Promotion on Acetone Sensing of Single SnO₂ Nanobelt by Eu Doping

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Abstract
SnO₂ nanobelts (NBs) have unique structural and functional properties which attract great attention in gas detecting. In this work, Eu doping is adopted to improve the gas sensitivity of pure SnO₂, especially to enhance the response to one single gas. The Eu-doped SnO₂ NBs, pure-SnO₂ NBs, and their single NB devices are fabricated by simple techniques. The sensing properties of the two sensors have been experimentally investigated. It is found that the two sensors possess long-term stability with rapid response performance, and Eu doping improves the electronic performance and the gas-sensing response, particularly to acetone. In addition, the effects aroused by Eu have been theoretically calculated, which indicates that Eu doping enhances the sensing performance of SnO₂. Consequently, Eu-doped SnO₂ NBs show great potential applications in the detection of acetone.

Keywords: Eu-doped SnO₂, Single nanobelt, Acetone sensor

Background
With the development of industry, as an important aspect of environmental problems, the leakage of harmful gases becomes more and more eye-catching. Many efforts of improving the gas sensor performance have been made in order to detect and monitor those gases. Excellent accomplishments have been reached in the field of gas sensor due to the remarkable advancement in novel nanomaterials [1–3].

Among various shapes of nanomaterials, nanobelt is a promising choice in gas sensing application [4, 5] since it could bear a large specific surface area, crystallographic perfection, and great electron transport properties. For instance, Khiabani et al. have reported that In₂O₃ NBs have excellent gas sensitive properties for NO₂ [6]. As to metal oxide semiconductors, their susceptibility coupled with stabilization makes it very applicable to the detection of various gases [7–9]. As an n-type wide-bandgap semiconductor, SnO₂ with a high gas-sensitive response to a variety of gases has attracted worldwide attention [10–12]. It has been proved by Huang et al. that SnO₂ nanorod arrays take the possession of unique performance as a hydrogen sensor [13]. In such materials, rare metal doping is often used to improve the sensitivity, especially to one single gas [14, 15]. As a typical rare earth metal, it has been proved to be effective for Eu to improve the sensing performance of various materials [16–19]. Especially, Hao et al. have testified the positive effects of Eu doping on the sensing and electrical conductivity of Eu-based metal-organic framework [20]. However, to the best of our knowledge, there are still very few studies about Eu doping effects on the gas-sensitive properties so far. Thus, it is a requisite to explore the gas-sensing properties of Eu-doped-SnO₂ nanobelts (Eu-SnO₂ NBs) to make progress in the sensitivity of pure-SnO₂ nanobelts (SnO₂ NBs).

In this work, we have made the synthesis of SnO₂ NBs and Eu-SnO₂ NBs by thermal evaporation method with simple conditions, low cost, and accessibility. The sensitivity of SnO₂ NBs and Eu-SnO₂ NBs to four gases was measured, and it is demonstrated that the Eu-SnO₂ NB sensor owns a higher response, especially to acetone. The conceivable mechanism was proposed on the basis of theoretical calculations. It turns out that Eu-SnO₂ NBs reveal great potential in acetone-sensing applications.
Methods
The synthesis of NBs was conducted in a horizontal tube furnace (HTF) with an alundum tube. The raw materials which provided Sn element were pure SnO2 powders, and Eu ions were supplied by pure Eu(O2CCH3)3 powders with a mass ratio of 19:1 for the preparation of the doped NBs. Then, the ingredients were filled into a ceramic boat being laid in the middle of the HTF and a silicon wafer plated with 10 nm Au film was positioned downstream 20 cm far away from the vessel. Subsequently, HTF was rinsed by argon, and then the temperature of the central region climbed up to 1355 °C with a ramp-up of 10 °C/min and then was kept at 1355 °C for 120 min. The flow of argon as carrier gas was at 20 sccm in the meantime, and the internal pressure was maintained at 200 torr by means of a mechanical pump. At last, the temperature declined naturally and the required NBs were obtained.

The specimens were characterized by X-ray diffraction (XRD) (D/max-3B Rigaku with Cu-Kα radiation, λ = 0.15406 nm), scanning electron microscopy (SEM) (Quanta 200 FEG, FEI Company), energy dispersive X-ray spectroscopy (EDS) (Octane Super, EDAX), X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versaprobe, ULVAC-PHI), and high-resolution transmission electron microscopy (HRTEM) attached with the selected area electron diffraction (SAED) (Tecnai G2 Transmission Electron Microscope, 200 kV).

