Electrically tunable electroluminescence from SiN$_x$-based light-emitting devices

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Abstract: Two obvious Gauss peaks are observed in SiN$_x$-based light-emitting devices with silver nanoparticles deposited onto the luminous layer, both of which are blue shifted with the increase of injected current. The origin of these two peaks is discussed by means of the changes of their positions, relative intensities, and full width at half maximum. We attribute the blue-shift of both electroluminescence peaks to the improvement of carrier injection as carriers can be injected into higher energy levels along their corresponding band tails, which is also confirmed by the changes of the transport mechanism.

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Reference and links


1. Introduction

In recent years, a lot of researches have been devoted to the optoelectronic properties of SiN$_x$ film due to its potential application as a candidate of Si-based light sources [1–7]. Although the fabrication of SiN$_x$-based light-emitting devices (LEDs) and their electroluminescence (EL) have been achieved by several groups [4–9], with the external quantum efficiency of $10^{-2}$–$10^{-4}$% [4,8,9], the origin of their EL was not actually clear.

Generally, the EL of SiN$_x$ films ranging from ~1.6 to 3.1 eV was attributed to the recombination between the defect states in SiN$_x$ [4,5,10]. However, there’s no further systematic discussion on the detailed defect energy levels of SiN$_x$ film for the origin of its EL. Besides, the increase of injected current could not only enhance the intensity of EL, but also induce the blue-shift of EL peaks from SiN$_x$-based LED [4–6,8,11]. Nevertheless, there’s a lack of interpretation on this blue-shift with the increase of applied voltage/injected current [4,5,8,11]. The only speculation was that holes in SiN$_x$ might gain higher energy under a higher voltage, which resulted in higher energy photons [4]. However, this explanation might not be sufficient as there were two Gauss peaks at least in SiN$_x$-based LED actually due to the asymmetry of the EL spectra observed in those works [4–6,8,11–13]. Cen et al. observed these two distinct EL peaks by implanting Si ions into Si$_3$N$_4$ films following a high temperature annealing (1100 °C) for 1 h to recover the implantation damages [6,12,13]. The blue-shift of EL peaks by increasing the injected current from their devices is originated from the modulation of the relative intensity of these two peaks [6]. No shifts of these two EL peaks that observed in other groups were obtained from their devices [12], which may result from its preferable carrier injection level. Obviously, without post treatment to improve its EL performance, the blue-shift of EL peaks might not be obvious in SiN$_x$ film due to its poor carrier injection level and stability [4,5,14]. Metal nanoparticles or island film was commonly used to enhance the carrier injection and improve the stability of EL performance of SiN$_x$-based LED [11,14], which would facilitate the observation of this blue-shift phenomenon.

In this work, Ag island film deposited on the SiN$_x$ luminous layer was employed to improve the EL performance of SiN$_x$-based LED for the facilitation of observing the changes of EL peaks position. SiN$_x$-based LED without the addition of Ag island film was also fabricated for comparison. The origin of EL peaks and the blue-shift of them with the increase of injected current are interpreted tentatively. The band diagram is also provided on the basis of...
predecessors’ researches and our works. Our work may provide a deep comprehension on the origin of EL from SiN_x-based LED as well as an alternative approach of tuning its EL wavelength.

2. Experimental

SiN_x film of ~50 nm was deposited onto the p/p^+ -Si(100) substrate by plasma enhanced chemical vapor deposition technical. N_2-diluted 10% SiH_4 and NH_3 were used as the reactant gas sources, where the flow rate ratio of them, the r.f. power density, deposition pressure, and substrate temperature were maintained at 10:1, ~1 kW/m^2, 0.1 Torr, and 400 °C, respectively. Ag island film with the average radii of ~50 nm was embedded between the ITO top electrode and SiN_x matrix for improving the luminescence performance of our devices. This island film deposited by magnetron sputtering was formed via a rapid thermal annealing process (500 °C, 60 s in Ar atmosphere). The detailed fabrication of SiN_x-based LEDs with and without Ag island film has been described in our previous paper [14].

The EL signals of SiN_x-based LEDs were recorded by an Acton SpectraPro-2500i monochromator coupled to a photomultiplier tube (PMT) at room temperature. A Keithley 4200 SCS semiconductor parameter analyzer was used for the measurement of current-voltage (I-V) characteristics of our devices.

3. Results and discussion

Fig. 1. EL spectra of the SiN_x-based LEDs with and without Ag island film deposited onto the luminous layer, injected by different currents.

