CO₂ laser rapid-thermal-annealing SiO_x based metal-oxide-semiconductor light emitting diode

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(Received 18 April 2007; accepted 19 July 2007; published online 16 August 2007)

Structural damage enhanced near-infrared electroluminescence (EL) of a metal-oxide-semiconductor light emitting diode (MOSLED) made on SiO_x film with buried nanocrystalline Si after CO₂ laser rapid thermal annealing (RTA) at an optimized intensity of 6 kW/cm² for 1 ms is demonstrated. CO₂ laser RTA induced oxygen-related defects are capable of improving Fowler-Nordheim tunneling mechanism of carriers at metal/SiO_x interface. The CO₂ laser RTA SiO_x film reduces Fowler-Nordheim tunneling threshold to 1.8 MV/cm, facilitating an enhanced EL power of an indium tin oxide/SiO_x/p-Si/Al MOSLED up to 50 nW at a current density of 2.3 mA/cm². © 2007 American Institute of Physics. [DOI: 10.1063/1.2769962]

Typically, the synthesis of Si nanocrystals (nc-Si) embedded in plasma-enhanced chemical-vapor deposition (PECVD)-grown silicon rich silicon dioxide (SiO_x, $x < 2$) film for efficient light emission requires a long-term and high-temperature furnace-annealing process (longer than 30 min).^{1–7} This approach meets the difficulty in its compatibility with current integrated-circuits processing limit at temperature < 600 °C. Furthermore, conventional annealing methods are not possible to *in situ* anneal a prescribed area on the SiO_x film with micron scale. In our previous research, the premier demonstration on synthesizing nc-Si in the SiO_x film by CO₂ laser rapid thermal annealing (RTA) process has been reported to overcome the aforementioned problems.^{8,9} Later on, Tewary *et al.*¹⁰ have also demonstrated the locally synthesize light emitting defects and Si nanoparticles in silicon rich oxynitride thin films by using a focused CO₂ laser beam with power densities in the range from 0 to 580 W/cm² and times of 5 s–60 min. Nonetheless, the CO₂ laser annealing SiO_x based light emitting diode has yet not been realized. In this work, we present the fabrication and the structural/electrical/optical characterization of a metal-oxide-semiconductor light emitting diode (MOSLED), whose oxide layer is the nc-Si embedded SiO_x film fabricated using a CO₂ laser RTA process. The carrier-transport mechanisms and the electroluminescent (EL) properties of such devices are explored in detail.

PECVD-grown SiO_x film was deposited on the *p*-type (100) Si substrate with a gas mixture of SiH₄ and N₂O. The process temperature, fluence ratio of SiH₄ to N₂O, the rf power, and the reaction gas pressure were 350 °C, 1:6, 40 W, and 60 mtorr, respectively. The thickness of PECVD-grown SiO_x film was 280 ± 10 nm measured by a surface profiler (KLA-Tencor, Alpha-Step 500). Afterward, the CO₂ laser RTA was performed in atmosphere using a continuous-wave CO₂ laser with ranging from 1.5 to 13.5 kW/cm². The laser spot was focused within 0.2 mm using a hemispherical lens. The CO₂ laser illuminating time was as short as 1 ms. The photoluminescence (PL) of CO₂ laser RTA SiO_x pumped by a HeCd laser at 5 W/cm² and 325 nm was detected by a

fluorescence spectrophotometer (Jobin Yvon, TRIAX-320). Indium tin oxide (ITO) and aluminum (Al) films with thicknesses of 200 and 500 nm were used as surface contact and backside contact, respectively. An ITO/SiO_{1.25}:nc-Si/*p*-Si/Al MOSLED with a contact diameter of 0.8 mm was made to perform EL. Rutherford backscattering spectroscopy (RBS) analysis at a detecting angle of 170° under 2 MeV He⁺-ion bombardment and a commercial software of “RAMP” reveals clear Si and O signals at energies of 1.147 MeV and 742.0 keV, respectively. The calculated O/Si ratio of 1.25 corresponds to a total Si concentration of 44.44 at. %.

