Significant Conductivity Enhancement of TiO$_2$ Films by Both Field Effect and Chemical Doping

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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 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 and chemical doping.

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 500$^\circ$C 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 ($\mu_{FE}$) and on/off ratio of FETs are quite different from each other. $V_{th}$, $\mu_{FE}$ 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.

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.

Next, we discuss the effect of PDA ambient on FET characteristics. Fig. 2 shows both $V_{th}$ and $\mu_{FE}$ 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 $\mu_{FE}$ 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 and in-plane XRD measurements. It was previously reported in other oxides that the...
Some of FETs have negative Vth decreased to 2 \times 10^{-3}\,\Omega^{-1}. Sheet conductivities of TiO\textsubscript{2} films immersed to TMAH with various concentration.

![Sheet conductivities of TiO\textsubscript{2} films immersed to TMAH with various concentration.](image)

The conductivity of TiO\textsubscript{2} films significantly increases, when the films are immersed to not only TMAH but also NH\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2}/SiO\textsubscript{2} interface. TiO\textsubscript{2} FETs annealed in O\textsubscript{2} have lower Vth and higher \( \mu_{FE} \) which is possibly due to the annihilation of acceptor type traps at TiO\textsubscript{2}/SiO\textsubscript{2} interface. In the latter, we have reported that the chemical doping significantly increases the sheet conductivity > 10\textsuperscript{-4}\,\Omega^{-1}\) which is recovered to the initial one in N\textsubscript{2} annealing.

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### References