Thin Solid Films 521 (2012) 54–59

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Thermal stability of Ag_XCu_{1-X} alloys and Pt capping layers for GaN vertical light emitting diodes

S.H. Kim [a], T.H. Kim [b], J.W. Bae [b], G.Y. Yeom [a,b,*]

[a] Sungkyun Advanced Institute of Nanotechnology (SAINT), Suwon, 440-746, Republic of Korea
[b] Department of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

ARTICLE INFO

Available online 26 March 2012

Keywords:
Reflectors
Ag–Cu
Vertical light emitting diode
GaN

ABSTRACT

In this paper, alloy metals of Ag–Cu (4.2–5.4 at.%) are investigated to achieve both ohmic contact and high reflectivity for vertical light emitting diode (VLED) applications. As the capping metal, platinum (Pt) is used to reduce the agglomeration of the metal alloy structures. At a high temperature of over 500 °C, pure Ag and Ag–Cu alloy metals without Pt show serious agglomeration, resulting in poor reflectance. It is found that the introduction of Cu to Ag and Pt capping layers could inhibit the agglomeration of the Ag-based alloy metals and hence sustain high reflectivity during the annealing process while making ohmic contact to p-GaN as low as 5×10^{-3} Ω-cm^2. The Ag–Cu 4.2 at.% alloy with a Pt capping layer annealed at 450 °C shows the highest level of reflectivity; 88% at the wavelength of 460 nm. The optical output power of the corresponding VLED is 14% higher than that of the VLED using pure Ag with a Pt layer.

1. Introduction

Recently, the GaN-based light emitting diode (LED) has attracted great attention as an environment-friendly next generation lighting device. However, conventional GaN-based LEDs have limits to their high power applications due to poor thermal and electrical conductivity of sapphire substrate and lateral arrangements of electrodes. GaN-based VLEDs are thus considered to be the strongest candidates for high power applications. In GaN-based VLEDs, the cathode and anode are vertically arranged to avoid current crowding so that a high current injection can be applied to the device without serious current crowding. The VLED is also formed on metal or thermally and electrically conductive substrate as opposed to sapphire, which shows very poor heat dissipation in high power situations. The sapphire substrate is removed from the LED wafer after bonding to the conductive support wafer by means of a laser lift-off (LLO) process. This LLO process has been the most widely used to remove the sapphire substrate. Additionally, VLEDs exhibit n-GaN side-up structural characteristics with highly conductive substrates, a structure that differs from the p-GaN side-up structure of conventional LEDs [1–3].

A high quality metal reflector is required for high power VLEDs. This reflector must exhibit the characteristics of low contact resistance to p-GaN, high reflectance, and good thermal stability. Ag (silver) has been a widely accepted material for this metal reflector of GaN-based VLEDs due to its high reflectance in the visible wavelength range and reasonable ohmic characteristics. However, the surface agglomeration caused by the annealing process reduces reflectance and weakens mechanical adhesion. In order to solve these issues, diverse approaches have been suggested. Recently, multi-layered Ag reflectors have been widely investigated [4–7]. However, other problems such as Ag migration into p-GaN during the annealing process, resulting in the aggravation of electrical property, are also exhibited by multi-layered Ag reflectors. In addition to these reflectors, several Ag alloys have been experimented with in attempts to overcome the problems.

Kim et al. investigate the electrical and optical properties of an Ag–Al alloy (3 at.% Al) contacts to p-GaN in their work [8]. Al (Aluminum) is thermally stable and exhibits good reflectance in the range of visible wavelengths [9]. However, the Ag–Al alloy displays a high potential barrier for ohmic contact to p-type GaN due to its low work function of 4.26 eV. An Ag–Cu alloy has also been investigated as an candidate for metal reflector [10,11]. Kim et al. [10] report that the Ag–Cu reflector shows a lower contact resistance and higher reflectance in the range of visible wavelength, compared to conventional Ag reflectors. Flip-chip LEDs fabricated with the Ag–Cu reflectors have been found to exhibit a 10% improvement in their light output power at 20 mA, when compared with those using the pure Ag reflector. However, more investigation is needed to understand the effect of Cu in the Ag–Cu alloy. This would facilitate optimization of ohmic contact to p-type GaN as well as a higher optical reflectance. Additionally, it is recommended to study the effectiveness of those alloy materials with a vertical LED structure at high forward currents over 350 mA. Lateral or flip-chip LED structures with low injection currents are less attractive prospects for study, because their properties can be degraded at high junction temperatures.

* Corresponding author at: Department of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon, 440-746, Republic of Korea.
E-mail address: gyyeom@skku.edu (G.Y. Yeom).

