

Evaluation of the Dopant Effects of ZnO-based Transparent Electrode on Electrochemical Characteristics for Biomedical Applications with Optical Devices

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Abstract

Transparent materials have been widely developed and used, for instance, in solar cells, flat panel displays, and so on. To enlarge the application of transparent materials into the biomedical field, their fundamental properties, such as transmittance and bioimpedance, need to be investigated. In this study, we evaluated the bioimpedance of Al-doped zinc oxide (AZO), B-doped zinc oxide (BZO), and non-doped zinc oxide (ZnO). Also, we discussed the effects of the deposition temperature of these ZnO-based transparent electrodes. This work helps realize biomedical applications with transparent electrodes such as neural probes for optogenetics and an artificial retina.

1. Introduction

Transparent materials, like ITO, PEDOT, SnO₂, and diamond, have been widely used in our life. An example of the applications of transparent material is the touch panel used in smartphones. Indium tin oxide (ITO) is commonly used as transparent electrodes for the touch panel, solar cells, and flat panel displays. Also, PEDOT, an intrinsically conductive polymer, has been paid much attention owing to high conductivity, high transparency, and flexibility. However, these materials also have disadvantages. For instance, indium oxide included in ITO is well known as toxic, and the environmental durability of PEDOT is not high. On the other hand, the diamond electrodes have been used in biomedical fields. However, as the deposition temperature of the diamond is fairly high (> 600 °C), their application area is limited. ZnO is transparent and nontoxic and is already used for cosmetics and other industrial products. Besides, ZnO can be deposited at low temperatures with the sputtering [1]. Especially, ZnO deposited by the magnetron sputtering can achieve low resistance without the post-annealing process [2].

Biomedical applications using optical devices, such as optogenetics and visual prosthesis, will be widely used by employing transparent electrodes. Fig. 1(a) shows the conventional opto-neural probe having both optical waveguide and metal electrodes for optogenetics. The light irradiation from the optical waveguide stimulates neurons, and the neuronal activity is recorded by the metal electrodes, simultaneously. As the recording electrodes are made of non-transparent metal material, the optical stimulation site is placed apart from the recording electrodes, which leads to a lower S/N ratio of the neuronal activity recording. In the case of the transparent electrode shown in Fig. 1(b), as the recording electrodes can be put on the optical stimulation site, the neuronal activity will be recorded with a higher S/N ratio.

In this study, to enhance the performance of optical biomedical devices, we evaluated the dopant effects of ZnO-based transparent electrodes, such as Al-doped ZnO (AZO) and B-doped ZnO (BZO), using electrochemical impedance spectroscopy (EIS), which have not become clear so far [3].

2. Results and discussion

Fig. 2 shows microscopic images of Pt and AZO electrodes deposited by sputtering on Au interconnect at 200 °C. Al concentration of AZO was 2%. Au can be observed under the AZO transparent electrodes, indicating that AZO with low deposition temperature has good transparency compared to Pt. Next, we measured the resistivity of AZO, BZO, and ZnO which were formed at various deposition temperatures of 50 °C, 200 °C, and 300 °C. Al and B concentrations of AZO and BZO were 2% and 1%, respectively. The measurement results are shown in Fig. 3. The resistivity of AZO was very close to ZnO and slightly changed accordingly with the deposition temperatures. On the one hand, the resistivity of BZO increased more than two orders of magnitude to the reference ZnO and decreased with the increased temperatures. Crystal structures were also investigated by X-ray diffraction (XRD) for AZO, BZO, and ZnO deposited at 200 °C, as shown in Fig. 4. The results indicated that AZO and ZnO were crystallized at 200 °C, which was adequate to fabricate transparent electrodes on active biomedical devices like sensors and ICs. In the case of BZO, strong intensity peaks induced by crystallization were not observed, which caused very high resistivity of BZO than AZO and ZnO.

For EIS measurement, test samples were fabricated following the process flow shown in Fig. 5. First, SiO₂ was deposited by PECVD as the insulator on both sides of Si substrates. Then, electrode materials such as ZnO, AZO, BZO, and Au were sputtered at 50 °C, 200 °C, and 300 °C, followed by patterning by wet etching. AZO and BZO sputtering targets contain dopants of 2% of Al₂O₃, 1% of B₂O₃, respectively. After that, SiO₂ was deposited, and finally, the electrode hole was formed by ICP-RIE. We measured electrochemical impedance of transparent electrodes with a 100-mV-AC voltage at room temperature. The reference electrode and the counter electrode were Ag/AgCl and Pt, respectively. Phosphate-buffered saline (PBS) was used as the electrolysis solution. An electrode area of 3 mm × 3 mm was exposed to PBS. Fig. 6 shows the impedance characteristics of transparent electrodes sputtered at 200 °C. Although the impedances of ZnO and AZO were higher than that of Au, these electrodes showed good characteristics. Also, ZnO and AZO showed smaller impedances than BZO. Lower electrode impedance enables lower power consumption in biomedical devices,

which leads to both less heat generation and fewer damages to neurons. Furthermore, electrode impedances changed with substrate temperature when sputtering, as shown in Fig. 7. ZnO deposited at 200°C showed smaller impedances, indicating that less dopant leads to smaller impedance. There is a possibility that dopant could influence the redox reaction at the electrode surface.

