Properties of the ITO layer in a novel red light-emitting diode*

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Abstract: An optically transparent electrode, indium tin oxide (ITO) film is fabricated by vacuum E-beam evaporation. The thermal annealing effects on the ITO/GaP contact have been investigated by means of the transmission line model method. Under 435 °C, with rapid thermal annealing for 40 s in N_2 ambient, the ITO contact resistance reaches the minimized value of $4.3 \times 10^{-3}\ \Omega \cdot cm^2$. The results from Hall testing and Auger spectra analysis indicate that the main reasons for the change of the contact resistance are the difference in the concentration of carriers and the diffusion of In, Ga, O. Furthermore, the reliability of AlGaInP LEDs with a 300-nm thickness transparent conducting ITO film is studied. The increase of LED chip voltage results from the degradation of ITO film. Moreover the difference between the thermal expansion coefficient of GaP and ITO results in the invalidation of the LED chip.

Key words: indium tin oxide; GaP; contact resistance; reliability
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1. Introduction

$(Al_xGa_{1-x})_{0.5}In_{0.5}P$ is an attractive material system for light-emitting diodes (LEDs) covering the red to green portion of the visible spectrum[1] . However, the poor current spreading effect of the p-type layer has localized the injected current just below the p-pad metal[2]. The emitted light under the p-pad electrode will be absorbed or reflected. Recently, an indium tin oxide (ITO) layer with high conductance and superior transparency (90%) was introduced to enhance the current spreading in AlGaInP-based LEDs[3–5]. Therefore, the thickness of the window layer in the AlGaInP LEDs could be effectively decreased by the insertion of ITO thin film.

It has been found that to use ITO advantageously, a reduction of the contact resistance between the window layer and the ITO layer is necessary in the design of these AlGaInP LEDs by introducing a thin highly doped p-type GaAs layer, forming a base for good ohmic contacts[6, 7]. However, it should be noted that the intensity of the emitted light still decreased because of the absorption of the inserted GaAs contact layer. To diminish the drawback of optical absorption, a heavily carbon-doped GaP (GaP : C) contact layer on the Mg-doped GaP window layer is proposed and thus enhances the light extraction efficiency. But the process is complicated[8, 9]. In this paper, the ITO film deposited on p-type Mg-doped GaP was fabricated by vacuum E-beam evaporation. The thermal annealing effects on the ITO have been investigated by means of the TLM method and Hall test. AlGaInP LEDs with a GaP contact layer and transparent conducting indium tin oxide film are fabricated and aged under a forward current of 120 mA for 4000 h.

2. Electrical properties of ITO

An electron beam evaporation system was used for ITO thin film deposition. The target material used in this study was an ITO pellet with a weight composition of 90% In_2O_3 and 10% SnO_2. The substrate temperature during the deposition process was kept at 300 °C, the rate was 0.4 nm/s, and the O_2 flow was 3.0 sccm. The thickness of deposited films was controlled using a quartz crystal thickness monitor.

A 300-nm thickness ITO film is deposited on glass and annealed in an RTA system at several temperatures: 360, 400, 435, 460, 500 °C under N_2 ambient for 40 s. The electrical properties of the ITO/glass were measured as a function of the annealing temperature by means of the Hall effect. The sample is a standard van der Pauw configuration. Four circular indium pads (2 mm diameter) were thermally evaporated in a symmetric arrangement at the corners of the substrates for the Hall measurement.

Figures 1 and 2 show the variation of the resistivity, carrier density, and Hall mobility as a function of RTA temperature.

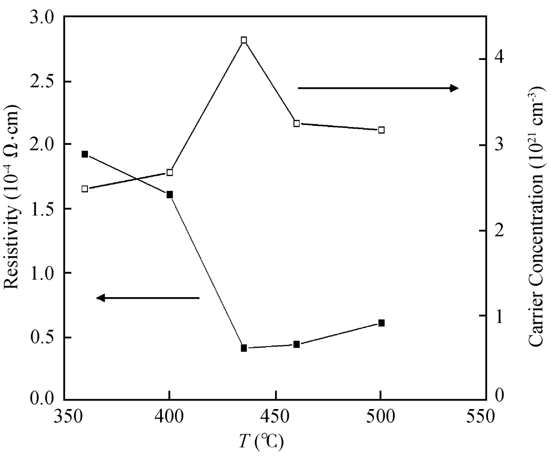

Fig. 1. Carrier concentration and resistance of ITO as a function of temperature.