The single nanobelt devices were manufactured by dual-ion beam deposition (LDJ-2a-F100-100 series) with an aid of the mesh-grid mask. First of all, a few nanobelts were dissolved into ethanol liquid to prepare a floating liquid, and then the floating liquid was dripped down to the surface of silicon wafer uniformly, which could result in the uniform distribution of nanobelts on the surface of silicon wafer. Thereafter, Ti (8 nm) and Au (80 nm) electrodes were deposited on the substrate in the conditions of the pressure of 2.2 × 10−2 Pa and argon ion flow of 10 mA/cm². After these, the preparation has been accomplished and the measurements would be conducted by Keithley 4200 SCS.

Results and discussion
The SEM images in Fig. 3a, d show that the widths of Eu-doped and pure SnO2 NBs with regular morphology are 1.661 μm and 543.8 nm, respectively. The TEM images in Fig. 3b, e reveal that the Eu-doped and pure SnO2 nanobelts are homogeneous with no remarkable surface defects. Their corresponding HRTEM and SAED patterns in Fig. 3c, f indicate that their growths are both directed along [0 0 3], since the measured inter-planar spacing of 0.47 and 0.48 nm corresponds to the spacing of the (0 0 3) planes. These diffraction spots formed a rectangular array in conformity with tetragonal structure SnO2 which could manifest crystallographic perfection.

The XRD spectra in Fig. 4a show that all diffraction peaks of Eu-SnO2 and SnO2 NBs can be indexed as the tetragonal rutile SnO2 phase (JCPDS card No.77-0450) with a = b = 0.473 nm and c = 0.318 nm. At the same time, it is revealed that the diffraction peaks of the

Fig. 1 Optical microscope photos of a Eu-SnO2 NB and b SnO2 NB devices
admixtures move toward low angles, and it could be proved that Eu has been doped into the lattice. This is reasonable, considering that the radius of Eu ion (94.7 pm) is larger than that of Sn ion (69 pm). The EDS spectra in Fig. 4b can confirm it that Eu ions have been doped into SnO$_2$ NBs. Based on the EDS data, it could be deduced that the ratios of Sn and O ions are 1:1.68 in Eu-SnO$_2$ NBs and 1:1.76 in SnO$_2$ NBs, indicating that there exist oxygen vacancies.

As shown in Fig. 4c, XPS spectrum displays that SnO$_2$ NBs contain Sn 3d, O 1s, Eu 4d, and C 1s states. It is indicative of the successful doping of Eu into SnO$_2$. In Fig. 4d, the Eu 4d peak having great symmetry could be well fitted by a Gaussian spectrum. It implies that there is only Eu 4d$_{5/2}$ located in a 128.9 eV state arising from trivalent Eu, so the main Eu element in Eu-SnO$_2$ NBs is Eu$^{3+}$.

From the I–V curves of the two sensors in Fig. 5a, it is known that the two sensors both have good ohmic contact but a noteworthy disparity in resistance. The resistance is found to be about 3.25 MΩ for Eu-SnO$_2$ NBs and 7.97 MΩ for SnO$_2$ NBs. Obviously, Eu doping has been successful in improving the conductivity of SnO$_2$ NBs. The sensitivity is defined as $R_a/R_g$, where $R_a$ is the resistance in air and $R_g$ is the resistance in target gas. With a reducing gas circulating inside, the tendency of change of the resistance of Eu-SnO$_2$ NB is the same as that of SnO$_2$ NB, which indicates that Eu-SnO$_2$ NB is a n-type semiconductor. As depicted in Fig. 5b, c, the gas responses of Eu-doped and pure sensors to 100 ppm of acetone, ethanol, methanal, and ethanediol at different temperatures have been investigated. The optimum working temperature of them is 210 °C. For different target gases, acetone, ethanol, methanal, and ethanediol, the highest sensitivities of the Eu-SnO$_2$ device are 8.56, 3.92, 2.54, and 2.17, respectively, while the corresponding values of the pure counterpart are 1.36, 1.43, 1.81, and 1.54. Evidently, the responses of Eu-SnO$_2$ sensor are much higher than those of the pure SnO$_2$ one. It is worth stressing that, for acetone gas, the response has reached 8.56, much higher than the values of the other gases. It could be demonstrated that the dopant Eu can effectively improve the response of SnO$_2$ NB.
Figure 5d displays the chemical resistance response of Eu-SnO$_2$ NB and SnO$_2$ NB sensors to different gas concentrations at 210 °C. With the concentration climbing up, the response/recovery time of Eu-SnO$_2$ NB (SnO$_2$ NB) sensor takes the values of 8/9 (5/7), 10/11 (12/14), 11/14 (12/13), 14/16 (14/16), and 15/19 (15/16) s. Their values are actually more or less the same in size. The detection lasted a few months and was repeated over and over again. Although during the period, the humidity ranged from 30 to 70 RH%, there is almost no fluctuation in the response, which could demonstrate that humidity has no effect on the sensor’s performance.

