

Increase in the Conductivity and Work Function of Pyrosol Indium Tin Oxide by Infrared Irradiation

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Abstract

The effect of infrared (IR) radiation on an indium tin oxide (ITO) transparent conductor, prepared by a pyrosol method, was investigated. As-deposited ITO was irradiated with IR in nitrogen gas at atmospheric pressure and temperatures ranging from 50 to 430 °C. Typically, IR irradiation of the as-deposited ITO at 400 °C for 60 minutes reduced the electrical resistance by 60%, raised the work function by 0.5 eV, and enlarged the optical energy band gap by 0.05 V. The resistance was mainly decreased during the initial 10 minutes of irradiation. The results of field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) analysis showed that the IR irradiation enhanced the crystallinity of the ITO. These results, derived from treatment at atmospheric pressure and using inexpensive equipment, suggest that IR irradiation should be an inexpensive method to reduce the resistance and raise the work function of as-deposited pyrosol ITO.

Keywords: Indium tin oxide; pyrosol process; infrared irradiation

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1. Introduction

Indium-tin-oxide (ITO) has been widely used, because of its transparency in the visible light region and high conductivity, as an electrode for several electronic devices, such as organic light emitting devices (OLEDs) [1], liquid crystal displays [2], and solar cells [3]. Various methods have been reported for preparing ITO, such as sputtering [4], chemical vapor deposition [5], electron beam deposition [6], and spray pyrolysis [7-10].

Among the methods listed above, the spray pyrolysis method, called 'pyrosol method' in this report, is unique because it is applied at atmospheric pressure. The method is based on the pyrolysis of an aerosol produced by ultrasonic spraying. For commercial production of ITO, the pyrosol process requires less initial investment and operational expense, because of its atmospheric pressure operation, in comparison with other methods conducted at a high vacuum.

The pyrosol method can prepare smoother ITO surfaces in comparison with most of the other methods, which makes the pyrosol method favorable for the preparation of ITO electrodes for OLEDs, because OLEDs require intimate surface contact between ITO and the organic thin film [11].

In application of pyrosol ITO for use as electrodes in OLEDs, however, the lowering of the ITO sheet resistance is desirable, because the lower electric resistance of ITO electrodes should result in less power consumption of the OLEDs.

The work function of pyrosol ITO is usually lower, by approximately 1 eV, than the highest occupied molecular orbital (HOMO) of the organic layer of OLEDs [12]. The larger energy difference between the ITO and the organic layer makes the interfacial Schottky barrier larger, which results in a smaller injected current at the interface. Raising the work function of pyrosol ITO to a level close to the HOMO of the organic layer, therefore, would minimize the Schottky barrier, and resultantly enhance hole injection from the ITO to the organic layer of OLED, reducing the required voltage of the OLED.

Several methods, such as plasma treatments [13], UV treatments [14, 15] and grafting of molecules [16], have been reported for treating ITO, in an effort to increase its work function. Among them, the oxygen plasma treatment is known as the most effective technique in increasing the work function of ITO prepared by sputtering [13].

In this work, as-deposited pyrosol ITO was exposed to infrared radiation (IR), in an effort to reduce the ITO sheet resistance, and increase its work function by

reorganizing the near surface structure. ITO partly absorbs infrared radiation, so that it was expected that the IR radiation could rapidly heat the ITO, and consequently enhance atom movement and induce restructuring of the ITO. The experimental results reported here, indicate that IR irradiation of pyrosol ITO decreased the sheet resistance, increased the work function, and enhanced crystallinity.

2. Experimental

The details of the pyrosol method have been previously reported [7-10]. ITO films were prepared using a reactant solution of 0.2 M indium acetylacetonate (III) and 0.01M di-n-butyl tin diacetate in acetyl acetone. Soda glass plates coated with SiO₂ were used as substrates. The reactant solution was atomized by ultrasonic vibration at 818 kHz and carried by 5 L/min air, flowing through a 50-mm diameter tube, to the surface of the substrate (50 mm × 50 mm) placed on an electric heater. The temperature of the substrate was controlled at a constant temperature, ranging from 400 to 590 °C, by adjusting the power input to the heater. The deposition time was 5 minutes.