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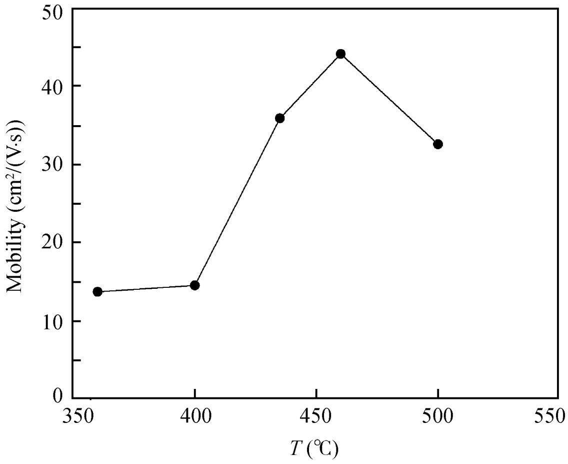

Fig. 2. Mobility of ITO as a function of temperature.

The carrier concentration of ITO increases when the RTA temperature $\leqslant$ 435 °C and decreases when the RTA temperature $>$ 435 °C. The resistivity and mobility of ITO firstly decrease and then increase as the RTA temperature increases.

It can be seen that the resistivity is strongly influenced by the RTA temperature. The resistivity of the film decreased to a lowest value of 4.3×10^{-3} $\Omega \cdot cm^2$ at an RTA temperature of 435 °C. The decrease in resistivity may be due to the increase of grain size as the RTA temperature increases[10]. Moreover, the RTA process enhances the crystallinity of the film. In ITO film, Sn atoms in crystal lattices (so called "activated Sn atoms") generate carrier electrons. Therefore, lower resistivity was obtained when RTA temperature was increased. However, the resistivity of the ITO film increased with a further increase at the RTA temperature ($>$ 435 °C), in spite of the largest grain size[11]. The reason for the resistivity increasing as the RTA temperature increases can be explained by the decrease of the number of oxygen vacancies in the ITO film. It seems that the enhancement of crystallinity of the film is a dominant factor which influences the resistance of ITO film[12−14].

Optical property is another important parameter for ITO. Zhang Guowei, who is in the same group as me, reported that the RTA process can improve the light transmittance of ITO film, and increase the refractive index[15].

3. Electrical properties of the ITO/GaP contact

ITO film with 300 nm thickness was deposited on p-type Mg-doped GaP using vacuum E-beam evaporation. The carrier concentration of the p-GaP layer was in the range of 10^{18} cm^{-3}. The TLM method was used to characterize the specific contact resistance of the ITO/GaP contact. Different samples were annealed using a rapid thermal annealing (RTA) system at several temperatures: 360, 400, 435, 460, 500 °C in N_2 ambient for 40 s.

The I–V characteristics of six samples at different annealing temperatures (T = no annealing, 360, 400, 435, 460, 500 °C) are shown in Fig. 3.

The contact characteristics of all samples, before and after annealing, are ohmic contact. The TLM measurement results in Fig. 4 present the values of the specific contact resistance. It was found that it is an ohmic contact when ITO

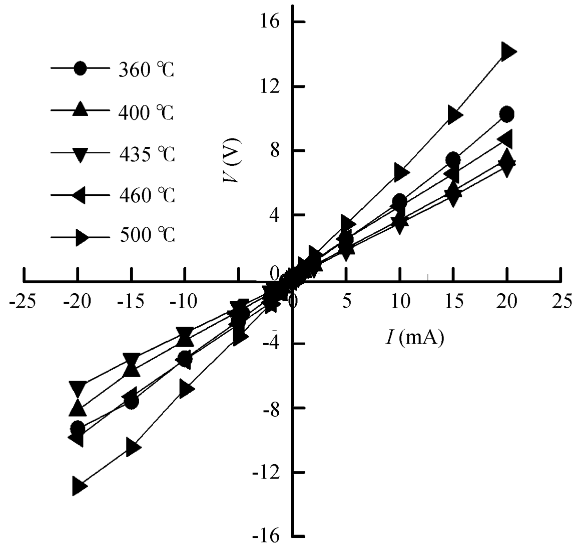

Fig. 3. I–V characteristics of the ITO /GaP contact as a function of temperature.

