Electroluminescence emission of crystalline silicon nanoclusters embedded in silicon nitride matrices

Ching-Ting Lee[*] and Tai-Cheng Tsai

Institute of Microelectronics, National Cheng Kung University
ctlee2ee.ncku.edu.tw

Because of the improvement of light emission efficiency due to quantum confinement and surface chemistry effects, monolithically integrated Si-based optoelectronic integrated circuits (OEICs) have become feasible. Recently, many efforts have been undertaken to study the optical emission mechanisms of low-dimensional Si nanostructures. Light emission under optical pumping in Si-based materials, such as porous silicon, erbiumdoped silicon, and silicon nanoclusters embedded in silicon oxide and silicon nitride matrices, have been demonstrated. However, very low light emission efficiency severely limits the possibility of porous silicon and erbium-doped silicon in applications of lightemitting devices. Furthermore, silicon nanoclusters embedded in silicon oxide matrices hinder the attainability of stable and efficient electrically driven light-emitting devices owing to a huge barrier mismatch between Si and SiO_2. Therefore, silicon nanoclusters embedded in silicon nitride matrices are a promising material for use in Si-based optoelectronic devices and OEICs. Many techniques and methods have been developed to grow silicon nanoclusters embedded in silicon nitride matrices. However, the formation of crystalline silicon nanoclusters must be grown or post-annealed at a high temperature to precipitate the crystalline silicon nanoclusters (Applied Physics Letters, 86, 091908(2005)). The high temperature process degrades the optical and electronic performance of the resultant devices. A laser-assisted chemical vapor deposition (LACVD) method has been previously used to deposit thin films and nanoclusters (Physical Review B, 48, 4883(1993)). In the present study, a LACVD method was used to grow crystalline silicon nanoclusters embedded in silicon nitride matrices at a low temperature and without a post thermal annealing process. The feasibility of electroluminescence emission from these devices was demonstrated.

In the LACVD system, an external CO2 laser beam was guided into the chamber of a conventional capacitively coupled plasmaenhanced chemical vapor deposition (PECVD) system through a ZnSe window. A He-Ne laser with a wavelength of 632.8 nm (visible red-light) was used to assist the alignment of the CO2 laser. To prevent heating the substrate, the substrate was illuminated with the CO2 laser beam at an incident angle of 88o. Argon-diluted SiH4 (4%) and NH3 reactant gases were used to deposit the silicon nitride films. The deposition conditions of the total working pressure, the radio frequency (RF, 13.56 MHz) power of the PECVD system, and the CO2 laser power were kept at 500 mTorr, 100 W, and 3 W/cm^2, respectively.
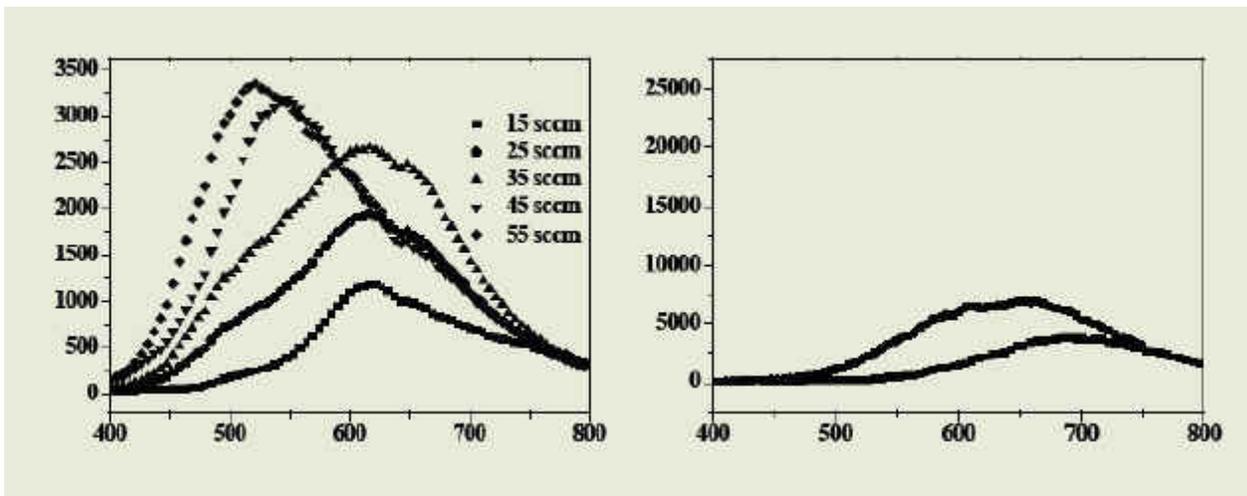
Fig. 1 PL spectra of silicon nitride films deposited (a) without laser assistance and (b) with laser assistance by varying the NH3 gas flow rate.

