Optimization of Sputtering Condition of IrOx Thin Film Stimulation Electrode for Retinal Prosthesis Application

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Abstract We have optimized the sputtering condition of the RF sputtering deposition for the fabrication of the iridium oxide thin film used in retinal prosthesis applications. The deposited IrOx thin films were characterized by using the cyclic voltammetry method and the charge delivery capacity was calculated from the integral of the generic CV curve. From the experimental results, the charge delivery capacity of IrOx under the best sputtering condition was improved to more than 50 times that of Pt. We also verified from our in vivo experiment results that IrOx has a better charge delivery capacity than that of Pt. The in vitro and in vivo experimental results also show that IrOx is a promising candidate for retinal prosthesis applications.

1. Introduction
A retinal prosthesis is developed for those who have lost their sight due to degenerative retinal diseases [1]. In these cases, only the photoreceptor cells are damaged, but a large portion of the neural cell on the retina is intact. It is believed that patterned electrical stimulation through a retinal prosthesis device onto the remaining retinal neural cells can partially restore a person’s visual sensation.

We proposed a multi-chip architecture-based neural stimulation device for a retinal prosthesis device in our previous research [2-3]. This architecture consists of small unit chips with Pt electrodes that work cooperatively with other unit chips, and the function of the developed retinal prosthesis device was verified from the results of in vitro and in vivo experiments. With this architecture, a thin and flexible multi-chip retinal stimulation device can be developed. The next stage is to increase the number of electrodes to enhance the spatial resolution of current retinal prostheses. However, the charge delivery capacity (CDC) of current electrode material Pt has been pointed out to be inefficient [4], and therefore, a higher charge delivery capacity material is required for a smaller electrode design in order to increase the number of electrodes in the limited area. Iridium oxide (IrOx) has been reported to hold a high charge delivery capacity and to have resistance to dissolution and corrosion in a saline environment [5-6]. IrOx thin film can be fabricated by electrochemical activating iridium metal (AIROF) [7] using reactive laser ablation [8] or by reactive sputtering from an iridium target (SIROF) [9-10]. IrOx thin film deposited by sputtering is compatible with CMOS process technology, and thus, has the advantage in that it can be multi-electrode array fabricated by using thin film
methods, and the CDC of sputtered IrOx thin film can be controlled by using the sputtering condition.

In this work, IrOx thin films were fabricated by using reactive sputtering deposition. Although sputtered IrOx has widely been made by other groups [9-10], little systematic analyses to optimize sputtering conditions have been appeared in the previous research. In order to optimize the sputtering condition to maximize the CDC of IrOx, we fabricated 16 IrOx thin film samples under different sputtering condition combinations, and Pt thin film was also sputter deposited for comparison. The IrOx thin films were characterized by using the cyclic voltammetry (CV) method, and the CDC were calculated from the integral of the CV generic curve and the effect on the CDC for each sputtering parameter was also evaluated. In addition, in vivo experiments were also carried out to compare the IrOx and Pt film performances. IrOx and Pt thin films were sputter deposited on a polyimide substrate with eight electrodes and implanted into the eye ball of a cat in the in vivo experiment.

2. Fabrication of Electrodes and Electrochemical Evaluation
We fabricated a thin film electrode using a RF reactive sputtering machine (Shibaura Mechatronics, CFS-4ES-231). The sputtering chamber was evacuated to $7 \times 10^{-4}$ Pa before the deposition by first using a rotary pump and then a turbo molecular pump. A 200-nm Ti adhesive layer was deposited on a glass substrate and then an Ar and O$_2$ gas flow ratio was controlled and introduced to the reactive chamber for IrOx thin film deposition. The CDC of IrOx is strongly related to the surface morphology and composition ratio and can be affected by the sputtering conditions. It is essential to optimize the sputtering conditions, such as the sputtering pressure, RF power, O$_2$ gas partial pressure, and sputtering time to maximize the CDC of IrOx. In this work, each parameter in the deposition process was set to the High (H) or Low (L) condition, for example the RF power was set at 200 W for the high condition and 50 W for the low condition. Table 1 lists the detailed sputtering conditions for each IrOx sample fabrication. There are a total of 16 IrOx samples that were fabricated under different sputtering condition combinations. In addition, Pt thin film was also deposited by DC sputtering deposition for comparison with IrOx. The deposition condition for Pt was set at 0.5 Pa, a DC power 500 W, an Ar gas flow of 20 sccm and then sputtered for 30 mins.