The surface morphology and the structural properties of the ITO films were examined by atomic force microscopy (AFM) (Seiko Instruments SPA 400), x-ray diffraction (XRD) (Rigaku, CN4148B2) with Cu K α radiation (40 kV, 30 mA), and field emission scanning electron microscopy (FE-SEM) (Hitachi Co. Ltd. S-5000). Visible-near-ultraviolet optical absorption was determined by transmittance measurements (Shimadzu UV-240). AFM was performed in the contact mode using triangular Si₃N₄ cantilevers in air, at room temperature. The thickness of ITO on the glass substrate was measured with an automatic ellipsometer equipped with a He-Ne laser (632.8 nm). The surface work function was determined with an atmospheric photoelectron spectroscope (Riken Keiki, AC-2). The sheet resistance of the ITO substrates was measured using a four-point probe resistance meter (Mitsubishi Yuka, Lorester IP MCP-T250).

The ITO substrate, set in a quartz tube filled with dry nitrogen gas, was irradiated, using an IR lamp (Ushiodenki, QIRZ 100-500/D), through the tube wall, at temperatures ranging from 50 to 430 °C for various time periods, from 10 minutes to 3 hours. The power supply to the IR lamp was adjusted for controlling the temperature of sample surface.

3. Results and Discussion

3.1. Characterization of as-deposited pyrosol ITO

3.1.1. Morphology and crystal structure

The AFM images (Fig.1) of ITO, deposited at various temperatures between 430 °C and 570 °C, show a remarkable increase in grain growth, with increasing deposition temperature. The surface roughness parameters, Ra and Rp-v, determined by AFM, which are typically 1.3 nm and 20 nm, respectively, did not show clear dependency on the deposition temperature (Fig.2).

The crystal structure of ITO, prepared at various temperatures ranging from 430 to 580 °C, was studied by XRD (Fig.3). From the XRD patterns, diffraction peaks specific to ITO [14] were identified, indicating the formation of a polycrystalline structure. For increased deposition temperatures, the diffraction peaks became larger, indicating that the ITO structure became more crystalline. While the dominant diffraction peak for ITO prepared by most other methods [18] is the (222) peak, the (400) peak is much larger than the (200) peak in case of the pyrosol ITO. It has been reported that the dominating diffraction peak is dependent on the type of substrate, the deposition temperature, and the film thickness [19]. For example, in unpublished work by the present authors, the (222) peak, rather than the (400) peak, was found to be dominant in the case of a pyrosol ITO on a mica substrate.

3.1.2. Conductivity and work function

The sheet resistance and the work function of ITO deposited at various temperatures are given in Fig.4 and Fig.5, respectively. The ITO resistance decreased from an order of $10^4 \Omega/\square$, to less than $10^2 \Omega/\square$, as the deposition temperature increased from 430 to 575 °C. The experimental temperature range was limited, as the soda glass substrates were thermally deformed beyond 575 °C. The crystal growth at the higher deposition temperatures, shown by the AFM images (Fig.1) and the XRD patterns (Fig.3), probably reduced the number of trap sites between the grains, and as a result the conductivity was improved.

The work functions did not show clear dependency on the deposition temperature and were distributed from 4.4 to 5.1 eV, as shown in Fig.5.

3.2. Effect of IR irradiation on ITO conductivity

3.2.1. Temperature dependency

As-deposited ITO samples, with sheet resistance of 200 to 400 Ω/\square , were irradiated with IR at various temperatures, ranging from 50 to 430 °C, for 1 hour. The IR irradiation remarkably improved the conductivity of the ITO, as illustrated in Fig.6, and the improvement became more conspicuous as the irradiation temperature increased. The reduction rate of the sheet resistance reached approximately 70% at 400 °C and 430 °C, the maximum available temperature of the irradiation system being 430 °C. Therefore, the irradiation temperature was set at 400 °C throughout the rest of the experiments.

3.2.2. Time dependency

Three as-deposited ITO samples were treated by IR irradiation for various time periods, ranging from 10 to 180 minutes. Fig.7 shows the rapid decrease in resistance over the initial ten minutes, and then a slow decrease over the following 50 minutes. For IR irradiation periods over 50 minutes, the resistance was slightly increased or displayed no change. For this reason, the irradiation time was set at 60 minutes during the rest of the experiments.