0040-6090/$ – see front matter
doi:10.1016/j.tsf.2012.03.072

Therefore, this study investigates the thermal stability of Ag_XCu_{1-X} reflectors for different atomic percentages of Cu in Ag–Cu alloys as a function of annealing temperatures ranging up to 550 °C. The weight percentages of Cu in Ag–Cu alloys are seen to be in the range of 0–10%. In addition, the effect of the Pt capping layer is investigated with a view to enhancing thermal stability [12,13]. Finally, this multilayer contact system is applied to a high power (HP) VLED and its electrical and optical characteristics are investigated. This is because the HP-VLED requires a lower p-contact resistivity to reduce power consumption and a higher reflectance of the contact system to increase the external quantum efficiency.

2. Experiment

In this experiment, metal organic chemical vapor deposition is used to grow InGaN/GaN multi quantum well (MWQ) LED structures. These structures have a peak wavelength of ~460 nm, on a c-plane sapphire substrate. The LED is structured with a 150 nm-thick p-type GaN:Mg layer, a 20 nm-thick AlGaN electron blocking layer, a 100 nm-thick active layer, a 80 nm-thick InGaN current spreading layer, a 3.5 μm-thick n-type GaN:Si layer, and a 2.0 μm-thick undoped-GaN layer on the sapphire substrate. First, the backside of the sapphire substrate is polished in preparation for the LLO process and the LED wafer is cleaned with a mixture of H_2SO_4 and H_2O_2 for 15 min. Next, it is ultrasonically degreased with acetone, isopropyl alcohol, and deionized water for 5 min. The metal alloys, consisting of 100–150 nm thick pure Ag, Ag–Cu 4.2 at.%, and Ag–Cu 5.4 at.% as well as 50–100 nm thick Pt are deposited on the sapphire substrate by electron beam evaporation. These metal alloys are then annealed in an O_2 atmosphere for 1 min at various temperatures ranging from 400 to 550 °C in a rapid thermal annealing system. Metal substrate was deposited on reflector layer. Subsequently, LLO process was performed using an ArF excimer laser operated. Through the transparent sapphire surface, the laser beam caused separation of the sapphire substrate from the LED structure. After this processing, undoped GaN surface was located on the top. It was etched off to expose the n-GaN layer by plasma etching. A KOH solution was used to roughen the n-GaN surface, and n-pad(Ti/Au) was deposited on the roughen n-GaN surface. Finally, each chip on the device is isolated by using plasma etch process (BCl_3/Cl_2 gas). Fig. 1 shows the process step for the vertical LED chips fabricated in this study. A circular transmission line model (CTLM) is used to calculate specific contact resistivity. The change in the reflectivity of each alloy is measured using a UV/Vis spectrophotometer (Shimadzu UV-3101PC). In order to find out the origin of the change as a function of the annealing temperature, the surface morphology and cross section images are observed using a scanning electron microscope (SEM 15.0 kV HITACHI S-4700) before and after the annealing. Real HP-VLED chips, having the 50 nm-thick Pt layer as the capping material and a size of 1 mm × 1 mm, are fabricated and examined in order to compare the light reflecting performance of each alloy reflector. The light output power–Current–voltage (L–I–V) characteristics of the HP-VLEDs with Ag-based reflectors are evaluated with a probe station (MICROMANIPULATOR QMP01), outfitted with a light integrating system. The I–V characteristics of chips are measured by a semiconductor parameter analyzer (HP 4145A) from 1 to 100 mA each few nA at −5 V, and until 1 A are measured other analyzer (Cascade Microtech Summit12201B).

3. Results and discussion

The e-beam source materials used for the reflector are composed of pure Ag, Ag–Cu 5%, and Ag–Cu 10%. Upon measurement of the Ag–Cu alloys' composition after the deposition, the Cu percentage in the deposited material is found to decrease to 4.2 at.% and 5.4 at.%, respectively. This indicates that the decreased Cu incorporation in the deposited Ag–Cu is due to the lower vapor pressure of Cu compared to Ag at the same evaporation temperature. However, the ratio of Cu between the Ag–Cu alloys in the source material remains similar after the deposition.

