Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp1218-1219

Significant Conductivity Enhancement of TiO_2 Films by Both Field Effect and Chemical Doping

Go Oike, Takeaki Yajima, Tomonori Nishimura, Kosuke Nagashio, and Akira Toriumi
Department of Materials Engineering, The University of Tokyo
7-3-1 Hongo, Tokyo 113-8656, Japan
Phone and Fax: +81-3-5841-7161, E-mail: oike@adam.t.u-tokyo.ac.jp

Abstract

We investigated the electrical conduction of TiO_2 films induced by both field-effect and chemical doping. We found that the former characteristics of TiO_2 were much improved by post-deposition annealing in O_2, and that the latter was significantly increased by immersing in acidic or alkaline solution.

1. Introduction

TiO_2 recently attracts much attention for various applications such as photo-catalyst, transparent semiconductor as well as resistive memory [1-3] in spite of a simple composition of "titanium" and "oxygen". Both field-effect and chemical doping techniques for TiO_2 are required to make electronic devices applicable. In this paper, we focus on electrical transport properties of TiO_2 films in terms of FET performance [2, 4, 5] and chemical doping [6].

2. Experimental

TiO_2 films (5-80nm) were prepared by pulsed laser deposition on 119-nm-thick SiO_2/n^+-Si, under an oxygen pressure of 1 Pa and room temperature. The gate electrode of TiO_2 FETs was n^+Si. Post deposition annealing (PDA) was performed for TiO_2 films at 500ºC for 30 min in various ambient. Source and drain electrodes were prepared by Al. Channel width and length were both 100 μm. The FET structure is schematically shown in **Fig. 1** On the other hand, the chemical doping was performed by immersing TiO_2 surface in various liquids.

3. Results and Discussion

First, we investigated the electrical conduction in TiO_2 films by field-effect doping. **Fig. 1** shows the transfer characteristics of TiO_2 FETs of 20 nm in O_2 and $He+H_2$ (1 %) PDA. Both of FETs show sufficiently low off currents, while the threshold voltage (V_{th}) and field-effect mobility (μ_{FE}) and on/off ratio of FETs are quite different from each other. V_{th}, μ_{FE} and on/off ratio in O_2 PDA are -3.30 V, 8.76 cm^2/Vs and ~10^6. To our knowledge, these are highest or comparable to highest ones reported in the literatures [4, 5].

We confirmed that V_{th} of TiO_2 FETs was independent of thickness (data not shown). If channels are formed in whole film, thicker TiO_2 FETs should have lower V_{th}. So, it is concluded that the channel is formed at TiO_2/SiO_2 interface and carriers are modulated at TiO_2/SiO_2 interface by field effect.

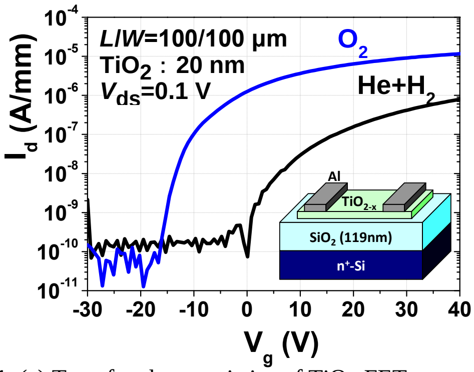

Fig. 1. (a) Transfer characteristics of TiO_2 FETs annealed in O_2 and $He+H_2$.

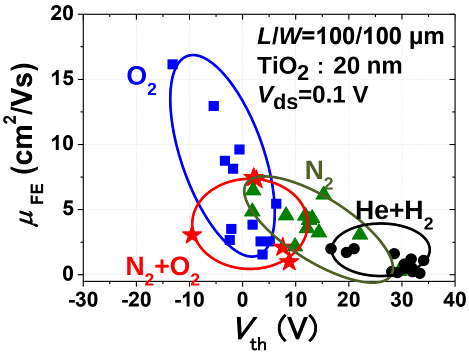

Fig. 2. Threshold voltage and field-effect mobility of TiO_2 TFTs in various PDA ambient.

Next, we discuss the effect of PDA ambient on FET characteristics. **Fig. 2** shows both V_{th} and μ_{FE} of TiO_2 FETs annealed in O_2, O_2+N_2, N_2 and $He+H_2$. The results clearly demonstrate that oxidative ambient PDA achieves a lower V_{th} and higher μ_{FE} simultaneously. Considering that the ideal value of V_{th} is approximately 0 V in terms of the band alignment, FETs annealed in O_2 have approximately an ideal V_{th}, while those annealed in reductive gas have higher V_{th}. It is expected that reductive PDA generates donor-type defects, such as Ti interstitials and oxygen vacancies, leading to lower V_{th}. The reductive PDA, however, caused higher V_{th}, so the results in the present experiment cannot be explained in terms of donor-type defects formation of in TiO_2. TiO_2 films annealed in any PDA ambient were crystallized to anatase, and no difference in the crystal structure was detected by Raman [7] and in-plane XRD measurements. It was previously reported in other oxides that the

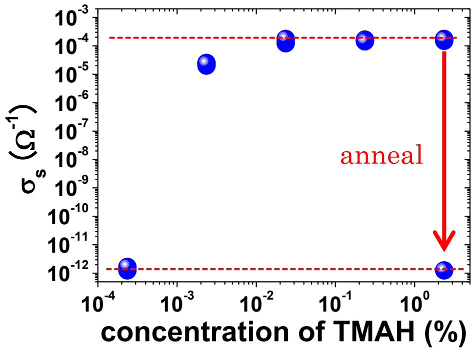

Fig. 3. Sheet conductivities of TiO_2 films immersed to TMAH with various concentration.

