Spectroscopic Study of TiO_x Film for Novel n-type Semiconductor/insulator/p-type Semiconductor Rechargeable Device

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ABSTRACT

We have demonstrated a novel semiconductor rechargeable battery (capacitor-like device), which uses electrons, holes and no mobile ions, having a $\text{TiO}_x/\text{SiN}_y/\text{NiO}_2$ laminated structure with a capacity 5000 times larger than that of a conventional parallel plate capacitor. In this study, photoluminescence, cathodoluminescence and Raman spectroscopy of TiO_x ($x = 1.92, 2.00$ and 2.04) films were carried out. We showed some correlations between these spectroscopic characteristics of TiO_x having different oxygen compositions and the capacitor performance of a $\text{TiO}_x/\text{SiN}_y/\text{NiO}_2$ laminated structure.

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1. Introduction

Secondary batteries have become essential components in a wide range of devices such as automobiles and mobile products.¹ However, lithium batteries, which are typical secondary batteries, have drawbacks, such as the use of a liquid electrolyte and combustibility. Recently, we have proposed a new type of semiconductor rechargeable battery or capacitor-like device having a semiconductor/insulator/semiconductor laminated structure. This device utilizes no mobile ions and only electrons and holes for charging and discharging. In fact, we fabricated a titanium oxide (300 nm in thickness)/silicon nitride (300 nm)/nickel oxide (300 nm) laminated structure and obtained charging and discharging characteristics with a capacity of at least 5000 times larger than that of a conventional parallel plate capacitor of the same size.² This capacitor-like device (hereafter simply referred to as a capacitor) has complete compatibility with semiconductor processes and can be easily applied to a battery-like power supply built in a sensor chip for IoT applications. Figure 1 shows the schematic structure of the capacitor using semiconductors and its measured four-cycle charging and discharging characteristics.² However, the charging and discharging mechanism of this type of semiconductor capacitor is not sufficiently understood. In this study, we investigated the relation between the capacitor performance of a $\text{TiO}_x/\text{SiN}_y/\text{NiO}_2$ laminated structure and the spectroscopic characteristics of TiO_x film having different oxygen compositions.

2. Experimental

TiO_x films were deposited by DC co-sputtering using Ti and TiO_{2-x} targets. In the sputtering process, oxygen and argon gases were used. The flow rate of Ar was fixed at 120 sccm, and the O_2 flow rate was set to 5, 7 or 20 sccm. The substrate temperature was kept at 200°C and the input power was 1 kW.² For spectroscopic analyses, a TiO_x film having a thickness of about 300 nm was deposited on a

glass substrate. Also, using a TiO_x film deposited by the same sputtering process, a capacitor having the laminated structure of $\text{Au}(200 \text{ nm})/\text{Ti}(30 \text{ nm})/\text{TiO}_x(300 \text{ nm})/\text{SiN}_y(300 \text{ nm})/\text{NiO}_2(300 \text{ nm})/\text{ITO}(150 \text{ nm})/\text{Mo}(30 \text{ nm})/\text{Au}(200 \text{ nm})$ shown in Fig. 1(a) was fabricated.² Next, the charging and discharging characteristics of this structure were measured. The areas of size of the top electrode (Au/Ti), TiO_x layer, SiN_y and NiO_2 layers and ITO electrode were $10 \text{ mm} \times 10 \text{ mm}$, $20 \text{ mm} \times 20 \text{ mm}$, $30 \text{ mm} \times 30 \text{ mm}$ and $50 \text{ mm} \times 50 \text{ mm}$, respectively. We evaluated the charging and discharging characteristics of the capacitors using electrochemical equipment (Toyo Technica SolarTron SI1287). As the charging condition, a constant-current (CC) charge of $5 \times 10^{-2} \text{ mA}/\text{cm}^2$ for 600 s was chosen. A constant-resistance (CR) discharge with a resistance of 100 kΩ was chosen for the discharge condition. The reason for carrying out a CR discharge measurement was to obtain more stable and reproducible results in our measurements. This measurement was continued until the capacitor voltage fell below 0.01 V.