It is accepted that when Cu is incorporated in Ag, the work function of Ag–Cu is increased from 4.2 eV to 4.7 eV, due to the increase of Cu in Ag–Cu [14]. However, the work function of p-type GaN is about 6.7 eV. Therefore, the contact between p-type GaN and the Ag–Cu alloy should be Schottky contact. However, previous studies have shown that an ohmic contact is possible between p-type GaN

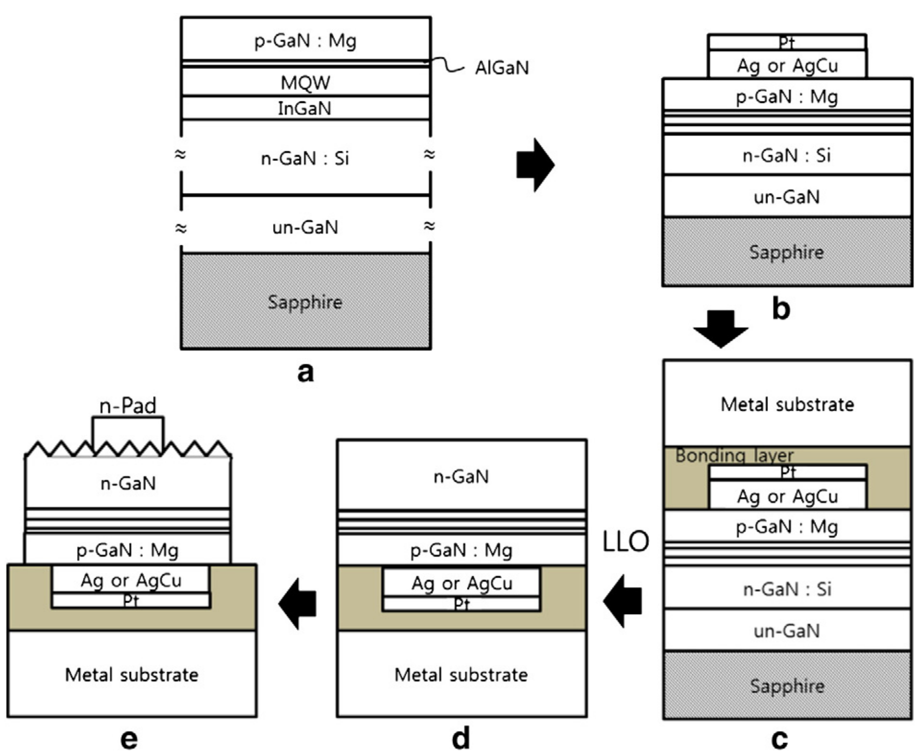

Fig. 1. (a) LED wafer structure, (b) reflector layer was deposited, (c) bonding to metal substrate, (d) LLO process, (E) roughening and n-pad was deposited.

and Ag–Cu. This is achieved by annealing in oxygen containing gas environment or by the formation of Ag–O–Ga at the interface [13–16]. Fig. 2 shows the I–V characteristics of Ag–Cu 4.2 at.% on p-GaN before and after annealing at various temperatures ranging from 450 to 550 °C. The I–V characteristics of Ag–Cu 5.4 at.% on p-GaN are also measured and exhibit similar I–V characteristics to those of Ag–Cu 4.2 at.%. This is despite the fact that the characteristics of Ag–Cu 5.4 at.% show a slightly higher resistance compared to those of Ag–Cu 4.2 at.% (not shown). For the measurement of the I–V characteristics and contact resistivity, CTLM patterns with distances of 5, 10, 15, 20, 30, and 50 μm on the p-GaN wafer are formed. The electrical characteristics are measured between −1.0 V and 1.0 V. As shown in the figure, Schottky contact characteristics are observed prior to annealing due to the differences in the work function between Ag–Cu alloy and the p-GaN. However, after annealing at a temperature higher than 450 °C, ohmic characteristics are observed. It is worth noting that the ohmic resistance is decreased by increasing the annealing temperature to 500 °C, yet raising the annealing temperature higher than 550 °C increases the resistance, similar to the results obtained by other researchers [15–19]. The p-contact resistivity measured by the CTLM pattern after the annealing at 450, 500, and 550 °C for Ag–Cu 4.2 at.% alloy is 3.8×10^{-3} Ω-cm^2, 3.4×10^{-3} Ω-cm^2 , and 4.5×10^{-3} Ω-cm^2, respectively.

Fig. 3(a) shows the reflectance of 150 nm thick Ag and Ag–Cu alloys deposited on p-GaN, measured using a UV–vis spectrometer after annealing at various temperatures. As shown in the figure, annealing up to 400 °C slightly improves the reflectance. The highest reflectance is obtained for pure Ag, while an increased Cu percentage decreases the reflectance. However, as the annealing temperature is increased further from 450 to 550 °C, the reflectance decreases. Pure Ag exhibits a more significant decrease in reflectance compared to the Ag–Cu 4.2 at.% alloy. Therefore, the Ag–Cu 4.2 at.% exhibits the highest reflectance among the Ag and Ag–Cu alloy thin films deposited in the experiment. This decreased reflectance with annealing temperatures higher than 450 °C is related to the agglomeration of the thin films at high annealing temperatures. In addition, the more significant decrease of reflectance for pure Ag compared to the Ag–Cu 4.2 at.% alloy indicates suppression of agglomeration by the addition of Cu in Ag. This is despite that fact that an excess of Cu in the Ag decreases the reflectance due to the severe absorption of the light in the film even though the agglomeration is improved.

