Surface & Coatings Technology 320 (2017) 421–425

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Performance of p-side-up thin-film AlGaInP light-emitting diodes with textured composite aluminum-doped zinc oxide transparent conductive layers

Ming-Chun Tseng [a], Dong-Sing Wuu [a,e], Chi-Lu Chen [b], Hsin-Ying Lee [c], Yu-Chang Lin [c], Ray-Hua Horng [b,d,*]

[a] Department of Materials Science and Engineering, National Chung Hsing University, Taichung 402, Taiwan, ROC
[b] Graduate Institute of Precision Engineering, National Chung Hsing University, Taichung 402, Taiwan, ROC
[c] Department of Photonics, National Cheng Kung University, Tainan 701, Taiwan, ROC
[d] Department of Electronics Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, ROC
[e] Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 701, Taiwan, ROC

ARTICLE INFO

Article history:
Received 18 August 2016
Revised 28 November 2016
Accepted in revised form 1 December 2016
Available online 6 December 2016

Keywords:
Texture surface
Light-emitting diodes
Composite aluminum-doped zinc oxide

ABSTRACT

Composite transparent conductive layers (TCLs) were deposited on the GaP window layer of *p*-side-up thin-film AlGaInP light-emitting diodes (LEDs) in order to enhance their light-extraction efficiency. The composite TCLs were fabricated from aluminum-doped zinc oxide (AZO) layers grown through atomic-layer deposition and pulsed-laser deposition. The results showed that wet-etching of composite AZO thin films improved the light-extraction efficiency of the corresponding LED devices. The droop efficiencies of LEDs with flat AZO thin films, composite AZO thin films, and optimum textured composite AZO thin films were 29%, 30%, and 22%, respectively. LEDs with textured composite AZO layers exhibited favorable optoelectronic performance. When the injection current was increased from 20 to 1000 mA, the emission wavelengths of LEDs with flat AZO thin films, composite AZO thin films, and optimum textured composite AZO thin films shifted by 3, 5, and 3 nm, respectively. The optimum textured composite AZO thin film can not only improve LED performance but also effectively substitute flat TCLs in AlGaInP LED applications.

1. Introduction

Light extraction from LED structures is a major challenge in the development of quaternary $(Al_{1-x}Ga_x)_{0.5}In_{0.5}P$-based light-emitting diodes (LEDs) owing to its being limited by substrate absorption and total internal reflection. One approach for improving light extraction is to minimize total internal reflection by inserting a middle-refractive-index material between the top layer and the epoxy layer of the LED structure [1]. Another approach is to mitigate light absorption by the semiconductor substrate through the application of thin-film technology: the epitaxial layers are separated from the semiconductor substrate to carrier substrate through the once or twice wafer-transferring technique [2–3].

Periodic-texturing and random-texturing surface techniques have been developed to improve the efficiency of light extraction. The effects of periodic texturing on the light-extraction efficiency of LED devices and components, such as LED surfaces that have been directly roughened, photonic crystals [4], *p*-GaP dish mirror arrays [5], nanomesh ZnO layers with a *p*-GaP window layer fabricated through nanosphere lithography [6], and stripe-patterned epilayer structures with an omni-directional reflector on the *p*-GaP surface [7], have been widely studied. Similarly, random-texturing surface techniques, such as the use of anti-reflective subwavelength structures on *p*-GaP surfaces [8], the use of porous anodic alumina film as a rough surface [9], *n*-side surface roughening [10], and pyramidal-patterned *p*-GaP:Mg spreading layers fabricated through a photoassisted chemical method [11], have been proposed for improving light extraction. These periodic- and random-texturing approaches have focused on *n*- or *p*-side semiconductor surface texturing to increase the probability of light scattering.

In our previous study, the Ohmic contact characteristics of aluminum-doped zinc oxide (AZO) thin films grown through atomic-layer deposition (ALD) with a *p*-GaP:C cap layer was found to strongly influence the performance of *p*-side-up thin-film AlGaInP LEDs [12]. The external quantum efficiency (EQE) of the AlGaInP LEDs was improved by enhancing light extraction through the use of ALD-AZO thin films. AZO plays the role to reduce the difference between the refractive indices of the semiconductor substrate and the epoxy layer in the LED structure. To increase the number of photons extracted from the LED structure, a thick AZO thin film was deposited on the ALD-AZO thin film through pulsed-laser deposition (PLD). After wet etching, this