We plotted the curves of the response of the two sensors and gas concentration at 210 °C, as shown in Fig. 6a. The gradient decreases with the increase in gas concentration may be caused by the increasing surface coverage.
by the adsorbed molecules [23]. As shown in Fig. 6b, the response versus the logarithm of the concentration can be well fitted by a straight line. From that, the sensitivity coefficients of Eu-SnO$_2$ and SnO$_2$ sensors could be calculated and the results are 4.6919 and 0.5963, indicating that Eu doping could improve the gas sensing performance effectively.

The fitting curves of the sensitivity versus gas concentration in low scales are presented in Fig. 6c. It reveals that the slopes are 0.1099 and 0.0069, respectively. The theoretical detection limit (TDL) of the sensor can be derived from the root-mean-square deviation $\text{RMSD} = \sqrt{\frac{S^2}{N}}$, where $N$ is the number of the selected points at the baseline in Fig. 5d and $S$ is the standard deviation of these points [24]. The TDLs of Eu-SnO$_2$ NB and SnO$_2$ NB sensors can be calculated based on $\text{TDL (ppm)} = 3 \times \frac{\text{RMSD/slope}}{\text{signal-to-noise ratio}}$ with the signal-to-noise ratio of 3 [25], and the results are 131 and 230 ppb. To understand the mechanism of the above observation, the calculation of the band structure of SnO$_2$ and Eu-SnO$_2$ was needed. As shown in Fig. 7, the top of the valence band and the bottom of the conduction band are located at point G in the Brillouin zone and it means that SnO$_2$ is a direct-band gap semiconductor with a band gap of 1.047 eV. The calculated band gap is lower than the experimental value of 3.6 eV, which is due to the use of DFT. After Eu doping, the bottom of the conduction band moves to lower energy, so the band gap is narrowed down to a value of 0.636 eV. As a result, the needed energy for the electrons jumping from the valence band to the conduction band becomes smaller, the electron excitation becoming easier, a red-shift occurring in the absorption band, the range of spectral response expanding, and the efficiency of electron excitation could be improved. In one word, Eu doping improves the electrochemical properties of SnO$_2$.
Figure 8 shows the density of states of Eu-SnO$_2$ and SnO$_2$, from which some changes caused by Eu doping can be observed. It shows that the low-energy parts (−20~0 eV), which are mainly composed of Sn 5s and O 2p states, are less influenced by Eu doping. As the inset of Fig. 8a shows, d and f orbits produce three peaks after Eu doping, and this means that there has appeared the impurity levels. As a result, the band gap becomes narrower, which could lead to an improvement in the conductive performance of SnO$_2$.

As a metal oxide material, SnO$_2$-based sensor belongs to the surface-controlled type [26]. The schematic diagram of the gas-sensing mechanism is shown in Fig. 9. Upon being exposed to air, the oxygen will be adsorbed on the surface, trapping free electrons, which could result in the formation of the depletion layer and the decline in conductivity according to Eq. 1

$$O_2 + e^- \rightarrow O^x \quad (1)$$

where O$^x$ means all kinds of oxygen ions [27, 28].

It is suggested that the oxygen-negative ions will react with the injected target gases and release the captured electrons back to the electron-depleted regions, reducing the resistance following these reactions [29, 30]

$$\text{CH}_3\text{COCH}_3 + O^x \rightarrow \text{CO}_2 + H_2O + e^- \quad (2)$$
$$\text{HCHO} + O^x \rightarrow \text{CO}_2 + H_2O + e^- \quad (3)$$

Eventually, due to the trapping and release of electrons, the conductivity of nanobelt generates an evident change and achieves the sensing improvement. Besides, the performance of the doped sensor is much higher than that of its counterpart. Therefore, it is possible that Eu plays a significant role. According to the theoretical results, Eu doping could improve the electrochemical properties and conductive performance of SnO$_2$. Then, the improved properties could contribute to a more rapid increase in the number of free electrons, narrow the electronic depletion layer, and enhance the deoxidation reaction on the surface. Just as a catalyst, Eu ions could promote the reactions around them [31]. Moreover, the possible reactions caused by Eu have been presented as below [32]:

$$\text{Eu}^{3+} + H_2O \rightarrow \text{EuO}^+ + H^+ \quad (4)$$
$$\text{EuO}^+ + O^x \rightarrow \text{Eu}_2\text{O}_3 + V_{O''} + e^- \quad (5)$$

According to Eqs. 4 and 5, more defects will be formed when Eu ions replace the position of Sn atoms in SnO$_2$ lattice, and this could lead to more active reactions at the same time. In addition, Eu doping can trigger the dehydrogenation which can lower down the energy of the redox reactions [33]. Through these ways, Eu realizes the boost of sensor performance.

