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Acceptor-Compensated Charge Transport and Surface Chemical Reactions in Au-Implanted SnO₂ Nanowires

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A new deep acceptor state is identified by density functional theory calculations, and physically activated by an Au ion implantation technique to overcome the high energy barriers. And an acceptor-compensated charge transport mechanism that controls the chemical sensing performance of Au-implanted SnO₂ nanowires is established. Subsequently, an equation of electrical resistance is set up as a function of the thermal vibrations, structural defects (Au implantation), surface chemistry (1 ppm NO₂), and solute concentration. We show that the electrical resistivity is affected predominantly not by the thermal vibrations, structural defects, or solid solution, but the surface chemistry, which is the source of the improved chemical sensing. The response and recovery time of chemical sensing is respectively interpreted from the transport behaviors of major and minor semiconductor carriers. This acceptor-compensated charge transport mechanism provides novel insights not only for sensor development but also for research in charge and chemical dynamics of nano-semiconductors.

Fabrication of p-type bulk SnO₂ is proven difficult due to the high formation energy of tin vacancies which are the only possible acceptor state in pure SnO₂¹. Recent developments in controlled synthesis and fabrication of metal-oxide-based nanomaterials such as nanowires², nanofibers³, and nanorods⁴ have, however, opened up new possibility to activate deep acceptor levels in nanocrystal SnO₂, which influence the surface charge transport process and may further enhance surface chemical reactions that are critical to gas sensing⁵.

Ion implantation involves the incorporation of energetic ions in the nanowires, where the depth of penetration of the ions can be controlled easily. Although ion implantation is widely reported for improved sensing performances^{6,7}, there has been no investigation about acceptor modified charge transport and the corresponding chemical reaction in metal-implanted nanowires.

In this work, an ion implantation technique is applied to activate a deep acceptor level in the electronic structure of SnO₂. On the basis of experiment and modeling approaches, a charge transport mechanism and a predominant factor controlling the chemical sensing are established. The electron-carrier concentrations in the Au-implanted SnO₂ nanowires are estimated, and a relationship between the carrier concentrations and electron scattering (due to structural defects and surface chemistry) is obtained. Furthermore, we speculate that the experimental sensor responses and recovery times are influenced by the electron-phonon coupling for the embedded electron gas from the Au atoms. This model shows that the surface chemistry is the predominant factor affecting the electrical resistivity, and is thus the source of the improved chemical sensing.

Results

DFT calculations. To locate the acceptor levels in Au-implanted SnO₂, its electronic properties were calculated by DFT methods. SnO₂ has a rutile crystal structure in the space group *P4₂/mnm* (No. 136). In this work, we have used a 2 × 2 × 3 unit cell of SnO₂ with one Sn atom substituted with Au giving a stoichiometry of AuSn₂₃O₄₈ as shown in Fig. 1a.

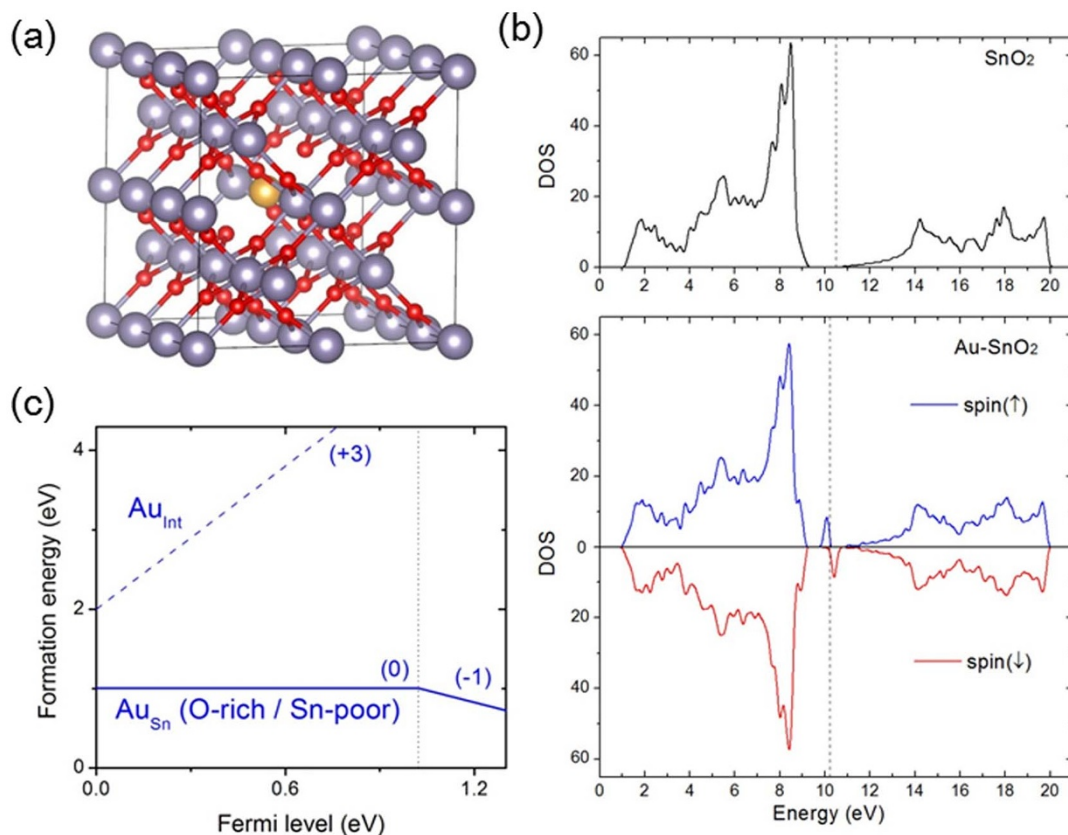


Figure 1 | DFT analysis. (a) Crystal structure of Au-SnO₂. (b) Density of states (DOS) of pristine SnO₂ and Au-implanted SnO₂. (c) Calculated formation energy for substitution Au impurity in SnO₂ under O-rich conditions. The dotted line indicates the case of interstitial Au in SnO₂.

