（一） 研究計畫中文摘要：

關鍵字： 氮化鎵，歐姆接觸，特徵接觸電阻，表面費米能階。

氮化鎵相關材料已被用於製作藍色發光二極體及雷射等光電元件，為改善元件的性能，必須有良好的p型及n型歐姆接觸特性。目前，p型氮化鎵的歐姆接觸製作較為困難，為達到p型氮化鎵之歐姆接觸需用較高溫之熱處理形成熱合金化歐姆接觸，此高溫處理將會對元件與材料造成某程度之影響，因此，本計畫重點在於發展p型氮化鎵非熱合金化歐姆接觸之外並與熱合金化歐姆接觸進行比較。茲分屬研究重點如下:

(A) p 型氮化鎵有效活化方式之開發與其對表面費米能階和產生自由載子濃度的特性分析，建立 p 型氮化鎵活化之機制

將 p 型氮化鎵經過不同形式之活化後經霍爾(Hall)觀測系統測量 p 型氮化鎵載子濃度，並以 x 光光電子能譜(XPS)術和深紫外光光電能譜(UPS)術觀測經活化的試片表面，整合分析 p 型氮化鎵的表面能帶分布情形。

(B) 金屬/p 型氮化鎵歐姆接觸特性分析

選擇合適之金屬蒸鍍在經有效活化後之 p 型氮化鎵上，以電流-電壓(I-V)法測量其特徵接觸電阻，並以 XPS 剖面分析技術深入研究熱處理前後金屬/p 型氮化鎵界面之特性。為了建立完善之歐姆接觸機制，也將製作金屬/p 型氮化鎵蕭特基二極體，以 I-V 和電容-電壓(C-V)法觀測界面之特性。

（二） 研究計畫英文摘要

Keywords: GaN, ohmic contact, specific contact resistance, surface Fermi level.

GaN has a 3.4 eV direct gap at room temperature and has attached much interest for its application in optical devices in the short-wavelength region such as blue light emitting diodes (LEDs) and laser diodes (LDs). Other devices that have been demonstrated so far include ultraviolet photoconductive detectors, ultraviolet

Schottky barrier photodetectors, metal – semiconductor field effect transistors, and high electron mobility transistors. Ohmic contacts to p-GaN with low resistance are essential in improving the performances of optical devices. In order to improve the ohmic performance of the metals/p-GaN samples, the samples were annealed at the higher temperature. High-temperature annealing led to the formation of defects, which resulted in degrading the performance of optical devices, in the p-GaN sample. So in this plan, we are devoted to improve the nonalloyed and alloyed ohmic contact of p-GaN samples under the various activations. Using the Van der Pauw-Hall measurement performed, the electron concentration of the p-GaN epilayer was determined. A specific contact resistance was measured using the transmission line method (TLM) for metals contacts to the p-GaN samples. In order to investigate the interfacial characteristics for the metal/p-GaN, all samples were measured using current-voltage (I-V) method, capacitance-voltage (C-V) measurement, x-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS).

(A) Study the activation of p-GaN under the various conditions:

In this work, the position of surface Fermi level of p-GaN samples under the various activations can be obtained using UPS measurement and XPS measurement. Using the Van der Pauw-Hall measurement performed, the electron concentration of the p-GaN epilayer was determined. The Ga/N atomic concentration ratio on the activated p-GaN samples was measured by XPS. In order to understand the activation mechanisms of p-GaN samples under the various activations, all observed results from Hall, XPS, and UPS were further analyzed.

(B) Study the characteristics of metals nonalloyed and alloyed ohmic contacts to p-GaN samples

The characteristics of Pt, Ni and Au (nonalloyed and alloyed) ohmic contacts to the activated p-GaN are measured using I-V in this work. The interfacial characteristics for metal/p-GaN are analyzed using XPS measurement. The formation mechanisms of ohmic contacts for the metals/p-GaN will be investigated in this study. In order to understand the interfacial characteristics of metal/p-GaN samples, the fabricated Schottky diodes of p-GaN were analyzed using the C-V measurements.

計畫成果自評：

本次計畫研究內容與原計畫相符程度達 90%，並達成預期目標，而且研究成果三篇論文均已發表於國際知名期刊 Applied Physics Letters，獲得國際學者肯定，極具學術與實際應用之價值。

報告內容：

此次專題計畫研究成果已撰寫成三篇論文並發表於美國 Applied Physice Letters 期刊，依序列於下：

1. **Y. J. Lin** and K. C. Wu, 2004, March "Electrical properties of Pt contacts on p-GaN activated in air", Appl. Phys. Lett. Vol.84, 1501. (NSC92-2215-E-035-003)
2. **Y. J. Lin**, W. F. Liu, and C. T. Lee, 2004, April "Excimer-laser-induced activation of Mg-doped GaN layers", Appl. Phys. Lett. Vol.84, 2515. (NSC92-2215-E-035-003)
3. **Y. J. Lin**, 2004, April "Activation mechanism of annealed Mg-doped GaN in air", Appl. Phys. Lett. Vol.84, 2760. (NSC92-2215-E-035-003)

論文詳細內容如下所示：

HTML ABSTRACT + LINKS

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 9 1 MARCH 2004

Electrical properties of Pt contacts on *p*-GaN activated in air

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(Received 30 October 2003; accepted 6 January 2004)

In this study, the electrical properties of Pt contacts on *p*-type GaN (*p*-GaN) activated in air were investigated. From the observed photoluminescence result, it is suggested that the hydrogenated Ga vacancies (i.e., $V_{Ga}H_2$) were formed during the activation process. However, $V_{Ga}H_2$ in *p*-GaN near the surface was transformed into V_{Ga} after Pt deposition, because Pt strongly absorbed hydrogen. A large number of V_{Ga} at the Pt/*p*-GaN interface would lead to the pinning of the Fermi level at 0.3 eV above the valence-band edge, as well as the formation of the low barrier at the interface, and the formation of the nonalloyed ohmic contacts due to the occurrence of the tunneling transmission for holes at the interface. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1651658]