The agglomeration can be further suppressed by depositing a capping layer which suppresses the agglomeration of Ag–Cu alloys and helps to obtain higher external quantum efficiency. In this experiment, a Pt thin film is used as the capping layer and Fig. 3(b) shows the reflectance of the pure Ag and Ag–Cu alloys measured as a function of the annealing temperature after the deposition of the 50 nm thick Pt capping layer. As shown, with an increase of the annealing temperature that remains below 400 °C, the pure Ag with the Pt capping layer shows the highest reflectance in addition to a slight increase of reflectance with the increase of annealing temperature. This is similar to the cases without the Pt capping layer. As the annealing temperature is increased further from 400 to 550 °C, the reflectance is significantly improved for all of the Ag and Ag–Cu alloy thin films with the Pt capping layer; showing the reflectance higher than 80% for all of the films annealed at 550 °C. In addition, the pure Ag with the Pt capping layer exhibits the lowest reflectance, indicating significant suppression of agglomeration for Ag–Cu alloys with the Pt layer by the combined effects of the Pt capping layer and Cu in Ag–Cu alloys.

Fig. 4 shows the SEM images of Ag and Ag–Cu alloys with and without the Pt capping layer annealed at various temperatures. As shown in the figure, pure Ag without the Pt layer displays a change in surface roughness from the annealing temperature of 450 °C by showing small crater-shaped features on the surface. At annealing temperatures higher than 500 °C, a significant increase of surface roughness is observed by showing big crater-shaped features (not shown for SEM images higher than 500 °C). However, for the Ag thin film with the Pt layer, a significant decrease of crater-shaped features is observed even at an annealing temperature of 500 °C, indicating a decrease of agglomeration by the Pt layer. In addition, a decrease

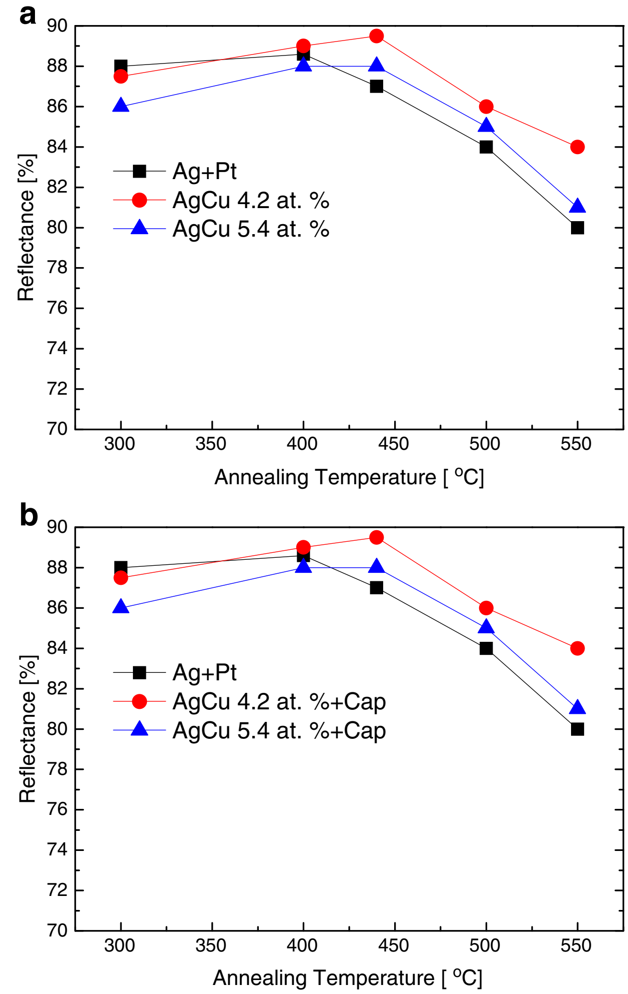

Fig. 3. Reflectance of pure Ag, Ag–Cu 4.2 at.%, and Ag–Cu 5.4 at.% contact layers without (a) and with (b) the Pt capping layer as a function of annealing temperature.