The formation energy of an impurity Au in a charge state q occupying Sn site is calculated by⁸

$$E_{form}(Au_{Sn}^q) = E[Au - SnO_2] - E[SnO_2] - \mu_{Au} + \mu_{Sn} + q(E_{VBM} + E_F + \Delta V) \quad (1)$$

where $E[Au - SnO_2]$ and $E[SnO_2]$ are the total energies of doped and perfect SnO₂, respectively, μ_{Au} and μ_{Sn} are the chemical potentials of Au and Sn, respectively. The last term describes the dependence on the Fermi level (E_F) measured from the valence band edge. E_{VBM} is a position of the valence band maximum (VBM) in the perfect system, and ΔV is a correction term aligning the VBM in the doped and perfect crystal supercells. Chemical potential $\mu_i = \mu_i^{ref} + \Delta\mu_i$ where μ_i^{ref} is calculated for the bulk phases of Au and Sn, while $\Delta\mu_i$ may vary corresponding to certain growth conditions (e.g. Sn-rich/O-poor or Sn-poor/O-rich). Since Perdew-Burke-Ernzerhof (PBE) calculations typically underestimate band gaps, we use an extrapolation correction in order to compare transition levels and formation energies with experimental band gaps.

The formation energy of neutral Au impurity under Sn-poor/O-rich conditions (which should be more suitable for doping at cation site in SnO₂) is found to be about 1 eV. The calculated value is quite large due to the larger atomic size in Au than in Sn. The positive sign of Au formation energy suggests that spontaneous incorporation of Au in SnO₂ is difficult to achieve under normal growth conditions. Therefore, high-energy implantation is required to activate the deep acceptors in Au-implanted SnO₂ samples.

Density of states (DOS) analysis shows that pure defect-free SnO₂ is a semiconductor with a band gap of 1.26 eV, being in reasonable agreement with existing theoretical studies on the same level of theory^{9–11}. Meanwhile, Au substitution causes a shift of the Fermi level in the direction of the valence band indicating a charge transfer from

SnO₂ to Au atom. When Au substitutes Sn atoms, it produces extra electronic states inside the SnO₂ band gap as shown in Fig. 1b. The impurity band contains a large contribution of Au 5*d*-orbitals and is spin-polarized. In addition, we observe hybridization between Au 5*d* and O 2*p* levels in the Fermi level region.

Figure 1(c) presents the formation energies of Au dopants in SnO₂ as a function of the Fermi level position. The range of the Fermi energy is given by the calculated valence-band maximum (VBM, 0 eV) and conduction-band minimum (CBM, 1.26 eV). For each dopant, only the charge states that are most energetically favorable at a given Fermi energy are shown. We find that Au impurities prefer the substitutional site. The interstitial site is not favorable at any conditions due to the large atomic size of Au. The 0/−1 ionization level for Au impurity is 1.02 eV (Fig. 1c), indicating that Au is a deep acceptor. Therefore, Au doping in SnO₂ may serve to “kill” the electrons in the system, and shift the Fermi level towards the valence band side. This is schematically described in Fig. 2. These findings explain a decrease in concentration of electron carriers in Au-implanted SnO₂ (to $\sim 10^5$ from $\sim 10^6$ cm^{−3}) which will be described in later sessions.

Microstructure of Au-implanted SnO₂ nanowires. Figure 3 shows the microstructure of the networked SnO₂ nanowires used for the sensor platform. Fig. 3a schematically shows the procedure used to grow the networked SnO₂ nanowires, which is described in detail in Methods part. The plan-view FE-SEM image in Fig. 3b clearly demonstrates the entanglement of nanowires grown selectively on the adjacent electrode pads, leading to an immense number of nanowires involved in the gas-sensing process, and thus, resulting in the fabrication of highly reproducible and reliable gas sensors. The inset figure shows the networking nature more clearly. Figure 3c shows a cross-section image showing the entanglement more

