Promotion of acceptor formation in SnO\textsubscript{2} nanowires by e-beam bombardment and impacts to sensor application

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We have realized a p-type-like conduction in initially n-type SnO\textsubscript{2} nanowires grown using a vapor-liquid-solid method. The transition was achieved by irradiating n-type SnO\textsubscript{2} nanowires with a high-energy electron beam, without intentional chemical doping. The nanowires were irradiated at doses of 50 and 150 kGy, and were then used to fabricate NO\textsubscript{2} gas sensors, which exhibited n-type and p-type conductivities, respectively. The tuneability of the conduction behavior is assumed to be governed by the formation of tin vacancies (under high-energy electron beam irradiation), because it is the only possible acceptor, excluding all possible defects via density functional theory (DFT) calculations. The effect of external electric fields on the defect stability was studied using DFT calculations. The measured NO\textsubscript{2} sensing dynamics, including response and recovery times, were well represented by the electron-hole compensation mechanism from standard electron-hole gas equilibrium statistics. This study elucidates the charge-transport characteristics of bipolar semiconductors that underlie surface chemical reactions. The principles derived will guide the development of future SnO\textsubscript{2}-based electronic and electrochemical devices.

Tin oxide (SnO\textsubscript{2}) is an n-type semiconductor and is employed in a wide range of applications, including sensors for a variety of oxidizing and reducing gases. This is because it can be produced cheaply using simple methods\textsuperscript{1}. On the other hand, sensors based on p-type SnO\textsubscript{2} have rarely been studied. Using density functional theory (DFT) calculations for almost all possible defects, Godinho et al. found that the only intrinsic defects that may induce p-type behavior in SnO\textsubscript{2} are Sn vacancies (and not interstitial oxygen as believed previously)\textsuperscript{2}. However, owing to their high energy of formation, Sn vacancies are unlikely to form under normal conditions. While p-type conductivity in SnO\textsubscript{2} has previously been achieved by chemically doping it with Fe\textsuperscript{3} or Rh\textsuperscript{4}, in this study, we explored a physical approach for realizing p-type behavior in SnO\textsubscript{2}.

Irradiation with an electron beam is known to be an effective technique for changing or modifying materials. Irradiating electron beams has also been used under atmospheric conditions for surface modification\textsuperscript{5}. In addition, electron-beam irradiation techniques have also been used to modify polymeric materials\textsuperscript{6} and fabricate power semiconductors\textsuperscript{7}. The electron-beam irradiation reduced the Schottky barrier height of ZnO nanowire based back-to-back double Schottky diode\textsuperscript{8}. Electron-beam irradiation of the PbO nanobelts resulted in the phase transformation from PbO\textsubscript{2} to PbO and finally to Pb\textsuperscript{9}. Edgell et al. reported the loss of oxygen by the electron-beam irradiation of SnO\textsubscript{2} single crystals\textsuperscript{10}. Komuro et al. reported the electron-beam irradiation-induced reduction of SnO\textsubscript{2} to Sn on TiO\textsubscript{2} surfaces\textsuperscript{11}. The Sn-SnO\textsubscript{2} coaxial nanocables were transformed to nanostructures consisting of SnO\textsubscript{2} trunks and Sn branches\textsuperscript{12}.

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Synthesis techniques based on electron-beam irradiation have numerous advantages: they are simple, allow for large-scale production, involve short reaction times, and do not generate chemical residues\(^{13-17}\). For instance, using such a technique, silver nanoparticles have been synthesized on a large scale\(^{13-19}\).

In this study, we fabricated SnO\(_2\) nanowires and used them in gas sensors to investigate the effect of electron-beam irradiation on the sensing behavior of the nanowires. We compared the sensing characteristics of the electron-beam-irradiated SnO\(_2\) nanowires with those of pristine ones with respect to NO\(_2\) gas. Using electron-beam irradiation, we were able to achieve a transition from \(n\)-type sensing behavior to \(p\)-type behavior.

Nitrogen oxide (NO\(_2\)) was adopted as the sensing gas not only because it is one of the gases most harmful to humans\(^{20}\) but also because NO\(_2\) sensors have been studied intensively in the past. One-dimensional (1D) SnO\(_2\) nanostructures (i.e., nanowires) were used as the sensing material, because, owing to their single crystalline structure and exceptionally high surface-to-volume ratio, they exhibit very high surface activity\(^{21,22}\). Finally, a network of multiple nanowires was used as the sensing scheme in the present work in order to circumvent the shortcomings associated with single-nanowire schemes\(^{23}\).

As mentioned previously, we were able to achieve a \(p\)-type-like semiconductor behavior in SnO\(_2\) nanofibers by means of electron-beam irradiation. We propose an underlying mechanism based on hole gas equilibrium statistics for the observed bipolar conduction and surface charge transport. Elucidation of the mechanism will result not only in a better understanding of charge transport in bipolar semiconductors but also lead to the development of SnO\(_2\)-based electronic and electrochemical devices.

**Results**

Figure 1a shows an SEM image of the electron-beam-irradiated SnO\(_2\) nanowires at doses of 150 kGy. Examination of the insets clearly reveals that no significant surface roughness was induced by the electron beam irradiation. By comparing the SEM images, it is reasonable to conclude that no significant change in the morphology and surface of the SnO\(_2\) nanowires resulted from electron-beam irradiation (Figure 1).
S1 in Supplementary Information). TEM analysis was performed on the electron-beam-irradiated SnO$_2$ nanowires, revealing that no significant change in the crystallinity of the SnO$_2$ nanowires was caused by electron-beam irradiation, Fig. 1b.