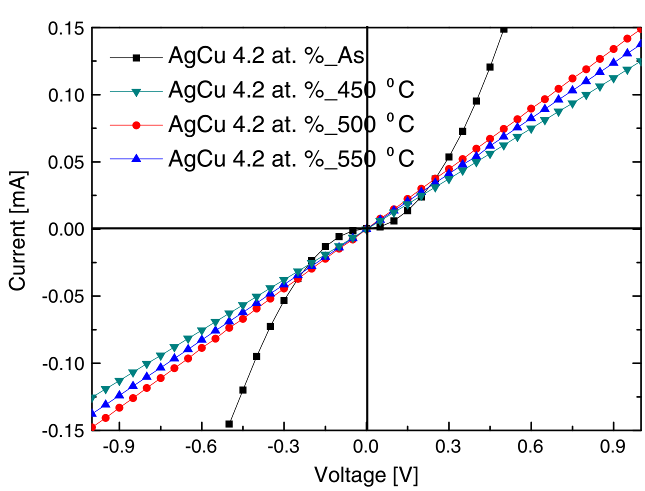

Fig. 2. I–V characteristics of Ag–Cu 4.2 at.% contacts to p-type GaN as a function of annealing temperature.

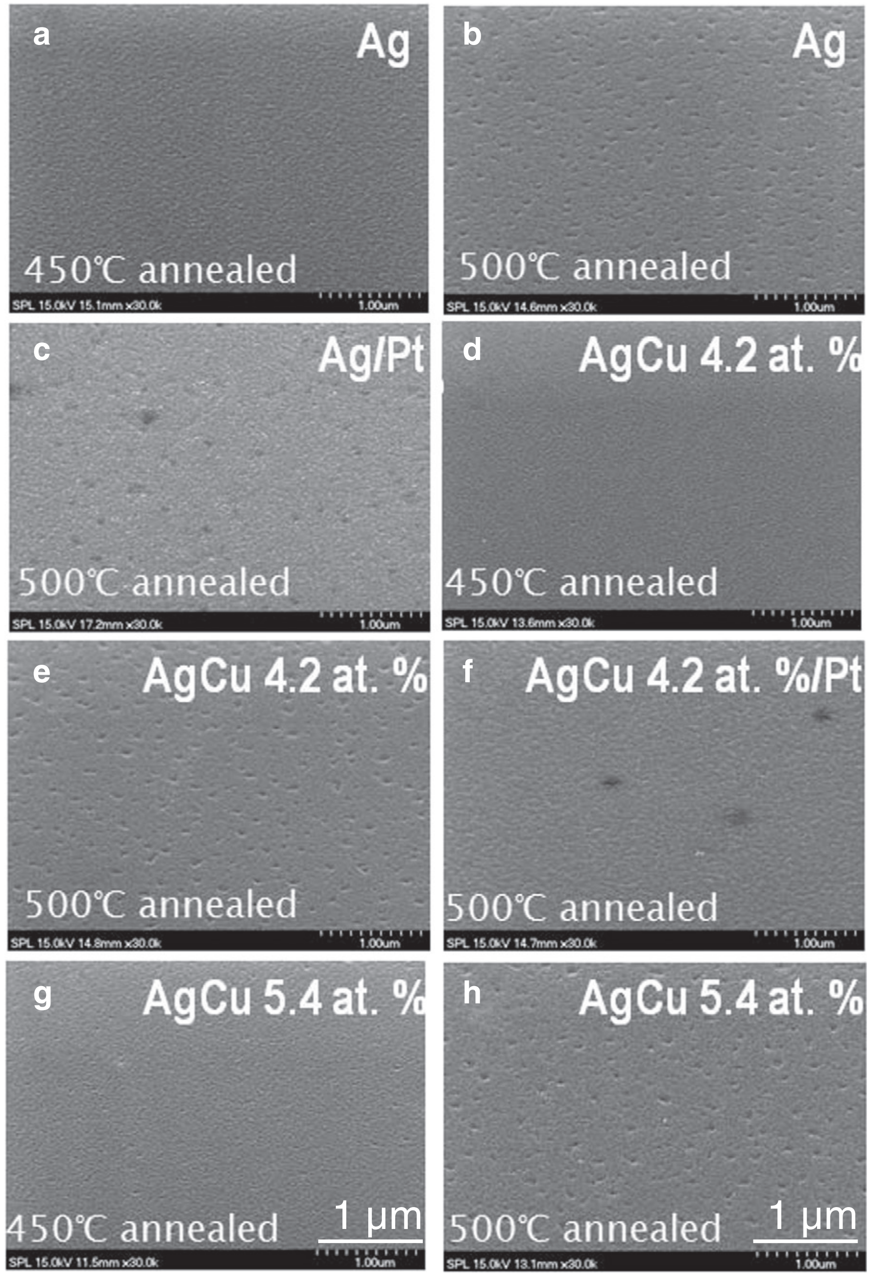

Fig. 4. SEM images of the metal reflector (Ag, Ag–Cu 4.2 at.%, and Ag–Cu 5.4 at.%) surface with and without the Pt capping layer after annealing at 450 and 500 °C for 1 min. Pure Ag: (a)–(c), Ag–Cu 4.2 at.%: (d)–(f), and Ag–Cu 5.4 at.%: (g)–(h).

of surface roughness with the addition of Cu (no significant change of surface roughness between 4.2 at.% Cu and 5.4 at.% Cu is observed) and with the Pt capping layer can be observed at the same annealing temperature, indicating the further suppression of agglomeration.