3.3. Effect of IR irradiation on work function

The work function of the pyrosol ITO, prepared at various deposition temperatures ranging from 430 to 570 °C, was measured using photoelectron spectroscopy before and after the IR irradiation, and the results are shown in Fig.5. The work functions of the as-deposited and the IR-irradiated samples are, on average, 4.7 eV and 5.2 eV, respectively. The 0.5 eV increment, achieved by IR irradiation, results in an ITO electrode work function that is closer to the ionization potential of the organic layer of an OLED, approximately 5.5 eV in many cases [12]. This is considered favorable for hole injection from ITO to the organic layer of an OLED, and therefore, could provide an effective method to improve the efficiency of hole injection. It is presumed that in the process of augmenting crystallinity in ITO by IR irradiation, less stable bonding, responsible for the lower work function could be converted to more stable bonding of crystals, thereby increasing the work function of the ITO. The augmentation of crystallinity in ITO is indicated by the XRD pattern and FE-SEM image shown later.

3.4. Effect of IR irradiation on the optical properties of ITO

Optical absorption of the ITO deposited at various temperatures was measured

before and after the IR irradiation. Using the results, the square of absorbance was then plotted against the photon energy (eV). The band gap energy of the ITO was estimated as the intersection of the tangential line of the plotted curve, with the horizontal axis [20]. The band gap energy increased by a few hundredths of an electron volt, when the ITO was IR-irradiated, which is possibly due to the Berstein-Moss effect [21-24]. From the improvement of the conductivity, it is presumed that the IR irradiation increased the number of carrier electrons, and the increased carrier electrons accumulated above the Fermi level, raising the upper edge of the conduction band.

3.5 .Effect of IR irradiation on the microstructure of ITO

Wide-angle XRD measurements of the ITO were conducted before and after IR irradiation, and an example of the patterns obtained is shown in Fig.8 (a). The intensity of the diffraction peaks became larger when the ITO sample was IR-irradiated, indicating that the IR irradiation enhanced crystallinity. The intensity ratio of the (222) peak to the (400) peak was calculated for the XRD patterns of various ITO samples, and plotted against the sheet resistance, as presented in Fig.8 (b). The ratio was strongly correlated to the sheet resistance of the ITO, although it is unknown whether this is a cause-and-effect relation. This strong correlation reflected the fact that the sheet resistance of the ITO was reduced (Fig.6) and the intensity ratio of the (222) peak to (400) peak decreased (Fig.3), as the deposition temperature increased.

The ITO surface was observed by FE-SEM, as shown in Figure 9. Many large triangle-shaped crystals, with a dimension of 100 nm, were observed at the surface of the IR-irradiated ITO, while not many were observed at the surface of the as-deposited ITO. This indicated that the IR irradiation enhanced crystal growth. In addition, these crystals seemed to grow in a certain regular plane, resulting in the triangular shape. The geometry suggests that growth was directed in the (111) plane of In_2O_3 . The (111) growth, however, may not be predominant, since the XRD charts indicated the growth of the (400) plane (Fig.8 (a)).

4. Conclusion

IR irradiation enhances crystallinity of the as-deposited pyrosol ITO, decreases its electrical resistance, and increases its work function. IR irradiation is a simple operation, performed at atmospheric pressures, and requiring no elaborate equipment, thereby providing an inexpensive, practical method for modifying the properties of pyrosol ITO.

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Figure captions

Fig. 1. The AFM images of ITO deposited on glass by the pyrosol process. Deposition temperatures are (1) 430 °C, (2) 540 °C, (3) 570 °C.

Fig. 2. The Ra and Rp-v surface roughness parameters of ITO, deposited on glass by the pyrosol process, at various deposition temperatures (●: Ra, Δ: Rp-v).

Fig. 3. The XRD patterns of ITO, deposited by the pyrosol process, at various deposition temperatures.

Fig. 4. Resistance of as-deposited pyrosol ITO vs. deposition temperature.

Fig. 5. Work function of as-deposited pyrosol ITO, and IR-irradiated ITO vs. deposition temperature. Irradiation temperature, 400 °C; irradiation time, 60min. (●: as-deposited, □: IR irradiation).

Fig. 6. Decrease in the resistance of pyrosol ITO vs. IR irradiation temperatures. Irradiation time: 60min.

Fig. 7. Decrease in the resistance of pyrosol ITO vs. IR irradiation time. Irradiation temperature: 400 °C.

Fig. 8. XRD measurement of pyrosol ITO (a) diffraction patterns of as-deposited and IR-irradiated ITO, (b) peak ratio vs. sheet resistance.

Fig. 9. FE-SEM micrograph of ITO deposited by the pyrosol process. (a) as-deposited. (b) IR irradiated. Magnification is $\times 60.0$ K.