Figure 2a shows the resistance curve for the sensor fabricated from the pristine SnO$_2$ nanowires (referred to as the pristine-nanowires sensor). Figure 2b,c are those of the sensors fabricated using the SnO$_2$ nanowires irradiated with the electron beam at doses of 50 and 150 kGy, respectively (referred to as the 50-kGy-nanowires sensor and the 150-kGy-nanowires sensor, respectively). The resistance curves were determined over the course of three introduction/stoppage cycles of 10 ppm NO$_2$.

In the undoped form, SnO$_2$ is an $n$-type semiconductor$^{24}$. The dominant species on the surfaces of SnO$_2$ nanowires at 573 K is O$^{-}$.$^{25,26}$ During the sensing experiments, the chemisorption of NO$_2$ leads to the following reaction: NO$_2$ (gas) + e$^{-}$ → NO$_2$-. $^{27,28}$ Electrons are extracted from the SnO$_2$ surface, increasing the resistance of the nanowires. The NO$_2$- ions are dissociated into NO (g) and O$^{-}$ by the following reaction: NO$_2$-→ NO (g) + O$^{-}$.$^{29}$ where the generated O$^{-}$ ions contribute to a further increase in the resistance.

In the case of the pristine-nanowires sensor, the resistance increases sharply to a high value upon exposure to NO$_2$ gas and then drops quickly to a low value upon the stoppage of the gas, resulting in a sensor response of 4.15 (Table 1). It is evident from Fig. 2a,b that the electron-beam irradiation caused a significant change in the sensitivity of the SnO$_2$ nanowires. The 50-kGy-nanowires sensor continued to exhibit $n$-type behavior; this was because the irradiation dose was low (50 kGy), resulting in the irradiated SnO$_2$ nanowires being similar to the pristine ones. However, the response of this sensor was estimated to be only approximately 1.02, indicating a significant degradation of the $n$-type sensing behavior. Additionally, the response time of the 50-kGy-nanowires sensor was as long as 277 s and much longer than that of the pristine-nanowires sensor, which was 28 s (Table 1). Furthermore, the recovery times of the pristine-nanowires and 50-kGy-nanowires sensors were 18 and 140 s, respectively. In case of the 150-kGy-nanowires sensor, the resistance decreases upon the introduction of the NO$_2$ gas and increases on the subsequent stoppage of its flow. This unexpected behavior is indicative of $p$-type conductivity. The introduction of NO$_2$ gas during the sensing experiments results in the extraction of electrons
the cation-vacancy model, in which positively charged holes are generated by the following reaction:

\[ \text{O}_2 \text{(gas)} \rightarrow \text{Vo}^{-} + 2 \text{e}^{-} + 1/2 \text{O}_2 \text{(gas)} \]

and the degree of ionization (\[\phi\]).

SnSn

When a low irradiation dose (50 kGy) is used, positive holes are generated: the positive holes are attributed to the newly formed acceptors, otherwise they will be unstable due to the electron-beam not only create oxygen vacancies but also tin vacancies which generate positive holes. Responses, response times, and recovery times of the sensors fabricated using the pristine and e-beam-irradiated SnO\textsubscript{2} nanowires are listed in Supplementary Information (Table S1). We calculate the concentrations for both carriers (electrons and holes) later in the paper.

To provide further insight into the origin of observed \(p\)-type behavior of SnO\textsubscript{2} under e-beam irradiation, the electronic properties of SnO\textsubscript{2} nanostructures were calculated by density functional theory

| Pristine-nanowires sensor | 50-kGy-nanowires sensor | 150-kGy-nanowires sensor |
|---------------------------|-------------------------|--------------------------|
| Response                   | 4.15                    | 1.02                     | 1.03                     |
| Response time (s)           | 28                      | 277                      | 16                       |
| Recovery time (s)           | 18                      | 140                      | 230                      |

Table 1. Responses, response times, and recovery times of the sensors fabricated using the pristine and e-beam-irradiated SnO\textsubscript{2} nanowires.

from the lattice. This further increases the number of positive holes, which are now the major carriers. The decrease in resistance owing to the increase in the number of hole carriers in a \(p\)-type semiconductor results in \(p\)-type sensing behavior. The response of the 150-kGy-nanowires sensor was estimated to be approximately 1.03. In addition, its response and recovery times were measured to be approximately 16 and 230 s, respectively. The Hall measurements confirm that the 150-kGy-nanowire is a \(p\)-type (Text S1 in Supplementary Information).

In order to investigate the origin of the \(p\)-type behavior observed in the 150-kGy-nanowires sensor, we performed XRD analyses and PL measurements. As mentioned previously, Fig. 1 shows that both the structural morphology and the surface roughness of the nanowires were not significantly affected by the electron-beam irradiation process. XRD spectra of the pristine and electron-beam-irradiated SnO\textsubscript{2} nanowires are shown in Supplementary Information (Figure S2). Irrespective of whether the nanowires were irradiated or not, all recognizable reflection peaks present in the spectra could be indexed to a tetragonal rutile SnO\textsubscript{2} phase (JCPDS card: No. 41-1445). The peak positions and full-width-at-half-maximum (FWHM) values of the (110), (101), and (211) diffraction peaks for the pristine and electron-beam-irradiated SnO\textsubscript{2} nanowires are listed in Supplementary Information (Table S1). It can be seen from the table that FWHM values of the irradiated nanowires were not significantly different from those of the pristine ones (Figure S3). Furthermore, the positions of the main peaks in the XRD spectrum of the pristine nanowires did not change noticeably after the nanowires were irradiated. Accordingly, we conclude that not only the crystalline integrity but also the interplanar distance of the SnO\textsubscript{2} structure remained unaffected by the electron-beam irradiation. Furthermore, by the examination of the XRD (Figure S4) and TEM data (Figure S5), the electron-beam irradiated SnO\textsubscript{2} nanowires did not exhibit other phases, including tetragonal SnO\textsubscript{2}.

