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Highly Stable Heavily-Doped Oxide Contacts on Oxide Nanowires: Reliable Low Contact Resistance and Enhancement of Long-term Sensor Response

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Abstract

A superior high temperature stability of SnO_2 nanowire devices was demonstrated by using heavily Sb-doped SnO_2 (ATO) as a contact layer. From contact resistance (R_c) evaluations with 200ºC air annealing, it is clarified that R_c of conventional Ti contacts significantly degrades due to Ti oxidation. Contrary, the R_c of ATO contact was almost constant over 400 hours. Furthermore, the practical stability of ATO contact was also confirmed by long-term gas sensor response measurements. Since the proposed concept can be applied for other oxide nanodevices, it enhances wider applications of oxide-based electronics.

Introduction

Recently, metal oxide nanowires have been intensively studied because of its various applications such as chemical/bio sensors, resistive switching memory, transparent electronics, etc. [1,2]. In terms of the practical application of oxide nanowires, contact resistance (R_c) is one of the critical issues because widely-used contact materials of low-work-function metal (Ti, Cr) are easily oxidized at operation temperature of typical chemical sensors around 200ºC [3]. Thus, stable contact materials to oxide nanowires are strongly desired for the oxide-based electron devices exposed to air and high temperatures.

In this work, we propose heavily Sb-doped SnO_2 (ATO) as a contact material on SnO_2 nanowires. The long-term stability of R_c of ATO and Ti were evaluated at a high temperature. A stability of SnO_2 gas sensors is also investigated for ATO and Ti contacts.

Experiments

Single crystalline Sb-doped SnO_2 nanowires were grown on Al_2O_3 (110) substrate by pulsed laser deposition technique using SnO_2 mixed with 0.5at%-Sb_2O_3 target [4]. The grown nanowires were dropped on SiO_2/Si substrate and electrodes were formed by electron-beam lithography and lift-off. As contact materials, Ti and heavily Sb-doped SnO_2 (ATO, Sb_2O_3 10at% target) were deposited by sputtering and PLD, respectively (Fig. 1). For ATO contact devices, Ar annealing was performed at 750ºC for 10 min to activate the dopant ions (Sb) in ATO. A schematic and SEM image of typical devices are shown in Fig. 2. For electrical characterizations, contact resistances (R_c) were extracted by 4-probe technique. A long-term stability was evaluated by annealing devices at 200ºC in air during intervals between electrical measurements.

Contact Resistances (R_c) of Ti and ATO

2-probe *I-V* characteristics of Ti and ATO contact devices were measured as fabricated, after 6- and 330- hours 200ºC annealing (Fig. 3). Although the current of Ti contact devices greatly decreases after annealing, that of ATO contact devices only slightly changes, indicating ATO contact devices are more stable at a high temperature operation. It is noted that the *I-V* curves of Ti contact devices show Schottky-diode like characteristics after annealing.

In order to clarify the origin of the current degradations in Ti contact devices, R_c was extracted from 4-probe measurements through 500 hours with 200ºC annealing (Fig. 4). The rapid increase in R_c of Ti contact was clearly observed during less than 200-hours annealing time. On the other hand, R_c of ATO contact devices was almost constant over 400 hours. Furthermore, it was confirmed that the slight current decrease of the ATO contact devices was results from the increase in nanowire resistivity by annealing (data not shown), namely the compensation of oxygen vacancies in SnO_2 nanowires which act as mobile carriers [5]. Thus, the advantage of ATO contacts compared to conventional Ti contacts was clearly shown in terms of stability of R_c.

The rapid increase in R_c of Ti contact is originated in the oxidation of Ti to TiO_x. As fabricated, Ti and n-type SnO_2 form a good Ohmic contact due to their band alignment (Fig. 5a). However, after Ti is oxidized, the contact stack changes to Pt/TiO_x/SnO_2 and a high and thick Schottky barrier is formed due to the low carrier density of TiO_x, resulting in rapid increase in R_c (Fig. 5b). For ATO contacts, because of a thin Schottky barrier in n+ ATO layer, electrons can easily tunnel through the barrier and a good Ohmic characteristics are obtained.

Long-term Sensor Response

A practical advantage of our concept was demonstrated by measuring gas sensor responses with high temperature annealing. Fig. 6 shows the relationship between the relative response to 100 ppm NO_2 and annealing time for Ti and ATO contact devices. The response of Ti contact sensors significantly degrades to around 1% within 100 hours due to Ti oxidation. Contrary, the response of ATO contact devices show only small decrease due to oxygen adsorption on SnO_2 nanowire surface. Thus, heavily-doped oxide contact devices shows superior long-term performances compared to the conventional metal contacts.

Conclusions

A stable Ohmic contact on SnO_2 nanowires was verified by using heavily Sb-doped SnO_2 (ATO) as a contact layer. Although the contact resistance of conventional Ti contact devices rapidly decreases at high temperatures due to Ti oxidation, that of ATO was almost constant over 400 hours. From the evaluation of NO_2 responses of Ti and ATO contact sensors, superior long-term response characteristics of ATO contact sensors were confirmed. Since proposed our concept can be applied for other oxide materials such as ZnO, MgO, etc., it enhances wider applications of oxide electronics.

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References

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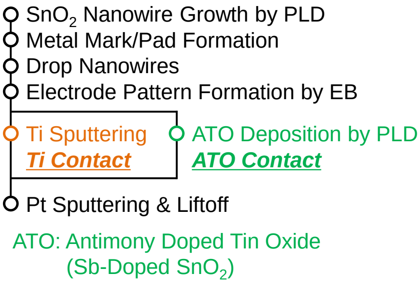

Fig. 1: Key fabrication processes of SnO_2 nanowire devices.

