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RESEARCH ARTICLE

Electron Beam Irradiated ITO Films as Highly Transparent *p*-Type Electrodes for GaN-Based LEDs

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We have investigated the effect of electron beam irradiation on the electrical and optical properties of ITO film prepared by magnetron sputtering method at room temperature. Electron beam irradiation to the ITO films resulted in a significant decrease in sheet resistance from 1.28×10^{-3} Ω cm to 2.55×10^{-4} Ω cm and in a great increase in optical band gap from 3.72 eV to 4.16 eV, followed by improved crystallization and high transparency of 97.1% at a wavelength of 485 nm. The overall change in electrical, optical and structural properties of ITO films is related to annealing effect and energy transfer of electron by electron beam irradiation. We also fabricated GaN-based light-emitting diodes (LEDs) by using the ITO *p*-type electrode with/without electron beam irradiation. The results show that the LEDs having ITO *p*-electrode with electron beam irradiation produced higher output power due to the low absorption of light in the *p*-type electrode.

Keywords: Indium Tin Oxide, Electron Beam, Light Emitting Diode.

1. INTRODUCTION

Indium tin oxide (ITO) thin films have been studied extensively for optoelectronic device applications because of their unique transparent and conducting properties. ITO is an *n*-type degenerate wide band gap semiconductor. The degeneracy is caused by both oxygen vacancy and substitutional tin created during deposition.[1] As a degenerate semiconductor, ITO can be used as the window layer in $n^+ - p$ heterojunctions.[2] Because ITO films have good efficiency for hole injection into organic materials, they have been widely utilized as the anode contact for organic light emitting diodes (OLEDs).[3] Various techniques, from low pressure to high vacuum, have been used to deposit ITO thin films.[4–8] Yao et al. fabricated ITO thin films by thermally evaporating indium and tin sequentially onto substrates kept at room temperature and subsequently annealing them in air to improve their transparency and conductivity.[7] Kulkarni et al. used a novel technique of layer-by-layer deposition of indium and tin by electron beam deposition and subsequent annealing in oxygen to form indium tin oxide.[8] However, films with the highest transmission and lowest resistivity have been prepared by sputtering. Kawada[9] has reported on ITO films deposited from metallic In–Sn alloy targets in a reactive sputtering process.

In this paper, we investigated the electrical and optical properties of ITO film deposited in electron beam assisted sputter system at room temperature as a function of the electron beam irradiation time (0–15 min). The results show that electron beam irradiation can significantly increase optical band gap and reduce resistivity of the ITO film, which can increase high output of GaN-based LEDs.

2. EXPERIMENTAL DETAILS

Deposition of ITO films was performed in a radio frequency (RF) magnetron sputtering system which (Infovion Co. EBAS model) was equipped with an electron-beam gun and three cathodes, RF (13.56 MHz) were applied to ITO (purity; 99.99%) targets, respectively.

The ITO films with a thickness of 200 nm were deposited by using an ITO target (10 wt% SnO_2-doped In_2O_3). At constant RF power of 80 W, Ar flow ratio of 20 sccm with 0.3 sccm of oxygen gas, and working pressure of 5 mTorr, a 200 nm thick ITO films were grown on a corning (Eagle 2000 Fusion Glass) substrate with a dimension of 10×10 mm at room temperature as well as on a LED wafer. After deposited as a ITO film, electron beam with a diameter of 2 inch was irradiated uniformly to the ITO films (20×20 mm) for 0–15 min with power of RF 150 W and DC 1500 V which has electron density of 1.59×10^9 cm^{-3} (measured by cut-off probe

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measurement), Ar flow ratio was 7 sccm and working pressure was 4×10^{-4} Torr. The sheet resistances of the ITO films were measured by four-point probe, and the carrier type, mobility as well as carrier concentration were determined using the Hall measurement system as a function of the electron beam irradiation time. The optical transmittance of the ITO films was measured in the wavelength range of 250–2300 nm using a High Resolution UV-visible-NIR spectrometer.

The structural properties of the ITO films were examined by X-ray diffraction (XRD). To compare the properties of the GaN based LEDs fabricated on the non-irradiated ITO film and electron beam irradiated ITO film grown under the optimized condition, Light-output versus current (L–I) measurements were made using a parameter analyzer.