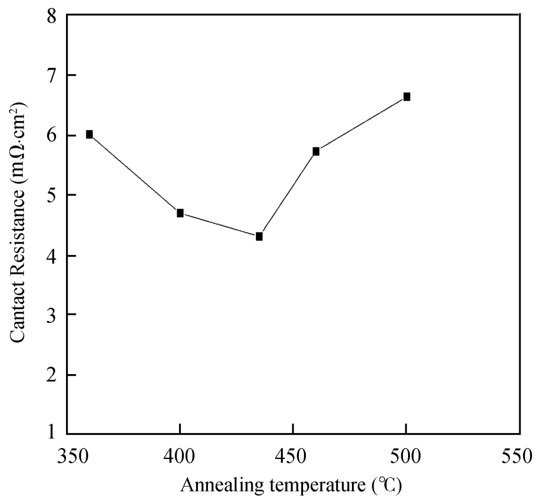

Fig. 4. Specific contact resistance of the ITO/GaP contact as a function of temperature.

is deposited directly on p-GaP. The specific contact resistance is increased and then decreased as the annealing temperature increases, so there is a optimal annealing temperature for the ITO/GaP contact as 435 °C, where resistance reaches a minimum at 4.3×10^{-3} $\Omega \cdot cm^2$.

Comparing Fig. 1 with Fig. 4, it is found that the change of carrier concentration is precisely opposite to the specific contact resistance as a function of the annealing temperature. Consequently, it can be thought that the main reason for the different contact resistance is the difference in the carrier's concentration of ITO film. However, from our experiment, the specific resistance without annealing is lower than that with annealing at 460 °C, and the carrier concentration of ITO without annealing is also lower than that with annealing. So there is another factor which may have an important effect on the contact resistance.

Auger spectra analysis of the sample can provide information on layer composition and thus will be helpful to explain this phenomenon. Figure 5 shows the Auger spectra of

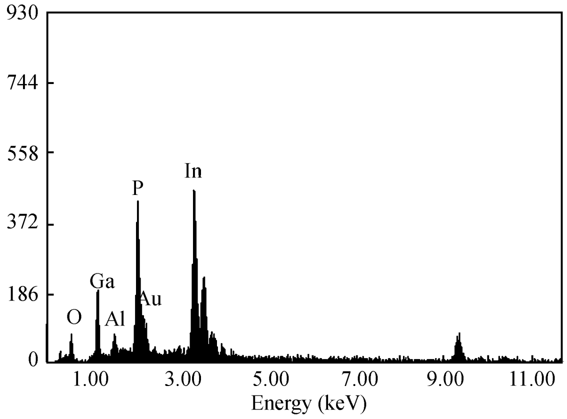

Fig. 5. Auger spectra of the ITO/GaP interface after 435 °C annealing.

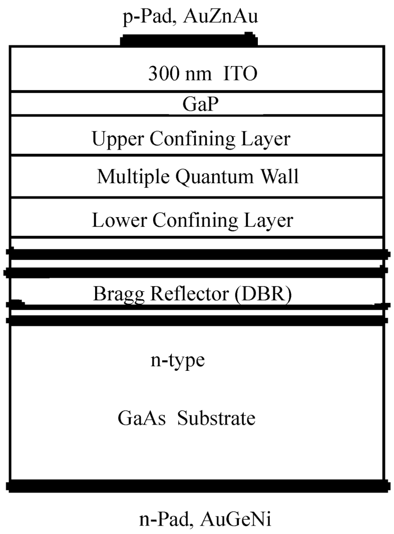

Fig. 6. Structure of AlGaInP LED.