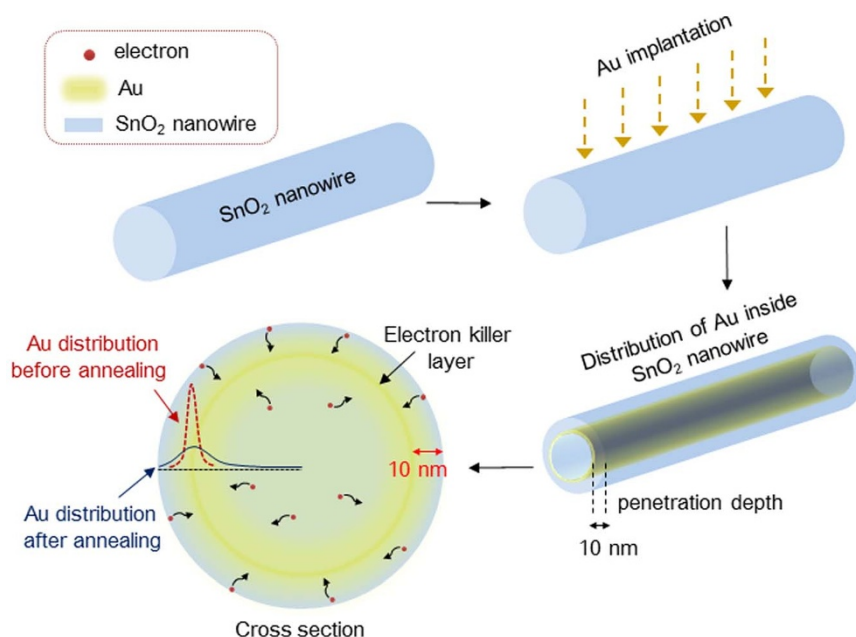


Figure 2 | Schematics of Au implantation. Schematics describing the penetration of Au into the SnO₂ nanowire, acting as an electron-killer layer.

clearly. Figure 3d shows a representative TEM image taken from an individual nanowire, revealing that it is single-crystalline. The inset figure is a selected-area electron diffraction pattern, again demonstrating its high crystalline quality. The shape and geometrical dimensions of the networked SnO₂ nanowires for superior sensing performances are discussed in detail in our previous report¹².

Au ions were implanted into these networked SnO₂ nanowires with different dose levels (10^{13} or $10^{14}/\text{cm}^2$). First, we investigated whether the implantation process influenced the surface morphology of the nanowires. Supplementary Fig. S1 displays typical

FE-SEM images of Au-implanted networked SnO₂ nanowires. The insets are the corresponding high-magnification images showing the surface morphology more obviously. For comparison, an image showing the microstructure of pristine SnO₂ nanowires (without Au implantation) is included in Supplementary Fig. S1a. As shown in Supplementary Fig. S1b, the surface of each SnO₂ nanowire implanted with a dose of $10^{13}/\text{cm}^2$ Au⁺ has a smooth surface similar to that of the pristine SnO₂ nanowires shown in Supplementary Fig. S1a. SnO₂ nanowires implanted with a dose of $10^{14}/\text{cm}^2$ Au⁺ (Supplementary Fig. S1c) also show

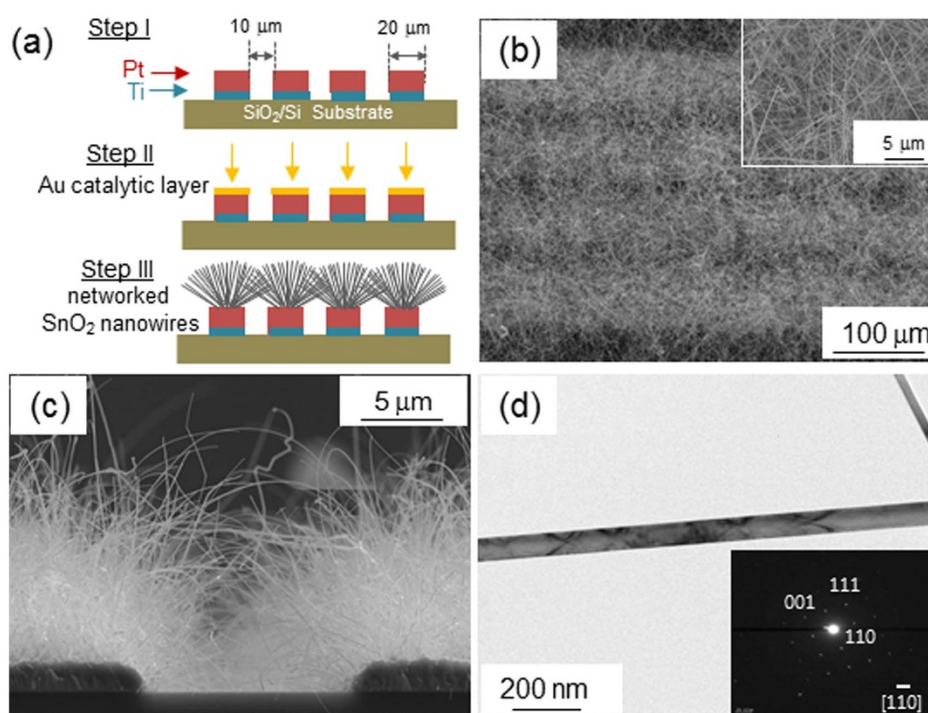


Figure 3 | Microstructure of Au-implanted SnO₂ nanowires(a) Schematic illustration of selectively-grown, networked SnO₂ nanowires on a patterned electrode. (b) Plane and (c) Cross-section field-emission scanning electron micrographs of networked SnO₂ nanowires. (d) Transmission electron micrograph of single SnO₂ nanowire. The inset shows a selected-area electron-diffraction pattern.



no distinctive difference in surface morphology from the pristine ones.

TEM observations were conducted for further investigation of the effect of Au implantation on the microstructure; the results are shown in Supplementary Fig. S2 (the insets are the corresponding low-magnification TEM images). As shown in Supplementary Fig. S2, there is no significant difference between the implanted samples and the pristine one. In addition, all the samples show clear lattice fringes, indicating that the subsequent thermal annealing completely eliminated any crystalline disorder in the nanowires that might have been incorporated during Au implantation. From these TEM results together with the FE-SEM results, we conclude that the Au implantation caused no detectable structural change in the pristine SnO₂ nanowires.