* Corresponding author at: Department of Electronics Engineering, National Chiao Tung University, 1001 University Road, Hsinchu 300, Taiwan, ROC.
E-mail address: rhh@nctu.edu.tw (R.-H. Horng).

http://dx.doi.org/10.1016/j.surfcoat.2016.12.002

thick PLD-AZO thin film functions as a textured surface; moreover, together with the ALD-AZO thin film, it forms a composite transparent conductive layer (TCL). In this study, composite AZO layers grown through ALD and PLD were deposited on the thin carbon-doped GaP cap layer of *p*-side-up thin-film AlGaInP LEDs with vertical electrode contacts, and the electrical properties of such LEDs with flat and textured composite AZO thin films were investigated.

2. Experimental details

The AlGaInP LED structure (Fig. 1) was grown on an *n*-type GaAs substrate through metal–organic chemical vapor deposition. The LED structure consists of a carbon-doped p^+-GaP Ohmic contact layer, a *p*-GaP:Mg window layer, a *p*-cladding AlGaInP layer, GaInP–AlGaInP multiple quantum wells, an *n*-cladding AlGaInP layer, an n^+-GaAs contact layer, and a GaInP etching-stop layer. This structure was fabricated through twice wafer-transferring technology, which has been described in detail in our previous study [1]; this structure exhibits a *p*-side up structure, which facilitates subsequent thin-film deposition and LED fabrication. The Cr/Au/In metals serve as the bonding layers and form an Ohmic contact with the n^+-type Si substrate. Two types of composite TCLs were fabricated through ALD and PLD. First, through ALD, the AZO layer was deposited on a *p*-side-up thin-film AlGaInP LED at a Zn:Al cycle ratio of 20:1, deposition temperature of 200 °C, and pressure of 0.6 Torr. Diethylzinc [$Zn(C_2H_5)_2$, DEZn], trimethylaluminum [$Al(CH_3)_3$], and de-ionized water were used as the Zn, Al, and O precursors for depositing the AZO thin film at a growth rate of 0.14 nm/cycle. The Al precursor as the dopant source in the ZnO film was introduced into the reaction chamber after 20 cycles of DEZn injections. The thick AZO layer deposited atop the ALD-AZO layer was then prepared by PLD (mode: PLD/MBE-2000, PVD products) using a 3″-diameter AZO ceramic target (99.999% purity; 98 wt% ZnO and 2 wt% Al_2O_3) at a growth temperature of 100 °C. The substrate and the target were placed 8 cm apart. A KrF excimer laser ($\lambda = 248$ nm, pulsed duration $= 25$ ns) was employed as the ablation source at a repetition rate of 2 Hz and energy flux of 600 mJ/pulse. Because the base pressure was less than 5×10^{-7} Torr, 15-sccm argon and 15-sccm oxygen gas were introduced into the chamber in order to recover the working pressure to 3×10^{-3} Torr. The thickness of the AZO thin films thus prepared through ALD and PLD were 230 nm and 1.45 μm, respectively. To examine the effect of surface texturing on light extraction, the AZO layer grown through PLD was etched in 0.5% diluted HCl for 15, 30, 45, and 60 s. Front-grid metal Ti/Al/Ti/Au (25/2000/50/100 nm) was deposited atop the composite TCL to form the *p*-contact pads, and the bottom electrode Ti/Au (5/100 nm) was deposited under the Si substrate with the LED thin epilayer to form the *n*-contact pads. Finally, the LED wafer was cut into 1010 μm × 1010 μm chips. AZO grown through ALD and PLD is referred to as ALD-AZO and PLD-AZO, respectively. The optical properties of the fabricated single and composite AZO thin films deposited on a glass substrate were characterized from their transmittance spectra (n&k analyzer 1280, n&k Technology, Inc), and their microstructure and surface roughness were characterized through high-resolution field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) and atomic force microscopy. To evaluate the effects of the AZO layer on LED performance, six types of LEDs were fabricated using the same epilayers: *p*-side-up thin-film AlGaInP LED with a flat AZO current-spreading layer (hereinafter, F-AZO-LED), *p*-side-up thin-film AlGaInP LED with a composite AZO thin film grown through ALD and PLD (hereinafter, D-AZO-LED), and *p*-side-up thin-film AlGaInP LEDs with composite AZO thin films etched for 15, 30, 45, and 60 s (hereinafter, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s, respectively). The current–voltage (I—V) characteristics of these LEDs were determined at room temperature by using an Agilent 4155B semiconductor parameter analyzer, and the output power of the LEDs was measured using a calibrated integrating sphere. The Al concentration in AZO thin film was measured through X-ray photoelectron spectroscopy by using an Al kα X-ray source at a resolution energy of 0.1 eV.