The cross-sectional SEM images of the annealed pure Ag and Ag–Cu 4.2 at.% (150 nm) without the Pt layer and Ag–Cu 4.2 at.% (100 nm) with the Pt layer (100 nm) are observed after annealing at 450 °C. The results are shown in Fig. 5. In the case of pure Ag, empty spaces are observed at some of the interfaces between the Ag thin film and the p-GaN, possibly due to the significant agglomeration of Ag thin film. However, for the Ag–Cu 4.2 at.% thin film, no significant empty spaces are observed, indicating a decrease of agglomeration. The Ag–Cu 4.2 at.% with the Pt layer displays the most uniformly thin film, showing almost no agglomeration of the Ag–Cu alloy. Therefore, the Ag–Cu 4.2 at.% with the Pt capping layer appears to be the best choice as a metal reflector in the current experimental conditions, judging by the factors of ohmic resistance and reflectance.

The I–V characteristics of the fabricated GaN HP-VLED chip are measured. Fig. 6 displays the results of I–V characteristics measured at five different locations of the two-inch diameter wafer. To facilitate measurement, the GaN LED structure grown on a two-inch diameter sapphire wafer is lifted-off using a typical LLO process. This occurs after the deposition of a metal reflector composed of Ag–Cu 4.2 at.% (150 nm) and Pt(50 nm) on p-GaN, annealing at 450 °C, and attachment of a supporting Si wafer. The size of the isolated GaN HP-VLED chip for the measurement of I–V characteristics is 1 mm × 1 mm and, as shown in the inserted picture, uniform emission in the area of the 1 mm × 1 mm GaN HP-VLED chip can be observed. As can also be seen in Fig. 6, the voltage is nearly uniform for the I–V characteristics of the GaN VLED chips measured at various locations of the two-inch diameter wafer, displaying a range of 3.3–3.45 V at 350 mA of forward current. In addition, at −5 V of reverse bias voltage, the leakage current is very small, at less than −2.0 μA.

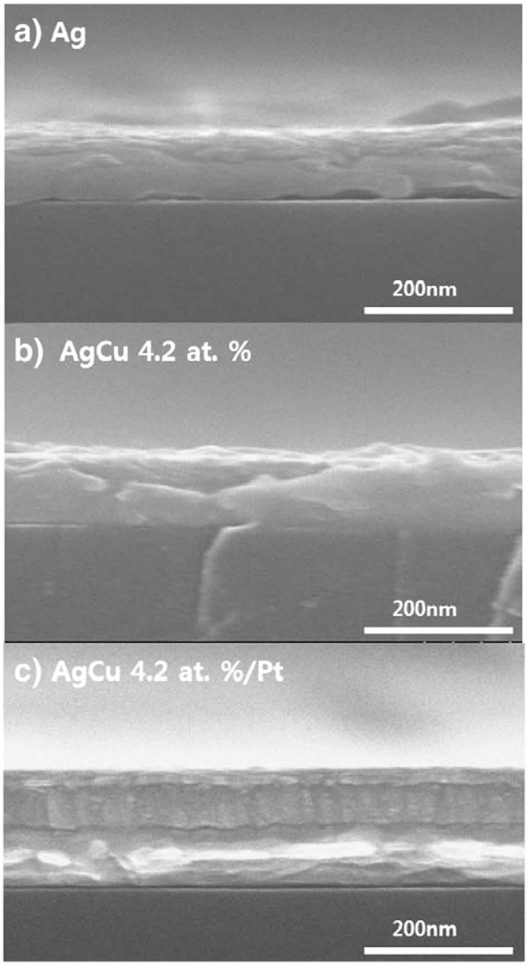

Fig. 5. Cross-sectional SEM images of pure Ag and Ag–Cu 4.2 at.% without the Pt capping layer and Ag–Cu 4.2 at.% reflector with the Pt capping layer after annealing at 450 °C for 1 min.

