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Enhancement of white luminescence from SiN_x films by surface roughening

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Abstract
White photoluminescence was obtained from multi-layered silicon nitride thin films prepared by plasma-enhanced chemical vapor deposition. The emission colors from single-layered silicon nitride films could be adjusted over the range of 440–660 nm by controlling the SiH_4/NH_3 flow ratio during deposition. Surface roughening by anisotropic KOH etching of the Si(100) substrate significantly improved the emission extraction efficiency and changed the color-rendering properties from the silicon nitride thin films. This was attributed to the suppression of internal reflection and interference effects from the thin films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Visible photoluminescence (PL) from Si nanoparticles embedded thin films has attracted great interest due to its potential application in low-cost Si-based optoelectronics [1–6]. Si nanoparticles can emit throughout the visible and near-infrared region through control of their size and/or the host matrix. Consequently, multiple-sized Si nanoparticle-embedded thin films can be used to produce white light sources with controlled spectral characteristics. When integrated with a blue/ultraviolet (UV)-emitting LED, a Si-based microelectronics compatible technology can be developed, providing a less expensive fabrication process to obtain advanced white light emitting solid-state lighting (SSL) devices.

Although various thin-film techniques can be used to prepare luminescent Si nanoparticles, plasma-enhanced chemical vapor deposition (PECVD) appears to have the advantage of making highly efficient emitters [7–9]. Park *et al* [6] and Wang *et al* [7, 8] reported efficient red to blue PL from SiO_x or SiN_x thin films prepared by PECVD, attributing it to amorphous Si nanoparticles embedded in the films. The host matrix and the film/nanoparticle interface both play significant roles in determining the PL properties of Si nanoparticles. For example, nitride-encapsulated Si nanoparticles exhibit shorter emission wavelengths and more intense PL compared to oxide-encapsulated ones [8]. Strong PL intensity was also observed by Kim *et al* [9] from SiN_x films containing a high density of crystalline Si nanoparticles which were grown by PECVD using SiH_4 and NH_3. The significant enhancement observed in the PL intensity of Si nanoparticles grown using SiH_4/NH_3 compared to that of Si nanoparticles grown using SiH_4/N_2 is attributed to hydrogen passivation of nonradiative defects. Although quantum efficiencies (QEs) up to 88% have been reported from a single Si nanoparticle at room temperature [10], the external QE of thin-film Si nanoparticles was much lower, in the range of 1–10% [8]. This is most probably due to thin-film entrapment effects and a statistical distribution in the QE of an individual nanoparticle resulting from the different quantum confinement and passivation conditions. Depending on the substrate and refractive indices, thin-film effects can limit the external efficiency of a 100% internal efficiency thin-film emitter to ∼5%. However, through the use of engineered optical structures, such as textured surfaces, antireflection coatings, filters, Bragg reflectors, and microcavities, the light extraction efficiency from these thin films can be significantly improved [1]. This implies that highly efficient engineered Si-based films/optical structures are achievable for SSL applications. In this research, white photoluminescence from SiN_x films was studied and surface roughening was utilizing to improve the light extraction efficiency.

2. Experimental details

SiN_x thin films were prepared in a PECVD system using SiH_4 and NH_3 as the gas sources. During deposition the N_2-diluted 2% SiH_4 gas was fixed at a flow rate of 650 sccm, and the flow rates of NH_3 were controlled between 10 and 150 sccm. Silicon (100) wafers were used as the substrates. The chamber pressure and growth temperature were maintained at 0.9 Torr and 300 °C, respectively, and the plasma power was fixed at 30 W. Surface roughening of the thin-film samples was carried out by etching the (100) Si substrate in potassium hydroxide (KOH, 0.56%) for 3–40 min at 80 °C before deposition. The PL spectra were obtained with a Spex1000M spectrometer using a 5 mW 275 nm UV Ar^+ laser as the excitation source. All the PL measurements were performed at room temperature and recorded with a GaAs photomultiplier tube (PMT). The reflectance spectra were recorded with a Filmetrics thin-film measurement system using a Hamamatsu (L7893) light source. Film thicknesses and refractive indices were obtained from fits to the reflectance spectra. The surface morphology of the samples was analyzed with a LEO 1530 scanning electron microscope (SEM).