By the electron-beam irradiation, the main PL emission peak at around 2.1 eV has been decreased (Figure S6, Text S2). With assumption that oxygen vacancies and tin interstitials are related to the yellow emission (~2.1 eV) in SnO\textsubscript{2}, it is possible that the electron-beam induced tin vacancies eliminate the tin interstitials or the electron-beam irradiation changed the characteristics of the oxygen vacancies.

Irradiation with an electron beam can generate holes by two mechanisms\textsuperscript{50}. One possibility is that positively charged holes are generated via the following reaction: \(1/2 \text{O}_2\text{(gas)} = \text{Vo}^{-} + 2 \text{e}^{-} + \text{h}^0\text{.31}\). This is the anion-interstitial model, in which \(\text{O}_{\text{an}}^{i-}\), \(h\), \(i\) are an interstitial oxygen ion, the associated hole, and the degree of ionization (\(i = 1\) or 2), respectively. The second possible mechanism is based on the cation-vacancy model, in which positively charged holes are generated by the following reaction: \(\text{O}_2\text{(gas)} = 2\text{Vo} + \text{V}_{\text{Sn}}^{i+} + \text{ih}^0\text{.32 or Sn Sn}^{+} = \text{V}_{\text{Sn}}^{i+} + \text{ih} + \text{Sn}_{\text{gap}}\), where \(\text{V}_{\text{Sn}}^{i+}\) is the Sn vacancy and \(i = 1\)–4. On the basis of both the fact that the interstitial sites in the SnO\textsubscript{2} lattice are much smaller than an oxygen ion in size and the results of the DFT calculations\textsuperscript{2}, it can be surmised that the second reaction must be the main source of holes. That is, a strong electron beam will directly expel Sn atoms out of their lattice positions. Accordingly, mechanism related to the introduction of other defects contributing to \(p\)-type conduction can be exclusively disregarded. The expelled atomic tin is sublimated into air through the surfaces of the SnO\textsubscript{2} nanowires, because tin cannot occupy the interstitial site, which will make SnO\textsubscript{2} an \(n\)-type semiconductor. In this manner, the generated holes may play a greater role than the electrons at the surfaces of the nanowires, resulting in the observed \(p\)-type behavior in the SnO\textsubscript{2} nanowires irradiated at a dose of 150 kGy. We calculate the concentrations for both carriers (electrons and holes) later in the paper.

We speculated the mechanisms on the changes induced by the electron-beam irradiation and showed the related schematic diagrams in Fig. 3. When the nanowires are irradiated with the electron beam, the beam electrons not only create oxygen vacancies but also tin vacancies which generate positive holes. The positive holes are attributed to the newly formed acceptors, otherwise they will be unstable due to their high formation energy. When a low irradiation dose (50 kGy) is used, positive holes are generated: \(\text{Sn}_{\text{gap}} = \text{V}_{\text{Sn}}^{i+} + \text{ih} + \text{Sn}_{\text{gap}}\) (Fig. 3c). In addition, negative electrons and oxygen vacancies are generated: \(\text{O}_2 = \text{V}_{\text{O}}^{2+} + 2 \text{e}^{-} + 1/2\text{O}_2\text{(gas)}\) (Fig. 3c). The overall conduction is still \(n\)-type due to insufficient amount of holes to match the increased oxygen vacancies. When a high irradiation dose (150 kGy) is used, a sufficient amount of positive holes are generated and positive holes become prevalent in the SnO\textsubscript{2} lattice (Fig. 3d).

To provide further insight into the origin of observed \(p\)-type behavior of SnO\textsubscript{2} under e-beam radiation, the electronic properties of SnO\textsubscript{2} nanostructures were calculated by density functional theory.
(DFT) methods. SnO₂ has a rutile crystal structure in the space group $P4_2/mmm$ (No. 136) as shown in Fig. 4a. The atomic structure of SnO₂ nanostructures thin film was initially constructed by cleaving the surface of the bulk structure of tin dioxide. Using this technique, it is possible to get nanostructures with a wide range of surface orientations and thicknesses while maintaining the bulk composition. The thickness of the studied SnO₂ thin film is equal to 1.2 nm. During geometry optimization, all atoms are allowed to relax freely to their new equilibrium positions in order to obtain the lowest-energy configuration. The optimized structure is shown in Fig. 4b. Our analysis shows that among the bulk terminated low-index SnO₂ surfaces (i.e. surfaces with surface-tin atoms in their bulk Sn$^{4+}$ oxidation state), the
(110) surface exhibits the lowest surface energy as compared to the (110) and (001) ones. This is in good agreement with experimental studies. Therefore, we will only focus on the thin film slabs with (110) surface orientation in our study.

We then calculate the formation energy of a defect $D$ in a charge state $q$ as follows

$$E_{\text{form}}(D^q; \text{SnO}_2) = E[D^q; \text{SnO}_2] - E[\text{SnO}_2] + \sum_i n_i \mu_i + q(E_{\text{VBM}} + E_F + \Delta V) \quad (1)$$

where $E[D^q; \text{SnO}_2]$ and $E[\text{SnO}_2]$ are the total energies of defected and perfect SnO$_2$, respectively, $n_i$ is the number of atoms being removed from the perfect system ($i = \text{Sn or O}$), $\mu_i$ is the chemical potential. The last term describes the dependence on the Fermi level ($E_F$) measured from the valence band edge, $E_{\text{VBM}}$ is a position of the valence band maximum (VBM) in the perfect system, and $\Delta V$ is a correction term aligning the VBM in the doped and perfect crystal supercells. Chemical potential $\mu_i = \mu_i^{\text{ref}} + \Delta \mu_i$ where $\mu_i^{\text{ref}}$ is calculated for the bulk Sn phase or O$_2$ molecule, while $\Delta \mu_i$ may vary corresponding to certain experimental growth conditions (e.g. Sn-rich/O-poor or Sn-poor/O-rich). Although PBE calculations typically underestimate band gaps of oxide semiconductors, they are proven efficient in predicting the general trends and defect formation energies.