The emission characteristics (total radial flux: TRF) of the GaN HF-VLED chip fabricated with the metal reflectors of pure Ag, Ag–Cu 4.2 at.%, and Ag–Cu 5.4 at.% are compared and the TRF is measured using a photometer at 350 mA of forward current, as shown in Fig. 7. Fig. 8 depicts optical output efficiency as a function of forward

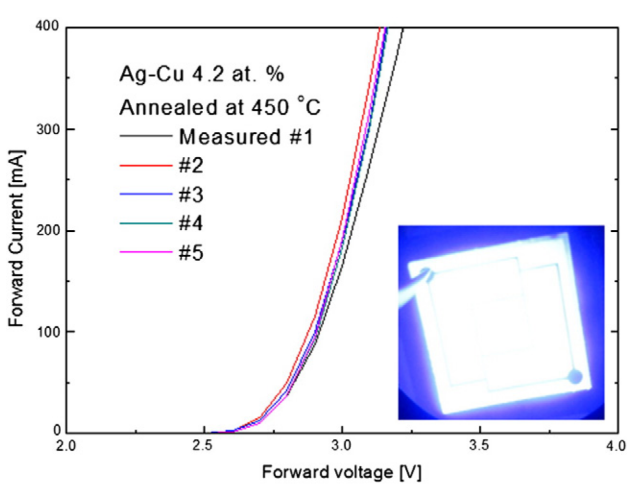

Fig. 6. I–V characteristics of vertical light emitting diodes with Ag–Cu 4.2 at.% reflectors and Pt capping layers, which are annealed at 450 °C for 1 min. Five different measurements are made with different chips on the same two inch diameter wafer. Inset shows the optical lighting image obtained from 1 mm × 1 mm GaN VLED.

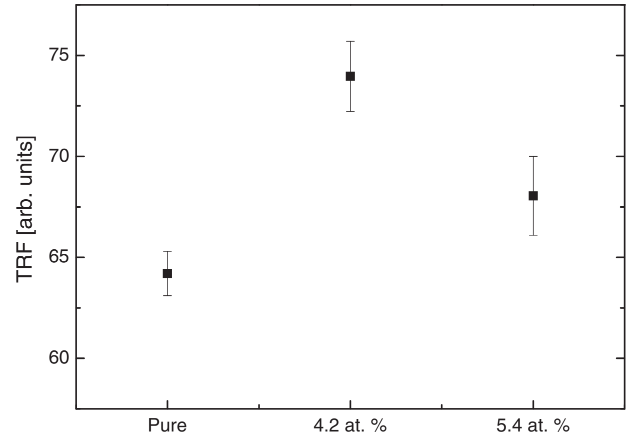

Fig. 7. Total radiant flux obtained from the GaN VLEDs fabricated with reflector layers of pure Ag, Ag–Cu 4.2 at.%, and Ag–Cu 5.4 at.% for the forward current fixed at 350 mA.

current from 50 mA to 500 mA. The metal reflectors are annealed at 450 °C after the deposition of the Pt capping layer. As shown in Fig. 7, the GaN HF-VLED chip fabricated with Ag–Cu 4.2 at.% with the Pt capping layer as the metal reflector shows an improvement of approximately 14% in the TRF, compared to that fabricated with pure Ag with the Pt capping layer.

4. Conclusion

This paper investigates the characteristics of Ag–Cu alloys as the metal reflector to p-GaN and the effect of a Pt layer as the capping layer on the metal reflector for GaN HP-VLED as a function of annealing temperature. It is shown that Ag–Cu alloy reflector is more thermally stable than pure Ag. This is because it exhibits less agglomeration after annealing at temperatures higher than 400 °C. However, due to the decrease of reflectance with the increase of Cu in Ag, the Cu in Ag must be limited to 4.2 at.%, considering both reflectance and ohmic contact resistance. Introducing a Pt capping layer to Ag and Ag–Cu alloys further improves the thermal stability and inhibits agglomeration. As a result, a metal reflector composed of Ag–Cu 4.2 at.% and a Pt capping layer annealed at 450 °C shows the highest reflectance of 89.5% at 460 nm. Additionally, the 1 mm × 1 mm size 1-W GaN HP-VLED chip fabricated with a metal reflector shows approximately a 14% improvement of extraction efficiency, compared to a chip fabricated with pure Ag and Pt capping layer annealed at 450 °C.