3. RESULTS AND DISCUSSION

Figure 1 shows the resistivity, carrier density and mobility of ITO films as a function of electron beam irradiation time. The resistivity of ITO films decreased as the electron beam irradiation time increased from 1.28×10^{-3} Ω cm to 2.55×10^{-4} Ω cm.

The carrier density of ITO films increased to 1.1×10^{21} cm^{-3} after 5 min electron beam irradiation, carrier concentration of ITO film with 15 min electron beam irradiation was slightly decreased to 8.5×10^{20} cm^{-3}, but it is also high carrier density. Mobility of ITO films increase to 26 cm^2/Vs after 15 min electron beam irradiation.

The electrical conductivity σ depends on both the concentration n and mobility μ of the free carrier Eq. (1).

$$\sigma = n \cdot e \cdot \mu \tag{1}$$

where e is the electron charge. High carrier concentration and mobility should be simultaneously realized to obtain films with high conductivity. It is generally reported that the use of a In_2O_3–(5–10) wt.% SnO_2 target is advantageous for obtaining ITO films with high conductivity.[10] In this case, films generally have $n \sim 10^{21}$ cm^{-3}, which is nearly the theoretical maximum carrier concentration due

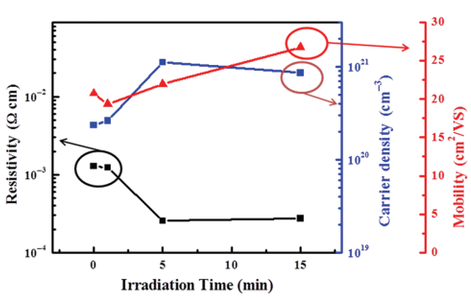

Fig. 1. Variation of sheet resistance, carrier density and mobility of ITO films as a function of the electron beam irradiation time.

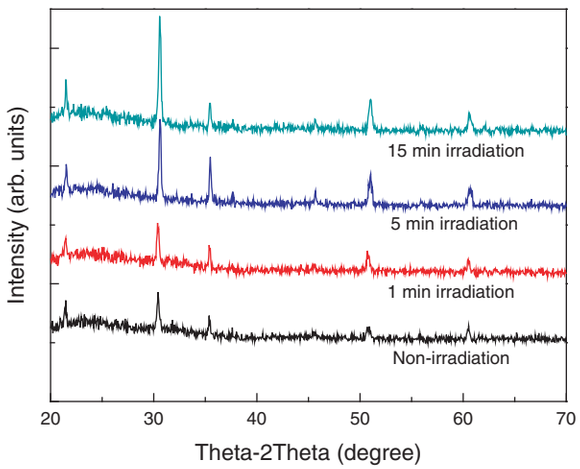

Fig. 2. XRD spectra of ITO films as a function of the electron beam irradiation time.

to Sn doping and oxygen vacancies. Therefore, we estimated that there is a possibility for improving the conductivity of ITO by accurate control of the parameters which affect the carrier mobility.

Figure 2 shows the X-ray diffraction of ITO films depending upon the electron beam irradiation time. The as-deposited ITO film showed (211), (222), (400), (440), (622) peaks. However, intensity of the ITO peaks significantly increased after electron beam irradiation for 15 min. It is implying much better crystal quality of ITO film after sufficient electron beam irradiation. The high intensity peak corresponding to the (222) plane has been observed as the predominant peak for all the films, which means that texturing is always normal to the (222) plane.[11] The improvement of crystallization can be explained as follow. One possible explanation is that the electron beam can result in momentum transfer of electron to ITO film, which can assist the substitution of Sn into the In site in ITO film. This can improve the crystallization of the ITO film during the electron beam irradiation, followed by increase in the carrier density after the electron beam treatment, as shown in Figure 2. However, electron mass (9.1×10^{-31} kg) is too small to cause the substitution of Sn into In site in ITO film, since the activation energy of the substitution was as high as 2.31 ± 0.06 eV.[17] Another possible mechanism is that the electron beam irradiation can cause energy transfer of electron beam to ITO film. This can increase the temperature of ITO film during the electron beam irradiation, which can improve the crystallization due to the crystallization in ITO film.