The effect of electron radiation on the system behavior was simulated by applying the external electric field, perpendicular to the SnO$_2$ thin film surface. We place a single tin or oxygen vacancy in the core region nearby the top surface of SnO$_2$ thin film. Under normal conditions (electric field is zero), the formation energies of neutral tin and oxygen vacancies are equal to 7.5 and 4.0 eV, respectively, at oxygen-rich limit. Note that at tin-rich limit, the formation energy of $V_{\text{Sn}}$ defect decreases to 1.2 eV. These values are very close to their respective bulk values and consistent with literature data. Under both tin-rich and oxygen-rich conditions, the donor defects are dominant in the system. Very high formation energy of Sn vacancy indicates that its concentration would be negligible under equilibrium conditions. This explains why $p$-type conductivity is very difficult to achieve in experimental SnO$_2$ samples.

We next studied the effect of an external electric field on the defect properties of SnO$_2$ nanostructures. Interestingly, the applied electric field has a substantial effect on the formation energies of both tin and oxygen vacancies. The calculated formation energies as a function of external electric field under oxygen-rich conditions (which should be more suitable for $p$-type defect formation) are shown in Fig. 5c. We notice that the formation energy of acceptor-type $V_{\text{Sn}}$ defect decreases with the increase in electric field. This suggests that the formation of acceptor defects becomes more likely under the external electron radiation. This result can be rationalized as follows: the presence of external electric field also leads to the large polarization of SnO$_2$ thin film with the formation of $p$-type-like region at the top surface of thin film and $n$-type region at the bottom. Inside the $p$-type-like zone at the surface of SnO$_2$ nanostructure, the formation energy of acceptor $V_{\text{Sn}}$ defects is slightly reduced.

In order to further investigate the origin of the observed $p$-type behavior, we measured the electrical resistances of the SnO$_2$ nanowires after irradiation at different doses (Table 2). These values were obtained from the initial resistance, which were measured from the dynamic resistance curves in Fig. 2 of our manuscript (i.e. $R_1$, $R_2$, and $R_3$ are 3000, 1245, and 935 Ω, for pristine (i.e., nonirradiated), 50-kGy-irradiated, and 150-kGy-irradiated SnO$_2$ nanowires, respectively). The specific resistivity of pristine SnO$_2$ ($n$-type) can be determined reasonably from basic semiconductor theory: specific resistivity $\rho = 1/(q\mu n)$, where $q$, $\mu$, and $n$ are the elementary charge of an electron, the mobility of the electrons, and their concentration, respectively. By assuming the values of $q = 1.6 \times 10^{-19}$ C, $\mu_e = 72$ cm$^2/(V\cdot s)$, and $n = 3.3 \times 10^{19}$ cm$^{-3}$, we obtain a specific resistivity of 2.63 Ωcm. On the basis of the measured resistance of the pristine SnO$_2$ nanowires and the specific resistivity of pristine SnO$_2$, the equivalent length of the nanowires was calculated to be approximately 1140 cm. This was used to convert the measured resistance data into specific resistivity as shown in Table 2.

Next, we discuss in detail the electrical transport mechanism in the SnO$_2$ nanowires under NO$_2$ exposure, on the basis of standard hole gas equilibrium statistics. As shown in Table 2, the specific resistivities of the pristine, 50-kGy-irradiated, and 150-kGy-irradiated nanowires are designated as $\rho_1$, $\rho_2$, and $\rho_3$, respectively. For the 50-kGy-irradiated nanowires,

$$\rho_2/\rho_1 = 2.41 = (\mu_e n + \mu_h p)/(72 \times 3.3 \times 10^{19}), \quad (2)$$

where $\mu_e$, $\mu_h$, $n$, and $p$ are the electron mobility, hole mobility, electron concentration, and hole concentration, respectively. Accordingly, $(\mu_e n + \mu_h p) = 5.73 \times 10^{19}$ (cm$^2/(V\cdot s)$). In the present work, we set the following two extreme conditions:

1. $\mu_n \gg \mu_e p$ (that is, the nanowires are very similar to pristine SnO$_2$ in nature)
2. $\mu_e n = \mu_h p$ (this corresponds to the exact point where the conduction behavior transitions from $n$- to $p$-type).

The hole mobility in SnO$_2$ (which is lower than the electron mobility) is reported to be ~6 cm$^2/(V\cdot s)$ in Mn-doped SnO$_2$ and ~39 cm$^2/(V\cdot s)$ in In-Ga codoped SnO$_2$. In this study, we assume $\mu_e = 5 \times \mu_h$. 
Figure 5. Preparation of sensor materials and devices. Schematic outline of preparation of sensor materials (i.e. SnO$_2$ nanowires), fabrication of SnO$_2$ nanowires gas sensors, and associated gas sensing mechanisms.
The factor 5 is assigned on the basis of the effective mass ratio of a hole and an electron. Therefore, we consider $\mu_h = 72/5 = 14.4 \text{ cm}^2/(V\cdot \text{s})$. This value falls between those measured previously.