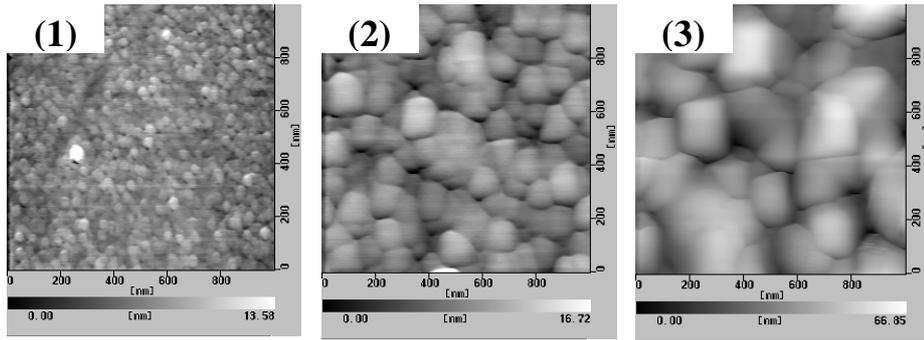


Fig. 1

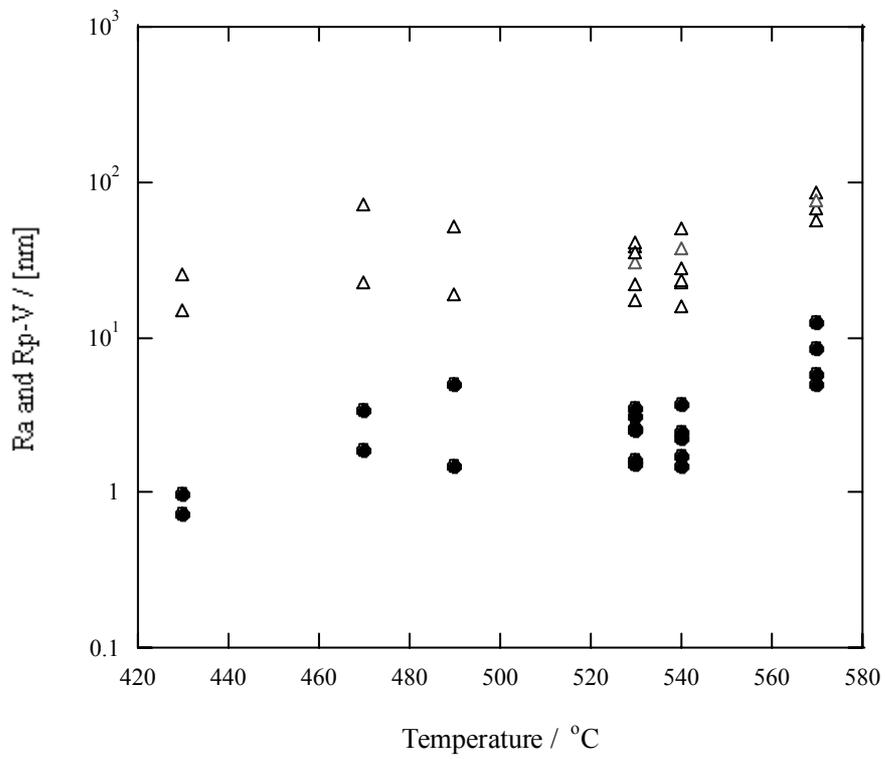


Fig. 2