3. Results and discussion

3.1. Controllable PL from single-layered SiN_x films

Intense visible emissions from blue to red were obtained from the as-deposited SiN_x thin films with a thickness between 300 and 400 nm. Figure 1(a) shows the room-temperature PL spectra of the samples as a function of the NH_3 flow rates. A continuous blue shift of the PL peak, from 660 to 440 nm, was observed with increasing NH_3 flow rate between 20 and 150 sccm. Typically, the three primary colors (blue, green, red) were observed at SiH_4/NH_3 gas flow ratios of 650 sccm/150 sccm (440 nm), 650 sccm/40 sccm (565 nm) and 650 sccm/20 sccm (660 nm), respectively, with a full width at half maximum (FWHM) of 150–170 nm. Figure 1(b) shows the images of several individual colors obtained from these samples and the white emission from a multi-layered sample, which will be discussed later. This ability to control the PL properties was attributed to the emission from Si nanoparticles due to the quantum confinement effect. With increasing NH_3 flow rate, the size of the Si nanoparticles decreases due to a decreased silicon to nitrogen ratio in the thin film. Similar results were also reported by Kim *et al* using SiH_4 and NH_3 as the reactant gas sources [9].

3.2. White PL from multi-layered SiN_x films

In order to obtain white emission, multi-layered SiN_x thin-film structures were deposited with a combination of emission colors by controlling the SiH_4/NH_3 flow ratio and deposition time. As shown in figure 1(c) various 'whitish' spectra were obtained due to a combination of emissions from multiple layers. Different structures were designed by sequentially depositing layers designed to individually emit colors from blue to red, or by gradually changing the composition of the layer during deposition to obtain a broad emission covering the whole visible region. For example, spectrum 3 results from three layers of SiN_x with total thickness of ~750 nm

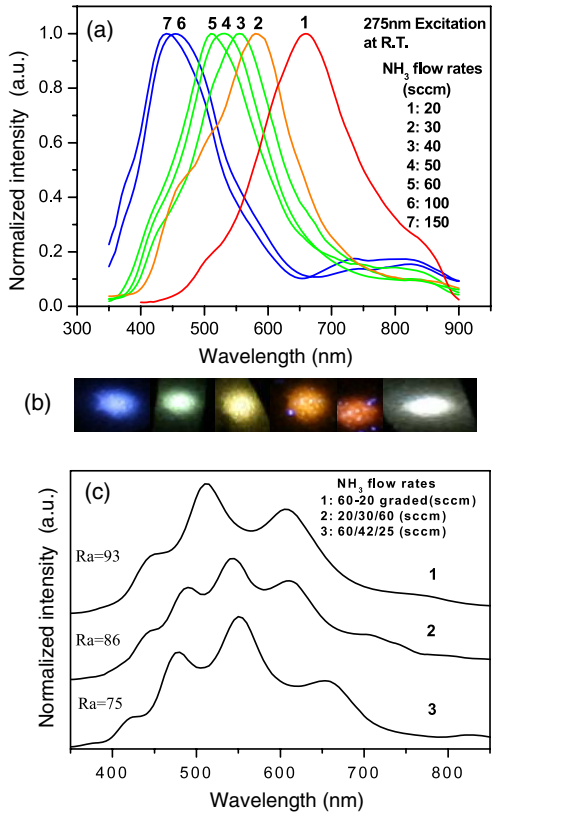

Figure 1. (a) PL spectra of silicon nitride films as a function of NH_3 flow rates (N_2-diluted 2% SiH_4 was fixed at a flow rate of 650 sccm for all the films); (b) images of colors emitted from SiN_x films excited by 275 nm UV radiation; (c) normalized PL spectra from multi-layered silicon nitride thin-film structures deposited with a combination of nanoparticle sizes and/or compositions by controlling the SiH_4/NH_3 flow ratio and deposition time.

deposited with NH_3 flow rates of 60, 42, and 25 sccm for a deposition time of 15 min for each layer. For spectrum 2, the film was designed to tune the emission from red to blue away from the substrate so as to minimize the self-absorption effects by depositing three layers with NH_3 flow rates of 20, 30, and 60 sccm for deposition times of 15, 20, 15 min, respectively. The total thickness of this film is about 990 nm. In addition, a film (spectrum 1) with a graded composition and total thickness of ~690 nm was prepared by gradually decreasing the NH_3 flow ratio from 60 to 20 sccm in 2 sccm steps for deposition times of 2 min for each step. It can be observed that the overall spectral characteristics of these white spectra are obviously affected by the luminescent property and thickness of each layer.

The color-rendering properties of a white light source is specified by its color-rendering index, R_a. This number is basically a measure of how realistically illuminated colors will be produced. It is measured by comparing the color rendering of the test source to that of a perfect source which is generally a black-body radiator. An R_a of 100 implies perfect color rendering. The R_a values can be calculated using a CIE Color Rendering Index calculation software by incorporating the spectrum data. For these spectra generated by the multi-layered thin films, the calculated R_a values are 93, 86, and 75 respectively, as shown in figure 1(c); while the R_a values