For condition 1, since $\mu_h n = 5.73 \times 10^{18} \text{ (cmV}\cdot\text{s})^{-1}$, the electron concentration is calculated to be approximately $8.0 \times 10^{16} \text{ cm}^{-3}$. For condition 2, $\mu_h n + \mu_e p = 5.73 \times 10^{18} \text{ (cmV}\cdot\text{s})^{-1}$, and thus the electron and hole concentrations are calculated to be approximately $4.0 \times 10^{16} \text{ cm}^{-3}$ and $2.0 \times 10^{17} \text{ cm}^{-3}$, respectively. Therefore, it is expected that electron and hole concentrations are in the ranges of $4.0 \times 10^{16}$ to $8.0 \times 10^{17} \text{ cm}^{-3}$ and 0 to $2.0 \times 10^{17} \text{ cm}^{-3}$, respectively.

In the case of the 150-kGy-irradiated nanowires, the ratio of the specific resistivities is

$$\rho_2/\rho_3 = (\mu_e n + \mu_p p)/(72 \times 3.3 \times 10^{16})$$

(3)

Then, $\mu_h n + \mu_e p = 7.63 \times 10^{18} \text{ (cmV}\cdot\text{s})^{-1}$. We again set two extreme conditions:

1. $\mu_h n \ll \mu_e p$
2. $\mu_h n = \mu_e p$

For condition 1, since $\mu_e p = 7.63 \times 10^{18} \text{ (cmV}\cdot\text{s})^{-1}$, by assuming $\mu_h = 14.4 \text{ cm}^2/(V\cdot \text{s})$, the hole concentration is calculated to be approximately $5.3 \times 10^{17} \text{ cm}^{-3}$. For condition 2, $\mu_h n + \mu_e p = 7.63 \times 10^{18} \text{ (cmV}\cdot\text{s})^{-1}$, and thus the electron and hole concentrations are calculated to be approximately $5.3 \times 10^{16} \text{ cm}^{-3}$ and $2.7 \times 10^{17} \text{ cm}^{-3}$, respectively. Therefore, it is expected that electron and hole concentrations are in the ranges of 0 to $5.3 \times 10^{16} \text{ cm}^{-3}$ and $2.7 \times 10^{17}$ to $5.3 \times 10^{17} \text{ cm}^{-3}$, respectively (Table 2).

In the SnO2 nanowire system, we have two major carriers to work with: electrons and holes. By the electron-beam irradiation, tin vacancies, holes, oxygen vacancies, and electrons will be generated in pristine and e-beam-irradiated SnO2 nanowires.

Table 2. Resistances, specific resistivities, and upper and lower electron and hole concentrations of the pristine and e-beam-irradiated SnO2 nanowires.

| Table 2. Resistances, specific resistivities, and upper and lower electron and hole concentrations of the pristine and e-beam-irradiated SnO2 nanowires. | SnO2 nanowires (50 kGy) | SnO2 nanowires (150 kGy) |
|---|---|---|
| Resistance (Ω) | $R_1 = 3000$ | $R_2 = 1245$ | $R_3 = 935$ |
| Specific resistivity (Ωcm) | $\rho_1 = 2.63$ | $\rho_2 = 1.09$ | $\rho_3 = 0.82$ |
| Upper limit of electron concentration (cm$^{-3}$) | $3.3 \times 10^{18}$ | $8.0 \times 10^{16}$ | $5.3 \times 10^{18}$ |
| Lower limit of electron concentration (cm$^{-3}$) | 0 | 0 | $2.7 \times 10^{17}$ |
| Upper limit of hole concentration (cm$^{-3}$) | $3.3 \times 10^{16}$ | $4.0 \times 10^{16}$ | 0 |
| Lower limit of hole concentration (cm$^{-3}$) | 0 | $2.0 \times 10^{17}$ | $5.3 \times 10^{17}$ |
explained on the basis of the reduction in the number of electrons that can move freely without interacting with holes/donor killer, which were generated by the electron-beam irradiation. This generates additional energy barriers for the transport of electrons. Similarly, during the recovery step, the recovery of electrons (major carriers) is very fast (the same as in regime I), but the recovery of holes (minor) is no longer ignorable due to the considerable amount of holes to recover. In other words, the remaining or newly-formed tin vacancies have to be recovered (or deactivated), which is a slow process leading to a longer recovery time (140 s).

In case of 150-kGy-irradiation (regime III), the acceptor killer is an oxygen vacancy. Therefore, the fast diffusion of oxygen vacancies will result in a shorter response time (16 s). The long recovery time (230 s) is determined by the slow diffusion of tin vacancies. It is noteworthy that the recovery time of 150-kGy-irradiated sample (230 s) is slightly shorter than response time of 50-kGy-irradiated sample (277 s), in spite of the fact that they are operated by the same process: deactivation of tin vacancies. It may be due to the compensation effects of the minor carrier electrons. In this case, the net hole concentration is higher than the electron concentration in the pristine SnO2 nanowires, even after the difference in the mobility has been into consideration (i.e. μ_e = 5 × μ_h).

In general, these gas response and recovery times are closely associated with catalysis on the surfaces of the nanowires; this process can be investigated using DFT calculations. Therefore, in the near future, it should be possible to design and test chemical sensors directly using computer modeling and simulations.