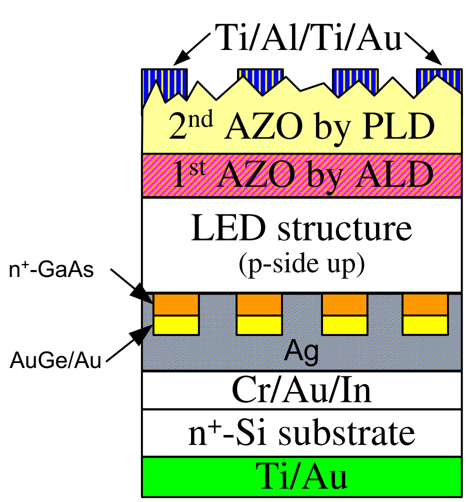

Fig. 1. Schematic of *p*-side up AlGaInP-based LED structure with composite AZO thin film fabricated through the twice wafer-transferring technique.

3. Results and discussion

That the ALD-AZO thin film can form Ohmic contact with a thin carbon-doped GaP cap layer has been demonstrated in our previous studies [1,12]. The electronic characteristics of AZO thin films are dependent on the Al doping concentration [13]. In this study, the Al composition in the ALD-AZO and PLD-AZO layers was 3.87% and 1.92%, respectively; both these layers possess the same material structure and differ only in their Al composition. The ALD can actualize to control the film thickness within a single atom layer scale and good thickness uniformity by binary reaction sequence precursor, which results in low growth rate of ALD. By contrast, PLD has a higher growth rate than does ALD. Therefore, the composite AZO thin film that consists of ALD-AZO and PLD-AZO thin films forms an Ohmic contact layer with the thin carbon-doped GaP cap layer.

Fig. 2 presents the transmittance spectra of the ALD-AZO, PLD-AZO, and composite AZO thin films in the wavelength range 200–1000 nm. The optimum AlGaInP LED performance (transmittance of approximately 85%–98% at 400–800 nm) was observed at an ALD-AZO thin-film thickness of 230 nm. The transmittance of PLD-AZO thin films at 400–800 nm was approximately 80%–91%. The transmittance of PLD-AZO film with optimum thickness of 1.45 μm is almost close to that of ALD-AZO thin film. At 610 nm, the ALD-AZO, PLD-AZO, and composite AZO thin films exhibited transmittance of 91%, 88%, and 85%, respectively.

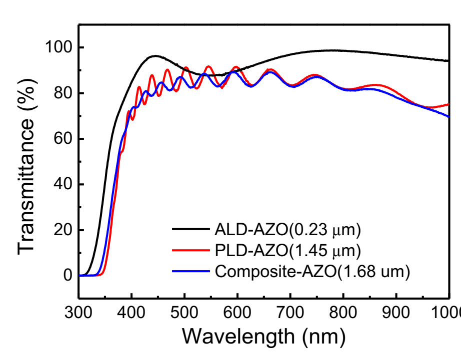

Fig. 2. Transmittance spectra of ALD-AZO, PLD-AZO, and composite AZO thin film.