XPS measurements were made to confirm the existence of Au-related species in the nanowires. Supplementary Fig. S3a shows the XPS spectrum taken from the networked SnO₂ nanowires implanted with 10¹⁴/cm² Au⁺. No peaks originating from Au-related species are observed. The spectrum from the pristine SnO₂ nanowire sample showed the same feature (Supplementary Fig. S4). According to the Monte Carlo simulation code SRIM, when 10¹⁴/cm² Au⁺ is implanted at an accelerating voltage of 30 kV into the SnO₂ lattice, the atomic concentration of Au in the implanted region is about 0.36 at%, and the penetration (implanted) depth is about 10 nm, which is deeper than the detection depth of XPS, meaning that most of the implanted Au ions are out of range for XPS measurements. Therefore, it is not so easy to detect the implanted Au in SnO₂ by XPS. Hence, we performed EDS analysis to confirm the implantation of Au ions in the networked SnO₂ nanowires using the EDS analyzer installed in the FE-SEM equipment. The EDS spectrum for SnO₂ nanowires implanted with a dose of 10¹⁴/cm² Au⁺ is shown in Supplementary Fig. S3b. The EDS analysis shows that the nanowires were composed of Sn, O, and Au. The peak at around 2.1 keV, which corresponds to the energy level of gold, is observed clearly, indicating the presence of Au⁺ in the SnO₂ nanowires. In order to further identify the presence of Au in the SnO₂ nanowires, EDS line scans for elemental analysis were performed using the EDS analyzer installed in the TEM equipment. The EDS line spectra are shown in Figure 4, obviously revealing the presence of Au in the SnO₂ nanowire.

Sensing behavior of Au-implanted SnO₂ nanowires. The sensing performances of the implanted nanowire sensors were investigated in terms of NO₂ detection. Figures 5a, 5b and 5c shows resistance curves of the pristine SnO₂ nanowires, and the Au-implanted SnO₂ nanowires with doses of 10¹³ and 10¹⁴/cm², respectively, for various concentrations of NO₂ at 300°C. For the pristine SnO₂ nanowires, the resistance increases sharply to a high value upon exposure to NO₂ gas, and drops quickly to a low value upon removal of the NO₂ gas, exhibiting a response of 18 for 1 ppm NO₂. This resistance change is well known in *n*-type semiconductor gas sensors; NO₂ molecules adsorbed on the surface of the SnO₂ nanowires are likely to extract electrons from them, eventually leading to the surface depletion of each SnO₂ nanowire. On the other hand, release of electrons occurs in conjunction with the desorption of NO₂ molecules. This charge transfer accounts for the resistance change observed in the sensors.

All the NO₂ sensing performances are summarized in Fig. 5d and 5e. It is evident that the Au implantation caused a significant change in the sensing performance. In the case of the Au-implanted SnO₂ nanowires with a dose of 10¹³/cm², the fabricated sensor showed a significant enhancement in sensing capability; the gas response, response time, and recovery time changed from 18, 120 s, and 241 s (pristine SnO₂ nanowires) to 90, 60 s, and 17 s, respectively, for 1 ppm NO₂. Even at the extremely low NO₂ concentration of 50 ppb, the Au-implanted SnO₂ nanowires showed a clear response curve. In sharp contrast, the pristine SnO₂ nanowires showed no

meaningful response to NO₂ for concentrations below 1 ppm. In the case of the Au-implanted SnO₂ nanowires with a dose of 10¹⁴/cm², the NO₂ sensing capabilities were enhanced further; the gas response, response time, and recovery time were 175, 48 s, and 11 s, respectively, for 1 ppm NO₂.

The responses of the Au-implanted SnO₂ nanowires were significantly higher than that of the pristine SnO₂ nanowires, suggesting that the implantation of Au ions in SnO₂ nanowires is a very efficient way to enhance the NO₂ sensing response. In addition, both the response and recovery times were shortened significantly upon Au implantation. These remarkable improvements are attributed to the amplification effects from both structural and surface chemical modifications, as shown below. The present results indicate that the synthesis of bimetallic catalysts would be a promising strategy for enhancing the sensing performances of nanowire gas sensors.

Electrical transport properties in Au-implanted SnO₂ nanowires.

In general, there are four components that contribute to the measured electrical resistivity:

$$\rho = \rho(T) + \rho(d) + \rho(c) + CX(1-X) \quad (2)$$

in which $\rho(i)$ ($i = T, d, c$) are the thermal, defect, and surface chemical catalysis contributions, respectively. The last term is the solid solution contribution (by Nordheim's rule)¹³, C is a constant, and X is the solute concentration (Au in this study). It is noteworthy that both the defect and surface chemical catalysis contribution terms are independent of the temperature. Besides the solid solution contribution, Au layers may also contribute to $\rho(c)$ even though they are about 10 nm below the surface of the nanowires. However, as described later, we do not have to single out such a contribution in this work, since our model (without this contribution) reproduces well our experiments. The $\rho(T)$ value is assigned as 2.63 ohm/cm (see details below), which is the value for pristine SnO₂ nanowires. Therefore, $\rho(d)$ takes pristine SnO₂ as its reference state.