The variation of resistivity by the electron-beam irradiation can be explained by means of the standard electron hole gas equilibrium statistics. In Table 2, for pristine SnO2 nanowires, the electron and hole concentrations are 3.3 × 10^16 electrons cm^-3 and 0 cm^-3, respectively. For SnO2 nanowires irradiated at 50 kGy, we check two cases; (a) upper limit electrons/lower limit holes: in case of full recombination, there will be 8.0 × 10^16 electrons cm^-3. Obviously, this is n-type and the electron concentration was increased by the electron-beam irradiation at 50 kGy; (b) lower limit electrons/upper limit holes: there will be 2.0 × 10^17 holes cm^-3 and 4.0 × 10^16 electrons cm^-3. In case (b), considering that μ_e = 5 × μ_h, n = μ_e = pμ_h. This matches with the sensor response data and specific resistivity data, indicating that the 50-kGy-irradiated sample is an n-type semiconductor. The specific resistivity data support that the resistance decreases by the electron-beam irradiation at 50 kGy. Accordingly, the electron concentration as an n-type will increase by the electron-beam irradiation at 50 kGy. For SnO2 nanowires irradiated at 150 kGy, we check two cases; (a) upper limit electrons/lower limit holes: there will be 2.7 × 10^17 holes cm^-3 and 5.3 × 10^16 electrons cm^-3, considering that μ_e = 5 μ_h, n = μ_e = pμ_h. (a) lower limit electrons/upper limit holes: there will be 5.3 × 10^17 holes cm^-3 and 0 electrons cm^-3. This is obviously p-type semiconductor. Our model shows the increase of hole concentration (from tin vacancy) by increasing the dose from 50 kGy to 150 kGy. However, the 50-kGy- and 150-kGy-irradiated samples are n-type and p-type, respectively. We check two cases; (a) upper limit electrons/lower limit holes: from Table 2, 150-kGy-irradiated sample has (8-5.3) × 10^16 less electrons (/cm^3) than the 50-kGy-irradiated one, but the difference in hole concentration is 2.7 × 10^17 (/cm^3), which is sufficient to make up for the conduction loss due to the electron even after taking into the factor of 5 (difference in mobility between electron and hole). We can justify that 150-kGy-irradiated sample has a little lower resistivity than the 50-kGy-irradiated one. (b), lower limit electrons/upper limit holes: from Table 2, 150-kGy-irradiated sample has (5.3-2) × 10^17 more holes (/cm^3) than the 50-kGy-irradiated one. This difference is sufficient to make up for the shortage due to the (4.0-0) × 10^16 electrons (/cm^3) in 150-kGy-irradiated sample. Therefore, our model (and data in Table 2) justifies the slight lower resistivity in 150 kGy-irradiated sample.

**Discussion**

Using the results of these calculations, we set the upper and lower limits for both carrier concentrations (Table 2), and explain the phenomena on experiment response and recovery times by a charge compensation mechanism. A typical charge compensation process on the Li- and Ti-codoping of NiO was studied by Wu et al.46; Li and Ti contributed to p-type and n-type conductions, respectively. On the basis of electron hole gas equilibrium statistics, the dependence of the Li-and Ti-generated states can be divided into three regimes: I, II, and III, as shown in Fig. 2 of Ref.46. The regimes I, II, and III correspond to the donor-dominated, compensated, and acceptor-dominated states, respectively. In the present work, transport behaviors associated with these three regimes were observed in zero, 50-, and 150-kGy-irradiated SnO2, where shallow donor and deep acceptor states are formed by oxygen vacancies and tin vacancies, respectively. In regime I, electrons are the only carriers. In regime II, electrons and holes are the major and minor carriers, respectively, leading to an n-type conduction. In regime III, holes and electrons are the major and minor carriers, respectively, leading to a p-type conduction.

Upon NO2 exposure, the concentrations of oxygen and tin vacancies will decrease and increase, respectively, and are responsible for the measured resistivity changes. The response time for resistivity change depends on the mobility of the minor carriers (non, holes and electrons respectively for regime I, II and III, respectively), via the charge compensation mechanism. There is negligible minority carrier in regime I and the minority carriers for regimes II and III are holes and electrons, respectively. For instance in regime III, newly generated holes (by NO2 exposure) have to first compensate the donor states (minor carriers) before contributing to the noticeable decrease in resistivity. Similarly the recovery time
depends on the mobility of the major carriers, which have to return to the original states. In SnO$_2$, it is believed that tin vacancies (for holes) diffuse slower than oxygen vacancies (for electrons)$^{43}$. Therefore, it predicts a prolonged response time if holes are the minor carriers and an extended recovery time if the holes are the major carriers.

In summary, we were able to achieve $p$-type-like conduction behavior in initially $n$-type SnO$_2$ nanowires via irradiation with a high-energy electron beam. We have proposed a mechanism for the transition from $n$-type to $p$-type conduction after electron-beam irradiation at a high dose (150 kGy). We explain that the electron-beam-induced loss of tin atoms (i.e. the generation of tin vacancies) in the SnO$_2$ lattice generates corresponding holes in the valence band of SnO$_2$, eventually leading to the $p$-type behavior. The concentrations of both carriers (electrons and holes) in the SnO$_2$ nanowires estimated on the basis of standard hole gas equilibrium statistics could explain the transition from $n$- to $p$-type transport behavior after the irradiation. The accompanying changes in the NO$_2$-sensing performances of the nanowires, including those in the response and recovery times, could also be explained. This study not only demonstrates that electron-beam irradiation can be an effective means of creating bipolar transport conduction in semiconductors but also provides a fundamental approach for developing SnO$_2$-based electronic and electrochemical devices.