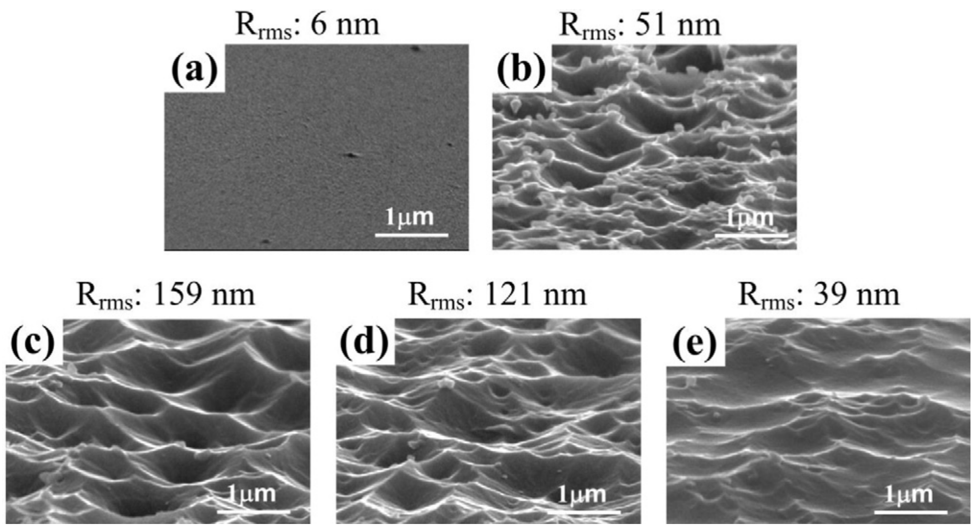

Fig. 3. SEM images of the surface morphologies of composite AZO thin films (a) before etching and after etching for (b) 15 s, (c) 30 s, (d) 45 s, and (e) 60 s.

Fig. 3 shows the top-view SEM images of a composite AZO thin film before and after HCl etching. Before etching, the composite AZO thin film has a flat surface with a root mean square (R_{rms}) roughness of 6 nm, and after etching for 15–60 s, it exhibits a distinctly different surface morphology. The R_{rms} roughness of composite AZO thin films etched for 15, 30, 45, and 60 s was 51, 159, 121, and 39 nm, respectively. The surface roughness of composite AZO thin films increased with etching time. Etching created a crater-like texture on the composite AZO. In addition, etching for 15, 30, 45, and 60 s decreased the thickness of the PLD-AZO layer to 1.05, 0.73, 0.42, and 0.24 μm, respectively; because of this reduction in thickness of PLD-AZO layer, the R_{rms} roughness of the thin film etched for 45 and 60 s was lower than that of the film etched for 30 s. The composited AZO thin films with a dense and compact surface texture facilitate effective light-extraction in LEDs. These results indicate that surface texturing composite AZO thin films reduce the total internal reflection of light between the AZO and epoxy layers.

Fig. 4 illustrates the forward I—V characteristics of F-AZO-LED, D-AZO-LED, and T-AZO-LED as a function of etching time. All LED structures exhibited normal *p*–*n* diode behaviors at a forward dc bias (Fig. 4(a)). At a current injection of 350 mA, the forward voltages of F-AZO-LED, D-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s were 2.34, 2.32, 2.31, 2.31, 2.31, and 2.39 V, respectively. Fig. 4(b) presents the output power of the LEDs (with epoxy package) as a function of the injection current. All LEDs exhibited stable output power, which increased with the injection current. The output power of D-AZO-LED was lower than that of F-AZO-LED by 4% at injection currents of 700 and 1000 mA; this is because the transmittance of composite AZO thin film was lower than that of single AZO thin film. Surface texturing by etching for up to 45 s improved the output power of the LEDs. This textured surface mitigated the internal reflection at the semiconductor–epoxy interface, thus facilitating the escape of more photons from the LEDs. In addition, using textured composite AZO thin films in AlGaInP-based LEDs not only effectively reduced the accumulation of Joule heat, but also increased light extraction. Therefore, at all etching times, the output power of T-AZO-LED was higher than that of F-AZO-LED. The output power of F-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s was 279, 309, 319, 339, and 290 mW at an inject current of 700 mA and 370, 412, 432, 460, and 382 mW at an injection current of 1000 mA, respectively. Compared with the output power of F-AZO-LED, that of T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s increased by 11%, 14%, 22%, and 4% at 700 mA and 11%, 17%, 24%, and 3% at 1000 mA, respectively. This result clarifies that the surface characteristics of T-AZO-LED-45 s has the highest light-extraction efficiency; this