GaN continues to grow in importance for the high-brightness light emitting diodes (LEDs) in the visible and ultraviolet wavelength regions.[1–3] For the case of the highly efficient LED, several critical problems must be addressed, such as high hole concentration (N_h) in *p*-type GaN (*p*-GaN) and low-resistance ohmic contact in the fabrication processes for the devices. To obtain a low-resistance ohmic contact to *p*-GaN, a variety of surface treatments of *p*-GaN using solutions such as H_3PO_4, KOH, HCl, and aqua regia, have been proposed.[4–6] In this study, we report on the results of activation time-dependent Hall effect measurements on *p*-GaN and investigate the mechanism of nonalloyed ohmic formation for Pt contacts to *p*-GaN activated in air.

The epitaxial layers used in the experiments were grown on *c*-plane sapphire substrates using a metalorganic chemical vapor deposition system. Trimethylgallium, ammonia, and bis-cyclopentadienylmagnesium were used as the Ga, N, and Mg sources, respectively. An undoped GaN buffer layer with a thickness of 650 nm was grown on the sapphire substrate at 520 °C, followed by the growth of an *p*-GaN layer (762 nm) at 1100 °C. The grown samples were annealed at 500 °C in air ambient using a thermal annealing furnace for the purpose of generating holes under various annealing times (i.e., 1, 2, 3, 4, 5, 6, and 8 h). The Hall and photoluminescence (PL) measurements were performed at room temperature in order to evaluate the electrical and optical properties of the *p*-GaN layers for each activation method. Using a He–Cd laser as an excitation source, the ~2.8 eV PL [blue luminescence (BL)] band was only observed for the all samples due to the heavily Mg doped.[7] For PL measurements, all activated samples were transferred to a loading chamber immediately after aqua regia treatment. The specific contact resistance (ρ_c) was measured using the transmission line method (TLM) for Pt contacts to the 1, 2, 3, 4, 5, 6, and 8 h activated samples. A Ni/Au (50/600 nm) metal mask was employed to form rectangular mesa regions with dimensions of 100 $\times$1000 μm^2. A reactive ion etching system was used with BCl_3 gas to etch the *p*-GaN wafers. The dimensions of the metal contact pads in the TLM pattern was 100$\times$100 μm^2. The gap spacing between the contact pads was designed to be 5, 10, 15, 25, 35, 50, and 60 μm, respectively. After the removal of the metallic mask, the samples were cleaned in chemical cleaning solutions of trichloroethylene, acetone, and methanol. The surfaces of as-cleaned samples were treated with aqua regia for 10 min prior to deposition of the Pt (30 nm) metal using an electron beam evaporator. The $I-V$ characteristics of the TLM patterns were measured using an HP4145B semiconductor parameter analyzer.

Figure 1(a) shows the normalized PL spectra of the *p*-GaN samples without and with 2 h activation, respectively. Figure 1(b) shows the difference between the PL spectrum of *p*-GaN without activation and the PL spectrum of *p*-GaN with 2 h activation. PL studies of the 2 h activated sample [see Fig. 1(a)] showed different features compared to those observed in the sample without activation. In Fig. 1(b), we can see that the difference spectrum is a broad peak in the region of 1.9–2.6 eV, which is the so-called yellow luminescence (YL). In this previous report,[8] we suggested that the hydrogenated gallium vacancies (i.e., $V_{Ga}H_2$) were sources of YL.[9,10] From this kinetic point of view,[10] the $V_{Ga}H_2$ complex is the most likely to be formed and contributes to YL.

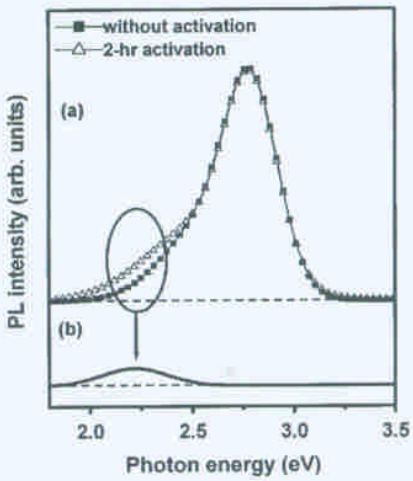

FIG. 1. (a) PL spectra of the *p*-GaN samples without and with 2 h activation. (b) The difference spectrum.

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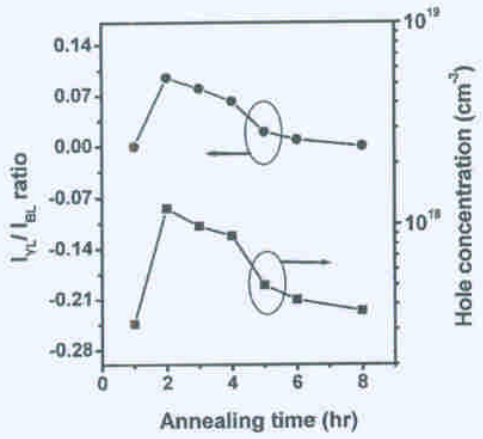

FIG. 2. Hole concentration and the relative intensity ratio of I_{YL}/I_{BL} as functions of activation time.