In Fig. 1, the EL spectra of SiN_x-based LEDs with and without Ag island film under different injected currents are presented. Two obvious peaks are observed for the device with Ag island film, as shown in Fig. 1(b). We label the peak with shorter wavelength as P1, while the one with longer wavelength as P2. However there is only one peak (labeled as PR) observed clearly in our reference device, as shown in Fig. 1(a), which may result from its poor electron injection as the barrier of electrons on ITO side (3.0 eV) is much higher than that of holes on p-Si side (1.9 eV) [4]. Furthermore, a blue-shift of about 0.10 eV (from 2.04 to 2.14 eV) is observed in the...
device without Ag island film, as shown in Fig. 2(a). This amount of blue-shift is a little smaller than that of P1 (from 2.23 to 2.45 eV) and P2 (from 1.81 to 1.94 eV), as shown in Fig. 2(b) (left). The smaller amount of blue-shift for PR may result from its higher turn-on voltage as well as higher injected current for the measurement of its initial EL signal, as shown in Figs. 2(a) and 2(b). By comparing the integrated area of P1 and P2, \(I_{P1}/I_{P2}\), we can get that P1 is dominated at a lower injected current, while they are almost equivalent at a higher injected current, as shown in Fig. 2(b) (right). It stabilizes at about 1.0 with the increase of injected current, eventually.

Furthermore, the full width at half maximum (FWHM) of PR and P1 is much larger than that of P2, as shown in Fig. 2(c). The FWHM of P1 decreases gradually with the blue-shift of its EL peak, while that of P2 is completely opposite.

An approximate relationship of \(\Delta \lambda \approx \lambda^2 \Delta E_p / hc\) can be obtained by simply differentiating \(\lambda\) with respect to the photo energy \(E_p\) in the Eq. of \(\lambda = c/\nu = hc/E_p\) and representing small intervals (\(\Delta\)) by differentials. A linear relationship between FWHM (\(\Delta \lambda\)) and the square of the central wavelength (\(\lambda^2\)) is obtained for P1 and P2, as shown in Fig. 2(d). The decrease of the FWHM for P1 with the blue-shift of its EL peak can be explained by this reason. For P2, the opposite phenomenon may result from its improved carrier injection due to the significantly enhanced local electromagnetic field surrounding Ag particles [11,14–16], as more carriers can be injected into a higher energy level.

Fig. 2. (a) The dependence of EL peak (PR) position on the injected current for the SiN\(_x\)-based LED without Ag island film. (b) The dependence of EL peak positions (left) and \(I_{P1}/I_{P2}\) (right) on the injected current for the SiN\(_x\)-based LED with Ag island film, where \(I_{P1}\) and \(I_{P2}\) stand for the integrated area of the Gauss peak1 (P1) and peak2 (P2), respectively. (c) The dependence of full width at half maximum (FWHM) of EL peaks on the injected current for SiN\(_x\)-based LEDs with and without Ag island film. (d) Plots of \(\Delta \lambda\) vs. \(\lambda^2\) accompanied with its linear fittings.
In order to study the origin of these two EL peaks, $J$-$V$ characteristic for the device with Ag island film was carried out, as shown in Fig. 3(a). The structure we investigated here is shown in the inset. The threshold voltage ($V_{th}$) of the device with Ag island film is around 2.3 V, which is much lower than that of the device with only a single SiN$_x$ layer ~5.5 V [14]. This voltage is also a little lower than the electron barrier on ITO side (~3.0 eV) [4,17] for the device investigated here due to the significantly enhanced local electromagnetic field surrounding Ag particles [11,14–16]. This enhancement of the local electromagnetic field can improve the carrier injection or/and shorten the transport path of localized carriers. Consequently, we speculate that the carrier injection under low injected current may result from thermal emission. Hence, we fit the $J$-$V$ curve by Poole-Frenkel (P-F) model for which the carrier injection is thermally activated [18], as shown in Fig. 3(b), like being commonly used in SiN$_x$ matrix [4,19].

