

## ***In-situ* Raman Spectroscopy of Amorphous Hydrrous RuO<sub>2</sub> Thin Films**

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### **Abstract**

Amorphous hydrrous ruthenium oxide thin films have attracted much interest owing to the possibility of using this material in electrochemical supercapacitors. Recently, it was found that this material is also electrochromic: during the charging/discharging cycle, the optical transmittance of the thin film is modulated. The physical and chemical origin of this phenomenon is not fully understood yet. In this work, we performed *in-situ* Raman spectroscopy measurements on amorphous hydrrous ruthenium oxide thin films during the charging/discharging cycles. Unambiguous changes in the Raman spectrum were observed as protons were injected or extracted from the thin film. When the samples were annealed to reduce the water content, there is a consistent trend in the Raman spectrum. The origins of the Raman features and their relation to the electrochromic and/or supercapacitor characteristics is discussed.

**Keywords** : ruthenium oxide, electrochromic, supercapacitor, Raman

### **1. Introduction**

Growing demands for power sources for transient high-power density have stimulated great interest in electrochemical capacitors in recent years [1-5]. An electrochemical capacitor of large specific capacitance (supercapacitor) results when an electrode material with large specific surface area is combined with a material that can be reversibly oxidized or reduced over a wide potential range. For example, the oxides of multivalent metals such as ruthenium and iridium exhibit large faradaic pseudocapacitance [4-6]. Consequently, these materials have often been studied for applications as supercapacitors. Amorphous hydrrous ruthenium oxide thin films have attracted much interest owing to the possibility of using this material in electrochemical supercapacitors. Recently, it was found that this material is also electrochromic: during the charging/discharging

cycle, the optical transmittance of the thin film is modulated. The physical and chemical origin of this phenomenon is not fully understood yet. In this work, we performed *in-situ* Raman spectroscopy measurements on amorphous hydrrous ruthenium oxide thin films during the charging/discharging cycles.

### **2. Experiment**

Hydrrous ruthenium oxide thin films were prepared on polished titanium substrates for Raman scattering measurements. The films were electroplated from the plating solution containing 5 mM RuCl<sub>3</sub> · (xH<sub>2</sub>O). Pt gauze was used as the counter electrode and Ag/AgCl as the reference electrode. Cyclic voltammetry (CV) was employed for the electrolysis procedure and performed at room temperature between 0 and 1000 mV at a scan rate of 50 mVs<sup>-1</sup>. Electrochemical behavior of the

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ruthenium oxide film electrodes was examined using cyclic voltammetry in a 0.5M H<sub>2</sub>SO<sub>4</sub> electrolyte solution.

For the *in-situ* measurement, the sample was held in an electrochemical cell with a 0.5M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. The deuterated sample was prepared from a solution of 5 mM RuCl<sub>3</sub> · xH<sub>2</sub>O in D<sub>2</sub>O, and the electrolyte used was 0.5M D<sub>2</sub>SO<sub>4</sub>. The Raman spectra were taken in the quasi-backscattering geometry using 100 mW of the 514.5 nm line of an Ar ion laser, focused to a line of 5 mm × 100 μm, as the excitation source. The signal was dispersed by a Spex 0.55-m spectrometer with a notch filter and detected with a liquid-nitrogen-cooled charge-coupled-device (CCD) detector array.

### 3. Results and Discussion

Figure 1 shows the Raman spectra of samples annealed at different temperatures. All the spectra except the one for the 300°C-annealed sample are essentially the same with a broad peak centered at ~400 cm<sup>-1</sup> with some substructures. At 300°C the film exhibits sharp crystalline features of the rutile tetragonal phase of RuO<sub>2</sub>. The three major Raman bands, namely E<sub>g</sub>, A<sub>1g</sub>, and B<sub>2g</sub> modes of RuO<sub>2</sub> are located at about 523, 645, and 710 cm<sup>-1</sup>, respectively [7]. It has been reported that the RuO<sub>2</sub> · xH<sub>2</sub>O films lose high specific capacitance upon crystallization [8]. The water content x, as determined

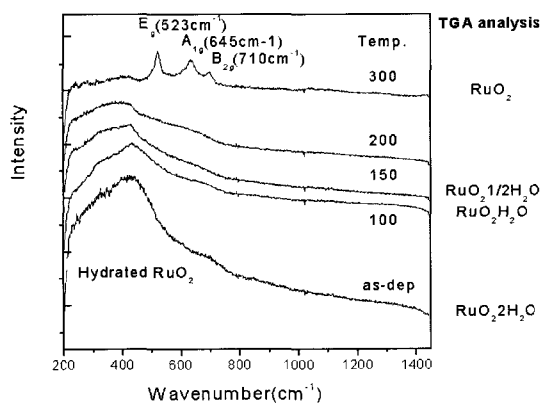


Fig. 1. Raman spectra of RuO<sub>2</sub> · xH<sub>2</sub>O annealed at different temperatures.