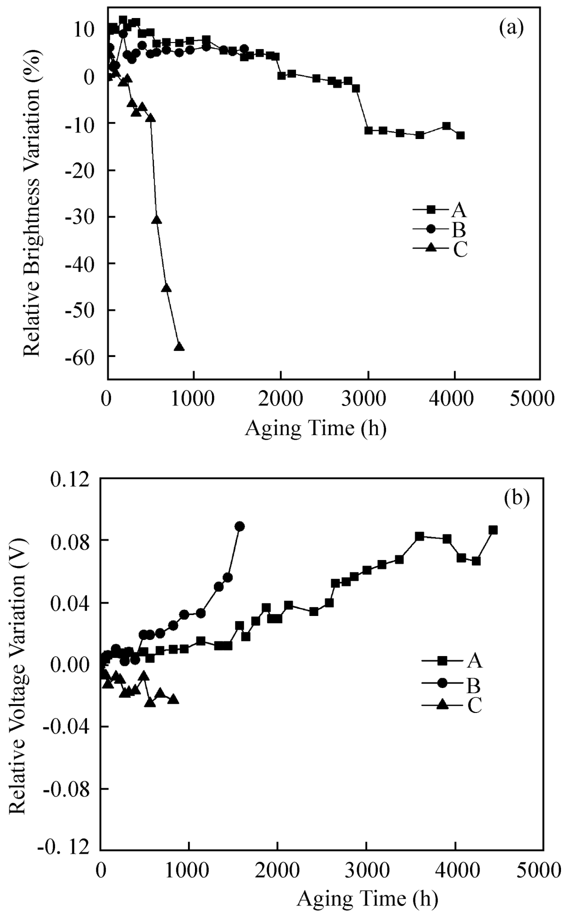

Fig. 7. (a) Output light intensity and (b) voltage variation of the novel LED versus aging time.

Table 1. Last-time test result.

Sample	Aging time (h)	Output light variation (%)	Voltage variation (V)
A: 300 × 300, unpackaged	4427	35	1.21
B: 200 × 200, unpackaged	1644	42	1.89
C: 200 × 200, packaged	830	58	−0.02

the ITO/GaP interface after annealing at 435 °C. Indium atoms are found to exhibit significant diffusion and O atoms also diffuse into the GaP layer. It is supposed that, during the contact annealing, gallium atoms diffuse out from the GaP substrate to the ITO contact and create gallium vacancies and indium atoms diffuse from the ITO contact to gallium vacancy sites in addition to the diffusion of O to GaP, therefore forming a mixed interfacial layer composed of $In_xGa_yP_z$, $In_xGa_yO_z$, etc[16] at the ITO/GaP interface. Also, it is possible that this mixed interfacial layer and created gallium vacancies could reduce the barrier height and decrease the sheet resistance of the substrate at the interface. The carrier concentration of ITO increased at the same time. So the specific contact resistance of GaP/ITO decreased. However, it is also possible that excessive intermixing of the materials at the ITO/GaP interface due to excessive annealing will increase the barrier width, and therefore, increase the contact resistance[16, 17].

4. Effect of ITO on the reliability of AlGaInP light-emitting diodes

The AlGaInP LEDs were grown on a GaAs substrate by MOCVD (metal organic chemical vapor deposition). The ITO layer, which was used as a current spreading layer, was deposited on top of the LED epi-layer by electron beam evaporation. Figure 6 shows the structure of the AlGaInP LED. These AlGaInP LEDs give a high performance under the optimal RTA condition. Unpackaged LEDs with chip sizes of 300 × 300 μm^2(sample A), 200 × 200 μm^2 (sample B) and epoxy resin packaged LEDs with chip size 200 × 200 μm^2 (sample C) were fabricated for the aging test.

Lifetime tests of the LEDs were performed at a forward current of 120 mA and at room temperature. Figure 7 and Table 1 show the test results.