In order to study the electron transport process and calculate carrier concentrations, we must deduct the solid solution effect from the measured electrical resistivity data. Our measured resistivity of pristine SnO₂ (*n*-type) can be reproduced reasonably from the semiconductor theory; specific resistivity = $1/(q\mu_e n)$, in which q , μ_e , and n are the elementary charge, mobility, and concentration of electrons, respectively. By taking the values of $q = 1.6 \times 10^{-19}$ C, $\mu_e = 72$ cm²/(V·s)¹⁴, and $n = 3.3 \times 10^{16}$ cm⁻³¹⁵, we obtain a specific resistivity of 2.63 ohm/cm. Using our measured resistivity, the equivalent length of nanowires is calculated to be 38023 cm, which will be applied to convert the measured resistance data to the specific resistivity, as shown below. By using equation (2) and assuming $\rho_2(d,c) = A \times \rho_3(d,c)$, where $\rho_i(d,c) = \rho_i(d) + \rho_i(c)$ and A is a constant ($A = 0.5$), we can derive the values of $C = 8219$, $\rho_2(d,c) = 10.19$, and $\rho_3(d,c) = 20.38$. Furthermore, the electron carrier concentrations in SnO₂, n_i , are 3.3×10^6 , 5.2×10^5 , and 2.9×10^5 cm⁻³ for pristine SnO₂ and SnO₂ with 10¹³ and 10¹⁴/cm² dosages, respectively. If we select $A = 0.33$, the above carrier concentrations are 3.3×10^6 , 5.7×10^5 , and 1.9×10^5 cm⁻³, respectively. Therefore, a different estimation of the constant A may not change significantly the magnitudes of the carrier concentrations. In this study $A = 0.5$ is applied, which will enable discussions on the basis of the carrier transport properties. For the partitioning of the measured overall resistivity into the four terms in equation (2), the following calculation procedures are used:

1. $\rho(\text{ohm/cm})$ at NO₂ = 0 is 2.63 (=100000/38023), 15.78 (=600000/38023), and 52.60 (=2000000/38023), respectively, for the three dosages.
2. $CX(1-X)$ is 0 (=8219 × 0 × (1 - 0)), 2.96 (=8219 × 0.00036 × (1 - 0.00036)), and 29.55 (=8219 × 0.0036 × (1 - 0.0036)), respectively, for the three dosages.

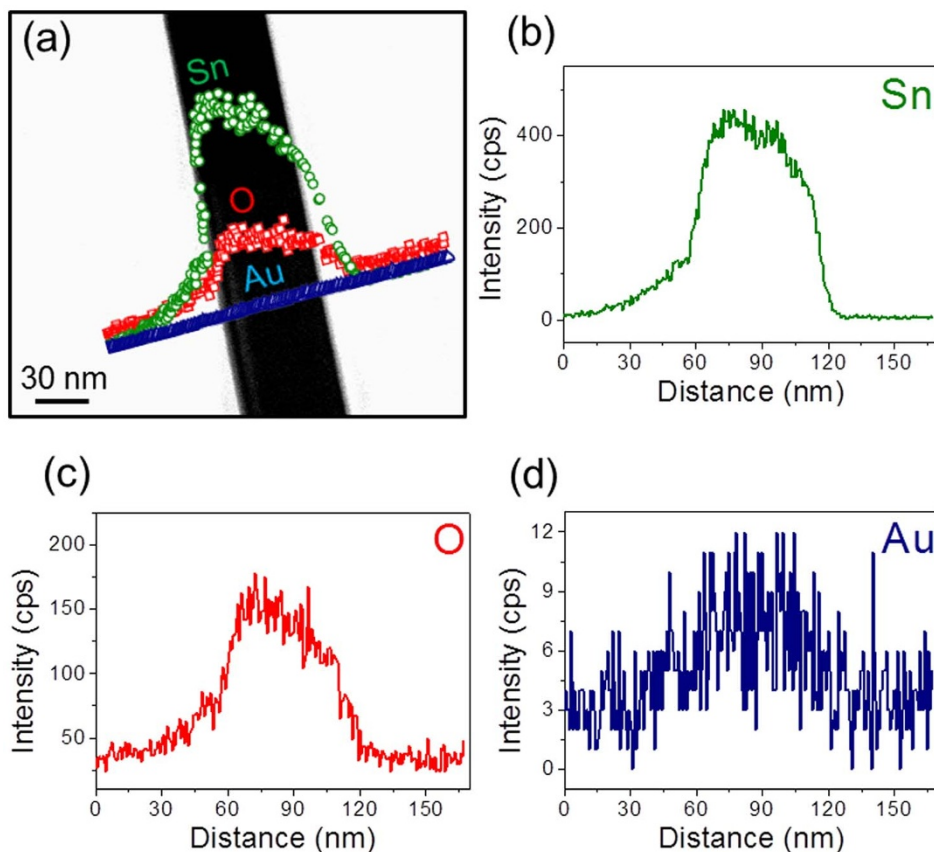


Figure 4 | Elemental analysis of Au-implanted SnO₂ nanowires. EDS line scans for (a) an Au-implanted SnO₂ nanowire with a dose of 10¹⁴/cm². (b, c, d) Line spectra of Sn, O and Au, respectively.