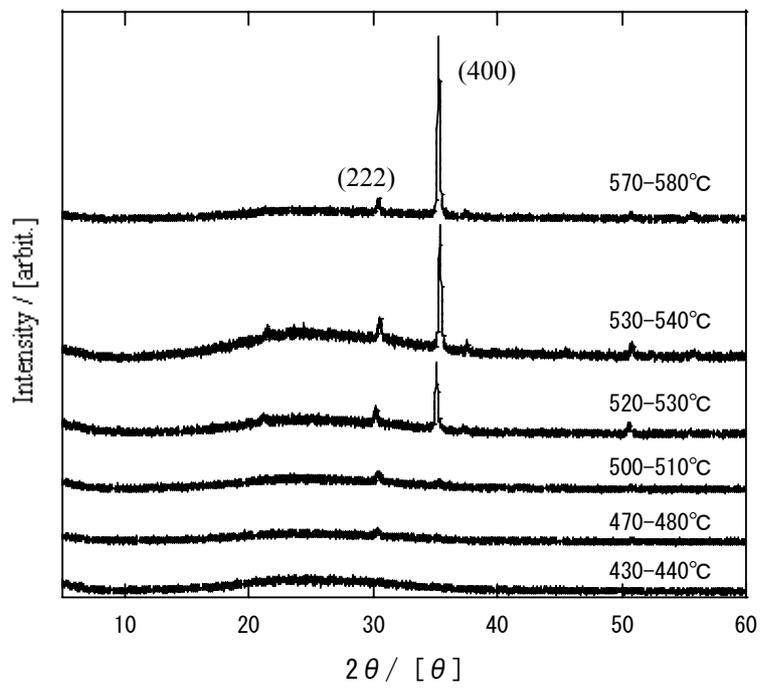


Fig. 3

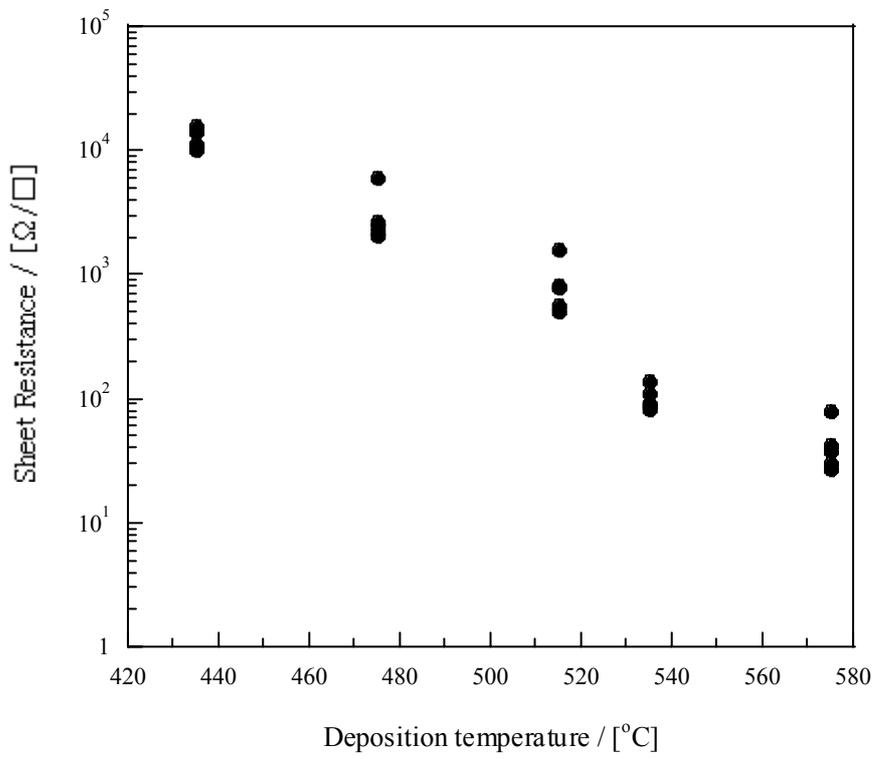


Fig. 4

