Near-infrared light emission from Si-rich oxynitride nanostructures

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Abstract: Near-infrared (NIR) luminescent Si-rich oxynitride nanostructures were fabricated by very high frequency plasma enhanced chemical vapor deposition followed by thermal annealing. By increasing the annealing temperature from 600 °C to 1100 °C, the intensity of NIR emission can be remarkably improved by more than three times. Si nanocrystals (NCs) with diameters ranging from 2 nm to 4 nm are found to play a decisive role in the enhanced NIR emission. The PLE spectra indicate a band-to-band excitation process with a quantum confinement feature in Si nanocrystals. Combining with the infrared absorption spectra and X-ray photoelectron spectra analyses, it is suggested that the photoexcited carriers for the enhanced NIR emission mainly originate in the quantum confined Si NCs, while their radiative recombination occurs in the surface states related to N-Si-O bonds.

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References and links


1. Introduction

Si-based light sources compatible with the mainstream complementary metal-oxide semiconductor technology are highly desirable owing to their potential application in monolithic Si optoelectronic integrated circuits [1–6]. In the past decades, to overcome the insufficient light efficiency from bulk Si, enormous efforts have been devoted to Si nanostructures due to their novel quantum-confined optical emission. The previous interest was on the light emission from silicon nanostructures embedded in silicon oxide and silicon nitride systems [7–16]. Up to now, strong and tunable light emissions in the blue, green, yellow, red and near-infrared ranges have been discovered in these two systems [7–16]. However, for the silicon oxide system, high potential barrier for silicon oxide with silicon nanostructures seriously decreases the carrier injection efficiency, making it unfavorable for designing stable and efficient electroluminescent devices. Moreover, the unbalanced carrier injection in light-emitting devices (LEDs) based on silicon oxide and silicon nitride systems yields a low electron-hole pair recombination probability, and thus lowers the electroluminescence efficiency [17]. In recent years, much attention has been paid on the silicon oxynitride system [18–23]. It has been reported that silicon oxynitride in comparison to silicon oxide and silicon nitride can more effectively improve the equivalent carrier injections in LEDs and thus significantly increase the carrier recombination probability [21]. Besides, silicon oxynitride materials exhibit intense light emission due to the nanoseconds...
recombination lifetime [19, 23]. Therefore, silicon oxynitride system has become an alternative for efficient Si-based LEDs. So far, visible light emission from the nonstoichiometric silicon oxynitride films have been investigated, and several kinds of radiative recombination centers have been proposed [19, 23–26]. However, silicon oxynitride system is still a subject of current experimental investigations. In particular, the report on the near-infrared (NIR) light emission from Si-rich oxynitride nanostructures has not been revealed so far.

Here, based on our previous work on silicon oxynitride films [23], NIR luminescent Si-rich oxynitride nanostructures were fabricated by very high frequency plasma enhanced chemical vapor deposition followed by thermal annealing. It is interesting to find that the intensity of NIR emission can be significantly improved by more than three times with increasing the annealing temperature from 600 °C to 1100 °C. The mechanism of the enhanced NIR emission is discussed in detail on basis of its annealing behavior.

2. Experimental

The amorphous Si-rich silicon oxynitride films with thickness of ~200 nm were prepared in VHF-PECVD system using the gas mixture of SiH₄, NH₃, and O₂ as the precursor, as was described in previous work [23]. After deposition, the pristine samples were first dehydrogenated at 400 °C and then annealed at different temperatures in a N₂ atmosphere for 60 min. The microstructure of samples was characterized by Raman Spectrometer (Renisha, Gloucestershire, UK) equipped with 514 nm green laser and JEOL high-resolution transmission electron microscope (2010F), respectively. The photoluminescence (PL) measurements were performed at room temperature using Jobin Yvon fluorolog-3 spectrophotometer, and the excitation sources were a 450W steady Xe lamp and a 10 mW He-Cd laser (325 nm), respectively. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo-VG Scientific photoelectron spectrometer to investigate the chemical environment of Si, N, and O contents in samples. A Fourier transform infrared (FTIR) spectroscope (Shimadzu IR Pretige-21) was employed to record the bonding configurations of samples.