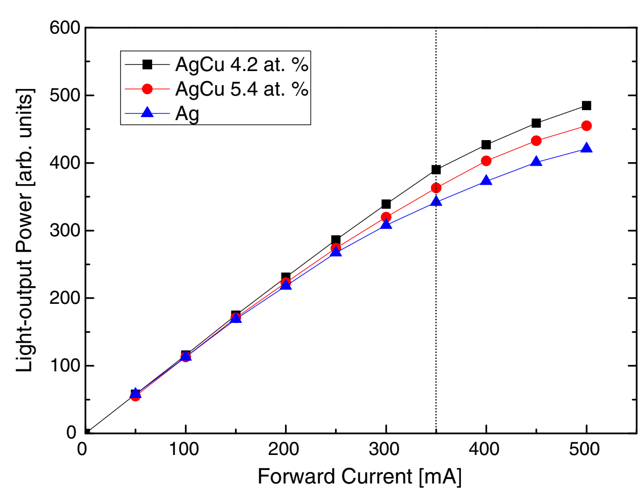

Fig. 8. Light-output power measured from the GaN VLEDs fabricated with reflector layers of pure Ag, Ag–Cu 4.2 at.%, and Ag–Cu 5.4 at.% for the forward current.

Acknowledgments

This work is partially supported by the Industrial Strategic Technology Development Program funded by the Gyeonggi Province (No. A080923) and the World Class University Program of National Research Foundation of Korea (Grant No. R32-2008-000-10124-0).

References

[1] S.J. Wang, K.M. Uang, S.L. Chen, Y.C. Yang, S.C. Chang, T.M. Chen, C.H. Chen, B.W. Liou, Appl. Phys. Lett. 87 (2005) 011111.
[2] W.S. Wong, T. Sands, N.W. Cheung, M. Kneissl, D.P. Bour, P. Mei, L.T. Romano, N.M. Johnson, Appl. Phys. Lett. 77 (2000) 2822.
[3] W.Y. Lin, D.S. Wuu, K.F. Pan, S.H. Huang, C.E. Lee, W.K. Wang, S.C. Hsu, Y.Y. Su, S.Y. Huang, R.H. Horng, IEEE Photon. Technol. Lett. 17 (2005) 1809.
[4] C.H. Chou, C.L. Lin, Y.C. Chuang, H.Y. Bor, C.Y. Liu, Appl. Phys. Lett. 90 (2007) 022103.
[5] D.L. Hibbard, S.P. Jung, C. Wang, D. Ullery, Y.S. Zhao, H.P. Lee, Appl. Phys. Lett. 83 (2003) 311.
[6] J.O. Song, W.K. Hong, Y. Park, J.S. Kwak, T.Y. Seong, Appl. Phys. Lett. 86 (2005) 133503.
[7] L.B. Chang, C.C. Shiue, M.J. Jeng, Appl. Surf. Sci. 255 (2009) 6155.
[8] J.Y. Kim, S.I. Na, G.Y. Ha, M. K. K, I.K. Park, J.H. Lim, S.J. Park, M.H. Kim, D.Y. Choi, K.I. Min, Appl. Phys. Lett. 88 (2006) 043507.
[9] D.R. Lide, Handbook of Chemistry and Physics, CRC Press, New York, 2003.
[10] H.S. Kim, K.H. Baik, J.H. Cho, J.W. Lee, S. Ho Yoon, H.K. Kim, S.N. Lee, C.S. Sone, Y.J. Park, T.Y. Seong, IEEE Photon. Technol. Lett. 19 (2007) 336.
[11] J.H. Son, G.H. Jung, J.L. Lee, Appl. Phys. Lett. 93 (2008) 012102.
[12] T. Jeong, S.H. Lee, H.H. Lee, S.H. Jeong, J.G. Jhin, J.H. Baek, S.H. Park, J.K. Lee, J. Korean Phys. Soc. 55 (2009) 1615.
[13] T. Jeong, K.H. Kim, H.H. Lee, S.J. Lee, S.H. Lee, J.H. Baek, J.K. Lee, IEEE Photon. Technol. Lett. 20 (2008) 1932.
[14] A.C. Schmitz, A.T. Ping, M. Asif Khan, Q. Chen, J.W. Yang, I. Adesida, J. Electron. Mater. 27 (1998) 4.
[15] J.O. Song, J.S. Kwak, T.Y. Seong, Appl. Phys. Lett. 86 (2005) 062103.
[16] J.Y. Kim, S.I. Na, G.Y. Ha, M.K. Kwon, I.K. Park, J.H. Lim, S.J. Park, M.H. Kim, D. Choi, K. Min, Appl. Phys. Lett. 88 (2006) 043507.
[17] H.W. Jang, J.-L. Lee, Appl. Phys. Lett. 85 (2004) 5920.
[18] J.O. Song, J.S. Kwak, Y. Park, T.Y. Seong, Appl. Phys. Lett. 86 (2005) 062104.
[19] D.L. Hibbard, S.P. Jung, C. Wang, D. Ullery, Y.S. Zhao, H.P. Lee, W. So, H. Liu, Appl. Phys. Lett. 83 (2003) 311.