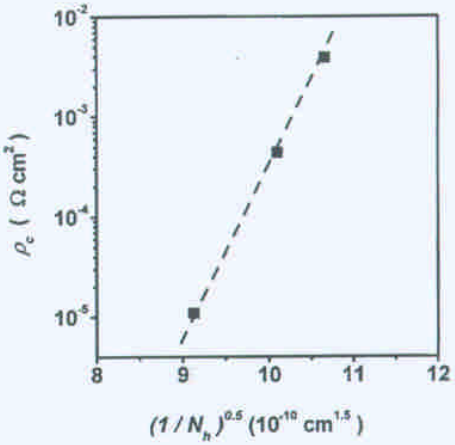

FIG. 3. A plot of the calculated values of ρ_c as a function of $1/\sqrt{N_h}$.

For the 1, 2, 3, 4, 5, 6, and 8 h activated samples, the relative intensity ratio of I_{YL}/I_{BL} is shown in Fig. 2, respectively.

In Fig. 2, the hole concentration and the relative intensity ratio of I_{YL}/I_{BL} are shown as functions of activation time. It can be seen that by increasing the activation time from 1 to 2 h, the hole concentration increases from 3.2×10^{17} cm^{-3} to 1.2×10^{18} cm^{-3}, respectively. However, the hole concentration decreases from 1.2×10^{18} cm^{-3} to 3.7×10^{17} cm^{-3} for the activation time increasing from 2 to 8 h, respectively. Figure 2 shows the relative intensity ratio of I_{YL}/I_{BL} to increase with increasing activation time to a minimum at 2 h, and decrease with increasing activation time beyond that point. Figure 2 also shows that the relative intensity ratio of I_{YL}/I_{BL} increases (decreases) with increasing (decreasing) hole concentration of p-GaN. This implied that the generation of $V_{Ga}H_2$ would result in the reduction of the amount of nitrogen vacancies (V_N), as well as the reduction of the self-compensation in the p-GaN layer, and the increase of the hole concentration. In addition, in $V_{Ga}H_2$, two electrons are contributed, leading to a single acceptor.[10] On the other hand, when the activation time is longer than 2 h, the relative intensity ratio of I_{YL}/I_{BL} decreases because of the formation of V_N. The generation of V_N could be attributed to the nitrogen desorption due to an excess of $V_{Ga}H_2$.

When Pt was deposited on the 1, 2, 3, 4, 5, 6, and 8 h activated samples, the nonalloyed ohmic contact of Pt/p-GaN was obtained from the 2, 3, and 4 h activated samples due to the formation of the higher hole concentration in the p-GaN films after activation. Figure 3 shows the plot of the measured values of ρ_c for Pt contacts to the 2, 3, and 4 h activated samples as a function of $1/\sqrt{N_h}$. When the contact with high hole concentration occurs, the tunneling process will dominate, and the ρ_c is given as

$$\rho_c \propto \exp\left(\frac{q\phi_B}{E_{oo}}\right) = \exp\left[\frac{\sqrt{\epsilon m^*}}{1.85\times10^{-11}}\left(\frac{q\phi_B}{\sqrt{N_h}}\right)\right], \quad (1)$$

where ϵ is the dielectric constant of p-GaN (ϵ=9.5), m^* is the effective hole mass constant of p-GaN (m^*=0.8), and $q\phi_B$ is the barrier height at the metal/semiconductor interface. For the 2, 3, and 4 h activated samples with high hole concentration ($N_h > 8.7\times10^{17}$ cm^{-3}), plotting $\ln(\rho_c)$ vs $1/\sqrt{N_h}$ gives a linear curve with the slop $(q\phi_B\sqrt{\epsilon m^*})/(1.85\times10^{-11})=4.4\times10^{10}$ using the Eq. (1), the $q\phi_B$ is calculated to be approximately 0.3 eV. This indicates that the formation of nonalloyed ohmic contact for Pt contacts to 2, 3, and 4 h actived samples can be attributed to the occurrence of the tunneling transmission of holes and the formation of a barrier height of 0.3 eV at the Pt/p-GaN interface. Besides, this previous experimental result reported by Kim *et al.* indicated that the energy level of V_{Ga} is located at 0.3 eV above the valence-band edge.[11] On the basis of the evidence, we deduced that the pinning of the surface Fermi level was deeply related to the V_{Ga} formation. Therefore, the formation of a low barrier at the Pt/p-GaN interface could be associated with the generation of a large number of V_{Ga} after the Pt deposition. Because Pt strongly absorbed hydrogen,[12] a large number of $V_{Ga}H_2$ induced by activation were transformed into V_{Ga}, pinning the Fermi level, and playing a role in forming nonalloyed ohmic contact. This explained why the observed barrier height for Pt contacts to 2, 3, or 4 h activated samples is equal to 0.3 eV. On the other hand, the formation of more V_{Ga} (V_{Ga} as an acceptor)[13] would cause an increase of the hole concentration in p-GaN near the interface and the occurrence of the tunneling transmission for holes at the interface.

In summary, the electrical properties of Pt contacts on p-GaN activated in air were investigated in this study. Pt onto the 2, 3, and 4 h activated p-GaN samples led to an increase in the amount of V_{Ga} due to the retention of hydrogen in the Pt layer,[12] resulting in the formation of a nonalloyed ohmic contact, the pinning of the Fermi level in the vicinity of valence band, and the occurrence of the tunneling transmission for holes at the interface of Pt with p-GaN.