3. Results and discussion

![Fig. 1. PL spectra obtained from (a) pristine and (b) annealed silicon oxynitride samples, respectively. The PL measurements were carried out using a He-Cd laser (325 nm) as the excitation source.](image)

Figure 1 shows the PL spectra of pristine and annealed silicon oxynitride samples. An unsymmetrical emission band centered at ~700 nm can be observed from pristine sample. This emission band can be divided into two Gaussian profiles. The one on the high energy side corresponds to the orange-red band at ~680 nm, whereas the other one on the low energy side is red band at ~835 nm, as is shown in Fig. 1(a). According to our previous work, the orange-red band originates from the radiative N-Si-O bond centers in the silicon oxynitride matrix [23]. From Fig. 1(b), one can see that the intensity of the orange-red band significantly decreases after the sample was annealed at 600 °C. Meanwhile, a weak emission band
centered at \(~920\) nm becomes dominant in the PL spectrum. The intensity of this band gradually decreases with increasing the annealing temperature up to \(800\) °C. However, with further increasing the annealing temperature, the intensity of this band tends to increase. In particular, at the annealing temperature of \(1100\) °C, the PL intensity significantly increases by more than three times as compared with the sample annealed at \(600\) °C. Interestingly, an enhanced NIR emission from silicon oxynitride films can be obtained by means of thermal annealing. To clarify the origin of the enhanced NIR emission, we examined the microstructure of the samples and the corresponding results are presented in Fig. 2(a) and 2(b). It is found that the pristine sample exhibits a weak Raman spectrum with a main peak (TO mode) at about \(480\) cm\(^{-1}\). This feature is typical of amorphous Si clusters. The \(480\) cm\(^{-1}\) Raman band becomes intense after the samples were thermally annealed. Moreover, with increasing the annealing temperature from \(600\) °C to \(1000\) °C, one can see that the intensity ratio of the TA mode (150 cm\(^{-1}\)) to the TO mode (480 cm\(^{-1}\)) tends to decrease. These observations suggest a reduced short-range and medium-range disorder of the Si-Si\(_4\) network as a result of increased Si particle size in the samples. The broad Raman band gets sharpened and moves to \(513\) cm\(^{-1}\) on further annealing at \(1100\) °C, implying an increase in the ordering of the amorphous Si clusters and an amorphous-to-crystalline transition in Si clusters. The formation of Si nanocrystals in the annealed sample was further confirmed by the cross-sectional HRTEM image, as is shown in Fig. 2(b). Based on the investigation of PL behavior with annealing temperatures, Si nanocrystals are considered to play main contribution to the NIR emission. From Fig. 2(b), one can see that the Si nanocrystals with diameters ranging from \(2.0\) to \(4.0\) nm are distributed throughout the silicon oxynitride matrix. The mean size is about \(3.5\) nm. According to the effective mass theory, the nanocrystal size dependence of the band gap can be expressed as follows [27]: \(E (eV) = 1.12 + 11.8/d^2\), where \(1.12\) is the band gap value of bulk Si and \(d\) (nm) is the grain size. For the grain size of \(3.5\) nm, the \(E\) is estimated to be \(~2.08\) eV, which is much larger than the PL peak energy (1.35 eV) observed in the corresponding sample. This indicates that the 1.35 eV NIR emission in our case is not resulted from the band-to-band recombination of photoexcited carriers in Si nanocrystals.

Figure 3 further shows several typical PL spectra of the annealed sample at \(1100\) °C, excited at \(325\) nm, \(350\) nm, \(375\) nm, and \(400\) nm, respectively. As the excitation wavelength increases from \(325\) nm to \(400\) nm, shape line of NIR emission spectra show no any recognized change and emission peaks are pinned at \(~920\) nm. It is worth noticing that the behavior of PL in our case is identical to that of surface states related PL which peak position is independent of the excitation wavelengths because of the narrow distribution of surface localized states [28]. Therefore, in our case the 1.35 eV NIR emission is suggested from the radiative recombination via surface states of Si nanocrystals.
Fig. 3. PL spectra of sample annealed at 1100 °C, excited by the wavelengths of 325 nm, 350 nm, 375 nm, and 400 nm from Xe lamp, respectively.

Fig. 4. (a) FTIR absorption spectra of pristine and annealed samples. (b) The experimental Si 2p spectra (dotted lines) and component peaks (green lines) obtained from the spectral deconvolution for the as-deposited and annealed films.

