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Strong violet and green-yellow electroluminescence from silicon nitride thin films multiply implanted with Si ions

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Strong visible electroluminescence (EL) has been observed from a 30 nm silicon nitride thin film multiply implanted with Si ions and annealed at 1100 °C. The EL intensity shows a linear relationship with the current transport in the thin film at lower voltages, but a departure from the linear relationship with a quenching in the EL intensity is observed at higher voltages. The EL spectra show two primary EL bands including the predominant violet band at ~ 3.0 eV (415 nm) and the strong green-yellow band at ~ 2.2 eV (560 nm). Two weak bands including the ultraviolet band at ~ 3.8 eV and the near infrared band at ~ 1.45 eV emerge at high voltages. The evolution of each EL band with the voltage has been examined. The phenomena observed are explained, and the EL mechanisms are discussed. © 2009 American Institute of Physics.

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Enormous efforts have been devoted to the research for efficient Si-based light source to realize monolithic Si optoelectronic integrated circuit since the observation of strong room-temperature photoluminescence (PL) from porous Si.^{1–10} Electroluminescence (EL) has been observed from the Si-rich oxide systems.^{3,4} However, low carrier injection due to the large band discontinuity between Si and silicon oxide constrains their applications in light-emitting devices (LEDs).^{5,6} Furthermore, it is reported in theories and experiments that the luminescence produced by Si nanostructures saturates with decreasing size in the presence of oxygen.⁷ Si-rich nitride (SRN) materials that have a lower band discontinuity compared with silicon oxide have become an alternative for efficient Si-based LEDs. PL tunable from red to violet has been observed from the SRN systems,⁸ and visible EL has been obtained from the LED structures with the SRN materials.^{6,9,10} To date, the technique commonly used to synthesize the luminescent SRN materials is chemical vapor deposition (CVD).^{6,8–10} Si ion implantation is one of the techniques that can introduce excess Si ions into the silicon nitride matrix. However, the reports on the light emissions from Si-implanted silicon nitride are rare. In this work, strong EL was observed from the silicon nitride thin films multiply implanted with Si ions and annealed at 1100 °C. The observed EL spectra consist of a main violet band, a strong green-yellow band, and two other minor bands. The change in the EL with the applied gate voltage has been studied.

A silicon nitride thin film with the thickness of 30 nm was deposited on a *p*-type Si (100) wafer by the low-pressure CVD technique. In order to enhance the injection current and improve the LED performance, a close-to-uniform distribu-

tion of the implanted Si ions in the nitride thin film was achieved by multiple implantations. The following Si ion implantations were carried out: the first implantation at the energy of 25 keV with the dose of 4×10^{16} atoms/cm², the second implantation at 8 keV with the dose of 8×10^{15} atoms/cm², and the third implantation at 2 keV with the dose of 3×10^{15} atoms/cm². Figure 1 shows the overall depth distribution of the implanted Si ions in the nitride thin film obtained from the stopping and range of ions in matter (SRIM) simulation.¹¹ After the Si implantations, thermal annealing was conducted in nitrogen ambient at 1100 °C for 1 h to precipitate the implanted Si ions and to eliminate the damages of the silicon nitride matrix caused by the ion implantations.² To fabricate the LED structure, a 200 nm thick Al layer was deposited onto the back side of the Si substrate to form the Ohmic contact. A circular transparent gate electrode with the diameter of 1.2 mm was formed by depositing an indium tin oxide (ITO) film of 100 nm with the sputtering technique. A schematic cross section of the LED

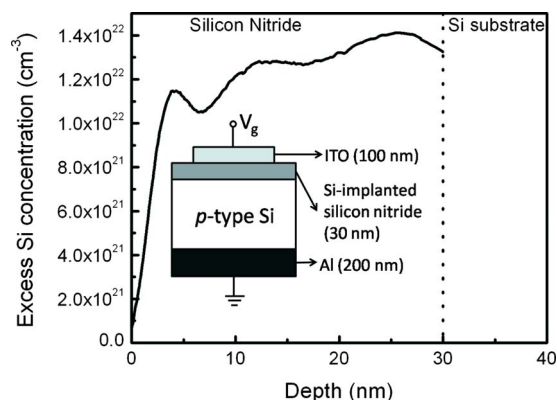


FIG. 1. (Color online) Distribution of the implanted Si ions in the silicon nitride thin film obtained from the SRIM simulation. The inset shows a schematic cross section of the EL device structure.