**Methods**

**E-beam irradiation.** The SnO$_2$ nanowires were fabricated by heating Sn powders via a vapor-liquid-solid (VLS) method (Fig. 5). The substrate temperature was kept at 800°C, while a mixture of Ar and O$_2$ gases was made to flow through the growth chamber. The fabrication procedure used was similar to one previously reported$^{49}$. Once fabricated, the SnO$_2$ nanowires were irradiated with an electron beam. The apparatus used for the process was the ELV-8 electron accelerator (EBTech, Daejeon, Korea). Electron beams with an accelerating voltage, dose, beam current, and pulse duration of 1.5 MeV, 50–150 kGy, 1 mA, and 400 ps, respectively, were used. The KGy is equal to 1,000 Gy, and the Gy is defined as the absorption of one joule of ionizing radiation by one kilogram of matter. The synthesized SnO$_2$ nanowires were irradiated in air ambient at room temperature. For precise comparison, the pristine and electron-beam irradiated samples not only are the same size but also contained nearly the same amount of SnO$_2$ nanowires within the error range, being confirmed by the analytical balance (readability: 0.01 mg, XR 205SM-DR, PreCISA Instruments AG, Swiss).

**Characterization.** The phases and crystalline qualities of the nanowires were determined via X-ray diffraction (XRD) analyses performed using a Philips X’pert MRD diffractometer and CuK$_\alpha$ radiation. The microstructures of the nanowires were observed using field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4200). In order to investigate the nature of the defects in the nanowires, the photoluminescence (PL) spectra of the nanowires were recorded at room temperature using a SPEC-1403 photoluminescence spectrometer and the 325-nm line of an He-Cd laser (Kimon, Japan).

**Sensing measurement.** For the NO$_2$ sensing measurements, an electrode layer comprising a 300-nm-thick layer of Au and a 50-nm-thick layer of Ti was sequentially sputtered on the specimens with an interdigital electrode mask (Fig. 5). A preliminary study performed by us had indicated that this Ti/Au system is very effective for making the ohmic contacts for the sensors. The fabricated sensors were placed in a horizontal-type tube furnace; the operating temperature was fixed at 300°C, because the NO$_2$-sensing performances of the sensors were the best at this temperature during preliminary tests. The concentration of NO$_2$ was controlled by changing the mixing ratio of dry air to NO$_2$ gas using high-precision mass flow controllers. The total flow rate was set to 500 sccm to prevent any possible variation in the sensing properties of the nanowires. According to the specifications provided by the gas manufacturer (Daeduk Gas Co., Korea), the water content in both the dry air/NO$_2$ gas mixture and the dry air was negligible. In case of the sensor showing $n$-type sensing behavior, the response was determined using $R = R_a/R_g$, where $R_a$ and $R_g$ are the resistances of the sensor in the absence and presence of NO$_2$, respectively. In case of the sensor showing $p$-type sensing behavior, the response was determined using $R = R_a/R_g$. The response and recovery times of the sensors were defined as the times taken for the resistance to change by 90% on exposure to the target gas (NO$_2$) and air, respectively.

**DFT studies.** Our spin-polarized calculations were performed using Quantum Espresso package$^{50}$. The exchange-correlation potential is approximated by generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) functional$^{51}$. The kinetic-energy cutoffs for valence electron wave functions and charge density are set as 35 Ry and 350 Ry, respectively. The optimized structures are 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$^{-1}$. 
References

