Spectroscopic Study of TiO$_2$ 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 TiO$_2$/SiN$_x$/NiO$_x$ 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$_2$ ($x = 1.92, 2.00$ and $2.04$) films were carried out. We showed some correlations between these spectroscopic characteristics of TiO$_2$ having different oxygen compositions and the capacitor performance of a TiO$_2$/SiN$_x$/NiO$_x$ laminated structure.

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Keywords : Battery, Capacitor, Titanium Oxide, Photoluminescence

1. Introduction

Secondary batteries have become essential components in a wide range of devices such as automobiles and mobile products. 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 capacitor 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. 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. 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 TiO$_2$/SiN$_x$/NiO$_x$ laminated structure and the spectroscopic characteristics of TiO$_2$ film having different oxygen compositions.

2. Experimental

TiO$_2$ films were deposited by DC co-sputtering using Ti and TiO$_2$ 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. For spectroscopic analyses, a TiO$_2$ film having a thickness of about 300 nm was deposited on a glass substrate. Also, using a TiO$_2$ film deposited by the same sputtering process, a capacitor having the laminated structure of Au(200 nm)/Ti(30 nm)/TiO$_2$(300 nm)/SiN$_x$(300 nm)/NiO$_x$(300 nm)/ITO(150 nm)/Mo(30 nm)/Au(200 nm) shown in Fig. 1(a) was fabricated. Next, the charging and discharging characteristics of this type of capacitor were measured. The areas of size of the top electrode (Au/Ti), TiO$_2$ layer, SiN$_x$ and NiO$_x$ layers and ITO electrode were 10 mm × 10 mm, 20 mm × 20 mm, 30 mm × 30 mm and 50 mm × 50 mm, respectively. We evaluated the charging and discharging characteristics of the capacitors using electrochemical equipment (Toyo Technica SolarTorr ST1287). As the charging condition, a constant-current (CC) charge of 5 × 10$^{-5}$ mA/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$_2$ 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$_2$ films for the three different oxygen flow rates employed in sputtering deposition showed that the composition of oxygen in TiO$_2$, 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
The CC charging and CR discharging characteristics of the TiO$_x$/SiN$_y$/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

$$Q_c = \int \frac{V_d(t)}{R_{\text{const}}} \, dt.$$  

Here, $R_{\text{const}}$ is a constant resistance of 100 kΩ and $V_d(t)$ 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 TiO$_{1.92}$ (Sample A) has the highest capacity and the capacitor with 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 TiO$_x$/SiN$_y$/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 TiO$_{2.04}$.
may be some relation between the capacity of the device and the crystal structure of the TiO₂ film. One possibility is that the rutile crystalline structure is more suitable for the charge storage in TiO₂ 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 TiO₂ films with different oxygen composition. The highest capacity was obtained using the TiO₁.₉₂, 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 TiO₂ film is strongly related to the charging mechanism of the TiO₂/SiN/NiO₂ laminated device.

4. Conclusions

The spectroscopic evaluation of TiO₂ films was performed to investigate the relations with the capacity of a TiO₂/SiN/NiO₂ laminate-structured capacitor-like device. It was found that there is a correlation between the capacity and the oxygen composition of TiO₂, and that this oxygen composition is related to (1) PL/CL intensity, (2) TiO₂ 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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Table 1. Summary of relationship between spectroscopic measurement results and capacity.

| TiO₂ film sample | A (Sample A) | B (Sample B) | C (Sample C) |
|------------------|-------------|-------------|-------------|
| O₂ flow rate in TiO₂ 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 TiO₂x | amorphous + microcrystalline rutile | amorphous + micro/poly-crystalline anatase | amorphous + polycrystalline anatase |

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