| Condition | Pressure [Pa] | RF Power [W] | O$_2$ Partial Pressure Ar [sccm] O$_2$ [sccm] Time [min] |
|-----------|--------------|--------------|-------------------------------|
| 1         | 0.5 (L)      | 50 (L)       | (L) 8 2 30 (L)                |
| 2         | 0.5 (L)      | 50 (L)       | (L) 8 2 60 (H)               |
| 3         | 0.5 (L)      | 50 (L)       | (H) 0 10 30 (L)             |
| 4         | 0.5 (L)      | 50 (L)       | (H) 0 10 60 (H)             |
| 5         | 0.5 (L)      | 200 (H)      | (L) 8 2 30 (L)              |
| 6         | 0.5 (L)      | 200 (H)      | (L) 8 2 60 (H)              |
| 7         | 0.5 (L)      | 200 (H)      | (H) 0 10 30 (L)             |
| 8         | 0.5 (L)      | 200 (H)      | (H) 0 10 60 (H)             |
| 9         | 1.0 (H)      | 50 (L)       | (L) 8 2 30 (L)              |
| 10        | 1.0 (H)      | 50 (L)       | (L) 8 2 60 (H)              |
| 11        | 1.0 (H)      | 50 (L)       | (H) 0 10 30 (L)             |
| 12        | 1.0 (H)      | 50 (L)       | (H) 0 10 60 (H)             |
| 13        | 1.0 (H)      | 200 (H)      | (L) 8 2 30 (L)              |
| 14        | 1.0 (H)      | 200 (H)      | (L) 8 2 60 (H)              |
| 15        | 1.0 (H)      | 200 (H)      | (H) 0 10 30 (L)             |
| 16        | 1.0 (H)      | 200 (H)      | (H) 0 10 60 (H)             |
The objective of this work is to optimize the charge delivery capacity of sputtered IrOx film for a smaller electrode design and increase the special resolution for a retinal prosthesis device. In order to fabricate mechanically stable amorphous sputtered iridium oxide thin film, an IrOx thin film was deposited at a low temperature without heating the substrate [11]. The electrochemical characteristic was evaluated by using the cyclic voltammetry (CV) method and was measured within the potential limits without causing any irreversible redox reactions. Irreversible processes are avoided because they will generate undesirable toxic species and lead to electrode corrosion. The cyclic voltammetry (CV) measurement method uses an Ag/AgCl reference electrode and a Pt wire counter electrode in 0.01M PBS (Phosphate Buffered Saline). Prior to CV testing, the IrOx film was electrically connected to a lead wire via electrically conductive paste. Figure 1 shows a schematic diagram of the cyclic voltammetry measurement system used in this work. The IrOx film sample was fixed by a jig and the lead wire was electrically connected to the potentiostat. The area of the IrOx defined by the jig for cyclic voltammetry evaluation was 0.5 cm$^2$. The cyclic voltamogram was taken by being activated using a triangular wave and repetitive potential cycling at a scan rate of 50 mV/s in a potential range from -0.65 to 0.85 V for the IrOx and -0.6 to 1.05 V for the Pt without H$_2$ and O$_2$ evolution. The CV generic curve was monitored through a PC and measured when the potential of the IrOx film was stable after being activated for three cycles. The CDC [$Q_a$] of IrOx can be calculated using equation 1.

$$Q_a = \frac{1}{\nu} \int_{E_c}^{E_a} i dE,$$

where $E$ is the electrode potential, $i$ is the measured current, $\nu$ is the scan rate, and $E_c$ and $E_a$ are the cathodic and anodic potential limits, respectively [11]. Therefore, the $Q_a$ for each sample can be calculated by integrating the generic CV curve for a sample evaluation. The thickness of the fabricated IrOx thin film was measured by using a Alpha-step 500 surface profiler.