During CO₂ laser annealing, the temperature $T(r, z)$ of the annealed SiO_{1.25} film is expressed by the following equation:¹¹

$$T(r, z) = \frac{4(1-R)}{\rho C_p} \frac{P_{\text{laser}} \tau}{\pi D^2 d_{\text{absorb}}} \exp\left(\frac{-4r^2}{D^2}\right) \exp(-\alpha|z|), \quad (1)$$

where r , z , τ , ρ , and C_p are the radial distance, the depth, the illuminating time, the density, and the specific heat of the SiO_x film, respectively.⁸ After CO₂ laser annealing at laser intensity (P_{laser}) of 6 kW/cm² and furnace annealing at 1100 °C for 30 min, broadband near-infrared PL spectra with peak wavelengths of 810 and 760 nm as well as spectral linewidths of 106 and 135 nm are observed [see Figs. 1(a) and 1(b)], respectively, which are attributed to the emission of nc-Si embedded in SiO_{1.25}. The estimated surface temperature of the SiO_{1.25} film at P_{laser} of 6 kW/cm² was about 1350 °C.⁹ The average size of nc-Si buried in CO₂ laser annealed SiO_{1.25} is larger than that of furnace-annealed SiO_{1.25}, which contributes the decreasing band gap of nc-Si and the redshift of PL peak wavelength from 760 to 810 nm.¹² The existence and the size distribution of nc-Si embedded in SiO_{1.25} film annealed at P_{laser} of 6 kW/cm² are confirmed by cross-sectional high resolution transmission electron microscopy (HRTEM) images. HRTEM images reveal that the average diameter of nc-Si is about 5.3 nm. The volume density of nc-Si buried in CO₂ laser annealed SiO_{1.25} film is around 1.9×10^{18} cm⁻³. Another significant PL at 400–650 nm from the CO₂ laser-annealed sample is attributed to incomplete Si precipitation and slight damage of oxide matrix under CO₂ laser annealing

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FIG. 1. (Color online) PL spectra of CO₂ laser annealed SiO_x at (a) 6 kW/cm², (b) furnace annealing at 1100 °C for 30 min, and CO₂ laser annealed SiO_x at (c) 12 kW/cm².

within 1 ms.^{2,3} Such a phenomenon has never been observed in the furnace-annealed sample since the high-temperature and long-term furnace annealing usually cause a gradual recovery on the compressing strain of the SiO₂ matrix nearby the nc-Si.

As the CO₂ laser intensity was larger than the ablation threshold of SiO_x film (6 kW/cm²), the surface of SiO_x film was sputtered and damaged, which induced oxygen related irradiative defects. The ablation of the SiO_x layer occurs at the CO₂ laser annealing of $P_{\text{laser}} = 12 \text{ kW/cm}^2$ and leads to another featured PL at 400 nm due to structural damage [see Fig. 1(c)]. This results in a concurrent decrease in the near-infrared PL intensity by an order of magnitude, whereas the intensity of blue PL at 400 nm varies oppositely. In fact, the 400 nm PL intensity is increased by one order of magnitude as the P_{laser} increases from 7.5 to 11 kW/cm², while the surface temperature has already exceeded the melting temperature of fused silica. Curve fitting of the broadband PL spectrum from 350 to 700 nm reveals three peak wavelengths at 415, 455, and 520 nm with associated linewidths of 40, 66, and 113 nm as well as the associated irradiative defects of weak-oxygen bond, neutral oxygen vacancy (NOV) defect, and E'_δ center, respectively.²⁻⁴ Most of these defects are oxygen dependent, and some of them are NOV defects originated from the nc-Si precipitation process as many excessive Si atoms occupied the sites of oxygen move away to precipitate nc-Si. Precipitated nc-Si inevitably compresses the SiO_x matrix and results in the formation of the interstitial oxygen dependent new defects, such as the weak-oxygen bond or ionized oxygen molecule (O_2^-).