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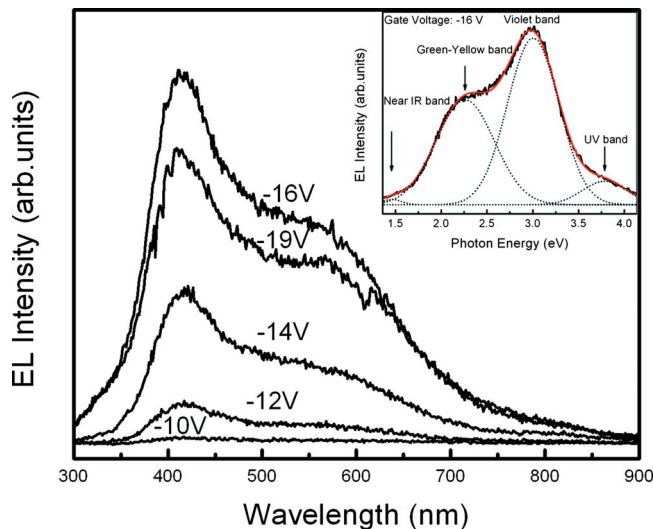


FIG. 2. (Color online) EL spectra measured at different gate voltages. The inset shows the deconvolution of the EL spectrum measured at the gate voltage of -16 V.

structure is presented in the inset of Fig. 1. The EL spectra were measured by a PDS-1 photomultiplier tube detector together with a monochromator. Figure 2 shows the EL spectra measured at various gate biases.

The current conduction of the silicon nitride thin film is greatly enhanced by the multiple Si ion implantations. The current-voltage (I - V) characteristic of the LED is shown in Fig. 3. As can be observed in Fig. 3, the current transport in the Si^+ -implanted nitride film follows a power law,¹²

$$I = \alpha_0(V - V_T)^\zeta, \quad (1)$$

where I is the current, V is the applied voltage, V_T is the global threshold voltage, α_0 is a coefficient, and ζ is the scaling exponent. The fitting to experimental data yielded a ζ value of 2.06, suggesting that the current conduction is close to two-dimensional transport.¹² The power-law behavior indicates that the enhancement in current conduction can be explained in terms of the formation of percolation tunneling paths by the excess Si atoms distributed in the nitride matrix.¹³

The evolution of the integrated EL intensity as a function of the gate voltage is also shown in Fig. 3. There is no light emission under a positive gate voltage due to insufficient hole injection from the gate. EL is observed under a negative

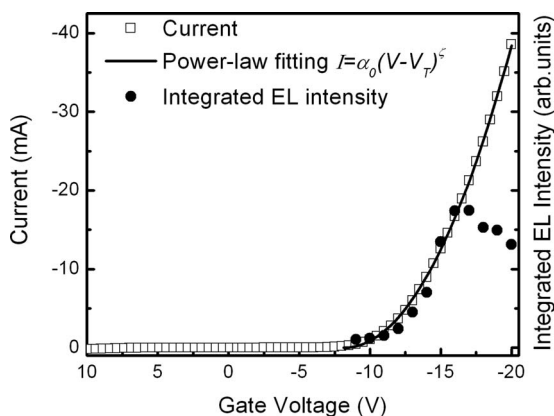


FIG. 3. Gate current and integrated EL intensity as functions of the gate voltage. The power-law fitting yields $\zeta = 2.06$, $\alpha_0 = 0.23 \text{ mA V}^{-\zeta}$, and $V_T = -8.1 \text{ V}$.