3. $\rho - CX(1 - X)$ at NO₂ = 0 is 2.63, 12.82 (=15.78 – 2.96), and 23.05 (=52.60 – 29.55), respectively, for the three dosages.
4. $\rho(T) = 2.63$, which is the resistivity of nanowires without exposure to chemical and ionic irradiation.
5. At NO₂ = 0, $\rho(c) = 0$, then $\rho(d) = \rho - \rho(T) - CX(1 - X)$ is calculated using the data from steps 2 and 3 above. Through regression of the three sets of data, the following equation is derived: $\log \rho(d) = 7.533 - 1.142 \times \log(n)$, where n is the carrier concentration.
6. Repeating the above steps from 1 to 4 for measurements at NO₂ = 1 ppm, the following equation is derived: $\log \rho(c) = 13.890 - 1.872 \times \log(n)$

Therefore, both $\rho(d)$ and $\rho(c)$ can be predicted from the carrier concentrations by using the following equations;

$$\log \rho(d) = 7.533 - 1.142 \times \log(n) \text{ for SnO}_2 \text{ nanowires in air} \quad (3)$$

$$\log \rho(c) = 13.890 - 1.872 \times \log(n) \text{ for SnO}_2 \text{ nanowires in 1 ppm NO}_2 \quad (4)$$

Equations (3) and (4) provide the relationship between the carrier concentration and resistivity caused by scattering from defects and the surface chemistry, respectively. Then, the overall resistivity of the SnO₂ nanowires is described as

$$\begin{aligned} \rho = & 2.63(\text{thermal term}) + 10^{7.533} / (10^{1.142 \log(n)}) (\text{defect term}) \\ & + 10^{13.890} / (10^{1.872 \log(n)}) (\text{surface chemistry term}) \\ & + 8219X(1 - X) (\text{solid solution term}) \end{aligned} \quad (5)$$

Figure 6 shows the relative contributions of each term (in log form). The surface chemistry term is the clear winner over the whole range

of carrier concentrations, and is the predominant control mechanism of the resistivity. The second place is occupied by the solid solution, defect, and thermal scattering contributions in the ranges of 10⁵ to 4 × 10⁵, 4 × 10⁵ to 1.7 × 10⁶, and >1.7 × 10⁶ cm⁻³, respectively. The revealed interplay between the carrier concentration, solid solution, defects, and thermal and surface chemistry, will aid in further study on the coupling of electronic and ionic conduction in semiconductors and theoretical investigation of electron-phonon coupling.

Discussion

This research may also provide insights into the sensing dynamics. As shown in Fig. 5, the sensor response time decreases from ≈120 (pristine) to ≈60 s (10¹³/cm² dose) for 1 ppm NO₂, which may be speculated from the relative strengths of the thermal and solid solution factors shown in Fig. 6, which crossover at the 10¹³/cm² dose. The response time records the speed of the physical event that leads to the increase of resistivity upon exposure to NO₂ gas, which is believed to be the reduced oxygen vacancies at increasing oxygen partial pressures. SnO₂ is an n-type semiconductor with tin vacancy as the only possible acceptor but of high formation energy¹, therefore, electron (from oxygen vacancy) and hole (from tin vacancy) are respectively the major and minor carrier. Our earlier DFT calculation identified new holes (deep acceptors by Au-implantation) which do not yet contribute to the electrical conductivity but compensate the electron charge of oxygen vacancies. Therefore the measured response time may indicate the speed of the hole compensation process which is about 120 s associated with tin vacancies in pristine, 60 s and 48 s with Au-implanted acceptor respectively under 10¹³/cm² and 10¹⁴/cm² dosages. The reduction in response time of Au-implanted samples results from the activation of “shallower” holes by Au implantation than these by tin vacancies. The response time

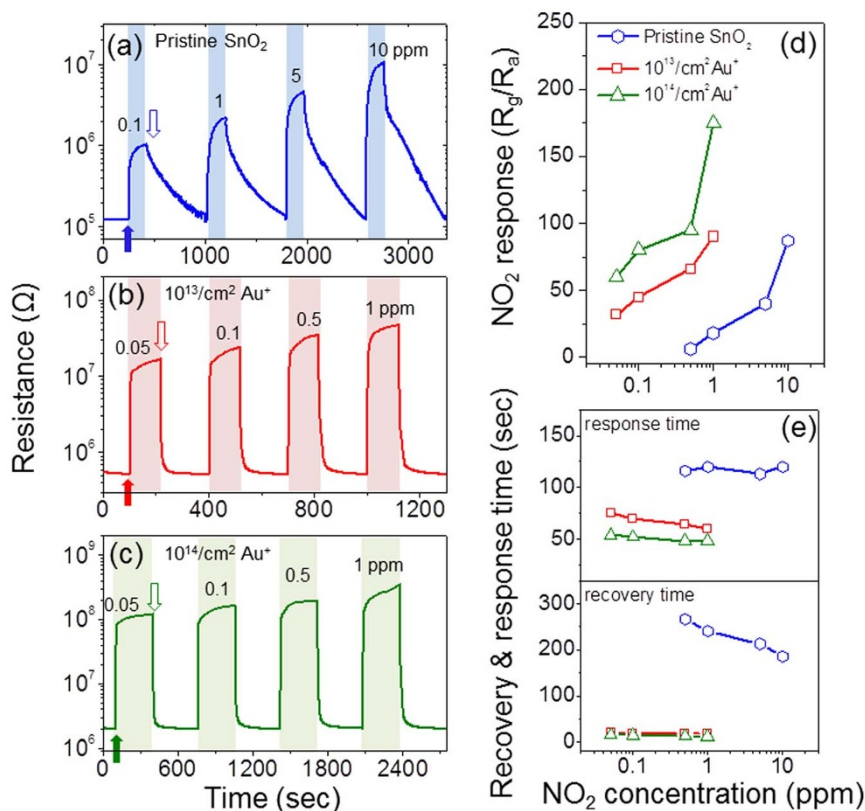


Figure 5 | Sensing performance of Au-implanted SnO₂ nanowires. Dynamic resistance curves of (a) pristine SnO₂ nanowires and (b,c) Au-implanted SnO₂ nanowires with doses of (b) 10¹³ and (c) 10¹⁴/cm² for various NO₂ concentrations. (d) NO₂ responses and (e) response and recovery times of pristine SnO₂ nanowires and Au-implanted SnO₂ nanowires with doses of 10¹³ and 10¹⁴/cm².