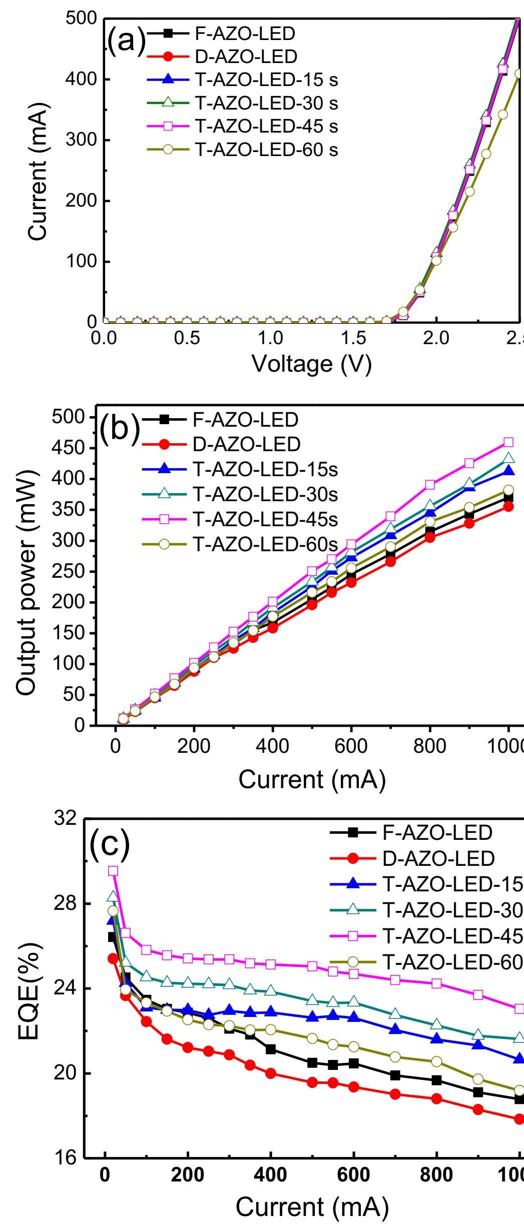

Fig. 4. (a) Forward I—V, (b) output power, and (c) EQE characteristics for F-AZO-LED, D-AZO-LED, and T-AZO-LED etched for 15, 30, 45, and 60 s.

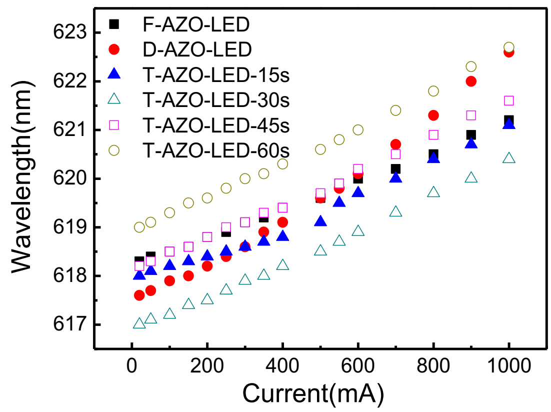

Fig. 5. Emission wavelengths of F-AZO-LED, D-AZO-LED, and T-AZO-LED fabricated under different etching time and injection current.

is because texturing reduced the thickness and produced optimum surface texture structure for the composite AZO thin film, as can be seen in Fig. 3(d).

We then evaluated the light-extraction efficiency (η_{extrac}) of the fabricated LEDs. The EQE of F-AZO-LED, D-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s was 26%, 25%, 27%, 28%, 30%, and 28% at an injection current of 20 mA, respectively (Fig. 4(c)). The droop efficiency (i.e., $[(EQE_{max} - EQE_{min})$ /-$EQE_{max}] \times 100\%$) of F-AZO-LED, D-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s was 29%, 30%, 24%, 24%, 22%, and 31%, respectively. The droop efficiency of the LED device improved markedly after etching the composite AZO thin film for 45 s.

Internal quantum efficiency (IQE; $EQE = IQE \times \eta_{extrac}$) is typically estimated through temperature-dependent photoluminescence measurements; the IQE of the *p*-side-up AlGaInP LED was 98% (data not shown). The η_{extrac} of F-AZO-LED, D-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s was 27%, 26%, 28%, 29%, 31%, and 29%, respectively. Compared with the light-extraction efficiency of F-AZO-LED, that of T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s was higher by 4%, 7%, 15%, and 7%, suggesting that textured composite AZO thin film can more effectively extract light from the GaP layer to the epoxy layer than can a single AZO thin film; this is due to the reduction in total internal reflection.