The P-F equation is given by:

$$J_{PF} = C E \exp\left(-q \left(\phi_B - \left(\frac{1}{N_{\epsilon_r} \epsilon_0}\right)^{1/2}\right) / kT\right)$$

(1)

where $J_{PF}$, $E$, $\phi_B$, $\epsilon_r$, and $\epsilon_0$ stand for the injected current density, the electric field applied on the active layer, the barrier for P-F emission, relative permittivity, and vacuum permittivity, respectively [20]. The value of $\epsilon_r$ can be extracted from the linear fitting of $\ln(J/E)$ vs. $E^{1/2}$. Good agreement is achieved by this P-F conduction mechanism under lower voltages (roughly to 1.7-3.5 V) with the fitting $\epsilon_r$ around 10.9, which is consistent with the value for SiN$_x$ films (between the relative permittivity of a-Si ~11.7 and Si$_3$N$_4$ ~7.5) [21]. Obviously, the value of threshold voltage $V_{th}$ is in the range of these fitting voltages, which confirms the speculation on the origin of carrier injection under a lower injected current. Therefore, we conclude that the EL of SiN$_x$-based LEDs under low current resulted from the recombination of electrons and holes injected by thermal emission from ITO electrode and $p$-type Si substrate, respectively. With the increase of voltage further, the $J$-$V$ curve is deviated from this P-F mechanism for the inconsistent of fitting $\epsilon_r$.

Usually, the carrier transport in SiN$_x$ matrix at high electrical fields is dominated by Fowler-Nordheim (F-N) tunneling mechanism [13], where $\ln(J/E)$ is proportional to $1/E$. The potential barrier height $\phi_{Si/SiN}$ between the Si substrate and SiN$_x$ matrix can be extracted from
the linear fitting of $\ln(J/E^2)$ vs. $1/E$ under a higher voltage. We exclude this mechanism for the carrier transport under a higher voltage due to its extremely small fitting value of this $\phi_{\text{SiN}}$ ($<0.1$ eV). To determine the carrier injection mechanism under higher voltages for our SiN$_x$-based LEDs, we transform the $J$-$V$ curve to the form of $\ln J$ vs. $\ln E$ for its distinct representation of power law ($J \propto E^n$) [10,18,22], as shown in Fig. 3(c). By the linear fitting of power law (P-L), we get the fitting parameter $n \approx 4.5$ for lower applied voltages (1.1-3.2 V) and $n \approx 2.0$ for higher applied voltages (6.0-11.0 V). From the discussion above, we attribute the carrier injection under low voltage to thermal emission as been confirmed by the fitting of P-F mechanism. While for the region with higher applied voltages (6.0-11.0 V), the conduction mechanism can be attributed to space charge limited conduction (SCLC) dominated by carrier transport between discrete trapping levels as the fitting index $n \approx 2.0$ [18,23]. The SCLC Eq. is given by [23]:

$$J = 9\varepsilon_i\varepsilon_0\mu E^2 / 8d$$  (2)

where $\mu$ and $d$ are the carrier drift mobility and the thickness of the active layer, respectively. Hence, we can extract the value of $\mu \approx 4 \times 10^{-8}$ cm$^2$/V*s for our SiN$_x$-based LEDs from the intercept of linear fitting of P-L relationship, as shown in Fig. 3(c). This value of $\mu$ is almost two orders of magnitude lower than that for SiN$_x$ films measured by T. Güngör et al. [24], which we attribute to a higher N content in the SiN$_x$ films by comparing the values of the optical band gap of SiN$_x$ films investigated in Ref. 24 with those of ours [14]. Besides, there are more dangling bonds in our SiN$_x$ films than those in Ref. 24 due to the high temperature annealing as H will be released during this process. More interfacial states produced by these dangling bonds will lower the carrier drift mobility further as carriers will be trapped or scattered [25]. Consequently, we conclude that the electrons (holes) can be injected into higher levels with the increase of applied voltages by the hopping along the valence (conduction) band tails. Meanwhile, we attribute the gradual blue-shift of EL peaks with the enhancement of injection current to the recombination of electrons and holes with higher energy, which result from the deeper injection of carriers into the band tails.

Besides, from the linear fitting shown in Fig. 3(c), the value of $V_{\text{TFL}}$, where the injected current increases significantly for our SiN$_x$-based LEDs with Ag island films is obtained at ~4.2 V [18]. Subsequently, the value of the state density $N_i$ for the trapped carriers can be extracted from the expression as follow [18]:

$$N_i = 2\varepsilon_i\varepsilon_0V_{\text{TFL}} / (qd^2)$$  (3)

Employing the values of $\varepsilon_i$ and $V_{\text{TFL}}$ obtained from the fittings shown above, we get that the density $N_i$ is on the order of $10^{10}$ cm$^{-2}$ magnitude, which corresponds to the defect tail level 0.9-1.1 eV above the valence band of SiN$_x$ as can be deduced from Ref. 26. This level, corresponding to the tail state composed by N dangling bands (= N), just lies 2.4-2.6 eV underneath the K center (=Si) [26], which is consistent with the cut-off wavelength for P1, as shown in Fig. 2(b). Meanwhile, the initial energy of EL peak1 (P1) is about 2.2 eV, which is consistent with the width between the K center and the center of = N (located at 1.6 eV above the valence band of SiN$_x$) [26]. Thus, the EL for P1 is originated from the recombination of the electrons confined in the K center and the holes located at the band tail formed by = N', which can also be observed in references 3 and 5.