The turn-on voltages of ITO/CO₂ laser RTA SiO_x/p-Si/Al and ITO/furnace-annealed SiO_x/p-Si/Al MOSLEDs are 79 and 87 V with slopes of 0.54 and 0.44 kV/mA, respectively. Lower turn-on voltage and higher slope of an ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED are attributed to the existence of defects buried in CO₂ laser RTA SiO_x film. The electric-field (E) dependent emission current (I) can be described and the current-field plot can thus be fitted by Fowler-Nordheim (FN) tunneling equations listed as below,¹³

$$I_{\text{FN}} = A_G A E^2 \exp\left(\frac{-B}{E}\right), \quad (2)$$

FIG. 2. (Color online) Plot of $\ln(J_0/E^2)$ as a function of $1/E$ for CO₂ laser-annealed and furnace-annealed MOSLEDs.

$$A = \frac{q^3(m/m_{\text{ox}})}{8\pi h \Phi_B} = 1.54 \times 10^{-6} \frac{(m/m_{\text{ox}})}{\Phi_B} (\text{A/V}^2), \quad (3)$$

$$B = \frac{8\pi\sqrt{2m_{\text{ox}}}\Phi_B^3}{3qh} = 6.83 \times 10^7 \sqrt{(m_{\text{ox}}/m)} \Phi_B^3 (\text{V/cm}), \quad (4)$$

where A_G is the gate area, E is the electric field, and A and B are usually considered to be constants. m_{ox} is the effective electron mass in the oxide, m is the free electron mass, and Φ_B is the effective barrier height. The FN tunneling behavior can be confirmed, due to the linear transferred function characteristic in the Arrhenius FN plot (see Fig. 2). The threshold electric fields to initiate FN tunneling for CO₂ RTA and furnace-annealed MOSLEDs are 1.8 and 3.2 MV/cm, respectively, which indicates that the effective potential barrier of the sample becomes smaller with the assistance of defects. This essentially corroborates with the reduction on threshold electric field of FN tunneling occurred in the CO₂ laser RTA sample. The gradients of power-current (P - I) plot of ITO/CO₂ laser RTA SiO_x/p-Si/Al and ITO/furnace-annealed SiO_x/p-Si/Al MOSLEDs are 6.7 and 3.5 μW/mA, respectively (see Fig. 3). The EL power of the ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED with oxygen-related defects can be enlarged by two times as compared to that of the

FIG. 3. (Color online) P - I curves of (a) ITO/CO₂ laser RTA SiO_x/p-Si/Al and (b) ITO/furnace-annealed SiO_x/p-Si/Al MOSLEDs. Inset: energy band diagram of a highly forward biased ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED.

FIG. 4. (Color online) EL spectra of MOSLEDs made by CO₂ laser RTA (dash line) and furnace-annealed (solid line) SiO_x. Inset: far-field EL patterns of CO₂ laser RTA (upper) and furnace-annealed (lower) MOSLEDs.

ITO/furnace-annealed SiO_x/p-Si/Al MOSLED with a higher turn-on voltage.

The barrier height of ITO-SiO_x junction is 3.7 eV with electric affinities of 4.7 eV for ITO and 1 eV for SiO₂. The electric affinity and band gap of Si substrate are 4 and 1.12 eV, respectively. Since the CO₂ rapid-laser-annealing process introduces oxygen-related defects buried in the ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED, these oxygen-related defects and interfacial states facilitate the carrier transport into nc-Si for the electron-hole pair recombination (see the inset of Fig. 3), and also decrease the turn-on voltage. This also elucidates the significant reduction of threshold electric field of the ITO/CO₂-laser-RTA SiO_x/p-Si/Al MOSLED. In contrast to the conventional furnace-annealed MOSLED, the high-temperature and long-term furnace annealing usually cause a gradual recovery on the compressing strain of the SiO₂ matrix nearby the nc-Si and also contributes a defect-free furnace-annealed SiO_x film, corresponding to the higher turn-on voltage, lower EL power, and the difficulty of carrier injection into nc-Si. Consequently, the electrons require a higher electric field to tunnel through the barriers of the MOS structure. Furthermore, the enhanced *P-I* slope and EL power from the CO₂ laser RTA SiO_x based MOSLED are due to the assistance of carrier injection via oxygen-related defects as compared to those of the furnace-annealed SiO_x based MOSLED at the same biased condition.