Fig. 5 shows the emission wavelengths of F-AZO-LED, D-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s; the electroluminescence peaks of these devices were at 618, 618, 618, 617, 618, and 619 nm at an injection current of 20 mA, respectively, and their wavelengths redshifted by approximately 3, 5, 3, 3, 3, and 3 nm at an injection current of 1000 mA, respectively. The wavelength redshift and the corresponding junction temperature of D-AZO-LED were higher than those of F-AZO-LED because D-AZO-LED provided a much longer optical path for light trapping, meaning that a part of the light is reflected into or re-absorbed by the device. Moreover, the low transmittance of composite AZO thin films in the D-AZO-LED could be a result of self-heating at the junction, which is due to the thermal-coefficient mismatch of the layers within the cavity. Clearly, LEDs with flat AZO layer and textured composite AZO thin film exhibit relatively low junction temperature, resulting in low wavelength variation.

To understand the optical properties and light-intensity distribution on the LED chip surface, the near-field optical images of the fabricated LED devices were captured and are presented in Fig. 6; this figure depicts the distribution of the output light intensity and the uniformity of the LED surfaces by using color bars. All of the LED devices were under injection current of 40 mA. The total intensity of F-AZO-LED, D-AZO-LED, T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s was 14.9, 13.2, 15.3, 15.4, 15.6 and 15.0, respectively, which is consistent with the optoelectronic performance trends of the LEDs (Fig. 4(b)). The light intensity uniformity of D-AZO-LED was lower than that of F-AZO-LED due to low transmittance of composite AZO thin films. After wet etching with different etching time, the light intensity uniformity of T-AZO-LED-15 s, T-AZO-LED-30 s, T-AZO-LED-45 s, and T-AZO-LED-60 s were changed with different etching time. The light intensity uniformity of T-AZO-LED improved markedly after etching the composite AZO thin film for 45 s. The light intensity uniformity of T-AZO-LED-60 s was lower than that of T-AZO-LED-45 s due to thinner composite AZO thin films and lower surface roughness. The tendency is consistent with the optoelectronic performance trends of the LEDs (Fig. 4(b)). Surface texturing improved the light-output intensity of the LEDs with composite AZO thin films, and the light-output intensity of all T-AZO-LEDs was higher than that of F-AZO-LED.

4. Conclusion

This study investigated the performance of *p*-side-up thin-film AlGaInP LEDs with flat AZO and textured composite AZO thin films. Compared with F-AZO-LED, T-AZO-LEDs etched for 15–60 s exhibited

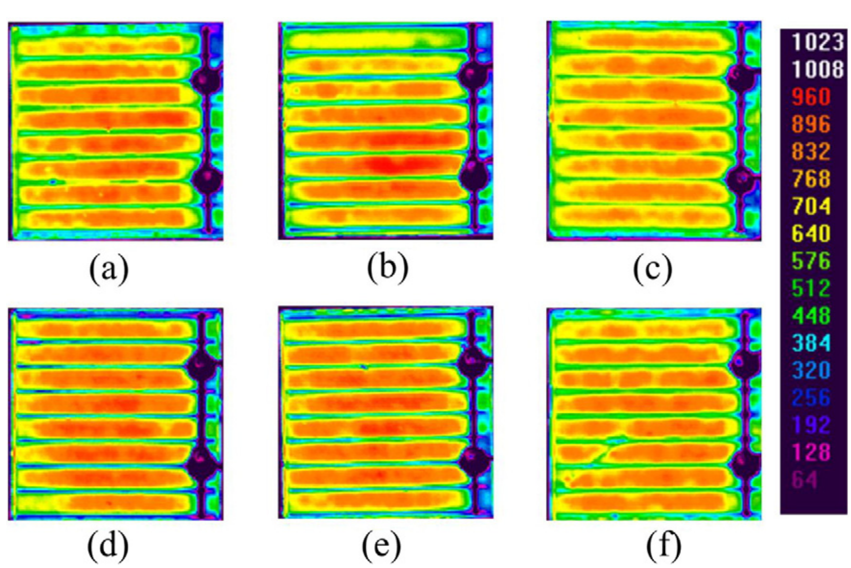

Fig. 6. Near-field optical images of (a) F-AZO-LED, (b) D-AZO-LED, (c) T-AZO-LED-15 s, (d) T-AZO-LED-30 s, (e) T-AZO-LED-45 s, and (f) T-AZO-LED-60 s.

not only improved light-extraction efficiency but also improved light-intensity distribution on the LED chip surface. Surface texturing of composite AZO mitigated total internal reflection within the device, which facilitated the extraction of more light into the epoxy from the GaP layer compared with the flat AZO thin film. Therefore, textured composite AZO thin films prepared through ALD and PLD have potential applications in AlGaInP LEDs and can reduce associated manufacturing costs.