For the argon-diluted SiH4 (4%) flow rate of 250 sccm and deposition conditions mentioned above, Fig. 1 (a) and (b) show the silicon nitride films deposited without and with laser assistance with various NH3 flow rates. In Fig. 1 (a), it can be seen that the PL peak positions located at 620 540 and 516 nm correspond to defects (Journal of Applied Physics, 73, 5185(1993)). Therefore, the PL emission of the silicon nitride films deposited without laser assistance can be attributed to the defects. For the PL spectra shown in Fig. 1 (b), not only is the PL intensity of the laserassisted silicon nitride films much larger than that of those without laser assistance, but the PL peak positions are not always located at defect energy levels. It can be deduced that the PL emission are not attributed to the defects in the laser-assisted silicon nitride films. According to a previous report (Applied Physics Letters, 88, 183103 (2006)), if light emission originates from the surface state of the nanoclusters, the associated energy gap is reduced by increasing nitrogen content on the surface of the nanoclusters. Therefore, the associated PL emission peak is red-shifted when the nitrogen content in the films is increased by increasing the flow rate of NH3 reactant gas. However, the experimental results shown in Fig. 1(b) indicate a blue-shift of the PL emission peaks with an increase of NH3 flow rate. Therefore, it can be deduced that the interface between a silicon nanocluster and the silicon nitride matrix is not a major mechanism of optical emission in the silicon nitride films.

High resolution transmission electron microscopy (HRTEM) was used to observe the silicon nanoclusters embedded in laserassisted silicon nitride matrices. Figure 2 (a) shows the HRTEM image of the laserassisted silicon nitride films deposited with SiH4 and NH3 flow rates of 250 and 55 sccm, respectively. Silicon nanoclusters embedded in the silicon nitride matrices can be clearly seen. The diameter of the silicon nanoclusters is approximately 2.9 nm. However, silicon nanoclusters were not observed in the silicon nitride films deposited without laser assistance. Figs. 2 (b) and (c) show the highresolution lattice image and electron diffraction pattern of the silicon nanoclusters,
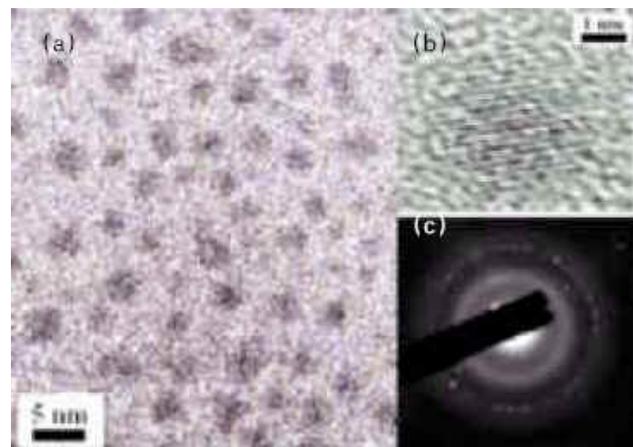

Fig. 2 (a) HRTEM image, (b) high-resolution lattice image and (c) Electron diffraction pattern of the laser-assisted silicon nitride films.

respectively. It can be seen that crystalline silicon nanoclusters were formed in laserassisted silicon

nitride films deposited at a low temperature and without post thermal annealing. To our knowledge, this is the first observation of crystalline silicon nanoclusters embedded in silicon nitride films which were deposited at a low temperature and without post-annealing process.

From the PL spectra shown in Fig. 1(b) and the HRTEM images, the PL peak energy and the diameter of silicon nanoclusters observed from HRTEM images as a function of NH3 flow rate are shown in Fig. 3. The diameter of silicon nanoclusters decreases with the increase of NH3 flow rate. According to the quantum confinement effect, the smaller diameter of nanoclusters would emit photons with a higher energy. Therefore, the PL peak position is shifted toward a higher energy by increasing the NH3 flow rate. By fitting the PL peak energy as a function of the diameter of the silicon nanoclusters, the dependence of associated energy gap E (eV) on diameter d (nm) of silicon nanoclusters can be expressed as E (eV) = 1.17 + (11.6 / d^2) (1)

Fig. 3 PL peak energy and diameter of silicon nanoclusters as a function of NH3 flow rate.