The changes on the energy of EL peak2 (P2) are also checked, which have the starting and ending values at ~1.8 and 1.9 eV, respectively. This energy range corresponded to the recombination of the electrons lay on the conduction band tail and the holes localized in the center of =Si$^0$ [26]. And the energy interval for P2 ~0.1 eV is a reasonable value for the width of conduction band tail. Consequently, the longer wavelength of EL may result from the
recombination of electrons and holes located at the conduction band tail and the center of $\equiv \text{Si}^0$, respectively.

![Band diagram of the SiN$_x$-based LED under forward bias.](image)

Based on the previous fundamental researches on the luminescence mechanisms and the properties for SiN$_x$-based LEDs [4,26] as well as the detailed discussions above, the band gap structure and carriers recombination schematic of the device is drawn in Fig. 4. Among the defect levels in SiN$_x$, $\equiv \text{Si}^-$ and $\equiv \text{Si}^0$ were considered as the electrons and holes trapped levels, respectively, with 80% of carriers localized on its corresponding central site [26]. While for carriers on the band tails, this confinement was not so strictly due to the larger distribution widths of state density [26]. As discussed above, electrons can be injected from ITO electrode to the conduction band tail and $\equiv \text{Si}^-$ center, while for holes from $p$-Si substrate to $=\text{N}^-$ and the center of $\equiv \text{Si}^0$, through thermal emission under lower voltages. Electrons (holes) would prefer to being injected into the center of $\equiv \text{Si}^-$ ($\equiv \text{Si}^0$) for its lower energy, which lead to the weak intensity of EL under low injected current due to the lower carrier injection onto its corresponding band tails. As the holes injection barrier is much lower than that for electrons, the integrated EL intensity for shorter wavelength ($I_{P1}$) is much higher than that for the longer one ($I_{P2}$) shown in Fig. 2b (right). It also explains the reason of the only one obvious EL peak (P1 or PR) for the device without Ag island films. The larger FWHM shown in Fig. 2(c) results from its larger width of valence-band tail composed by N dangling bands ($=\text{N}$) and Si-Si bonding states (Si-Si), both of which are recognized as the hole trapped levels [25]. For higher applied voltages, the injection by thermal emission becomes saturated and the SCLC dominated, subsequently. More carriers can be transported onto the higher energy levels of band tails with the increase of the injected current, which lead to the enhancement in EL intensities and the blue-shift of EL peaks, as shown in Fig. 1(a), Figs. 2(a) and 2(b) (left). For the structure with Ag island films on SiN$_x$, the injection of electrons from ITO side can be improved by the addition of Ag island films due to the significantly enhanced local electromagnetic field surrounding Ag particles [11,14–16]. Meanwhile, holes injected from $p$-Si substrate have more freedoms on its corresponding valence-band tails than electrons due to the larger width of valence-band tails [26]. It decreases the relative number of holes contributed to radiative recombination for central wavelength. Consequently, the integrated EL intensities with longer wavelength ($I_{P2}$) is comparable with that of P1 at higher voltages as well as the broadening of P2 with its blue-shift, as shown in Fig. 2(b) (right) and Fig. 2(c).
4. Conclusion

In conclusion, two Gauss peaks (P1 and P2) together with their blue-shift have been observed in our SiN$_x$-based LED with Ag island films. The peak with shorter wavelength ranging from ~2.2-2.5 eV is originated from the recombination of the electrons confined at the K center and the holes located at the band tail formed by = N'. While, we attribute the one with longer wavelength (~1.8-1.9 eV) to the recombination of the electrons located at conduction band tail and the holes confined in the center of =SiO. Electrons (holes) are injected by thermal emission from ITO electrode (p-type Si substrate) under lower applied voltages dominated by P-F conduction mechanism. While for higher applied voltages, electrons and holes are transported along their corresponding band tails which is confirmed by the SCLC model. The blue-shift of EL peaks in our SiN$_x$-based LEDs results from the enhancement of carrier injection that electrons (holes) can be injected into a higher level of the conduction (valence) band tails. Our work provides a deep comprehension on the origin of the EL of SiN$_x$-based LEDs. The tailoring of EL wavelength of SiN$_x$-based LEDs can be achieved by the modulation of the density of defect tails state.

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