Acknowledgment

This study was financially supported by the Ministry of Science and Technology under contracts MOST 102-2221-E-005-071-MY3 and 104-2221-E-005-031-MY3, Hsinchu Science Park under contract 101A08, and Southern Taiwan Science Park under contracts 102CE06 and 105CE01.

References

[1] M.C. Tseng, C.L. Chen, N.K. Lai, S.I. Chen, T.C. Hsu, Y.R. Peng, R.H. Horng, P-side-up thin-film AlGaInP-based light emitting diodes with direct ohmic contact of an ITO layer with a GaP window layer, Opt. Express 22 (2014) A1862–A1867.

[2] S.C. Hsu, D.S. Wuu, C.Y. Lee, J.Y. Su, Horng, high-efficiency 1 mm^2 AlGaInP LEDs sandwiched by ITO omni-directional reflector and current-spreading layer, IEEE Photon. Technol. Lett. 19 (2007) 492–494.

[3] R.H. Horng, B.R. Wu, C.F. Weng, P. Ravadgar, T.M. Wu, S.P. Wang, J.H. He, T.H. Yang, Y.M. Chen, T.C. Hsu, A.S. Liu, D.S. Wuu, P-side up AlGaInP-based light emitting diodes with dot-patterned GaAs contact layers, Opt. Express 21 (2013) 19668–19674.

[4] K. Bergenek, C. Wiesmann, R. Wirth, L. O'Faolain, N. Linder, K. Streubel, T.F. Krauss, Enhanced light extraction efficiency from AlGaInP thin-film light-emitting diodes with photonic crystals, Appl. Phys. Lett. 93 (2008) (041105–1-3).

[5] P.W. Huang, Y.C.S. Wu, Improved performance of AlGaInP LEDs by a periodic GaP-dish mirror array, IEEE Photon. Technol. Lett. 21 (2009) 1441–1443.

[6] J.J. Chen, Y.K. Su, C.L. Lin, C.C. Kao, Light output improvement of AlGaInP-based LEDs with nano-mesh ZnO layers by nanosphere lithography, IEEE Photon. Technol. Lett. 22 (2010) 383–385.

[7] Y.J. Lee, H.C. Tseng, H.C. Kuo, S.C. Wang, C.W. Chang, T.C. Hsu, Y.L. Yang, M.H. Hsieh, M.J. Jou, B.J. Lee, Improvement in light-output efficiency of AlGaInP LEDs fabricated on stripe patterned epitaxy, IEEE Photon. Technol. Lett. 17 (2005) 2532–2534.

[8] Y.M. Song, E.S. Choi, J.S. Yu, Y.T. Lee, Light-extraction enhancement of red AlGaInP light-emitting diodes with antireflective subwavelength structures, Opt. Express 17 (2009) 20991–20997.

[9] C.C. Liu, S.X. Lin, C.C. Wang, K.K. Chong, C.I. Hung, M.P. Houng, Light output enhancement of AlGaInP light emitting diodes with nanopores of anodic alumina, Jpn. J. Appl. Phys. 48 (2009) (082102–1-3).

[10] Y.J. Lee, H.C. Kuo, S.C. Wang, T.C. Hsu, M.H. Hsieh, M.J. Jou, B.J. Lee, Increasing the extraction efficiency of AlGaInP LEDs via n-side surface roughening, IEEE Photon. Technol. Lett. 17 (2005) 2289–2291.

[11] Z. Zuo, R. Wang, D. Liu, Q. Yu, Z. Feng, X. Xu, Ultra bright AlGaInP light emitting diodes with pyramidally patterned GaP spreading layer, Appl. Phys. Lett. 99 (2011) (121104–1-3).

[12] M.C. Tseng, D.S. Wuu, C.L. Chen, H.Y. Lee, Y.C. Lin, R.H. Horng, Performance comparison of p-side-up thin-film AlGaInP light emitting diodes with aluminum doped zinc oxide and indium tin oxide transparent conductive layers, Opt. Mater. Express 6 (2016) 1349–1357.

[13] S.P. Liu, D.S. Wuu, S.L. Ou, Y.C. Fu, P.R. Lin, M.T. Hung, R.H. Horng, Highly ultraviolet-transparent ZnO:Al conducting layers by pulsed laser deposition, J. Electrochem. Soc. 158 (2011) K127–K130.