The TiO_x films were analyzed by Rutherford backscattering spectrometry (RBS) to evaluate their compositions. Furthermore, to evaluate energy levels of defects, photoluminescence (PL) measurement (Renishaw inVia PL Microscope) using a He-Cd laser with a wavelength of 325 nm as the excitation light and cathodoluminescence (CL) measurement with an electron acceleration voltage of 5 kV were performed. To identify the crystal structures, Raman spectroscopy (Renishaw inVia PL Microscope) was also carried out using a He-Cd laser with a wavelength of 325 nm. We used this short wave length to avoid Raman signals from the substrate.

3. Results and Discussion

The results of RBS measurements of the TiO_x films for the three different oxygen flow rates employed in sputtering deposition showed that the composition of oxygen in TiO_x , that is, the composition ratio of oxygen to titanium, was 1.92 for an O_2 flow rate of 5 sccm (hereafter referred to as Sample A), 2.00 for a flow

Figure 1. (a) Schematic structure of fabricated semiconductor capacitor and (b) measured charging and discharging characteristics of the capacitor. The charging and discharging were repeated four times. The charging condition was a constant-current charge of $5 \times 10^{-2} \text{ mA/cm}^2$ for 60 s. The discharging condition was a constant-current discharge of $5 \times 10^{-3} \text{ mA/cm}^2$ until the voltage fell below 0.01 V.

rate of 7 sccm (Sample B) and 2.04 for a flow rate of 20 sccm (Sample C).

The CC charging and CR discharging characteristics of the $\text{TiO}_x/\text{SiN}_y/\text{NiO}_z$ laminated structure are shown in Fig. 2. The horizontal axis is the capacity and the vertical axis is the voltage of the capacitors. The capacity Q_c in the CR discharging was calculated from the measured discharge characteristics as

$$Q_c = \int \frac{V_c(t)}{R_{\text{const}}} dt. \quad (1)$$

Here, R_{const} is a constant resistance of 100 k Ω and $V_c(t)$ is the measured voltage across the resistance. The area of the top electrode was 1 cm^2 . The calculated capacity was 11.42 mC for Sample A, 9.53 mC for Sample B and 7.48 mC for Sample C. The results show that the capacitor with $\text{TiO}_{1.92}$ (Sample A) has the highest capacity and the capacitor with $\text{TiO}_{2.04}$ (Sample C) has the lowest capacity. This means that the composition of oxygen in the TiO_x film correlates with the capacity of the $\text{TiO}_x/\text{SiN}_y/\text{NiO}_z$ capacitor.

The results of PL and CL analysis for these three TiO_x films with different capacities are shown in Fig. 3 and 4. Samples A and B have a broad peak in the PL spectrum in the vicinity of the photon energy of 2.4 eV. In Sample C, the peak appears at around 2.2 eV. Similar to the PL measurement results, CL spectrum has a broad peak around 2.4 eV. The intensity of the peak is highest in $\text{TiO}_{2.04}$

Figure 2. Charging and discharging characteristics of $\text{TiO}_x/\text{SiN}_y/\text{NiO}_z$ laminated semiconductor capacitors with three different TiO_x films. The horizontal axis is the capacity of the fabricated capacitors and the vertical axis is the voltage of the capacitors. CC charge measurement was performed for 600 s. CR discharge measurement continued until the capacitor voltage fell below 0.01 V. The capacities were calculated from the CR discharge curves with Eq. (1).

Figure 3. PL spectra of TiO_x films having different capacities. The PL measurement was performed with an ultraviolet laser having an excitation photon energy of 3.81 eV (a wavelength of 325 nm).

Figure 4. CL spectra of TiO_x films having different capacities. CL was measured at room temperature and with the electron acceleration voltage of 5 kV.

Table 1. Summary of relationship between spectroscopic measurement results and capacity.

TiO _x film sample	A	B	C
O ₂ flow rate in TiO _x deposition (sccm)	5	7	20
O/Ti ratio (x)	1.92	2.00	2.04
Capacity (mC)	11.42	9.53	7.48
Relative intensity of PL peak at 2.4 eV (arb. unit)	1.0	2.3	3.4
Structure of TiO _x	amorphous + microcrystalline rutile	amorphous + micro/poly-crystalline anatase	amorphous + polycrystalline anatase

Figure 5. Raman spectra of TiO_x films having different capacities. “▲” indicates the peak position of the rutile TiO₂ crystalline structure and “○” indicates the peak position of the anatase TiO₂ crystalline structure.