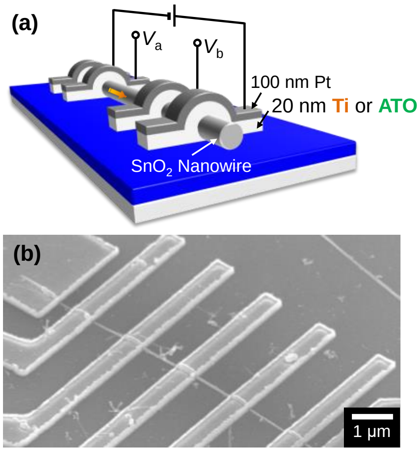

Fig. 2: (a) Device schematic and (b) SEM image of a typical 4-terminal device.

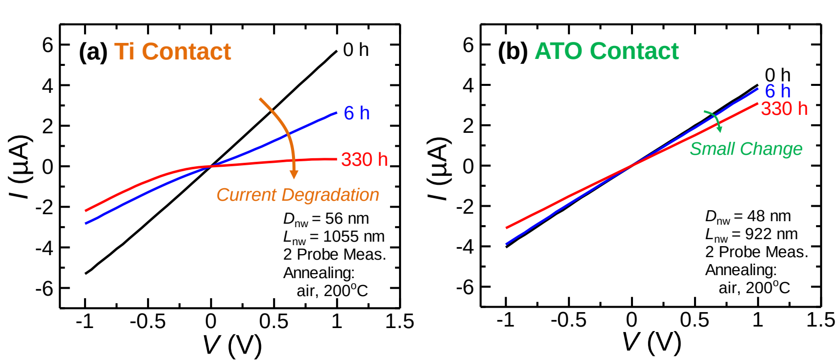

Fig. 3: *I-V* characteristics of (a) Ti and (b) heavily Sb-doped SnO_2 (ATO) contact SnO_2 nanowires as fabricated (0 h), after 6- and 330- hours 200ºC air annealing. Although the current of Ti contact devices greatly decrease after annealing, that of ATO contact devices only slightly changes due to the increase in resistivity of SnO_2 nanowire channel, indicating stable operations of ATO contact devices at a high temperature.

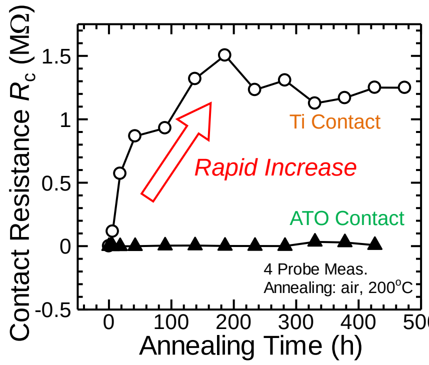

Fig. 4: Relationship between contact resistance (R_c) and annealing time for Ti and ATO contact devices extracted by 4-probe measurements. The rapid increase in R_c of Ti contact was clearly observed.

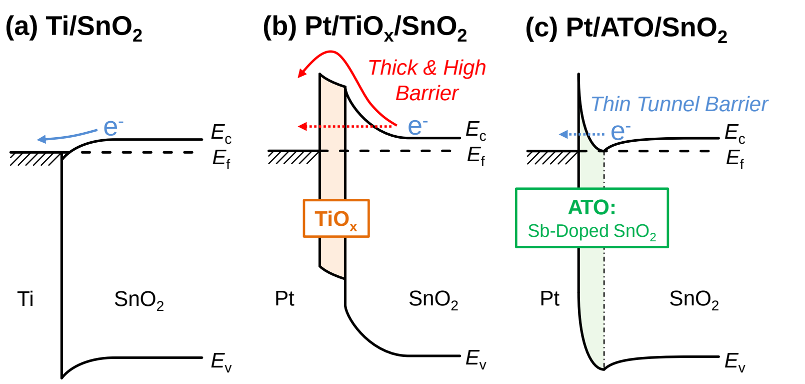

Fig. 5: Energy band diagrams at cross section between electrode and SnO_2 nanowire channel for (a) Ti/SnO_2, (b) $Pt/TiO_x/SnO_2$, and (c) $Pt/ATO/SnO_2$ stacks. As fabricated, Ti and n-type SnO_2 nanowire form a good Ohmic contact due to their band alignment. However, after Ti is oxidized to TiO_x, a high and thick Schottky barrier enlarge R_c. For ATO contacts, because of a thin Schottky barrier in n+ ATO layer, a good Ohmic contact are obtained.

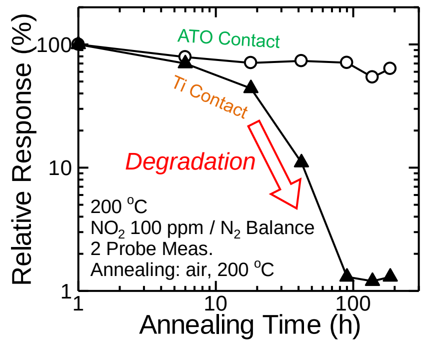

Fig. 6: Relationship between relative sensor response to 100 ppm NO_2 and annealing time for Ti and ATO contact SnO_2 nanowire gas sensors. Although the response of Ti contact sensor significantly degrades within 100 hours, that of ATO contact sensor show only small decrease due to oxygen adsorption on SnO_2 nanowire surface.