![Schematic diagram of cyclic voltammetry measurement system](image)
3. Experimental Results and Discussion

Figure 2 shows the measured thickness of the deposited IrOx thin film, and the thickness of the deposited Pt thin film for comparison is 862 nm. Figure 3 shows the CDC \(Q_a\) calculated from the integral of the CV generic curve for each IrOx sample, and Pt is shown for comparison. It is apparent that the CDC of the deposited IrOx films is strongly related to the sputtering conditions. The CDC of the sample deposited under conditions 7 and 8 are not available because the deposited film was brittle and easily peeled off. The calculated CDC \(Q_a\) of the deposited Pt thin film was 3 mC/cm\(^2\). From figures 2 and 3, the CDC of the deposited IrOx thin film has correlation with the thickness (sputtering time) while only sputtering time was varied and the other sputtering parameters were fixed.

Figure 4 shows the generic CV curve of the deposited IrOx thin film for the best four conditions and compared with Pt. The current peak in each CV curve of the IrOx occurred due to the redox reactions involving the changes in valence of the iridium between Ir\(^{+3}\) and Ir\(^{+4}\) within the multilayered metal oxide film [11]. The charge delivery capacity of IrOx, because of the multilayer nature, is much greater than that of the monolayer redox reactions on Pt. The larger the closed area of CV curve, the larger the CDC of IrOx thin film. In this work, the CDC of IrOx obtained under the best condition is over 50 times greater than that of Pt thin film.

![Figure 2. Thickness of deposited IrOx thin film](image1)

![Figure 3. CDC calculated from CV curve](image2)

![Figure 4. CV curve of deposited IrOx for best four conditions and compared with Pt](image3)
From the CV generic curve, the CDC of IrOx obviously varied by changing the sputtering conditions during the deposition process. This is because the composition and morphology of the deposited IrOx thin film can be altered under different sputtering conditions during the deposition process. The current peak in the CV generic curve represents that the iridium changes its oxidation state from Ir$^+$ to Ir$^{4+}$ during potential cycling. The possible redox reactions that occurred at these current peaks is described as follows [12]:

$$\text{Ir(OH)}_3 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{Ir(OH)}_2 \cdot 2\text{H}_2\text{O} + \text{H}^+ + e^-$$

$$\text{Ir(OH)}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ir(OH)}_3 \cdot \text{H}_2\text{O} + \text{H}^+ + e^-$$

$$\text{Ir(OH)}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{Ir(OH)}_4 + \text{H}^+ + e^-$$

In order to evaluate the effect of each sputtering parameter on CDC, the CDC ratio of the high condition/low condition for each sputtering parameter was calculated. Table 2 lists the representative CDC ratio of the high condition/low condition for each sputtering parameter. We can see from table 2 that the CDC ratio of O$_2$ partial pressure is the highest among the other sputtering parameters. Therefore O$_2$ partial pressure plays the most important role in determining the CDC of the sputtered IrOx thin film. The effect of O$_2$ partial pressure on CDC was also shown in CV curves. For example figure 5 shows the CV generic curve of the IrOx thin film deposited under conditions 14 and 16. Condition 14 was deposited at an oxygen gas flow of 2 sccm and condition 16 was deposited at an oxygen gas flow of 10 sccm. It is clear that the peak current varied with respect to O$_2$ partial pressure. With the increase in O$_2$ partial pressure, the iridium atoms were surrounded by more oxide radical and lead to the composition of the sputtered IrOx film deposited at a high O$_2$ partial pressure was different from that at low O$_2$ partial pressure.