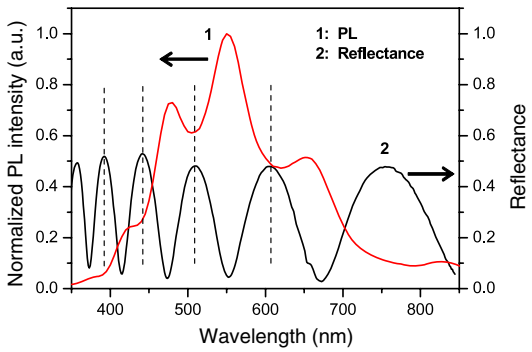

Figure 2. PL and reflective spectra of a three-layered silicon nitride film (NH_3: 60/42/25 sccm) with total thickness of ∼750 nm, showing thin-film interference effects and white emission.

for warm-white and daylight fluorescent lamps are 52 and 75, respectively. Thus, this film can produce superior color rendering compared to standard fluorescent bulbs.

To investigate the origin of the multiple emission peaks observed from the multi-layered samples, the reflectance spectra of these films were also measured and compared to the PL spectra, as shown in figure 2. These measurements showed that the valleys in the PL curve correspond exactly to the peak positions in the reflectance curve. This indicates that the modulation in the PL spectra was actually due to thin-film interference effects. Our observation of thin-film effect induced multiple PL peaks gives an alternative explanation to the controversial results on multiple PL peaks observed from SiN_x or SiO_x films [3, 11].

3.3. Surface roughening effects on light extraction

The effects of surface roughening on the spectral property and light extraction efficiencies from silicon nitride films were next investigated. Figure 3(a) shows an SEM image of the surface morphology of a Si substrate etched for 10 min. It can be observed that pyramid structures with dimensions ranging from 100 nm to 1 μm formed on the surface due to anisotropic etching. Figure 3(b) shows the surface morphology of a silicon nitride film sample with thickness ∼400 nm deposited on the 10 min etched substrate. Rounded bumps with dimensions in the range of 500 nm to 2 μm were observed after growth on the pyramid structures. As confirmed by the reflectance measurements shown in figure 4(a), the reflectivity from the etched Si substrates was ∼2 orders of magnitude lower than

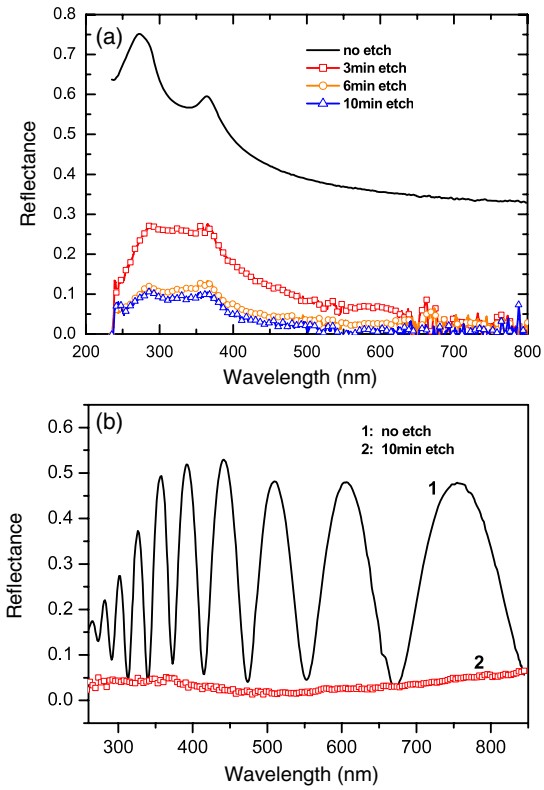

Figure 4. (a) Reflectance spectra from Si(100) substrates with smooth surface and roughened surfaces after etching for 3, 6 and 10 min (the reflectance of the etched samples are enlarged 20×). (b) Reflectance spectra from three-layered silicon nitride films deposited on unetched (1) and 10 min etched (2) substrate (the reflectance of the etched samples is enlarged 10×), indicating significant suppression of thin-film interference effects.

from the unetched substrate. With increased etching time, from 3 to 10 min, the reflectivity decreased due to increasing surface roughness. A further increase in etching time had little effect on the reflectivity and surface roughness.

Figure 5 compares the angle-dependent PL spectra from a white-emitting sample deposited on smooth and roughened substrates at measuring angles of 90°, 135° and 150°, which are the angles between the surface parallel direction and the detecting direction. Thus for 90° this means measuring in the direction normal to the sample surface. The PL intensity from the roughened surface was significantly higher than that from the smooth surface for all angles. An average increase

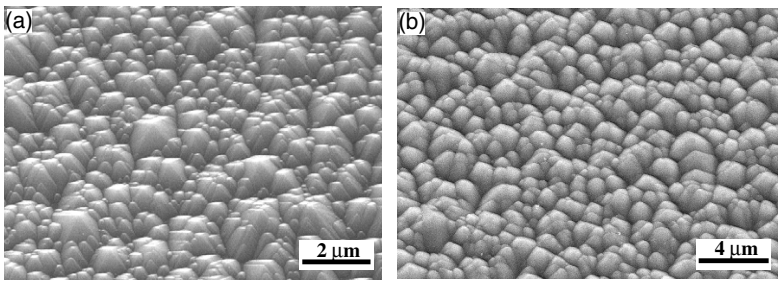

Figure 3. (a) Surface morphology of Si(100) substrate etched by 0.56% KOH solution for 10 min at 80 °C; (b) surface morphology of a ∼400 nm thick silicon nitride film deposited by PECVD on the 10 min etched Si substrate.