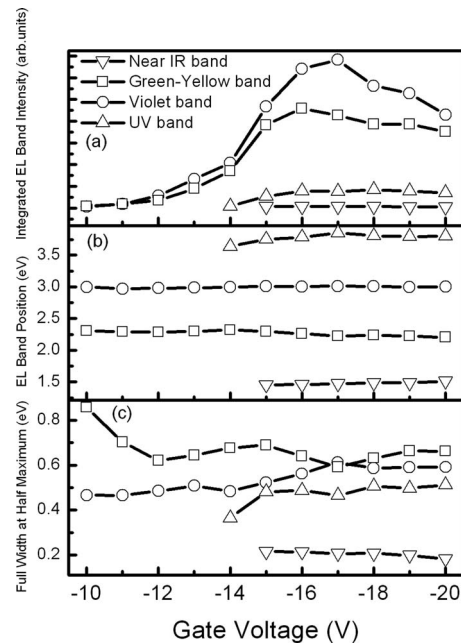


FIG. 4. Evolution of each EL band with the applied voltage: (a) integrated intensity, (b) peak position, and (c) FWHM.

gate voltage with the voltage magnitude larger than about 10 V. As shown in Fig. 3, there is a linear relationship between the integrated EL intensity and the injection current in the voltage range from -10 to -16 V, implying that the EL originated from the recombination of the electrons and holes injected from the ITO gate and the Si substrate, respectively. When the magnitude of the gate voltage is larger than ~ 16 V, the integrated EL intensity departs from the linear relationship, and it quenches and decreases gradually as the voltage magnitude further increases. It has been found in our experiment that such an EL quenching is strongly related to the charging effect, which reduces both the electron injection from the ITO gate and the hole injection from the p -Si substrate.¹⁴ Moreover, the high electric field in the silicon nitride film, which is estimated to be $\sim 6 \text{ MV/cm}$ for the gate voltages in the range from -17 to -20 V, has been shown to have an impact on the radiative lifetime of Si nanostructures and could lead to a quenching of the radiative recombination.¹⁵ In addition, nonradiative Auger recombination that plays an important role in the case of high-level carrier injection dominates the recombination process when multiple carriers are present in the same nanostructures.¹⁶ These mechanisms could explain the observed reduction in the integrated EL intensity at a large gate voltage.

As shown in the inset of Fig. 2, the EL spectra can be deconvoluted into two primary Gaussian-shaped EL bands, i.e., the violet EL band ($\sim 3.0 \text{ eV}$ or 415 nm) and the green-yellow EL band ($\sim 2.2 \text{ eV}$ or 560 nm). When the magnitude of the voltage is larger than 15 V, an ultraviolet (UV) band ($\sim 3.8 \text{ eV}$ or 327 nm) and a near infrared (IR) band ($\sim 1.45 \text{ eV}$ or 850 nm) emerge, although their contributions to the total EL intensity are much smaller compared to the two main EL bands. The evolutions of the integrated intensity of each EL band with the negative gate voltage are presented in Fig. 4(a). Figure 4(b) shows the peak positions for all the EL bands as a function of the gate voltage, and the corresponding full width at half maximum (FWHM) of each peak is shown in Fig. 4(c).

As can be seen in Fig. 4(a), the violet and green-yellow bands together contribute up to $\sim 90\%$ of the total EL intensity. When the voltage magnitude is larger than ~ 16 V, the intensity of the two EL bands (in particular, the violet band) decreases with the voltage magnitude, while the intensity of the UV band and the near-IR band becomes saturated. Obviously, the reductions in the intensity of the violet and green-yellow bands are responsible for the quenching of the total EL intensity at high voltages discussed earlier.