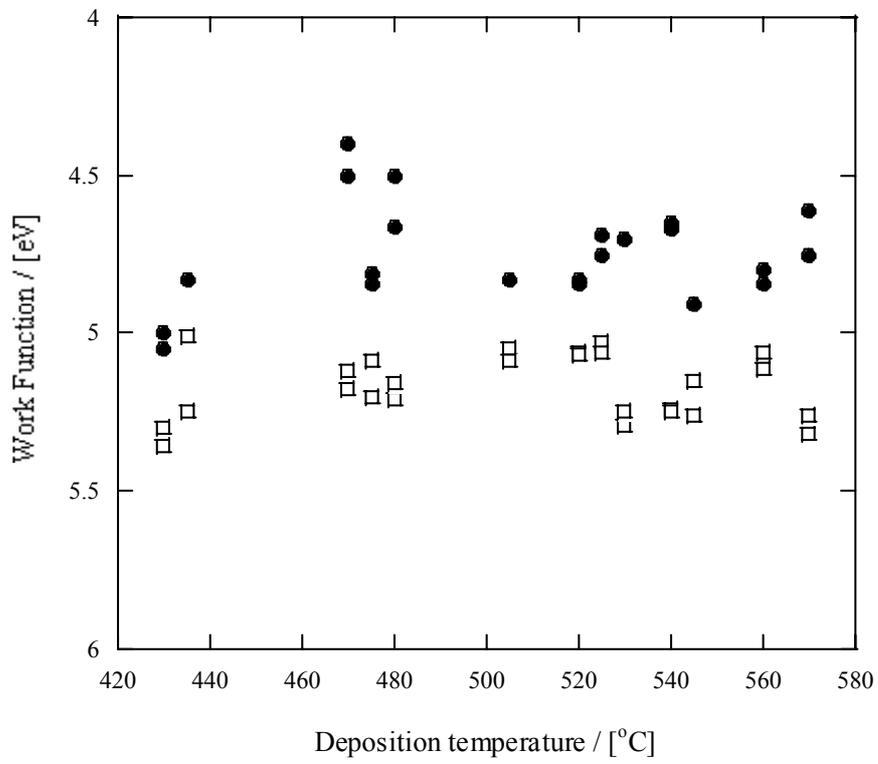


Fig. 5

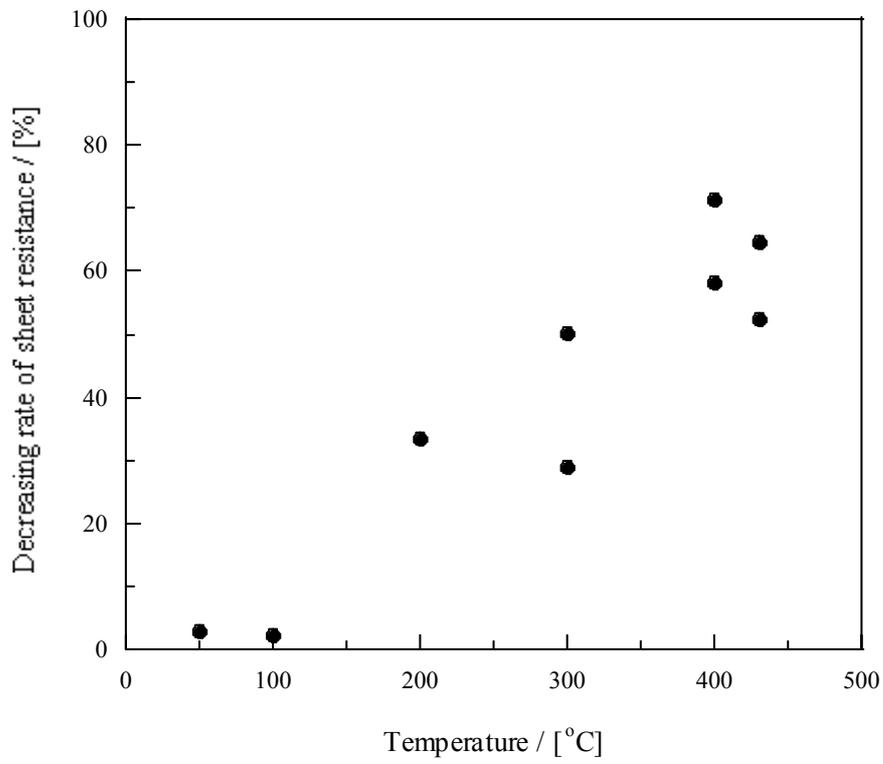


Fig. 6

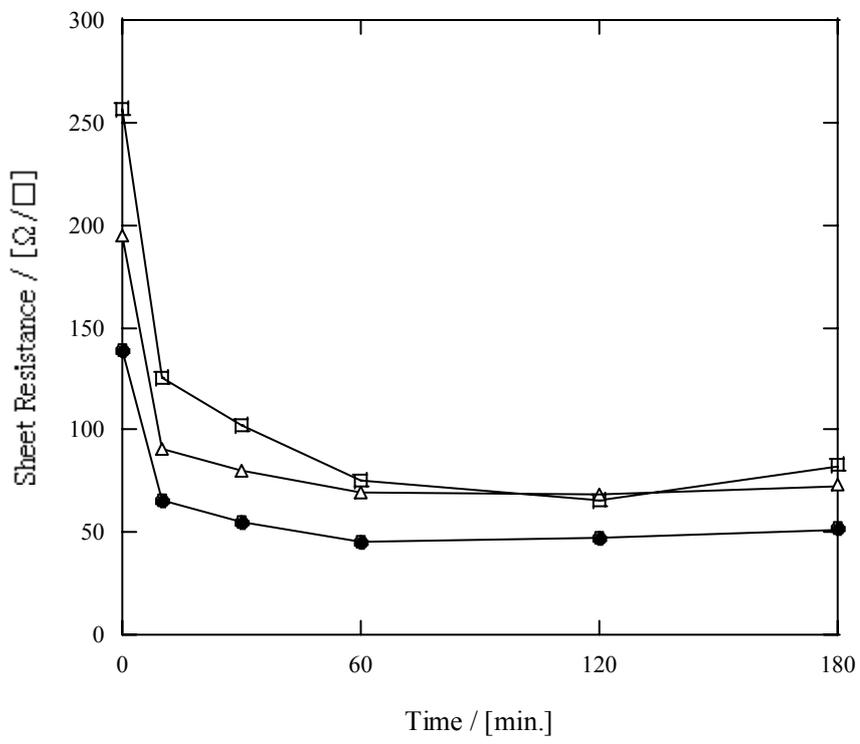