Figure 7(a) shows that the output light intensity of the three kinds of LEDs decreases as the aging time increases. The sample C (epoxy resin packaged) shows a faster decay than that of samples A and B. The voltages of the LEDs change as the aging time increases, as shown in Fig. 7(b). Sample A increases more slowly than sample B. The voltage of sample C does not

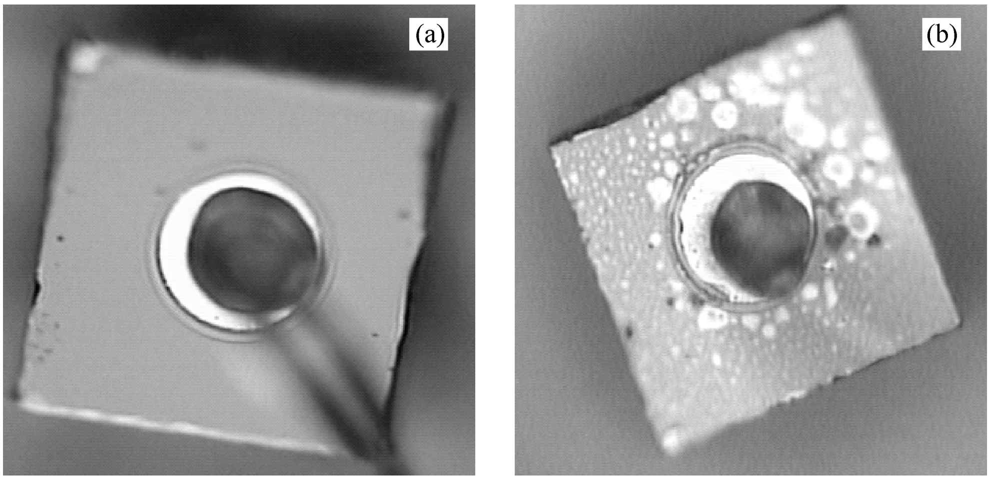

Fig. 8. Circuit diagram of the source coupled differential amplifier.

increase but slightly decreases. As shown in Table 1, as for sample A in last 200 h, the light output variation is down 35% and the voltage variation is up by 1.21 V. For sample B in last 90 h, the light output variation is under 42%, and the voltage variation is up by 1.89 V.

The aging results show that the failure model is different for different reasons of degradation. In particular, the voltage of sample C decreased while the other two curves increased as the aging time increased. The reason for the degradation of sample C may be due to the degradation of the epoxy resin. The heat generated from the LED chip could be great enough to carbonize the epoxy plastic in high current. From the result mentioned before, the degradation of the LED chip with ITO film is induced by the high current injected into the ITO layer, and the larger the injected current density is, the faster the voltage increases[18].

Figure 8 shows images of sample B before and after the aging test. There is notable degradation on the ITO film. Many small bubbles appear on the surface. It is possible that the degradation of ITO is due to the long time exposure in air ambient, which caused a reaction between the vapor, oxygen and ITO. Furthermore, the large injected current in ITO can catalyze the reaction process. As the voltage increases, the LED chip generates more heat. A higher junction temperature accelerates the failure process. The interface between GaP and ITO become laxative; then a bubble is formed and cracks due to the different thermal expansion coefficients for GaP (5.81×10^{-6} K^{-1}) and ITO (8.2×10^{-3} K^{-1}). The cracked ITO flakes off from the GaP layer. Finally, it results in the rapid voltage increase and the light intensity decrease.

5. Conclusion

In this paper, the effects of thermal annealing on the electrical properties of ITO and the ITO/GaP contact have been investigated by means of Hall testing and the TLM method. It showed that under 435 °C RTA for 40 s, the contacts between ITO and GaP have a minimized contact resistance of 4.3×10^{-3} $\Omega\cdot cm^2$. The results from Hall testing and Auger spectra analysis indicate that the differences in contact resistance are due to the change in the concentration of carriers and the diffusion of In, Ga, O atoms. Furthermore, AlGaInP LEDs with a GaP contact layer and an ITO current spreading layer were investigated under high current aging tests. At the beginning of the aging process, the main degradation is the voltage increase which is due to the degradation of ITO film in air ambient. In the last period, because of the different thermal expansion coefficients for GaP and ITO, the interface between GaP and ITO becomes laxative; then a bubble formed and cracked, finally resulting in the invalidation of the LED chip.

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