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APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 14 5 APRIL 2004

Excimer-laser-induced activation of Mg-doped GaN layers

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In this study, we investigated the 248 nm excimer-laser-induced activation of the Mg-doped GaN layers. According to the observed photoluminescence results and the x-ray photoelectron spectroscopy measurements, we found that the dissociation of the Mg–H complexes and the formation of hydrogenated Ga vacancies (i.e., $V_{Ga}H_2$) and/or the Ga vacancies occupied by interstitial Mg during the laser irradiation process, led to an increase in the hole concentration. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1695436]

Applications of wide bandgap GaN-based III–V nitride compounds in blue light-emitting diodes, laser diodes, and high-power electronic devices have been reported. One of the problems in GaN-based optoelectronic devices is the low hole concentration of Mg-doped GaN, which makes it difficult to form excellent ohmic contacts in metal/Mg-doped GaN samples. There have been a few recent studies on the effects of oxygen in the *p*-type activation process.[1,2] In addition, a low-energy electron-beam irradiation (LEEBI) treatment,[3,4] a microwave treatment,[5] a thermal annealing treatment,[6] and thermal annealing with a minority-carrier injection method[7] have been also employed for the effective activation and generation of holes. Jang *et al.*[8] have indicated that the acceptor concentration would increase by a factor of ~2 after KrF excimer laser irradiation. They suggested that the activation efficiency of Mg dopants was enhanced by the photon-assisted breaking of Mg—H bonds and/or the removal of hydrogen atoms in the presence of oxygen, which produced *p*-type GaN with an increased hole concentration.[8] However, they did not investigate the excimer-laser-induced activation mechanism further.[8] Therefore, to date, the excimer-laser-induced activation of Mg-doped GaN has not yet been well understood. For this study, we demonstrate that the activation of Mg-doped GaN could be achieved by repetitive laser beam irradiation with a pulsed KrF excimer laser under an air atmosphere. After laser irradiation, Ga oxides formed on the Mg-doped GaN surface, and hydrogenated Ga vacancies (i.e., $V_{Ga}H_2$) and/or Ga vacancies, occupied by the interstitial Mg (Mg_{Ga}), formed in the Mg-doped GaN film, due to Ga outdiffusion. Therefore, after laser irradiation, a hole concentration of 4.1×10^{17} cm^{-3} could be achieved in the Mg-doped GaN film.

The epitaxial layers used in the experiments were grown on *c*-plane sapphire substrates using a metalorganic chemical vapor deposition system. Trimethylgallium, ammonia, and bis-cyclopentadienylmagnesium, were used as the Ga, N, and Mg sources, respectively. An undoped GaN buffer layer with a thickness of 650 nm was grown on the sapphire substrate at 520 °C, followed by the growth of an Mg-doped GaN layer (762 nm) at 1100 °C. The grown samples (as-grown samples) were annealed for the purpose of generating holes at 750 °C for 30 min in an ambient N_2 (N_2-activated samples), then irradiated in air, by a single pulse from a KrF excimer laser (laser-irradiated samples). The laser was operated at 248 nm with a pulse duration of approximately 50 ns. The incident laser fluence was 250 mJ/cm^2 (<600 mJ/cm^2). It is known that the threshold fluence for the decomposition or damaged of GaN is above 600 mJ/cm^2, under which the GaN surface is heated to its decomposition temperature of ~900 to 1000 °C.[9,10] Next, all the samples were cleaned in chemical cleaning solutions of trichloroethylene, acetone, and methanol. Prior to the making of the Hall and photoluminescence (PL) measurements, the as-grown, N_2-activated, and laser-irradiated samples were treated in an aqua regia solution for 10 min. Hall and PL measurements were performed at room temperature in order to evaluate the electrical and optical properties of the Mg-doped GaN layers, for each activation method. When an He–Cd laser was used as an excitation source, only the 2.8 eV PL band was observed, in the all samples. Two Gaussian functions were used to fit the PL peak, neglecting interference effects. The van der Pauw–Hall measurements were used to determine the hole concentration of the Mg-doped GaN epilayer. From the observed Hall measurements, the hole concentration of the N_2-activated and laser-irradiated samples was calculated to be 3.6×10^{17} cm^{-3} and 4.1×10^{17} cm^{-3}, respectively. The hole mobility of the N_2-activated and laser-irradiated samples was calculated to be 11.1 $cm^2/V\,s$ and 10.9 $cm^2/V\,s$, respectively. For this work, the Ga $2p_{3/2}$ core-level spectrum was measured via x-ray photoelectron spectroscopy (XPS). The XPS measurements were performed using a monochromatic Mg $K\alpha$ x-ray source. For energy reference purposes, we took a Au $4f_{7/2}$ peak at 83.86 eV and a Cu $2p_{3/2}$ peak at 932.65 eV. The Ga $2p_{3/2}$ core-level peaks were deconvolved into their various components using an interactive least-squares computer program; the curves were assumed total 80% Gaussian and 20% Lorentzian mixed functions.

Figure 1 shows the Ga $2p_{3/2}$ core-level spectra of the N_2-activated and laser-irradiated samples, respectively, without aqua regia treatment. The Ga—N bonds and Ga—O bonds, were observed in the N_2-activated and laser-irradiated

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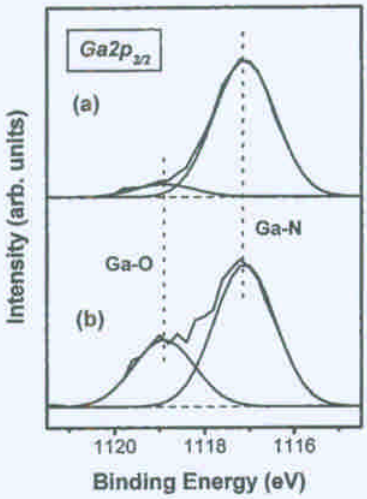

FIG. 1. Ga $2p_{3/2}$ core-level spectra of (a) N_2-activated Mg-doped GaN and (b) laser-irradiated Mg-doped GaN.