1. Kazar, I., Roy, S. C. & Bhatnagar, M. C. Effect of indium doped SnO2 nanoparticles on NO2 gas sensing properties. Sens. Actuators B 126, 478–484 (2007).
2. Godinho, K. G., Walsh, A. & Watson, G. W. Energetic and electronic structure analysis of intrinsic defects in SnO2. J. Phys. Chem. C 113, 439–448 (2009).
3. Galatiss, K. et al. p- and n-type Fe-doped SnO2 gas sensors fabricated by the mecanochemical processing technique. Sens. Actuators B 93, 562–565 (2003).
4. Licznarski, B. W., Nitsch, K., Teterycz, H. & Wisniewski, K. The influence of Rh surface doping on amorphous properties of thick-film SnO2 gas sensors. Sens. Actuators B 79, 157–162 (2001).
5. Kim, K. D. et al. Influence of electron-beam treatment of TiO2/Ti on properties of deposited Pt films. Surf. Interf. Anal. 42, 927–930 (2009).
6. Oshima, A., Shiraki, F., Fujita, H. & Washio, M. Surface modification of polymeric materials using ultra low energy electron beam irradiation. Radiat. Phys. Chem. 80, 196–200 (2011).
7. Lakdawala, V. K., Stoudt, D. C., Smith, T. F. & Brinkmann, R. P. Electron-beam-controlled high-power semiconductor switches. IEEE Transactions on Electron Devices 36, 1793–1802 (1989).
8. Li, X. et al. Investigation of electron beam detection properties of ZnO nanowire based back-to-back double Schottky diode. RSC Adv. 4, 12743–12747 (2014).
9. Pan, Z. W., Dai, Z. R. & Wang, Z. L. Lead oxide nanobelts and phase transformation induced by electron beam irradiation. Appl. Phys. Lett. 80, 309–311 (2002).
10. Edgell, R. G., Erikson, S. & Flavell, W. R. A spectroscopic study of electron and ion beam reduction of SnO2(110). Surf. Sci. 192, 265–274 (1987).
11. Komuro, Y. & Matsumoto, Y. Electron beam-induced reduction of SnO2 deposited on TiO2(110) surfaces. J. Phys. Chem. C 115, 6618–6621 (2011).
12. Wang, B., Yang, Y. H. & Yang, G. W. Electron-beam irradiation induced shape transformation of Sn-SnO2 nanocables. Nanotechnology 17, 5916–5921 (2006).
13. Belloni, J. et al. Radiation-induced synthesis of mono- and multi-metallic clusters and nanoclusters. New J. Chem. 22, 1239–1255 (1998).
14. Beloni, J. Nucleation, growth, and properties of nanoclusters studied by radiation chemistry application to catalysis. Catal. Today 113, 141–156 (2006).
15. Bogle, K. A. & Dhole, S. D. Silver nanoparticles: synthesis and size control by electron beam irradiation. Nanotechnology 17, 3204–3208 (2006).
16. Henglén, A. Physicochemical properties of small metal particles in solution: microelectrode reactions, chemisorptions composite metal particles, and the atom-to-atom transition. J. Phys. Chem. 97, 5457–5471 (1993).
17. Treguer, M. et al. Dose rate effects on radiolytic synthesis of gold-silver bimetallic clusters in solution. J. Phys. Chem. 102, 4310–4321 (1998).
18. Kim, S.-E., Han, Y.-H., Lee, B. C. & Lee, J.-C. One-spot fabrication of various silver nanostructures on substrates using electron beam irradiation. Nanotechnology 21, 075302–075308 (2010).
19. Marignier, J. L. Belloni, J., Delcourt, M. O. & Chevalier, J. P. Microaggregates of non-noble metals and bimetallic alloys prepared by radiation-induced reduction. Nature 317, 344–345 (1985).
20. Leo, G. et al. Sprayed SnO2 thin films for NO2 sensors. Sens. Actuators B 58, 370–374 (1999).
21. Lim, W. et al. Selective-hydrogen sensing at room temperature with Pt-coated InN nanobelts. Appl. Phys. Lett. 93, 072109 (2008).
22. Vomiero, A. et al. InN nanowires for gas sensors: morphology and sensing characterization. Thin Solid Films 515, 8356–8359 (2007).
23. Kim, S. S. et al. Significant enhancement of the sensing characteristics of In2O3 nanowires by functionalization with Pt nanoparticles. Nanotechnology 21, 415502 (2010).
24. Kim, S. S. et al. Novel growth of CuO-functionalized, branched SnO2 nanowires and their application to H2S sensors. J. Phys. D: Appl. Phys. 45, 205301 (2012).
25. Giannozzi, P. et al. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. J. Phys.: Condens. Matter. 21, 175306 (2009).
26. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
27. Iao, Z. et al. Effects of electron beam irradiation on tin dioxide gas sensors. Bull. Mater. Sci. 31, 83–86 (2008).
28. Cho, N. G. et al. Highly sensitive SnO2 hollow nanofiber-based NO2 gas sensors. Sens. Actuators B 128, 566–573 (2008).
29. Prades, J. D. et al. Effect study of SnO2 nanostructures by cathodoluminescence analysis: application to nanowires. Sens. Actuators B 126, 6–12 (2007).
30. Gaidi, M. et al. Structure and photoluminescence of ultrathin films of SnO2 nanoparticles synthesized by means of pulsed laser deposition. J. Appl. Phys. 108, 063537 (2010).
31. Wang, S. H., Chou T. C. & Liu, C. C. Nano-crystalline tungsten oxide NO2 sensor. Sens. Actuators B 94, 343–351 (2003).
32. Zhou, X. T. et al. Origin of the luminescence from SnO2 nanoribbons. In: The 13th International Conference on X-ray Absorption Fine Structure. Stanford, California, U. S. A. July 9–14 882, 777–779 (2006).
33. Doi, K., Sasaki, T. & Hukata, K. Electronic properties of TeO2. J. Bull. Chem. Soc. Jpn. 48, 144–146 (1975).
34. Doshi, E. E. & Mazloom, J. Optical, electrical and morphological properties of p-type Mn-doped SnO2 nanostructured thin films prepared by sol-gel process. Appl. Phys. A 108, 693–700 (2012).
35. Mao, Q. N., Ji, Z. G. & Zhao, L. N. Mobility enhancement of p-type SnO2 by In-Ga co-doping. Physica Status Solidi B-Basic Solid State Physics 247, 299–302 (2010).
36. Mi, Y., Ódaka, H. & Iwata, S. Electronic structure and optical properties of ZnO, SnO2 and In2O3. Jpn. J. Appl. Phys. 38, 3453–3458 (1999).
44. Sanon, G., Rup, R. & Mansingh. A. Band gap narrowing and band structure in degenerated tin oxide (SnO₂) films. Phys. Rev. B 44, 5672–5689 (1991).
45. Sakurai, T. & Takizawa, T. Thermal expansion of SnO₂ at high temperatures. High Temp. High Pressures 3, 325–331 (1971).
46. Kamp, B., Merkle, R., Lauck, R. & Maier, J. Chemical diffusion of oxygen in tin dioxide: effects of dopants and oxygen partial pressure. J. Sol. Stat. Chem. 178, 3027–3039 (2005).
47. Yoo, H. I. & Lee, C. E. Two-fold diffusion kinetics of oxygen re-equilibration in donor-doped BaTiO₃. J. Am. Ceram. Soc. 88, 617–623 (2005).
48. Zhang, J., Loh, K. P., Yang, S. W. & Wu, P. Exohedral doping of single-walled boron nitride nanotube by atomic chemisorptions. Appl. Phys. Lett. 87, 243105 (2005).
49. Zhang, J., Cao, X.-M., Hu, P. J. & Wu, P. Density functional theory studies of ethanol decomposition on Rh(211). J. Phys. Chem. C 115, 22429–22437 (2011).
50. Zhang, J. et al. Study of Pd-Au bimetallic catalysts for CO oxidation reaction by DFT calculations. Phys. Chem. Chem. Phys. 11, 1441–1446 (2009).
51. Wu, P. et al. Defects in codoped NiO with gigantic dielectric response. Phys. Rev. B 79, 235112 (2009).

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Author Contributions
H.W. and S.S.K. designed the experiments, analyzed the data. P.W. and V.K. planned and performed the models and calculations, designed the theoretical work. H.G.N. conducted the experiments. H.W.K. and P.W. wrote the manuscript. All authors participated in discussion and reviewed the manuscript.

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