The FTIR absorption spectra of all samples were examined to trace the chemical bonding changes at different annealing temperatures and are shown in Fig. 4(a). For the pristine sample, the FTIR spectrum shows a distinct ~855 cm⁻¹ absorption peak with a shoulder at ~920 cm⁻¹, which are assigned to the Si-N stretching vibration and the O-Si-N vibration, respectively [23, 26]. Another peak located at ~2150 cm⁻¹ is connected with the Si-H stretching vibration [23, 26]. After annealing, the signal of the Si-H stretching vibration is diminished. The absence of H in the samples implies that the Si nanostructures are in a hydrogen-free environment. With an increase of the annealing temperature, it is also found that the signal of the Si-N stretching vibration decreases and the signal of the O-Si-N vibration becomes dominant, indicating a SiNx-to-SiOxNy phase transformation. To gain more insight on the chemical environment of Si, N, and O in the samples, XPS measurements of the samples were conducted and the Si 2p core level spectra are shown in Fig. 4(b). The component peaks obtained from the deconvolution of the Si 2p core level spectra are also presented. For all the samples, a component peak at a binding energy of 99.3 eV related to the neutral Si state (Si-Si₄ tetrahedron) can be clearly observed, which is a strong evidence for the formation of Si nanostructures. In addition, the other three component peaks located at the binding energies of 100.2 eV, 101.2 eV, and 102.2 eV are associated with the Si-SiN, Si-SiO₂N, and Si-SiO₄N tetrahedrons [29]. One can see that the component peaks related to Si-Si₄, Si-Si₂N, and Si-SiO₂N tetrahedrons become intense after annealing at 1100 °C, while the peak connected with Si-SiN tetrahedron is significantly attenuated. These results indicate that N-Si-O bonding structures may exist at the surface of Si nanocrystals. It should be noted that Si nanocrystals may also be in part passivated by N. However, it has been found that the NIR emission induced by the incorporation of N on the surface of Si nanostructures is peaked at
950 nm [30], which are redshifted in comparison with the NIR emission peak (920 nm) in our case. Thus, the 920 nm NIR emission in our case is suggested from the contribution of N-Si-O bonds that acted as luminescent centers existing at the surface of Si nanostructures.

Fig. 5. (a) PLE spectra of pristine and annealed silicon oxynitride samples, taken by monitoring at 885 nm. (b) PLE spectra of sample annealed at 1100 °C, taken by monitoring at 885 nm, 910 nm, 923 nm, and 935 nm emission wavelengths.

The PLE spectra of pristine and annealed samples were also examined to understand the mechanism of NIR emission, as is shown in Fig. 5(a). The pristine sample shows a PLE band at 376 nm. In addition, there exists a very weak peak at about 390 nm. The weak 390 nm PLE band becomes obvious after the samples were annealed. With increasing the annealing temperature up to 1100 °C, the 376 nm PLE band disappears and the 390 nm PLE band becomes dominant in the spectrum. It is found that the evolution of the 390 nm PLE band on the annealing temperatures exhibits a similar tendency to that of Si nanostructure on the annealing temperatures as shown in Fig. 2. This indicates that Si nanostructures are responsible for the 390 nm PLE band, and the optical excitation process is governed by the Si nanostructures. Comparing with the PL results of the corresponding sample, a large Stokes shift (1.8 eV) between the PLE and PL spectra can be observed, which means that the excitation-transfer mechanism is responsible for the NIR light emission [31]. That is the photoexcited carriers mostly generated in the Si QDs can be transferred into the surface states of Si QDs and then radiatively recombine, contributing to the NIR light emission. In this case, the Si QDs play a role as a sensitizer of the NIR light emission, which well explains the fact that the intensity of NIR emission remarkably increases as the Si QDs are formed in the silicon oxynitride sample. From Fig. 5(a), it is noticed that the 390 nm PLE band redshifts in comparison to that observed in Si nanostructures with complete H passivation. Pi et al have found that paired interstitial N or doubly bonded O at the surface of Si nanocrystals would reduce the energy of the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) of Si nanocrystals at excited state [28]. Thus, combining with the FTIR and XPS spectra analyses mentioned above, the redshift of the 390 nm PLE band can be ascribed to the N-Si-O at the NCs surface. From Fig. 5(b), one can see that the PLE peak blueshifts with decreasing the monitoring wavelength. This behavior can be attributed to the fact that the HOMO–LUMO gap at excited state increases with the decrease of Si nanostructure size due to the quantum confinement effect [27]. Thus, based on the above results, we can infer that the photoexcited carriers for the enhanced NIR emission mainly originate in the quantum confined Si NCs, while their radiative recombination occurs in the surface states related to N-Si-O bonds.

4. Conclusion

In summary, NIR emission from Si-rich oxynitride nanostructures was obtained by VHF-PECVD followed by thermal annealing. By increasing the annealing temperature from 600 °C to 1100 °C, the NIR emission intensity can be significantly improved by more than three
times. Si nanocrystals with diameters ranging from 2 nm to 4 nm are demonstrated to play main contribution to the enhanced NIR emission. Combining with the PLE, FTIR, and XPS spectra analyses, it is suggested that the photoexcited carriers for the enhanced NIR emission mainly originate in the quantum confined Si NCs, while their radiative recombination occurs in the surface states related to N-Si-O bonds.

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