As shown in Fig. 4(b), the violet EL band (~ 3.0 eV), which is the dominant band in the EL spectra, is independent of the gate voltage, but its FWHM increases from 0.46 eV with the bias and becomes saturated at 0.59 eV at the large voltages. Such a strong violet EL band at 3.0 eV, which can be observed from the Ge-implanted SiO_2 layer,¹⁷ was seldom reported for silicon nitride based materials, although violet PL has been obtained from Si nanostructures in silicon nitride films.^{8,18} We have also observed PL with energies close to this violet EL band from thick Si-implanted silicon nitride films. One of the mechanisms usually used to explain the short wavelength light emission from silicon nitride films is the radiative recombination through the defect states within the silicon nitride bandgap.^{19,20} The defect-related mechanism should particularly play an important role in the present study, as various point defects could be introduced into the dielectric matrix during the Si implantation.²¹ This can explain the difference in light emission between the SRN materials fabricated by ion implantation and those by CVD. The emission at 3.0 eV could be attributed to the electronic transition of the defect states $\text{Si}^0 \rightarrow E_v$, which has been calculated in theory and testified by experiments in materials related to silicon nitride.^{19,20}

Being different from the violet EL band, the green-yellow EL band, one of the two primary bands, shifts slightly from 2.3 to 2.2 eV as the gate voltage is increased from -10 up to -20 V. Its FWHM decreases with the voltage in general, but is stabilized at around 0.66 eV at the high voltages. The green-yellow EL has been observed from the SRN materials by other groups.^{6,9} Band tail radiative recombination has been exploited to account for the emission of the green-yellow band;²² nevertheless the radiative recombination assisted by defect states could be the origin too.^{9,20}

The two minor EL bands, i.e., the UV band and the near-IR band, emerge at high voltages. One possible mechanism responsible for the UV band peaked at ~ 3.8 eV is explained in the following. As compared with the stoichiometric silicon nitride, SRN has been revealed to have a larger trap density of shallow energy level, which is ~ 1.1 eV below the silicon nitride conduction band minimum.²³ A significant amount of electrons can be captured by these shallow traps during the electron injection from the ITO gate under a high voltage. The radiative recombination between the electrons captured by the shallow traps and the holes in the valence band of silicon nitride injected from the p -type Si substrate produces an UV emission with the energy of ~ 3.8 eV. It is interesting to note that PL near the UV region has been observed from SRN films also.²⁴ On the other hand, at a high voltage, significant electron or hole injection into the conduction or valence bands of the Si nanocrystals embedded in the silicon nitride matrix, respectively, could also occur. The radiative recombination of the injected electrons and holes via the nanocrystal can produce EL in the near-IR

range. This mechanism could explain the near-IR band observed in this study. If this is the case, the near-IR band indicates that the bandgap of the Si nanocrystal is about 1.5 eV. The Si nanocrystal exhibits a bandgap expansion as compared to bulk crystalline Si, which is frequently explained by the quantum confinement effect.²⁵

In summary, luminescent silicon nitride thin films with nearly uniform distribution of excess Si are fabricated by Si implantation into silicon nitride and annealing at 1100°C in this study. Strong visible EL has been observed from the LED structures based on the Si-implanted silicon nitride thin films under negative bias with the turn on voltage of -10 V. The deconvolution of the EL spectra shows that there are two primary EL bands including the predominant violet EL band at ~ 3.0 eV and the strong green-yellow EL band at around 2.2 eV. At high gate voltages, two additional weak EL bands including the UV band at ~ 3.8 eV and the near-IR band at ~ 1.45 eV emerge.

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¹L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).

²Z. H. Cen, T. P. Chen, L. Ding, Y. Liu, M. Yang, J. I. Wong, Z. Liu, Y. C. Liu, and S. Fung, *Appl. Phys. Lett.* **93**, 023122 (2008).

³L. Ding, T. P. Chen, Y. Liu, M. Yang, J. I. Wong, K. Y. Liu, F. R. Zhu, and S. Fung, *Nanotechnology* **18**, 455306 (2007).