Although it is not as obvious as that for the O$_2$ partial pressure, we found that thickness is another factor that affects the CDC of the sputtered IrOx film from the electrochemical experimental results. A thicker sputtered IrOx film and high O$_2$ partial pressure sputtered IrOx film has a larger CDC probably because the rougher surface, which increases the contact area between the electrode and the electrolyte, and thus, also increases the CDC of the electrode. Figure 6 shows the SEM imaging results for No. 14~No. 16 IrOx samples. From SEM imaging results, No. 16 (sputtered at high O$_2$ partial pressure and high sputtering time) shows the densely microporous surface lead to the rougher surface than No. 14 (sputtered at low O$_2$ partial pressure) and No. 15 (thin thickness). However, the pressure in the chamber and the RF power during the deposition process don’t have an obvious influence on the CDC from the experimental results.

The CDC of the electrode not only depends on the material but also the electrolyte and stimulation waveforms. However, in this work we only focus on the material. The CDC of the sputtered IrOx film obtained under the best sputtering condition was around 170 mC/cm$^2$ in this work. However, because the current pulses used in vivo are much faster than the scan rates in the CV experiment, only part of the charge injection is available during the real stimulation.

**Table 2.** Representative CDC ratio of high condition/low condition for each sputtering parameter

| Sputtering parameter | RF power | O$_2$ partial pressure | Sputtering pressure | Sputtering time |
|----------------------|----------|------------------------|---------------------|-----------------|
| CDC ratio            | 0.86     | 29.06                  | 0.83                | 1.79            |
| condition H/L        |          |                        |                     |                 |
4. In Vivo Evaluation
An in vivo experiment was also conducted to compare the performances of the IrOx and Pt electrodes. The IrOx electrode was sputtered at the same condition with No. 16. Figure 7 shows the IrOx and Pt thin film electrodes fabricated on a polyimide substrate for the in vivo experiment. The diameter of each electrode was 0.3 mm and the distance between two electrodes was 0.4 mm. The polyimide substrate was implanted into the eye ball of a cat for the in vivo experiment. The current controlled retinal stimulations were performed in a Suprachoroidal Transretinal Stimulations (STS) configuration [13-14]. In this method, the retinal prosthesis device was implanted in a sclera pocket and the reference electrode was inserted into the vitreous. Cathodic first charge-balanced biphasic current pulse that was input and the pulse width for the in vivo experiment were 0.3 mA and 0.5 ms, respectively, and the electrical potential of the IrOx and Pt electrodes were then measured. The electrical stimulation in cat’s eye ball was performed and the responses of retinal cell evoked by the stimulation were observed successfully. Figure 8 shows the electrical potential of the IrOx and Pt electrodes measured in the in vivo experiment. We found from the experimental result that IrOx has a lower maximum electrical potential than that of Pt, which means that IrOx has a lower impedance compared with Pt, and therefore, we were also able to verify in this experiment that IrOx has a better charge delivery capacity than that of Pt.
5. Conclusion
This research focuses on the optimization of the RF sputtering conditions for fabricating IrOx thin film electrodes in retinal prosthesis devices. We found from the electrochemical experimental results when using the cyclic voltammetry method that the \( O_2 \) partial pressure and thickness strongly effect the CDC of the sputter deposited IrOx films due to the morphology and the composition of the sputtered IrOx film was altered. The CDC of the sputtered IrOx thin film obtained under the best sputtering condition was over 50 times that of Pt thin film. With the increase in charge delivery capability of the electrode, a smaller electrode design is possible to increase the number of electrodes to 1000 for retinal prosthesis devices. In addition, IrOx has a better CDC than Pt and this was also verified in the results from our \textit{in vivo} experiment. The IrOx electrode fabricated by sputter deposition clearly improved the CDC compared with a Pt one, and thus, is a promising candidate for retinal prosthesis application.

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