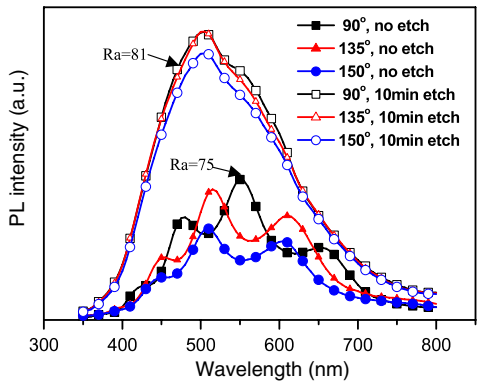

Figure 5. Angle-dependent photoluminescence from a white-emitting silicon nitride film grown on smooth and roughened surfaces.

of 260% was observed from the etched sample compared to the unetched one. For the surface-roughened sample, the PL intensity showed little dependence on angles. However, for the smooth sample, an obvious decrease of 28% from 90° to 150°, was observed with increase of measuring angle due to total internal reflection. In addition, surface scattering related to the rough surface of etched sample may also account for the little change in PL intensity with angle. Moreover, multiple peaks observed from the smooth surface were not present in the roughened sample, because of the suppression of thin-film interference effects by surface roughening, as indicated from the reflectance spectra of films shown in figure 4(b). By dividing the PL spectrum of the etched sample (90°, 10 min etch) shown in figure 5 with the reflective spectrum of the unetched one shown in figure 2, five emission peaks located at 375, 415, 475, 555, 675 nm were calculated, which closely matched the multiple PL peaks of the unetched sample shown in figure 2. Thus, the overall PL intensity increase was attributed to the suppression of the total internal reflection as well as the interference effects on thin films resulting from the increase of surface roughness. In addition, the elimination of the multiple emission peaks by surface roughening significantly affected the color coordinates of the output spectrum. The calculated R_a for the PL of etched sample (90°, 10 min etch) is 81, which produces superior color rendering compared to the unetched sample ($R_a = 75$) shown in figure 5.

4. Conclusion

In conclusion, strong visible photoluminescence ranging from blue to red was obtained from silicon nitride films grown by PECVD using SiH_4 and NH_3 as the source material. The emission wavelength was controlled over the range 440–660 nm by varying the flow ratios of SiH_4 and NH_3 precursors, which is most probably attributed to the change of the size of Si nanoparticles embedded in the films. Various shades of 'white' could be obtained from multi-layered silicon nitride thin-film structures deposited using a combination of nanoparticle sizes and/or compositions by controlling the SiH_4/NH_3 flow ratio and layer thickness. Surface roughening by anisotropic KOH etching a Si(100) substrate greatly improved the emission extraction efficiency from the silicon nitride thin films, due to a significant suppression of the total internal reflection and interference effects by surface roughening.

References

[1] Fauchet P M 2005 *Mater. Today* **8** 26
[2] Wilson W L, Szajowski Pl F and Brus L E 1993 *Science* **262** 1242
[3] Pei Z, Chang Y R and Hwang H L 2002 *Appl. Phys. Lett.* **80** 2839
[4] Kahler U and Hofmeister H 2002 *Appl. Phys.* A **74** 13
[5] Zacharias M, Heitmann J, Scholz R, Kahler U, Schmidt M and Blasing J 2002 *Appl. Phys. Lett.* **80** 661
[6] Park N M, Kim T S and Park S J 2001 *Appl. Phys. Lett.* **78** 2575
[7] Ma L B, Ji A L, Liu C, Wang Y Q and Ca Z X 2004 *J. Vac. Sci. Technol.* B **22** 2654
[8] Wang Y Q, Wang Y G, Cao L and Cao Z X 2003 *Appl. Phys. Lett.* **83** 3474
[9] Kim B H, Cho C H, Kim T W, Park N M, Sung G Y and Park S J 2005 *Appl. Phys. Lett.* **86** 091908
[10] Credo G M, Mason M D and Buratto S K 1999 *Appl. Phys. Lett.* **74** 1978
[11] Tong J F, Hsiao H L and Hwang H L 1999 *Appl. Phys. Lett.* **74** 2316