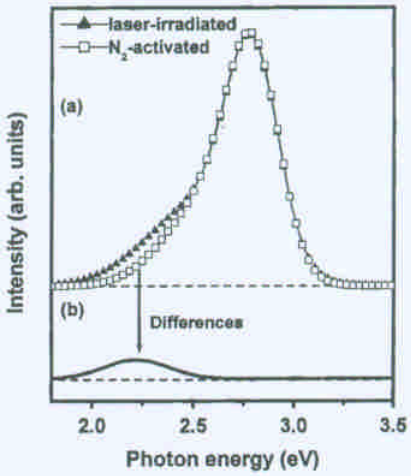

FIG. 3. (a) PL spectra of the laser-irradiated and N_2-activated Mg-doped GaN. (b) The difference spectrum (laser-irradiated minus N_2 activated).

samples. The intensity of the spectral component from the Ga—O bond increased significantly after laser irradiation. This suggests that Ga oxides (i.e., Ga_2O_3)[11] had formed on the laser-irradiated sample surface due to Ga outdiffusion. Wolter *et al.*[12] suggested that the transformation of Ga into Ga oxide during irradiation would be thermodynamically most favorable in air.[12] Figure 2 shows the respective normalized PL spectra of the N_2-activated and as-grown samples, after aqua regia treatment. In Fig. 2, we find that both samples had a similarly shaped curve.

Figure 3 shows the respective normalized PL spectra of the N_2-activated and laser-irradiated samples, after aqua regia treatment. In Fig. 3(a), we find that the samples do not show a similarly shaped curve. The difference [laser irradiated minus N_2 activated, shown in Fig. 3(b)] is a broad peak in the 1.9–2.6 eV region, the so-called yellow luminescence (YL). Basak *et al.*[13] have indicated that the Ga vacancies (V_{Ga}) are the source of the YL.[13] In addition, van de Wall has suggested that hydrogenated Ga vacancies (i.e., $V_{Ga}H$ and $V_{Ga}H_2$) also contribute to YL.[14] This implies that the Ga outdiffusion induced by laser irradiation will lead to an increase in the amount of Ga vacancies in Mg-doped GaN film. It is possible that the vacancies caused by Ga oxidation will be good paths for Ga atoms to diffuse out of the GaN substrate.[15] However, Wright has indicated that, for extreme p-type conditions, the formation energy of the V_{Ga} or $V_{Ga}H$ complex is quite high.[16] In this case, the V_{Ga} and $V_{Ga}H$ complexes are unlikely to occur. From this kinetic point of view,[16] the $V_{Ga}H_2$ complex is the most likely to be formed if contributes to YL, as shown in Fig. 3(b). During the laser irradiation process, the following reactions will occur for Mg–H and $V_{Ga}H_2$:

$$2GaN + 3/2O_2 \rightarrow Ga_2O_3 + 2(V_{Ga}\text{–}N), \quad (1)$$

$$Mg\text{–}H \rightarrow Mg + H, \quad (2)$$

$$V_{Ga} + 2H \rightarrow V_{Ga}H_2, \quad (3)$$

Wright has also suggested that $V_{Ga}H_2$ has a negative formation energy and that the removal energy of $V_{Ga}H_2$ is approximately equal to 2.5 eV for p-type GaN.[16] Wampler *et al.*[17] have indicated that Mg–H has a positive formation energy, and the formation energy for, Mg–H→Mg+H, is equal to 0.8 eV. Therefore, we deduce that the occurrence of the reaction, Mg–H→Mg+H, and the formation of V_{Ga} during laser irradiation, may lead to the generation of $V_{Ga}H_2$.

According to previous reports,[14,18] we understand that in Mg-doped GaN hydrogen prefers a positively charged state (H^+) and is attracted by negatively charged Ga vacancies (V_{Ga}^{3-}). This suggests that the formation of Ga vacancies significantly enhances hydrogen desorption from the Mg–H complexes, to form $V_{Ga}H_2$. This results in the activation of Mg-doped GaN. In addition, the Mg–H complexes may be also broken by laser irradiation to form the positive charged hydrogen. $V_{Ga}H_2$ contributes two electrons, leading to a single acceptor.[14] Gelhausen *et al.*[3] found that the YL band evolved, following the LEEBI treatment for the metalorganic vapor phase epitaxy-grown Mg-doped GaN. They proposed that electron irradiation will head to the dissociating of hydrogenated Ga vacancies, resulting in an activation of V_{Ga}-related complexes, thus inducing the radiative recombi-

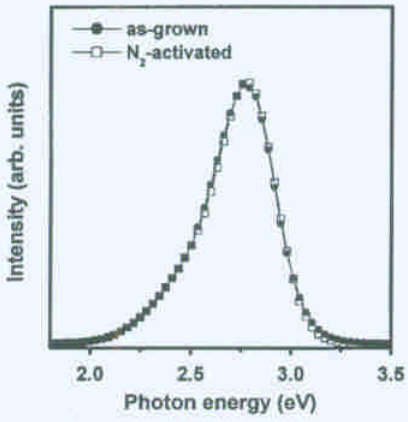

FIG. 2. PL spectra of the as-grown and N_2-activated Mg-doped GaN samples.

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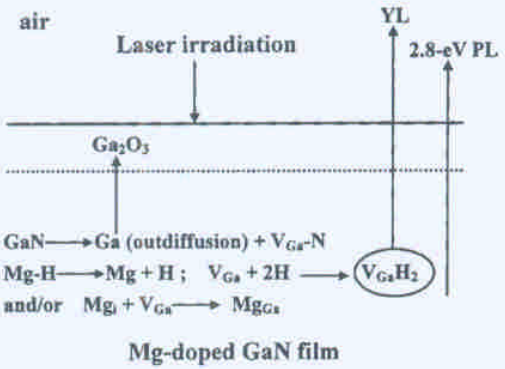

FIG. 4. Schematic illustration of the p-type laser-irradiation mechanisms in Mg-doped GaN films.

nation responsible for the observed YL.[3] In addition, the increase in the number of Ga vacancies caused by Ga outdiffusion may improve the activation efficiency, by promoting the following reaction $Mg_i + V_{Ga} \rightarrow Mg_{Ga}$ (Mg_i: The interstitial Mg).[19] This is another possible explanation for the increased hole concentration. A schematic drawing summarizing the laser-irradiation activation mechanisms described above shown in Fig. 4.