⁴G.-R. Lin, C.-J. Lin, C.-K. Lin, L.-J. Chou, and Y.-L. Chueh, *J. Appl. Phys.* **97**, 094306 (2005).

⁵L. Rebohle, J. Von Borany, H. Fröb, and W. Skorupa, *Appl. Phys. B: Lasers Opt.* **71**, 131 (2000).

⁶R. Huang, H. P. Dong, D. Q. Wang, K. J. Chen, H. L. Ding, X. Wang, W. Li, J. Xu, and Z. Y. Ma, *Appl. Phys. Lett.* **92**, 181106 (2008).

⁷M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, *Phys. Rev. Lett.* **82**, 197 (1999).

⁸N.-M. Park, T.-S. Kim, and S.-J. Park, *Appl. Phys. Lett.* **78**, 2575 (2001).

⁹Z. Pei, Y. R. Chang, and H. L. Hwang, *Appl. Phys. Lett.* **80**, 2839 (2002).

¹⁰L.-Y. Chen, W.-H. Chen, and F. C.-N. Hong, *Appl. Phys. Lett.* **86**, 193506 (2005).

¹¹J. F. Ziegler, J. P. Biersach, and U. Littmark, *SRIM* (Pergamon, New York, 2006) (available from www.srim.org).

¹²H. E. Romero and M. Drndic, *Phys. Rev. Lett.* **95**, 156801 (2005).

¹³Y. Liu, T. P. Chen, H. W. Lau, J. I. Wong, L. Ding, S. Zhang, and S. Fung, *Appl. Phys. Lett.* **89**, 123101 (2006).

¹⁴Y. Liu, T. P. Chen, L. Ding, M. Yang, J. I. Wong, C. Y. Ng, S. F. Yu, Z. X. Li, C. Yuen, F. R. Zhu, M. C. Tan, and S. Fung, *J. Appl. Phys.* **101**, 104306 (2007).

¹⁵P. Photopoulos and A. G. Nassiopoulou, *Appl. Phys. Lett.* **77**, 1816 (2000).

¹⁶C. Delerue, M. Lannoo, G. Allan, E. Martin, I. Mihalcescu, J. C. Vial, R. Romestain, F. Muller, and A. Biesy, *Phys. Rev. Lett.* **75**, 2228 (1995).

¹⁷L. Rebohle, J. V. Borany, R. A. Yankov, W. Skorupa, I. E. Tyschenko, H. Fröb, and K. Leo, *Appl. Phys. Lett.* **71**, 2809 (1997).

¹⁸L. B. Ma, R. Song, Y. M. Miao, C. R. Li, Y. Q. Wang, and Z. X. Cao, *Appl. Phys. Lett.* **88**, 093102 (2006).

¹⁹J. Robertson and M. J. Powell, *Appl. Phys. Lett.* **44**, 415 (1984).

²⁰C. M. Mo, L. Zhang, C. Xie, and T. Wang, *J. Appl. Phys.* **73**, 5185 (1993).

²¹H. Z. Song and X. M. Bao, *Phys. Rev. B* **55**, 6988 (1997).

²²H. L. Hao, L. K. Wu, W. Z. Shen, and F. W. Dekkers, *Appl. Phys. Lett.* **91**, 201922 (2007).

²³T. H. Kim, I. H. Park, J. D. Lee, H. C. Shin, and B.-G. Park, *Appl. Phys. Lett.* **89**, 063508 (2006).

²⁴V. A. Gritsenko, K. S. Zhuravlev, A. D. Milov, H. Wong, R. W. M. Kwok, and J. B. Xu, *Thin Solid Films* **353**, 20 (1999).

²⁵L. Ding, T. P. Chen, Y. Liu, C. Y. Ng, and S. Fung, *Phys. Rev. B* **72**, 125419 (2005).