating larger devices intended for future high-density applications, it is possible to engineer the length and width of nanowires, as well as the size of the contact pads and interconnects. We also suggest the ambipolar transistors have potential for achieving highly selective and sensitive gas detection by leveraging their dual response alongside JNT parameters such as “on”-current, threshold voltage, and charge mobility, especially when combined with additional rigorous machine learning experiments involving cross-reactive gases.

4. Experimental Section

Fabrication of Si-JNT Devices: Nanowire devices were fabricated from ultra-thin silicon-on-insulator (SOI) substrates, comprising stacked layers of silicon-insulator-silicon. The layer specifications were: a 775 μm thick *p*-doped bulk Si carrier substrate, a thermally grown SiO_2 buried oxide layer with a thickness of 102 nm and a 20 nm intrinsic top Si layer (device layer) as shown in the schematic in Supporting Information (Figure S1, Supporting Information). SOI substrates were employed to minimize parasitic capacitance within the substrate, thereby enhancing device performance. The diced SOI substrate dimensions for device fabrication were 1 cm $\times$ 1 cm. Ion implantation and flash lamp annealing (FLA) of the SOI substrates were undertaken, with doping via a chain implantation process using phosphorus (*n*-type doping). Nanowires were fabricated through a top-down approach using electron beam lithography (EBL) and reactive ion etching (RIE).^[35,46] A negative tone resist, 2% hydrogen silsesquioxane (HSQ) (XR-1541 from DuPont), was used to create the nanowire pattern via EBL. Nanowires were exposed using a RAITH e-LINE PLUS EBL system, with exposure parameters optimized to obtain specific dimensions and morphology. A SENTECH inductively coupled plasma reactive ion etching (ICP-RIE) Si 500 system was used to anisotropically transfer the HSQ pattern into the device layer. After nanowire fabrication by EBL and RIE, thermal oxidation of the nanowires was performed to obtain a uniform SiO_2 layer (3 and 10 nm) on the surfaces of the nanowires. The oxidation process was conducted at a temperature of 900 $^{\circ}\text{C}$ under an O_2 atmosphere for several seconds to achieve thin, high-quality oxide films. Lastly, contact pads were patterned using EBL, and nickel (20 nm) and gold (140 nm) were deposited on the substrate using e-beam deposition to form source-drain contacts. Samples were annealed using FLA (at 3.6 kV for 3 ms under N_2 atmosphere) to reduce contact resistance.^[47] A new process based on rapid thermal annealing (RTA) was implemented to further reduce contact resistance. After fabrication of the metal contacts and initial characterization, RTA was performed in a N_2 environment at a temperature of 450 $^{\circ}\text{C}$ for 30 s. RTA facilitates vertical diffusion of silicide to create Schottky junctions at the source and drain contacts, enabling both electron and hole conduction, resulting in device performance similar to Schottky barrier-based FETs.^[48] Detail of the silicide formation at the Ni-Si contacts under RTA and FLA conditions is described in our previous works.^[47,49]

Morphological Characterization of Si-JNTs: Si-JNTs morphology were analyzed using a FEI quanta 650 scanning electron microscope (SEM) and a Jeol 2100 transmission electron microscope (TEM) operated at 200 kV. Samples were prepared for TEM cross-sectional imaging with an FEI Helios Nanolab 600i system. The sectioned Si-JNT device was transferred to a TEM grid and imaged by transmission electron microscopy (TEM, FEI Titan 80 operating at 300 kV).

Electrical Characterization of Si-JNTs: The electrical characterization of Si-JNTs was performed using an electrical analysis setup consisting of two Keithley 2450 source meters interfaced to a Nextron probe station. All electrical measurements (*I*-*V* characteristics) were performed using the Keithley Kickstart software, version 2.2.1.

Si-JNTs were exposed to and compared under various NO_2 flowing environments with different mixing ratios ranging from 2.5 to 50 ppm. Experiments examining the interaction of NO_2 with Si-JNTs were performed in a

semi-customized gas-tight micro probe station with a volume of 100 cm^3 (Nextron). Zero air (ZA), that is, mixture of nitrogen and oxygen without any trace gas, particles, and humidity, was introduced at a rate of 10 standard litres per minute (SLPM) for 20 min, followed by exposure to specific NO_2 mixing ratios for 30 min. Prior to exposure to ZA, Si-JNTs were dried under vacuum for 45 min. All experiments were carried out at room temperature and atmospheric pressure. The transfer characteristics of Si-JNTs were recorded under ZA and at each NO_2 exposure to evaluate the transistor parameters such as threshold voltage (V_{th}), field-effect mobility (μ_h , μ_e), and on-current (I_{on}), as well as to analyze the effect of NO_2 concentrations on these parameters.

Density Functional Theory (DFT) Calculations: To elucidate the atomic-scale details for key interactions between NO_2 molecules and the oxidized surfaces of the Si nanowires (in the Si-JNTs), quantum-mechanical DFT calculations were undertaken. The calculations were performed using the DFT code VASP^[50] employing with an energy cutoff of 500 eV, projector augmented waves (PAWs),^[51] and the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof^[52] exchange-correlation (xc) functional. Non-bonding Van der Waals interactions were accounted for within the DFT-D3 scheme.^[53] Structural representations were generated using the software VESTA.^[54]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ambipolar device, density functional theory, junction less transistor, nitrogen dioxide, pseudo molecular doping, silicon nanowire

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