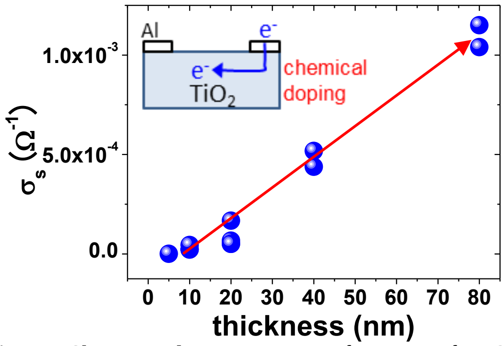

Fig. 4. Sheet conductivities as a function of TiO_2 film thickness.

oxygen vacancies formed in reductive atmosphere cause not only donor levels, but also acceptor levels by structural disorder [8]. Therefore, we think for the present that the observed V_{th} increase in reductive atmosphere is caused by acceptor levels caused by oxygen vacancies, and the annihilation of oxygen deficiencies is the most critical for the performance improvement in TiO_2 FETs. Note some of FETs have negative V_{th} although we mentioned the ideal value of V_{th} is 0 V. Actually in the fabricated TiO_2 FETs, decrease of V_{th} with time was observed, also slightly shifting V_{th} to negative values in **Fig. 2**.

Next, we discuss the chemical doping [6] on the electrical conduction of TiO_2. TMAH ($[N(CH_3)_4]^+OH^-$) was first employed for introducing electrons into TiO_2 films. TMAH is the typical developer in the photo-lithography process. As shown in **Fig. 3**, the sheet conductivity dramatically increase $>10^{-4}$ (Ω^{-1}) when immersed to TMAH with concentration of more than 0.001 %, while the sheet conductivity decreased to the original value when annealed in N_2 at 400ºC. It indicates that TMAH does not change intrinsic properties of TiO_2 films.

Fig. 4 shows the sheet conductivity of TiO_2 films with various thicknesses. The almost linear relationship except in a very thin region implies that electrons introduced by TMAH will not be localized at the surface of TiO_2 but spread over the whole TiO_2 film.

Finally, the sheet conductivity of TiO_2 films immersed to various liquids is shown in **Fig. 5**. Note that

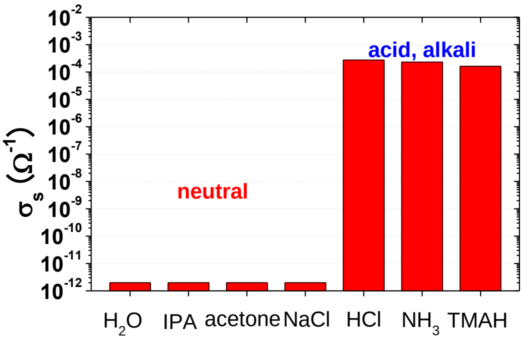

Fig. 5. Sheet conductivities of TiO_2 films immersed to various liquids.

the conductivity of TiO_2 films significantly increases, when the films are immersed to not only TMAH but also NH_3 and HCl solutions. We have confirmed that the induced carrier type is "electron" by the Hall effect measurement. Considering that the doped carriers are spread throughout the film while the sheet conductivity of TiO_2 is recovered by annealing (**Fig. 3**), it is suggested that electron may be injected not inside grains, but at grain boundaries. Moreover, considering that only acid and alkaline liquids make TiO_2 film conductive, this doping cannot be explained in terms of ions or pH. It is known that both acid and alkaline liquids have corrosiveness to TiO_2. Therefore, they are likely to generate the O-atom deficiencies at grain boundaries, which results in the electron doping. Although details of chemical doping into TiO_2 are not clear now, the chemical doping will enable to reduce the parasitic resistances in the gate fringe and contact regions for electronic applications.

4. Conclusion

This paper has discussed the electrical conduction both by electric field (FET operation) and by chemical doping. The field-effect doping modulates carriers at TiO_2/SiO_2 interface. TiO_2 FETs annealed in O_2 have lower V_{th} and higher μ_{FE}, which is possibly due to the annihilation of acceptor type traps at TiO_2/SiO_2 interface. In the latter, we have reported that the chemical doping significantly increases the sheet conductivity $> 10^{-4}$ (Ω^{-1}) which is recovered to the initial one in N_2 annealing.

Acknowledgements

This work was partly in collaboration with STARC.

References

1) M. R. Hoffmann *et al*., *Chem. Rev.* **95**, 69 (1995).
2) N. Zhong, H. Shima, and H. Akinaga, Adv. *Appl. Phys.* **1**. 032167 (2011).
3) H. Akinaga and H. Shima, *Proc. IEEE* **98**, 2237 (2010).
4) Kwang-Hyuk Choi and Han-Ki Kim, *Electrochem. Solid ST.* **14**, H314 (2011)
5) Y. Nagao *et al.*, *Appl. Phys. Lett.* **97**, 172112 (2010)
6) M. Kubo *et al.*, *Appl. Phys. Lett.*, **98**, 073311 (2011)
7) T. Ohsaka *et al.*, *J. Raman Spectroscopy*, **7**, 321 (1978).
8) T. Kamiya *et al.*., *Journal of Display Technology* **5**,7 (2009)