From the HRTEM images of the laserassisted silicon nitride films, the silicon nanocluster density of the silicon nitride films deposited with NH3 flow rates of 25 sccm, 35 sccm, and 55 sccm were approximately about 8×10^{11}cm^{-2}, 2.1×10^{12} cm^{-2}, and 4.6×10^{12} cm^{-2}, respectively. The error estimate for the silicon nanocluster density is approximately 5 %. The silicon nanocluster density increased with the NH3 flow rate. Since the PL intensity depends on the silicon nanocluster density, it can be deduced that the PL intensity increases with the NH3 flow rate. This phenomenon is demonstrated in the PL spectra shown in Fig. 1 (b).
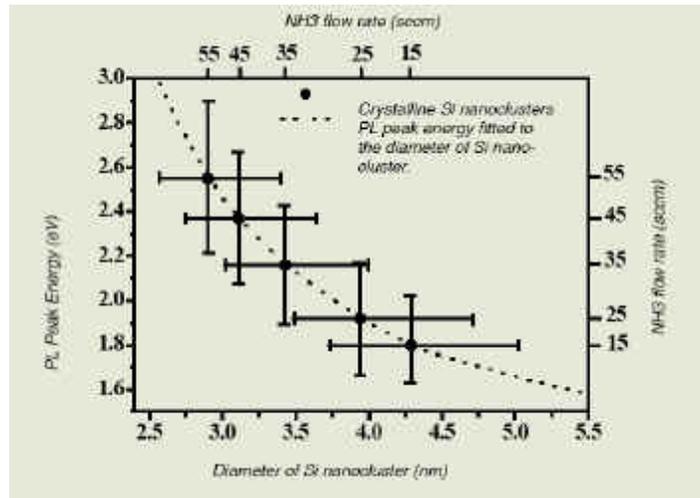

Fig. 4 The current-voltage characteristic of light-emitting devices.

A p-type (100)-oriented silicon wafer with a resistivity of 20 Ω·cm was polished to a thickness of 150 μ m. A 100 nm-thick laserassisted silicon nitride film was deposited on the silicon wafer using SiH4 and NH3 flow rates of 250 sccm and 55 sccm, respectively, under deposition conditions mentioned above. A 300 nm-thick transparent n-type indium tin oxide (ITO) film and a 200 nmthick aluminum were deposited on the silicon nitride film and the bottom surface of the p-type silicon wafer, respectively. For the structure of the light-emitting devices using crystalline silicon nanoclusters embedded in silicon nitride matrices mentioned above, the current-voltage characteristics measured using an HP4145B semiconductor parameter analyzer are shown in Fig. 4. Figure 5 shows the electroluminescence (EL) spectrum of the light-emitting devices measured at

room temperature and biased at a current of 50 mA. The PL spectrum of the device without an ITO layer is also shown in Fig. 5. It can be seen that the peak energy of 590 nm in the EL spectrum was red-shifted with respect to the 486 nm emission of the PL spectrum. The extended quantum confinement/ luminescence center (QCLC) model (Solid State Communication, 94, 607(1995)) states that the light emission is from the competition between three different recombination processes. In our experimental results, electron-hole pairs were generated by photoexcitation and PL is mainly due to electronhole recombination within silicon nanoclusters. However, under forward bias, the EL spectrum would be caused by the radiative recombination of charge carriers that tunnel into luminescence centers in the silicon nitride films, and the luminescence center being responsible for the light emission at 590 nm (Journal of Physics I, 1, 1335(1991)).
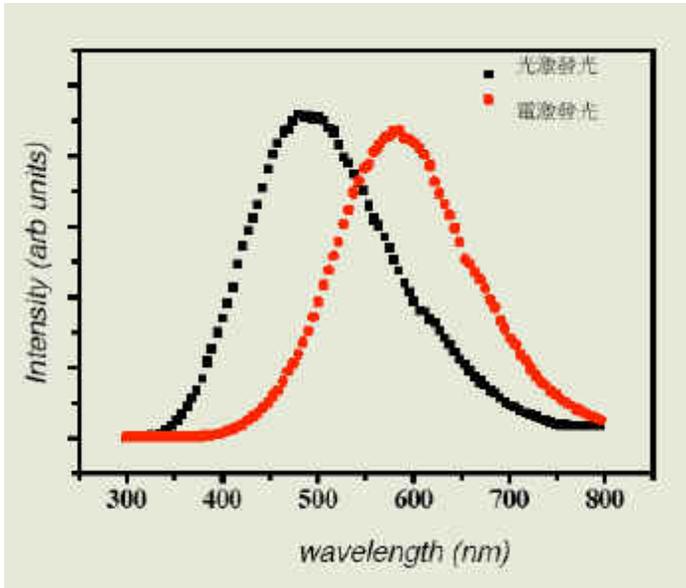

Fig. 5 The PL and EL spectra of lightemitting devices.

Crystalline silicon nanoclusters embedded in laser-assisted silicon nitride matrices were deposited at a low temperature and without post-annealing using an LACVD system. The dimensions of the crystalline silicon nanoclusters and the associated PL peak position of the deposited silicon nitride films could be controlled by varying the NH3 flow rate. According to the PL emission spectra, it can be concluded that the light emission from the laser-assisted silicon nitride films is attributed to the silicon nanoclusters embedded in silicon nitride matrices, which can be clearly seen in the HRTEM images. According to the electron diffraction pattern of the silicon nanoclusters, crystalline silicon nanoclusters are formed in the laser-assisted silicon nitride films. The silicon nanoclusters related electroluminescence shows that silicon nitride films deposited using an LACVD system can be applied in light emitting devices.