**Conclusions**

The Eu-doped and pure SnO$_2$ NBs with regular morphology and great flakiness ratio have been fabricated and the relevant single nanobelt devices have been prepared. Certainly, their electrical- and gas-sensing properties
have been investigated and it is found that the conductivity of Eu-SnO\textsubscript{2} is higher than that of the pure one. The results of their sensitive measurements show that the optimum working temperatures of them are both 210 °C, and the highest sensitivity of Eu-SnO\textsubscript{2} device to 100 ppm of acetone is 8.56, which is 6.29 times as large as that of its pure counterpart (1.36). The response recovery time of the two devices is less than 20 s. The TDL of the Eu-SnO\textsubscript{2} is higher than that of the pure one. The results have proved that Eu doping could improve the sensitivity of sensing response of SnO\textsubscript{2} NB, especially to acetone gas.

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Authors’ Contributions
YLiu and HZS guided the experiments and revised the final edition of the manuscript. YC and ZG performed the experiments and wrote the manuscript. YZ guided the simulations. YL, SS, and ZMW improved the manuscript. All authors read and approved the final manuscript.

Competing Interests
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References
1. Bai J, Zhou B (2014) Titanium dioxide nanomaterials for sensor applications. Chem Rev 114:10131–10176
2. Luo L, Liang F, Jie J (2011) Sn-catalyzed synthesis of SnO\textsubscript{2} nanowires and their optoelectronic characteristics. Nanotechnology 22485701
3. Luo L, Yang X, Liang F, Jie J, Wu C, Wang L, Yu Y, Zhu Z (2011) Surface dangling bond-mediated molecules doping of germanium nanowires. J Phys Chem C 115:24029–24039
4. Zhao Z, Tian J, Sang Y, Gobat A, Liu H (2015) Structure, synthesis, and applications of TiO\textsubscript{2} nanobelts. Adv Mater 27:2557–2582
5. Fu H, Xie H, Yang X, An X, Jiang X, Yu A (2015) Hydrothermal synthesis of silver vanadium oxide (Ag\textsubscript{2}V\textsubscript{2}O\textsubscript{7}) nanobelts for sensing amines. Nanoscale Res Lett 10:11
6. Khbani PS, Hosseinmardi A, Marzbanrad E, Ghahshgeha S, Zamani C, Keyanpour-Rad M, Raisi B (2012) NO\textsubscript{2} gas sensor fabrication through AC electrophoretic deposition from electrospray In\textsubscript{2}O\textsubscript{3} nanoribbons. Sens Actuators B Chem 162:102–107
7. Zhang J, Liu X, Neri G, Pinna N (2016) Nanostructured materials for room-temperature gas sensors. Adv Mater 28:795–831
8. Liu L, Li S, Guo X, He Y, Wang L (2016) Excellent performance of gas sensor based on In\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3} nanotubes. J Semicond 37:013005
9. Wu WY, Ting JM, Huang PJ (2009) Electrospray ZnO nanowires as gas sensors for ethanol detection. Nanoscale Res Lett 4:513–517
10. Chen Z, Pan D, Li Z, Jiao Z, Wu M, Shek CH, Wu CM, Lai JKL (2014) Recent advances in tin dioxide materials: some developments in thin films, nanowires, and nanorods. Chem Rev 114:7442–7486
11. Ma J, Liu Y, Zhang H, Ai P, Gong N, Zhang Y (2014) Synthesis and high-sensing properties of a single Pd-doped SnO\textsubscript{2} nanoribbon. Nanoscale Res Lett 9:503
12. Zhang H, Zhuo M, Luo Y, Chen Y (2017) Mesoporous tin oxide nanospheres for a NO\textsubscript{x} in air sensor. J Semicond 38:203003
13. Huang H, Gong H, Chow CL, Guo J, White TJ, Tse MS, Tan OK (2011) Low-temperature growth of SnO\textsubscript{2} nanorod arrays and tunable n–p–n sensing response of a ZnO/SnO\textsubscript{2} heterojunction for exclusive hydrogen sensors. Adv Funct Mater 21:2680–2686