In summary, the activation mechanism of laser-irradiated Mg-doped GaN has been investigated for this study. According to the experimental results, we deduce that Ga oxidation will lead to an increase in Ga-vacancy-related defects and the acceleration of Ga outdiffusion during laser irradiation. Therefore, excimer-laser-induced activation is attributed to the dissociation of the Mg–H complexes and the strengthened formation of the hydrogenated Ga vacancies and/or the Ga vacancies occupied by interstitial Mg.

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HTML ABSTRACT + LINKS

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 15 12 APRIL 2004

Activation mechanism of annealed Mg-doped GaN in air

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In this study, the activation mechanism of annealed Mg-doped GaN in air and the influence of ambient on activation of Mg-doped GaN were investigated. According to the experimental results, we found that the dissociation of Mg_{Ga}–H, and the formation of hydrogenated gallium vacancies ($V_{Ga}H_2$) and gallium vacancies occupied by interstitial Mg during the air-activation process, led to an increase in the hole concentration. In addition, from the observed photoluminescence results and the secondary ion mass spectroscopy measurements, it is suggested that the formation of $V_{Ga}H_2$ will result in an enhancement of hydrogen desorption from the Mg_{Ga}–H complexes. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1704873]

Wide-band-gap semiconductors are of fundamental interest for optoelectronic applications. High hole conductivity in GaN is the key for producing short-wavelength optical devices as well as high-power and high-frequency electronic devices. However, there are still some problems that are unresolved. One of the problems in GaN-based optoelectronic devices is the low hole concentration (N_h) of Mg-doped GaN, which makes it difficult to form excellent ohmic contacts in metal/Mg-doped GaN samples. There have been a few recent studies on the effects of oxygen in the p-type activation process.[1,2] They demonstrated that the incorporation of oxygen into the activation ambient resulted in the resistance reduction[1] and an increase in the hole concentration[1,2] due to the outdiffusion of hydrogen (H) from the Mg-doped GaN layer. A low-energy electron-beam irradiation (LEEBI) treatment,[3] a microwave treatment,[4] a thermal annealing treatment,[5] and thermal annealing with a minority-carrier injection method[6] have been employed for the effective activation and generation of holes. Takeya and Ikeda have indicated that hole concentration increased in proportion to the square root of annealing time in low-temperature long-time annealing method and it took ~2 h to obtain hole concentration of $\sim 10^{18}$ cm^{-3} at 485 °C annealed in air.[2] However, they did not investigate the activation mechanism further.[2] To date, there have as yet been no studies into the long-time-activation mechanism of Mg-doped GaN annealed in air. This is an important key for improving the performance of the GaN-related devices. In this study, we found the specific difference from the long-time-thermal annealing method under air ambient. The formation of hydrogenated gallium vacancies (i.e., $V_{Ga}H_2$)[7] during the air-activation process could strongly influence the activation of Mg-doped GaN. After 2-h-air activation, the N_h of 1.2×10^{18} cm^{-3} was obtained, due to the dissociation of Mg_{Ga}–H, and the formation of hydrogenated gallium vacancies and gallium vacancies occupied by interstitial Mg.

The epitaxial layers used in the experiments were grown on c-plane sapphire substrates using a metalorganic chemical vapor deposition (MOCVD) system. Trimethylgallium (TMG), ammonia (NH_3), and bis-cyclopentadienylmagnesium (CP_2–Mg), were used as the Ga, N, and Mg sources, respectively. An undoped GaN buffer layer with a thickness of 650 nm was grown on the sapphire substrate at 520 °C, followed by the growth of a Mg-doped GaN layer (762 nm) at 1100 °C. Mg concentration ([Mg]) was 6×10^{19} cm^{-3} for all samples. The [Mg] in Mg-doped GaN was measured using secondary ion mass spectroscopy (SIMS). The grown samples (as-grown samples) were annealed for the purpose of generating holes, at 750 °C for 30 min in ambient N_2 (750 °C-N_2-activated samples), at 500 °C for 2 h in ambient N_2 (500 °C-N_2-activated samples) and at 500 °C for 2 h in air (air-activated samples), respectively. The samples were cleaned in chemical cleaning solutions of trichloroethylene, acetone, and methanol. Prior to Hall, photoluminescence (PL), and SIMS measurements, the as-grown, 750 °C-N_2-activated, 500 °C-N_2-activated, and air-activated samples were treated in an aqua regia solution for 10 min. Hall and PL measurements were performed at room temperature (RT) in order to evaluate the electrical and optical properties of the Mg-doped GaN layers for each activated method. When a He–Cd laser was used as an excitation source, only the 2.8-eV-PL band was observed, in all the heavily doped samples.[8] The Ga depth profile and the H depth profile were obtained from the SIMS measurements (Cameca IMS-4f system). According to the Van der Pauw–Hall measurements, we found that the hole concentration of 750 °C-N_2-activated, 500 °C-N_2-activated, and air-activated samples was, respectively, calculated to be 3.6×10^{17}, 9.3×10^{16}, and 1.2×10^{18} cm^{-3}. An explanation for this will be given.

Figure 1 shows the respective normalized PL spectra of the as-grown, 750 °C-N_2-activated and 500 °C-N_2-activated samples. In Fig. 1, we found that the PL spectra of the 750 °C-N_2-activated, 500 °C-N_2-activated and as-grown samples had a similarly shaped curve. This suggested that extrinsic optical characteristic was not induced after N_2 activation.