(Sample C) and lowest in TiO_{1.92} (Sample A). Namely, the luminescence intensity decreases with increasing capacity. Although the luminescence intensity may not be quantitatively compared with each other only from these results, the order of the intensity obtained by the two different excitations, i.e. UV light in PL and higher energy electron in CL, showed the same tendency. Therefore, it seems highly probable that there is a correlation between the luminescence intensity and the oxygen composition of TiO_x, that is, the capacity of the laminated TiO_x/SiN_y/NiO_z capacitor-like device.

The broad emission spectra with the peak at 2.4 eV observed in the PL and CL measurements could be attributed to the luminescence generated by oxygen vacancies or self-trapped excitons.^{3–6} However, the TiO_{1.92}, which has probably the largest amount of oxygen vacancy between the three TiO_x samples, showed the smallest luminescence intensity. It appears that the measured luminescence does not simply related to the oxygen vacancies.

The Raman spectra of the TiO_x films with three different oxygen composition are shown in Fig. 5. For Sample A (TiO_{1.92}), two weak peaks (▲ in Fig. 5) were observed, corresponding to TiO_x with the rutile crystalline structure.⁷ On the other hand, for Samples B (TiO_{2.00}) and C (TiO_{2.04}), three peaks (○ in Fig. 5) were observed, corresponding to TiO_x with the anatase crystalline structure.⁷ Moreover, the peak intensity is much higher for TiO_{2.04} than for TiO_{2.00}. This result indicates that the TiO_{2.04} film has a polycrystalline or microcrystalline phase in an amorphous structure, the TiO_{2.00} film has a smaller amount of the polycrystalline or microcrystalline phase in the amorphous structure. The TiO_{1.92} is assumed to be an amorphous structure with a microcrystalline phase of the rutile crystalline structure. Raman spectroscopy results suggest that there

may be some relation between the capacity of the device and the crystal structure of the TiO_x film. One possibility is that the rutile crystalline structure is more suitable for the charge storage in TiO_x than the anatase crystalline structure. Another possibility is that amorphous structure is effective for the charge storage.

We summarize the measured results in Table 1. The capacity of the semiconductor batteries differs for the TiO_x films with different oxygen composition. The highest capacity was obtained by using the TiO_{1.92}, which has the smallest oxygen composition in this study. From the relation between the capacity and the Raman spectra, it may be reasonable to assume that crystal structures and/or structure-related defects may affect this correlation, though further study is needed. There is also some correlation between the PL and CL spectra and the capacity. As mentioned above, oxygen vacancies could not simply explain this correlation. Although the detailed mechanism of charging in the device is not yet understood, our experimental results indicate that the oxygen composition of the TiO_x film is strongly related to the charging mechanism of the TiO_x/SiN_y/NiO_z laminated device.

4. Conclusions

The spectroscopic evaluation of TiO_x films was performed to investigate the relations with the capacity of a TiO_x/SiN_y/NiO_z laminate-structured capacitor-like device. It was found that there is a correlation between the capacity and the oxygen composition of TiO_x and that this oxygen composition is related to (1) PL/CL intensity, (2) TiO_x crystalline structure and/or (3) structure-related defects. However, further work is needed to understand the mechanism of the charging and discharging of this device.

Acknowledgments

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References

1. J. Xu, H. R. Thomas, R. W. Francis, K. R. Lum, J. Wang, and B. Liang, *J. Power Sources*, **177**, 512 (2008).
2. A. Sasaki, A. Sasaki, H. Hirabayashi, S. Saito, K. Aoki, Y. Kataoka, K. Suzuki, H. Yabuhara, T. Ito, and S. Takagi, *Jpn. J. Appl. Phys.*, **57**, 041201 (2018).
3. M. C. Fravventura, L. D. A. Siebbeles, and T. J. Savenije, *J. Phys. Chem. C*, **118**, 7337 (2014).
4. H. Tang, K. Prasad, R. Sanjines, P. E. Schmid, and F. Levy, *J. Appl. Phys.*, **75**, 2042 (1994).
5. M. Watanabe and T. Hayashi, *J. Lumin.*, **112**, 88 (2005).
6. J. B. Varley, A. Janotti, C. Franchini, and C. G. Van de Walle, *Phys. Rev. B*, **85**, 081109 (2012).
7. T. Mazza, E. Barborini, P. Piseri, P. Milani, D. Cattaneo, A. Li Bassi, C. E. Bottani, and C. Ducati, *Phys. Rev. B*, **75**, 045416 (2007).