14. Li X, Zhang F, Zhao D (2015) Lab on upconversion nanoparticles: optical properties and applications engineering via designed nanostructure. Chem Soc Rev 44:1346–1378
15. Li X, Liu Y, Li S, Huang J, Wu Y, Yu D (2016) The sensing properties of single Y-doped SnO\textsubscript{2} nanobelts device to acetone. Nanoscale Res Lett 11:470
16. Lee JJ, Xing GZ, Yi JB, Chen T, Ionescu M, Li S (2014) Tailoring the coercivity in ferromagnetic tin oxide thin films by 3d and 4f elements doping. Appl Phys Lett 104:12405
17. Wegh RT, Donker H, Oskam KD, Meijerink A (1999) Visible quantum cutting in LiGD\textsubscript{3}F\textsubscript{2}Eu\textsuperscript{3+} through down-conversion. Science 283:666–666
18. Luo M, Cheng K, Weng W, Song C, Du P, Shen G, Xu G, Han G (2009) Enhanced luminescence of Eu-doped TiO\textsubscript{2} nanodots. Nanoscale Res Lett 4:809
19. Mou P, Umapada P, Justo MGY, Felipe PR (2012) Effects of crystallization and dopant concentration on the emission behavior of TiO\textsubscript{2} Eu nanophosphors. Nanoscale Res Lett 7:1
20. Zhao Z, Yang G, Song X, Zhu M, Meng X, Zhao S, Song S, Zhang H (2013) A europium(ii) based metal-organic framework: bifunctional properties related to sensing and electronic conductivity. J Mater Chem A 2:237–244
21. Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865
22. Schleife A, Varley JB, Fuchs F, Rodl C, Bechtstedt F, Rinke P, Janotti A, van de Walle CG (2011) Tin dioxide from first principles: quasiparticle electronic states and optical properties. Phys Rev B 83:035116
23. Zheng JY, Yan Y, Wang X, Shi W, Ma H, Zhao YS, Yao J (2012) Hydrogen peroxide vapor sensing with organic core/sheath nanowire optical waveguides. Adv Mater 24:OP194–OP199. doi:10.1002/adma.201200867
24. Dua V, Surwade SP, Ammu S, Agnihotra SR, Jain S, Roberts KE, Park S, Rudolf, Manohar SK (2010) All-organic vapor sensor using inkjet-printed reduced graphene oxide. Angew Chem Int Ed 49:2154–2157
25. Duy LT, Kim DJ, Trung TQ, Dang VQ, Kim BY, Moon HK, Lee NE (2015) High performance three-dimensional chemical sensor platform using reduced graphene oxide on high aspect-ratio micro-pillars. Adv Funct Mater 25:883–890
26. Wagner T, Haffer S, Weinberger C, Klaus D, Tiemann M (2013) Mesoporous materials as gas sensors. Chem Soc Rev 42:4036–4053
27. Wang SB, Huang YT, Chattopadhyay S, Chang SJ, Chen RS, Chong CW, Hu MS, Chen LC, Chen KH (2013) Surface plasmon-enhanced gas sensing in single gold-peapodded silica nanowires. NPG Asia Mater 5:e49. doi:10.1038/am.2013.17
28. Chen W, Liu Y, Qin Z, Wu Y, Li S, Gong N (2016) Improved ethanol-sensing with single Yb ions doped SnO\textsubscript{2} nanobelt. Ceram Int 42:10902–10907
29. Ou JZ, Ge W, Carey B, Dameneke T, Roibat A, Shan W, Wang Y, Fu Z, Chrimes AF, Wlodarski W, Russo SP, Li YX, Kalantar-zadeh K (2013) Physisorption based charge transfer in two-dimensional SnS\textsubscript{2} for selective and reversible NO\textsubscript{2} gas sensing. ACS Nano 9:10313–10323
30. He Y, Wang D, Ge F, Liu L (2015) SnO\textsubscript{2}-doped α-Fe\textsubscript{2}O\textsubscript{3} patulous microtubes for high performance formaldehyde sensing. J Semicond 36:383005
31. Jeong SH, Kim S, Cho J, San MS, Park SH, Kim HY, Choi MH, Whangbo MH, Yoo KH, Kim SJ (2013) Hydrogen sensing under ambient conditions using SnO\textsubscript{2} nanowires: synergetic effect of Pd/Sn codeposition. Nano Lett 13:5938–5943
32. Klug C, Zunger A (2002) Origins of coexistence of conductivity and transparency in SnO\textsubscript{2}. Phys Rev Lett 88:095501
33. Zhang G, Zhang S, Yang L, Zou Z, Zeng D, Xie C (2013) La\textsubscript{2}O\textsubscript{3}-sensitized SnO\textsubscript{2} nanocrystalline porous film gas sensors and sensing mechanism toward formaldehyde. Sens Actuators B Chem 188:137–146