reduced a little further to 48 s in the case of 10¹⁴/cm² dose where the new acceptor state may move closer to the valence band under the higher Au implantation dosage. In addition, the extra electrons (by Au implantation) at the region about 10 nm below the SnO₂ surface via either interstitial or work function mechanisms have to couple with the surrounding lattice represented by the thermal scattering factor (2.63 ohm/cm). It seems that the crossover shown in Fig. 6 indicates the effective coupling of electrons and phonons, which also contributes to a short response time.

Similarly the recovery time records the speed of the physical event that removes the electron loss upon switching off the NO₂ gas. The

recovery time is dependent on the mobility of electrons (major carrier) which is higher than that of holes (minor carriers). Therefore, it is not surprised that the recovery time is about 4 times shorter than the corresponding response time under Au implantation (17 to 60 s and 11 to 48 s), considering the fact that the electron mobility is about 5 times higher than the hole mobility in SnO₂^{16,17}. This trend does not hold for the pristine SnO₂ somehow, which may involve more complicated mechanism that results in a strong dependence between the NO₂ gas concentration and recovery time (Fig. 5e), unlike the other two Au-implanted cases. In general, the gas response and recovery times are closely associated with the exact surface catalysis involving electron and hole transport, which can be established by DFT calculations^{18–20}. In the future work, detailed study of the surface catalysis under the influence of deep acceptors and the electron gas (produced by Au implantation) will be made through DFT calculations. In addition, the effect of hindering the adsorption of both atmospheric oxygen and NO₂ by limiting the available free charge carriers on sensing performances needs to be investigated to further clarify the acceptor role of Au in SnO₂.

Recently, it was revealed that the role of Au as an additive in SnO₂ is mainly chemical and can be described in terms of enhanced reactivity to oxygen²¹, being in contrast to the effect of Pd and Pt promoters which were found to be distributed at an atomic level on the surface and in the bulk of the supporting sensing material and therefore have a tremendous effect on its bulk and surface electronic properties²². According to the results presented in the reference²¹, Au is present in the form of small metallic particles at the surface of the host metal oxide, leading to the “spill-over effect”, meaning that the Au particles enrich the surface of the active metal oxide with oxygen species. However, the Au-implanted SnO₂ nanowires in this work showed no evidence of forming metallic particles either at the surface or in the interior of SnO₂ nanowires. This is confirmed by the

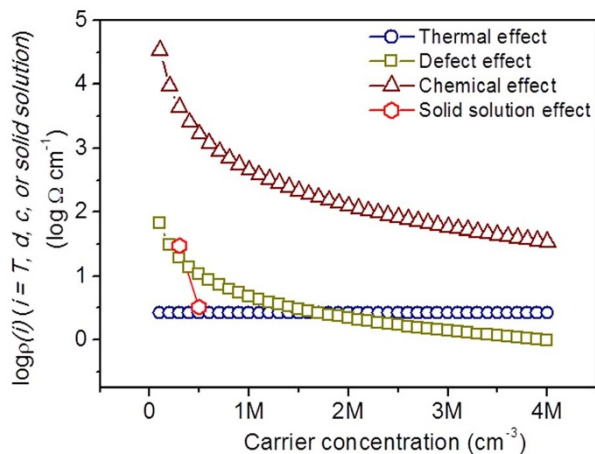


Figure 6 | Electrical resistivity contributions. Changes in relative resistivity contributions ($\log p(i)$ ($i = T, d, c, \text{ or solid solution}$)) with carrier concentrations.



TEM observations. Figure 1d and Figure S5 show the detailed microstructures of an Au-implanted SnO₂ nanowire with a dose of 10¹⁴/cm², confirming no evidence of Au metallic particles or clusters. Usually in the implantation process, when the amount of an implanted element is very small or the post heat-treatment is not enough, it is more likely that they exist in the form of point defects such as interstitial or substitutional impurities in the host material^{23,24}. On the basis of the TEM observations, the general characteristic of the implantation process^{23,24}, and the first principle calculations for the formation energies of Au dopants in SnO₂ revealing that Au prefers the substitutional site (see Figure 1), it is reasonable to claim that Au can play the role of a deep acceptor particularly in the Au-implanted SnO₂ nanowires.

Another point that should be noted is the effect of the back to back Schottky barriers formed at the nanowires contacts. According to a literature survey^{25,26}, the Schottky barriers can be one of the key sources of resistance change because the barrier height will be modulated by adsorption and desorption of gas molecules, consequently intensifying the resistance change. However, in our networked SnO₂ nanowires, the contact is minimal. That is, one or two contacts are produced while making a linkage from one electrode to the other one¹². In this case, the dominant source of resistance change is likely to come from the radial modulation of the electron-depleted layer in the surface region of nanowires, which was elucidated in our previous reports^{27,28}. A systematic study based on the impedance spectroscopy may reveal more clearly the contributions from the Schottky barrier and the radial modulation of the electron-depleted layer, which needs to be performed in the future.