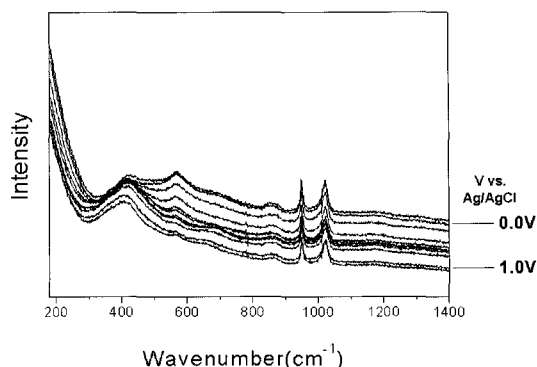


Fig. 2. In-situ Raman spectra of RuO<sub>2</sub> · xH<sub>2</sub>O for various potentials relative to the Ag/AgCl reference electrode.

from thermo-gravimetric analysis (TGA), for each sample is also indicated.

Figure 2 shows the *in-situ* Raman spectra of an unannealed RuO<sub>2</sub> · xH<sub>2</sub>O thin film sample at a series of potentials relative to the Ag/AgCl reference electrode. As the potential changes from 1.0 volt to 0.0 volt, the film becomes more transparent (bleached). The most striking change is the emergence of a Raman peak at about 570 cm<sup>-1</sup> as the film is bleached. The peaks in the range of 800 to 1100 cm<sup>-1</sup> are due to the H<sub>2</sub>SO<sub>4</sub> electrolyte. It is evident that the emergence of the 570 cm<sup>-1</sup> peak is related with the electrochemical bleaching of RuO<sub>2</sub> · xH<sub>2</sub>O.

Figure 3 shows a series of Raman spectra for a film annealed at 300°C. It is seen that there is no

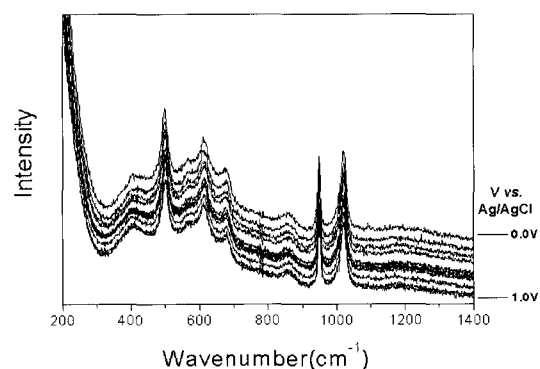


Fig. 3. *In-situ* Raman spectra of RuO<sub>2</sub> · xH<sub>2</sub>O for annealed at 300°C.

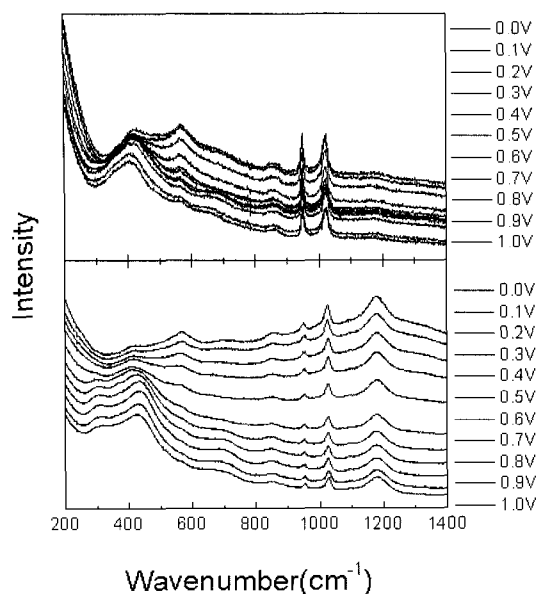


Fig. 4. Comparison of in-situ Raman spectra of RuO<sub>2</sub> · xH<sub>2</sub>O (top) and RuO<sub>2</sub> · xD<sub>2</sub>O (bottom) for various potentials relative to the Ag/AgCl reference electrode.

obvious change in the spectra as the potential is varied. This is consistent with the fact that this crystallized film shows little electrochemical charging.

In order to investigate the origin of the new peak at 570 cm<sup>-1</sup>, we studied the isotope effect. Fig. 4 show the the *in-situ* Raman spectra of a RuO<sub>2</sub> · xH<sub>2</sub>O thin film at a series of potentials relative to the reference electrode. It is seen that the 570 cm<sup>-1</sup> peak appears as the potential is lowered just as in the case of the RuO<sub>2</sub> · xH<sub>2</sub>O thin film. The peaks in the range of 800 to 1300 cm<sup>-1</sup> are due to the D<sub>2</sub>SO<sub>4</sub> electrolyte. From this result, we can conclude that the new peak is not related with hydrogen (or deuterium) atom. It has been suggested that upon charging the Ru<sup>4+</sup>-O<sup>2-</sup> bonds change to Ru<sup>3+</sup>-OH<sup>-</sup> [9]. But our result show that the new peak is not related with hydrogen bonds.

## 4. Conclusions

In-situ Raman spectra of amorphous hydrated ruthenium oxide thin films has been measured. The electrochemical charging/discharging of the thin films strongly correlates with the changes in the Raman spectra. Investigation of the isotope effect, though, reveal that the main change in the Raman spectra is not related with hydrogen atoms as suggested previously.

## Acknowledgments

This work was supported by KOSEF through the Quantum Photonic Science Center at Hanyang University.

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