nc-Si related EL spectra of ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED with a bright color far-field pattern was decomposed into three luminescent peaks at 590, 715, and 810 nm with the spectral linewidths of 203, 117, and 54 nm as well as peak ratios of 1.65:1.47:1, respectively (see the lower inset of Fig. 4). The luminescent peaks at 590 and 810 nm emitting from different sizes of nc-Si were observed; however, the luminescent peak at 715 nm was not obviously found in the PL spectrum. Because of oxygen-related defects, such as weak-oxygen bond and NOV defects, behave high energy band gaps, carriers favor to inject into smaller nc-Si with higher energy band gaps and approximate excited level via oxygen-related defects, and then recombine in the nc-Si. This result corresponds to the largest decomposed-EL intensity at 590 nm and the reduction of the decomposed-EL intensity as the increasing size of nc-Si. Hence, the EL emission from nc-Si at 715 nm can be enhanced and observed.

The EL spectrum of ITO/furnace-annealed SiO_x/p-Si/Al MOSLED, biased at higher electric-field without the carrier-transport assistant of oxygen-related defects, reveals a deep-red far-field pattern (see the upper inset of Fig. 4) and dual luminescent peaks at wavelengths of 625 and 768 nm with spectral linewidths of 189 and 154 nm, respectively. The EL component at longer wavelength coincides well with that of PL, revealing that the nc-Si-related PL and EL are attributed to the same carrier recombination mechanism. The mechanism of secondary EL peak expanded to shorter-wavelength region (500–700 nm) is possibly attributed to the cold-carrier-tunneling process under appropriate bias.³ The band bending becomes serious under an extremely high electric-field, leading to the carriers between adjacent nc-Si tunneled from first-order quantized state ($n=1$) to second-order quantized state ($n=2$), providing a higher population in the second-order state as well as an enhanced spontaneous emission at larger energy.

In conclusion, the enhanced near-infrared EL of an ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED is preliminarily demonstrated. Dense nc-Si can be synthesized in the SiO_{1.25} film by using CO₂ laser RTA at P_{laser} of 6 kW/cm² for 1 ms. The comparison on PL spectra of CO₂ laser annealed and furnace-annealed PECVD-grown SiO_{1.25} samples reveals the contribution of oxygen related defects. Since the CO₂ laser annealing time is only 1 ms and much shorter than furnace-annealing time (3 h), the annealing time is insufficient for precipitating larger-size nc-Si, whereas the oxygen-related defects are generated in the CO₂ laser annealed SiO_x film. These defects enhance the carrier transport through the MOSLED, reducing the tunneling threshold from 3.2 to 1.8 MV/cm as compared to the furnace-annealed sample. The elucidation on the role of the oxygen-related defects played on the improved carrier transport and enhanced light emission properties is addressed. A maximum EL power of nearly 50 nW from the ITO/CO₂ laser RTA SiO_x/p-Si/Al MOSLED under a biased voltage of 85 V and current density of 2.3 mA/cm² is reported to date.

This work was supported in part by National Science Council (NSC) of Republic of China under Grant Nos. NSC96-2221-E-002-448, NSC96-2221-E-009-282, NSC96-2752-E-229-007-PAE, and NSC96-2752-E-009-007-PAE.

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