In summary, the NO₂ sensing performances of SnO₂ nanowires were improved greatly by Au implantation. The response of pristine SnO₂ nanowires for 1 ppm NO₂ was improved about ten folds upon Au implantation with a dose of 10¹⁴/cm², while a clear response curve was shown even at 50 ppb NO₂. In addition, the response and recovery times were shortened significantly by the Au implantation. The surface chemistry was found to be the predominant control mechanism of NO₂-gas sensors based on the Au-implanted SnO₂ nanowires. An equation of electrical resistance has been established as a function of thermal vibration, structural defects (Au implantation), surface chemistry (1 ppm NO₂), and solute concentration. The electron carrier concentrations in the Au-implanted SnO₂ nanowires were calculated and used to predict the strength of the electron scattering of structural defects and surface adsorbents. The sensor performance, in terms of response and recovery times, was discussed in relation to the acceptor compensation and the electron-phonon coupling mechanism. We further investigated the feasibility of using sensor response and recovery time to determine fundamental physics governing the electron/hole transport in semiconductors. This study provides novel insights into the fundamental carrier dynamics in semiconductors as well as aids the development of next-generation chemical sensors.

Methods

DFT calculation. Our spin-polarized calculations were performed using *Quantum Espresso* package. The exchange-correlation potential was approximated by generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) functional. A Monkhorst-Pack mesh with (3 × 3 × 3) k-point sampling was used for geometry optimizations, while a denser k-point grid of (8 × 8 × 8) was employed in the case of density of states (DOS) calculations. The kinetic-energy cutoffs for valence electron wave functions and charge density were set as 37 Ry and 370 Ry, respectively. The optimized structures were obtained by relaxing all atomic positions using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm until the interatomic forces are less than 0.01 eV Å⁻¹.

Fabrication of nanowire sensors. For the sensor platform, SnO₂ nanowires were grown selectively through the vapor-liquid-solid (VLS) method on a SiO₂-grown Si(100) substrate, on which patterned interdigital electrodes (PIEs) had been formed by using a conventional photolithographic process. The electrode was a layer consisting of Au(3 nm)/Pt(200 nm)/Ti(50 nm), deposited in sequence through a sputtering method. The Si substrate was introduced into a horizontal quartz tube furnace in which an alumina crucible containing Sn powders (Aldrich, 99.9%) was

placed. The furnace was then evacuated with a pump down to a pressure of 8 × 10⁻² torr and heated to 900°C for 5 min. During the VLS growth of the SnO₂ nanowires, N₂ and O₂ were flowed through the tube at rates of 300 and 10 standard cubic centimeters per minute, respectively. The experimental conditions used to synthesize the SnO₂ nanowires and the sensor design are described in detail in our previous reports^{12,28}.

Ion implantation. The Au implantation in SnO₂ nanowires was performed with a conventional ion implanter (Nissin Electric Co., Ltd., Japan). Au⁺ ions with an energy of 30 keV were implanted into the SnO₂ nanowires under a pressure of 1 × 10⁻⁷ torr with an ion current density of 10 nA/cm², without any intentional heating. After the Au implantation, the samples were annealed at 500°C for 1 h in air to repair the structural damage that might be caused by the implantation process.

Materials characterization. The microstructure of the pristine and Au-implanted SnO₂ nanowires was examined through field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4200) and transmission electron microscopy (TEM, Philips CM-200). The bulk and surface chemistries were characterized through energy-dispersive X-ray spectroscopy (EDS, Oxford INCA energy) installed in the FE-SEM equipment and X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha), respectively. For further elemental analysis, EDS line scans were performed using the EDS analyzer (EDS, Oxford INCA energy) installed in the TEM equipment.

Sensing measurement. The sensing performances of the sensors fabricated from the Au-implanted SnO₂ nanowires were investigated for a representative oxidizing gas (NO₂) with a custom-made gas-sensing system, and compared with the performance of pristine SnO₂ nanowires. The fabricated sensors were placed in a horizontal tube furnace, and the operating temperature was fixed to 300°C because the NO₂ sensing performances were found to be best at that temperature in preliminary tests. The NO₂ gas has a concentration of 100 ppm in dry air, and the gas concentration was controlled by changing the ratio of this mixture gas to dry air by using accurate mass flow controllers. The total flow rate was set to 500 sccm to avoid any possible variation in sensing properties. According to the specifications provided by the gas manufacturer (Daeduk Gas Co., Korea), the content of water vapor in both the dry-air-balanced NO₂ gas and the dry air was negligible. The response (*R*) for NO₂ was estimated with the following formula: $R = R_g/R_a$, where *R_g* and *R_a* are the resistances in the absence and presence of NO₂, respectively. The response time and recovery time were defined as the time taken for a 90% variation of the resistances upon exposure to the target gas and air, respectively.

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Author contributions

S.S.K. designed the experiments, analyzed the data and prepared the manuscript. P.W. planned and performed the models and calculations, designed the theoretical work and prepared the manuscript. A.K., G.-J.S. and S.W.C. conducted the experiments. S.H. organized the implantation process. V.V.K. carried out the DFT calculations. All authors participated in discussion. A.K. and S.W.C. contributed equally as first authors.

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