Figure 2(a) shows the respective normalized PL spectra of the air activated and 500 °C-N_2-activated samples. PL studies of the air-activated sample [see Fig. 2(a)] showed different features compared to those observed in the 500 °C-

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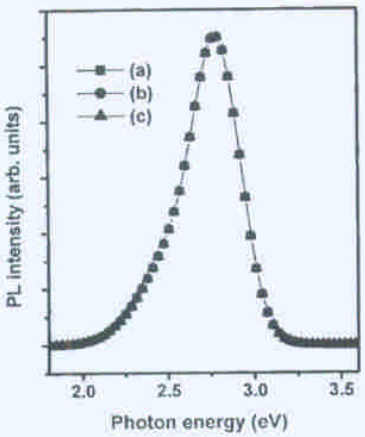

FIG. 1. PL spectra of the (a) as-grown, (b) 750 °C-N_2-activated, and (c) 500 °C-N_2-activated Mg-doped GaN samples.

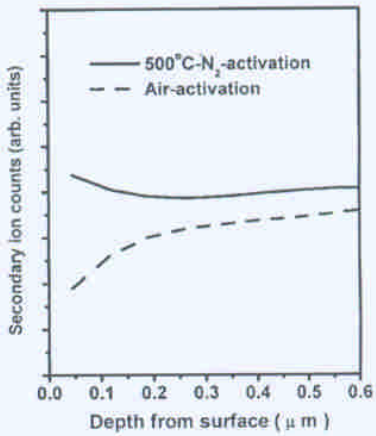

FIG. 3. Ga SIMS depth profiles of the 500 °C-N_2-activated and air-activated Mg-doped GaN samples.

N_2-activated sample. In Fig. 2(b), we can see that the difference (air-activated minus 500 °C-N_2-activated) is a broad peak in the 1.9–2.6 eV region, the so-called yellow luminescence (YL). Basak *et al.* have indicated that the gallium vacancies (V_{Ga}) were sources of YL.[9] In addition, Van de Walle has suggested that hydrogenated gallium vacancies ($V_{Ga}H$ and $V_{Ga}H_2$) also contributed to YL.[10] Van de Walle has also indicated that, for extreme p-type conditions, the formation energy of V_{Ga} or $V_{Ga}H$ complex is quite high.[10,11] In this case, the V_{Ga} and $V_{Ga}H$ complexes are unlikely to occur. From this kinetic point of view,[10,11] $V_{Ga}H_2$ complex is the most likely to be formed and contributes to YL, as shown in Fig. 2(b), which also shows that the air activation produces a broad luminescent band (centered on ~2.25 eV) which is slightly blueshifted relative to the YL peak (centered on ~2.2 eV) reported by Pearton *et al.*[12] Kucheyev *et al.* indicated that the H-related YL peak exhibits a blueshift.[13] According to previous reports,[10,14] we understand that hydrogen in Mg-doped GaN prefers a positively charged state (H^+) and is attracted by negatively charged gallium vacancies (V_{Ga}^{3-}). These results suggest that the formation of V_{Ga}-related defects significantly enhances hydrogen desorption from the Mg_{Ga}–H complexes, to form $V_{Ga}H_2$. This results in the activation of Mg-doped GaN. In addition, in $V_{Ga}H_2$, two electrons are contributed, leading to a single acceptor.[10] During the air-activation process, the following reactions will occur for Mg_{Ga}–H and $V_{Ga}H_2$ complexes:

$$GaN+(x/2)O_2+2(Mg_{Ga}\text{–}H) \rightarrow (V_{Ga}H_2)N+2Mg_{Ga}+GaO_x, \quad (1)$$

$$GaN+(x/2)O_2+Mg_i \rightarrow Mg_{Ga}N+GaO_x, \quad (2)$$

$$2(Mg_{Ga}\text{–}H)+(1/2)O_2 \rightarrow 2Mg_{Ga}+H_2O.[15] \quad (3)$$

where Mg_i is the interstitial Mg. Van de Walle *et al.* have indicated that the formation energy of Mg_i will be close to that of Mg_{Ga} when the Fermi level is near the valence band edge.[16] An increase in the number of Ga vacancies caused by air activation may improve the activation efficiency, by promoting the following reaction of Eq. (2). This is also another possible explanation for the increased hole concentration. Koide *et al.* have concluded that oxygen reacts with hydrogen to form H_2O, which helps to decrease the H concentration during the alloying process.[15] This is also another possible explanation for the increased hole concentration. On the other hand, during the 500 °C-N_2-activation (or 750 °C-N_2-activation) process, the following reaction will occur for Mg_{Ga}–H complexes:

$$Mg_{Ga}\text{–}H \rightarrow Mg_{Ga}+H. \quad (4)$$

In order to further confirm whether the $V_{Ga}H_2$ complexes were really formed after the air activation or not, the Ga SIMS depth profile and the H SIMS depth profile must be, respectively, obtained. Figure 3 shows the Ga SIMS depth profiles of the 500 °C-N_2-activated and air-activated samples, respectively. In Fig. 3, we find that the intensity of Ga SIMS of the 500 °C-N_2-activated samples is larger than that of the air-activated samples. This implies that the Ga-vacancy-related defects were formed in the air-activated samples. We find that the value of the depth from the surface decreases with increasing the Ga-vacancy-related defects for

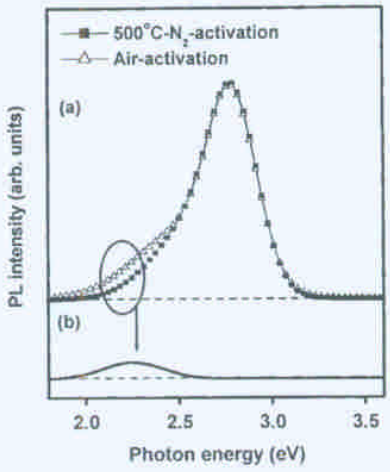

FIG. 2. (a) PL spectra of the 500 °C-N_2-activated and air-activated Mg-doped GaN samples, (b) the difference spectrum (air-activated minus 500 °C-N_2-activated).