Figure 3 shows the change of transmittance of the ITO films as a function of the electron beam irradiation time. The highest transmittance of 91.5% was obtained at wavelength of 540 nm for the ITO film without electron beam irradiation. However, for the ITO film with 15 min electron beam irradiation, the highest transmittance of 97.1% at wavelength of 485 nm.

RESEARCH ARTICLE

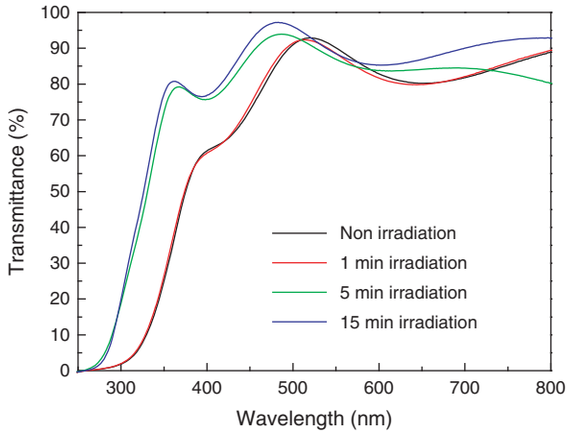

Fig. 3. The transmittance of ITO films as a function of the electron beam irradiation time.

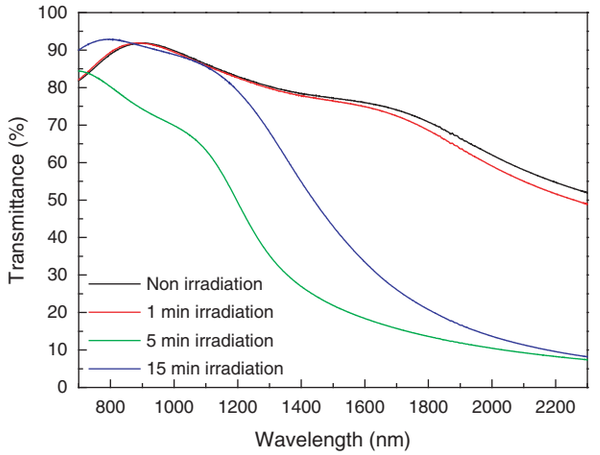

Fig. 5. The transmittance of ITO at wavelength of IR region as a function of the electron beam irradiation.

This result clearly shows that electron beam irradiation to the ITO film increases the transmittance and lead to blue-shifted. Figure 4 shows the optical band gap of ITO film as a function of the electron beam irradiation time. Optical band gap of the ITO films with/without the electron beam irradiation was calculated following relation, in Eq. (2).[12]

$$\alpha h\upsilon = A(h\upsilon - Eq)^n \tag{2}$$

where α is absorption coefficient, $h\upsilon$ is the photon energy, and Eq is the optical band gap, A is constant, $n = 0.5$ for direct band gap material, $n = 2$ for indirect band gap material. The optical band gap of the ITO films increased from 3.72 eV to 4.16 eV after the electron beam irradiation, which clearly shows that the electron beam irradiation can greatly increase optical band gap of ITO films. This shift of the band gap with change in carrier density can be explained by the Burstein-Moss (BS) shift.[13–14]

To evaluate the Burstein-Moss effect, we investigated the IR region of transmittance of ITO films. In the IR region, the free carrier absorption becomes important for the transmittance for the transmittance and reflectance of the ITO films. The optical phenomena in this region can be explained on the basis of classical Drude's theory.[15–16] Figure 5 shows the transmittance of ITO films as a function of the electron beam irradiation at the wavelength of 700 nm to 2300 nm.

This result shows that high transmittance is kept in the low carrier density film in the whole IR region. And this phenomenon will cause a partial filling of the conduction band and result in blocking of the lowest states and then a widening of the optical band gap known as the Burstein-Moss shift.