Fig. 7

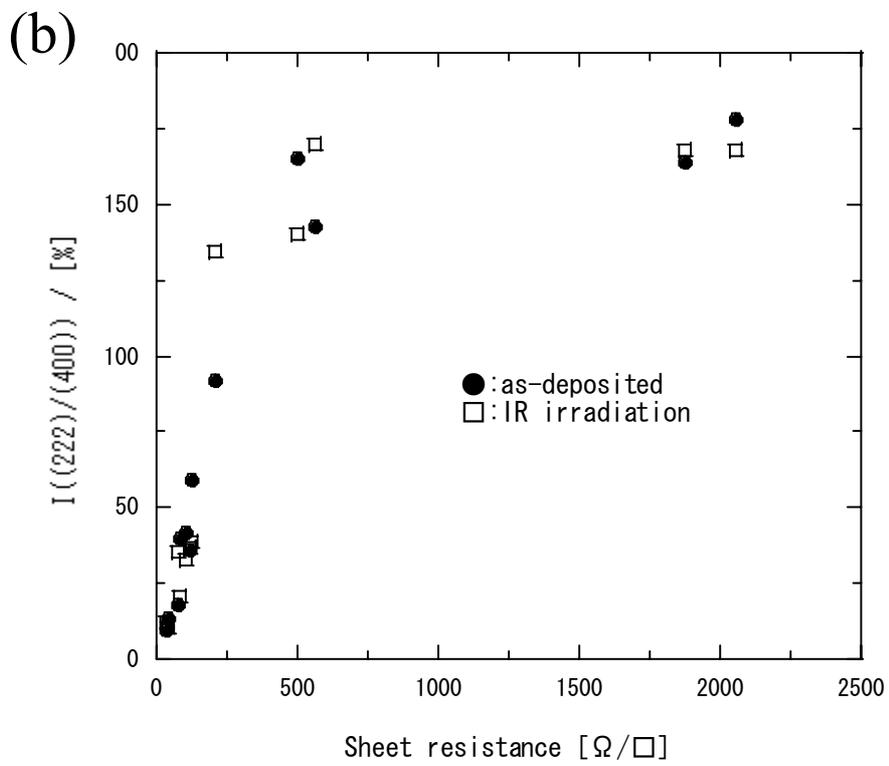
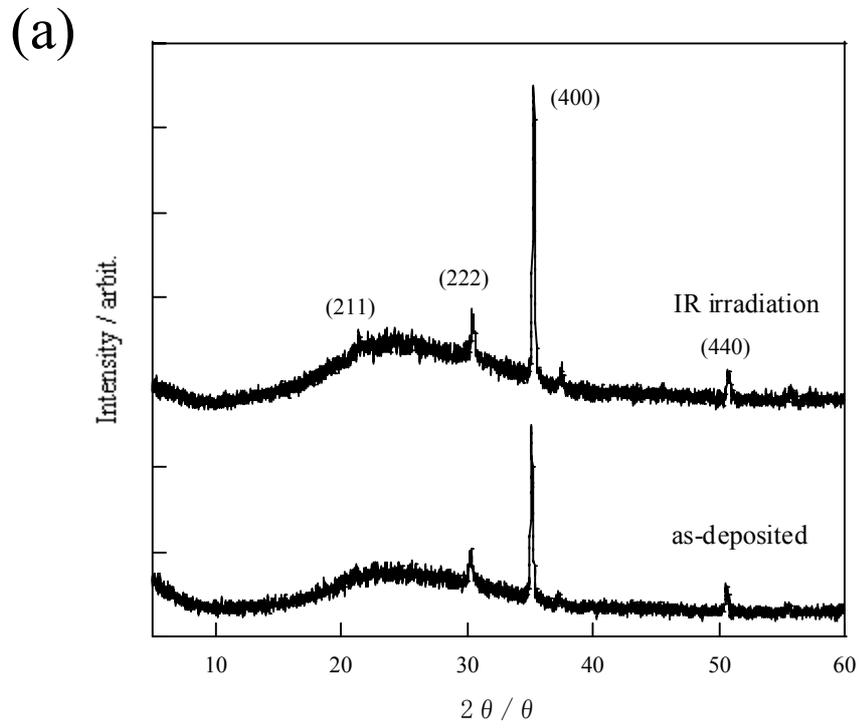