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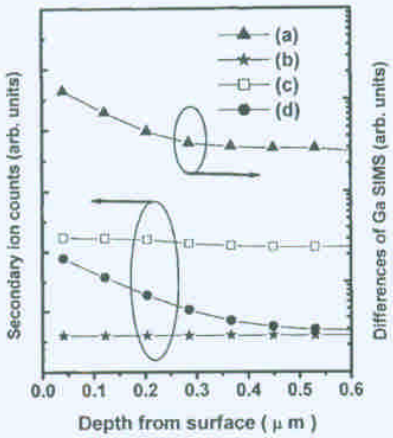

FIG. 4. (a) Difference between Ga SIMS depth profiles of the 500 °C-N_2-activated and air-activated Mg-doped GaN samples (500 °C-N_2-activated minus air activated). The H SIMS depth profiles of the (b) 750 °C-N_2-activated, (c) 500 °C-N_2-activated, and (d) air-activated Mg-doped GaN samples.

the air-activated sample, according to the observation on the difference [500 °C-N_2-activated minus air activated, as shown in Fig. 4(a)] between the intensity of Ga SIMS of the 500 °C-N_2-activated sample and the intensity of Ga SIMS of the air-activated sample. This indirectly indicated the difference between the intensity of Ga SIMS of the 500 °C-N_2-activated sample and the intensity of Ga SIMS of the air-activated sample has a relationship with the concentration of the Ga-vacancy-related defects.

Figure 4 also shows the H SIMS depth profiles of the 750 °C-N_2-activated, 500 °C-N_2-activated and air-activated samples, respectively. We find that the intensity of H SIMS of the 500 °C-N_2-activated sample has no relationship with the depth [shown in Fig. 4(c)] and the intensity of H SIMS of the air-activated sample decreases with increasing the depth from the surface [shown in Fig. 4(d)]. Similarly, the Ga-vacancy-related defects of the air-activated sample decrease with increasing the depth from the surface, as shown in Fig. 4(a). This implies that the Ga-vacancy-related defects are the hydrogenated Ga vacancies (i.e., $V_{Ga}H_2$).

On the other hand, SIMS analysis shows that the intensity of H SIMS of the air-activated samples is lower than that of the 500 °C-N_2-activated samples, which may improve the activation efficiency. This result is in agreement with the report by Koide *et al.*[15] The reaction of oxygen with hydrogen to form H_2O [shown in Eq. (3)] will help to decrease the H concentration during the air-activation process. This explained why the Hall concentration of the air-activated samples is higher than that of the 500 °C-N_2-activated samples. SIMS analysis also shows that the intensity of H SIMS of the air-activated samples is higher than that of the 750 °C-N_2-activated samples. However, the Hall concentration of the air-activated samples is higher than that of the 750 °C-N_2-activated samples. This suggests that most of H atoms existed in the air-activated samples bond with V_{Ga}, not Mg_{Ga}. The formation of hydrogenated gallium vacancies (i.e., $V_{Ga}H_2$) during the air-activation process can strongly influence the activation of Mg-doped GaN, as shown in Eq. (1). Besides, we find that the intensity of H SIMS of the 500 °C-N_2-activated samples is higher than that of the 750 °C-N_2-activated samples. Nakamura *et al.* have indicated that the low-resistivity *p*-type GaN films were obtained by N_2-ambient thermal annealing above 700 °C.[5] This explained why the Hall concentration of the 500 °C-N_2-activated samples is lower than that of the 750 °C-N_2-activated samples.

In summary, for Mg-doped GaN, the air-activation mechanism and the influence of ambient on activation were investigated. According to the experimental results, we found that the dissociation of Mg_{Ga}–H, and the formation of $V_{Ga}H_2$ and gallium vacancies occupied by interstitial Mg during the air-activation process, led to an increase in hole concentration. From the observed SIMS result, it is suggested that the formation of hydrogenated gallium vacancies (i.e., $V_{Ga}H_2$) during the air-activation process could enhance hydrogen desorption from the Mg_{Ga}–H complexes and strongly influence the activation of Mg-doped GaN.

This project is supported by National Science Council of Taiwan, Republic of China, under Contract No. NSC 92-2215-E-035-003. The secondary ion mass spectroscopy was kindly provided from the NTHU Instrumentation Center at Hsinchu National Tsing Hua University.

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國科會補助計畫	計畫名稱：P 型氮化鎵非熱合金化與熱合金化歐姆接觸研究 計畫主持人：林祐仲 計畫編號：NSC 92-2215-E-035-003-　學門領域：光電
技術/創作名稱	以準分子雷射照射技術活化 P 型氮化鎵
發明人/創作人	李清庭/林祐仲
技術說明	中文： 本技術利用準分子雷射照射鎂摻雜氮化鎵使之活化，並藉由 X 光光電子能譜及光致發光量測系統進行分析，其結果顯示雷射照射後使鎂氫鍵結解離，且由於鎵原子向外擴散至表面，導致形成氧化鎵，並產生氫化鎵空位，大量鎂摻雜之鎂間隙原子亦可能佔據鎵空位，因而使得電洞濃度因此而提升。
	英文： In this study, we investigated the 248 nm excimer-laser-induced activation of the Mg-doped GaN layers. According to the observed photoluminescence results and the x-ray photoelectron spectroscopy measurements, we found that the dissociation of the Mg-H complexes and the formation of hydrogenated Ga vacancies (i.e. $V_{Ga}H_2$) and/or the Ga vacancies occupied by interstitial Mg during the laser irradiation process, led to an increase in the hole concentration.
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