Finally, we fabricated GaN-based LEDs by using the ITO *p*-type electrode with/without electron beam irradiation. Figure 6 shows the integrated intensity of the ITO film of applied to LEDs as a function of the electron beam irradiation (0 and 15 min). As shown in Figure 6, for the LEDs having ITO *p*-electrode with electron beam

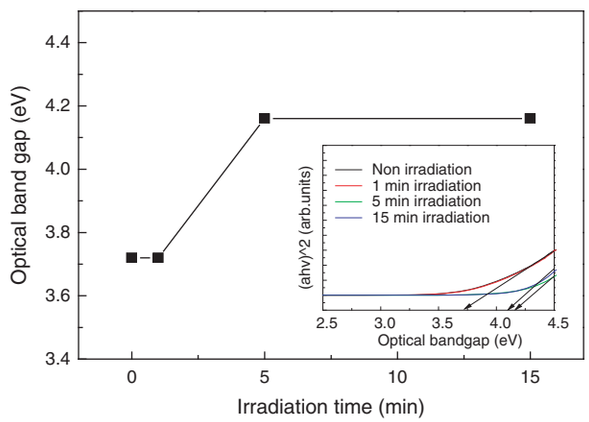

Fig. 4. Variation of optical band gap of ITO films as a function of the electron beam irradiation time.

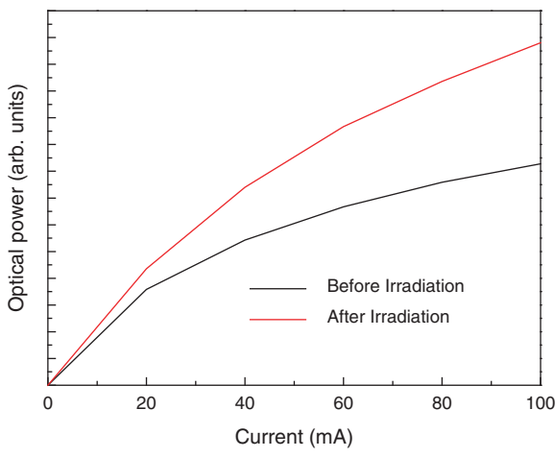

Fig. 6. Light output power–current (L–I) characteristics of ITO film contacts before and after electron beam irradiation.

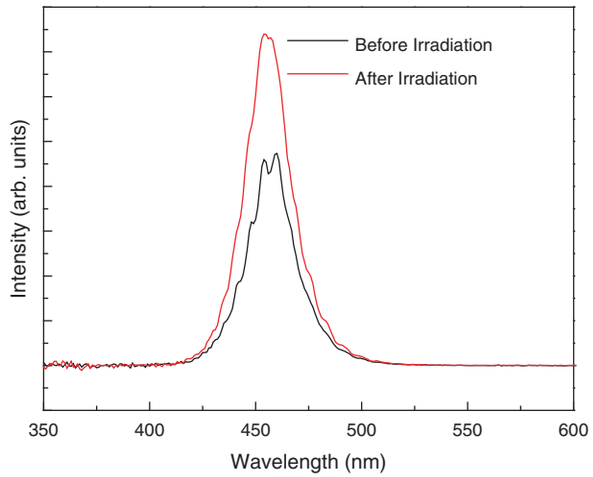

Fig. 7. Integration intensity of ITO film contacts before and after electron beam irradiation.

irradiation, optical power increased, when compared to that of the LEDs without electron beam irradiation.

Figure 7 shows the change of the electroluminescence (EL) of the LEDs at 60 mA with/without electron beam irradiation. The EL intensity shows that electron beam irradiation did not change the peak wavelength of the LED, meanwhile it significantly increased the integrated intensity. These results strongly suggest that electron beam irradiated ITO films is a good candidate as a *p*-type electrode for realization of high power LEDs.

4. CONCLUSION

In this paper, we have investigated the electrical and optical properties of ITO film deposited in electron beam assisted sputter system at room temperature as a function of the electron beam irradiation time (0–15 min). The electron beam irradiation to the ITO films resulted in a significant decrease in resistivity from 1.28×10^{-3} Ω cm to 2.55×10^{-4} Ω cm, increase in carrier density and their mobility. In addition, after electron beam irradiation, transmittance increased in the visible region caused by improved crystallization of ITO film but transmittance decreased in the IR region. These results indicate that the absorption edge is blue-shifted in the high carrier density film due to a Burstein-Moss effect. Moreover, the overall change in electrical, optical and structural properties of ITO films is related to annealing effect and energy transfer of electron by electron beam irradiation. The results show that the GaN-based LEDs having ITO *p*-electrode with electron beam irradiation produced higher optical output power due to the low absorption of light as the *p*-type electrode. Therefore, the ITO film with electron beam irradiation can represent a highly promising *p*-type contact for high brightness LEDs.

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