Fig. 8

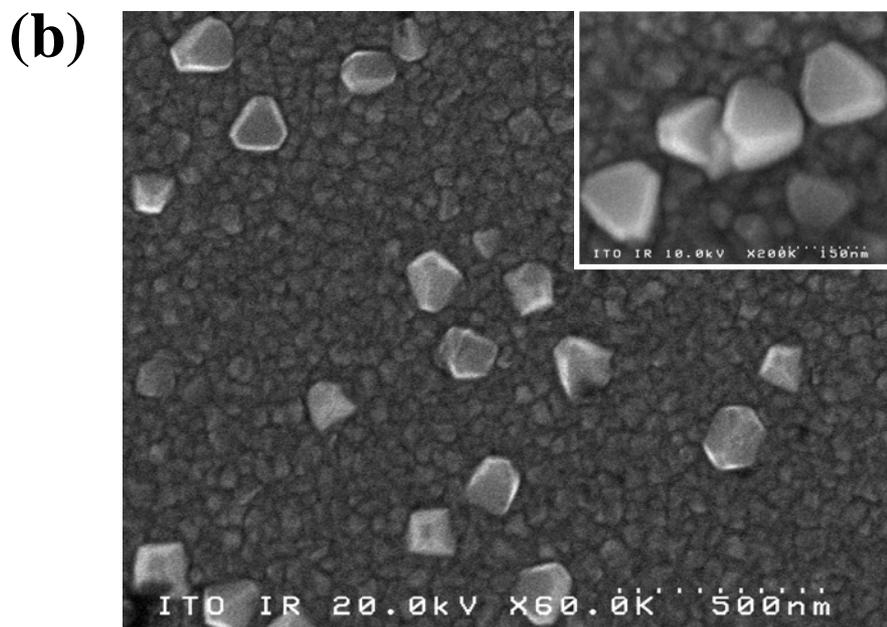
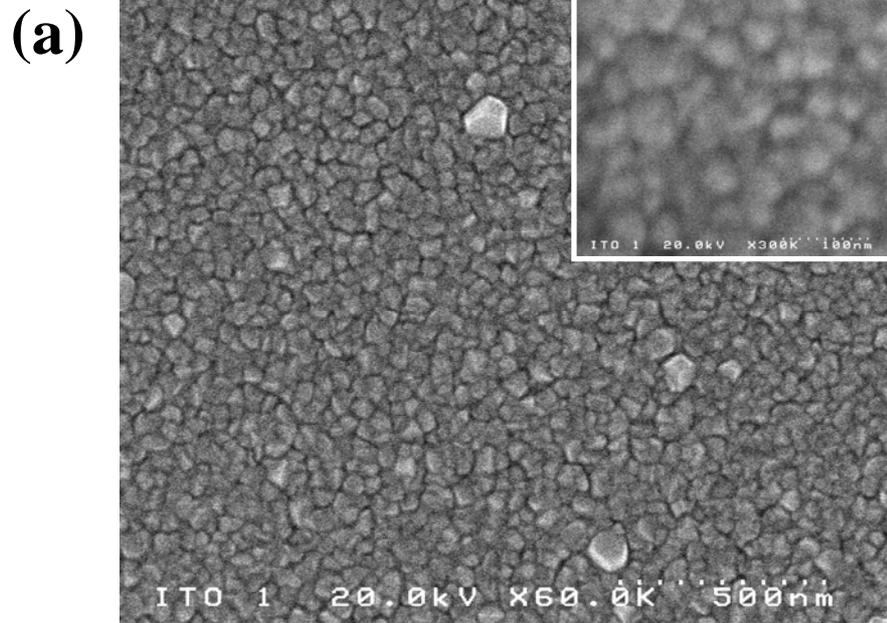


Fig. 9