3. Conclusions

For evaluation of the ZnO-based transparent electrode to enhance the performance of optical biomedical devices, the fundamental characteristics of AZO, BZO, and ZnO were measured by EIS and XRD. It was found that dopant material played an important role in obtaining good crystal structure and electrochemical characteristics. These results also showed AZO had good electrical characteristics as a recording electrode for biomedical devices. Further investigations of dopant effects are necessary from the viewpoint of charge injection capacity for the ZnO-based transparent stimulus electrode.

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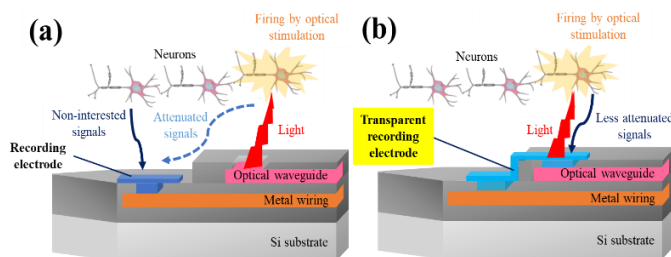


Fig. 1. Schematic cross-sections at the tip of the opto-neural probe with stimulus light irradiation and the neuronal activity recording using electrodes made of (a) conventional metal and (b) transparent material.

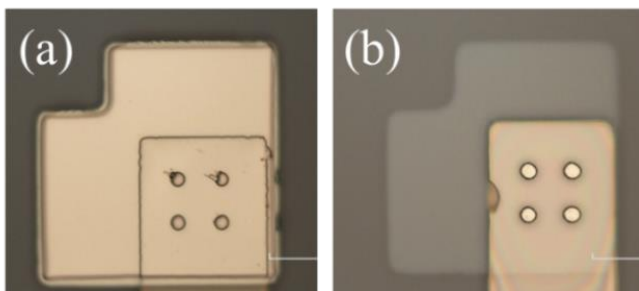


Fig. 2. Microscope images of (a) Pt electrode and (b) AZO electrode.

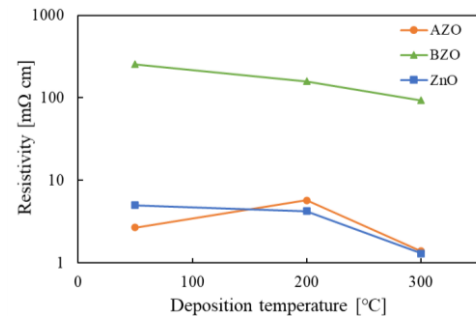


Fig. 3. The resistivity of AZO, BZO, and ZnO with various deposition temperatures.

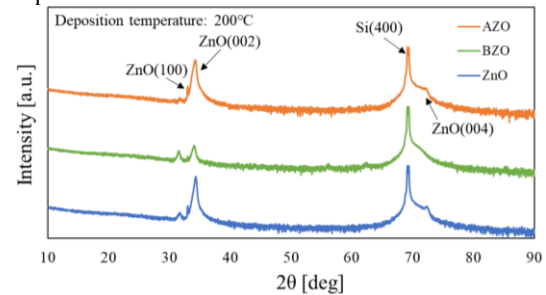


Fig. 4. XRD profiles of AZO, BZO, and ZnO with a deposition temperature of 200°C.

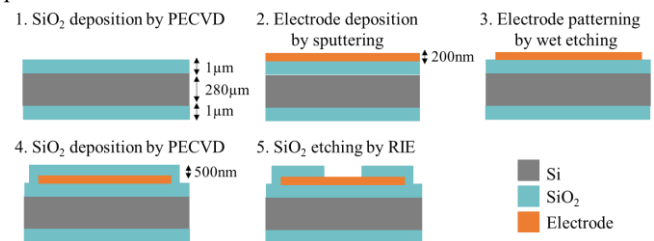


Fig. 5. Process flow of the test samples to evaluate the electrochemical impedance of the electrodes.

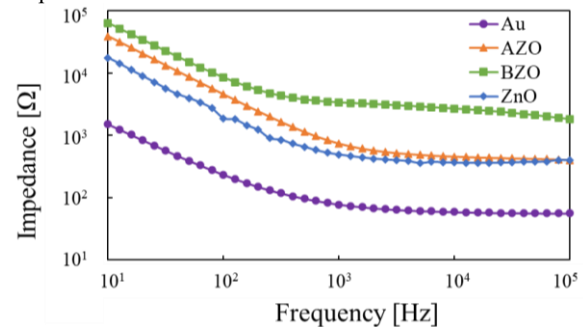


Fig. 6. Impedance measurement results of AZO, BZO, and ZnO with a deposition temperature of 200°C.

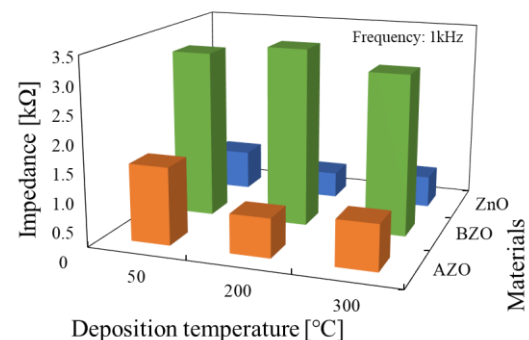


Fig. 7. Impedance comparison at 1 kHz with various deposition temperatures.