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Adjustable emissions from silicon-rich oxide films prepared by plasma-enhanced chemical-vapor deposition

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Observation of sequentially adjustable, intense, and stable emissions at room temperature from amorphous silicon-rich oxide thin films without any thermal annealing is reported. Hydrogenated amorphous silicon-rich oxide (SiO$_x$:N:H, 0<x<2) thin films were deposited by plasma-enhanced chemical-vapor deposition with a mixture of 5% silane in argon and nitrous oxide gases. The strong naked-eye-seeing photoluminescence (blue–white–orange) could be adjusted by changing the process gases flow rate ratio $G$ ($=\frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi}$). The degree of silicon richness was determined from secondary ion mass spectrometry. The microstructure-bonding configuration was examined by Fourier transform infrared spectroscopy. The implications of these studies for understanding the origins of silicon-based luminescence are discussed. © 1999 American Institute of Physics.

TABLE I. The thickness, optical gap, refractive index, and SIMS measured $x$ value of SiO$_x$:H thin films prepared at various [SiH$_4$][N$_2$O] gas-phase compositions.

| Sample | $\Gamma = 0.3$ | $\Gamma = 0.4$ | $\Gamma = 0.5$ | $\Gamma = 0.6$ | $\Gamma = 0.7$ | SiO$_2$
|-------|-------------|-------------|-------------|-------------|-------------|-------------------|--------|------------------------|------------------------|
| Thickness (nm) | 570 | 725 | 766 | 912 | 964 | 501
| Optical gap (eV) | 7.27 | 6.92 | 6.61 | 6.22 | 5.14 | 8.47
| Refractive index | 1.564 | 1.622 | 1.66 | 1.558 | 1.626 | 1.487
| $x$ value | 1.94 | 1.2 | 0.89 | 0.78 | 0.67 | 2.0

Observation of visible room-temperature photoluminescence (PL) from silicon nanostructures has attracted considerable interest in understanding the optical properties of group-IV semiconductor nanostructures and fabricating silicon-based optoelectronic devices. In particular, porous silicon and oxidized silicon nanoclusters are receiving widespread attentions. Qin, Lin, and Yao demonstrated an ultraviolet photoluminescence observation including peaks at 340, 355, and 370 nm from thermally oxidized porous silicon. Kim et al. observed a weak ultraviolet photoluminescence band centered at 365 nm, together with other stronger visible bands from the silicon-rich oxide layers deposited by electron cyclotron resonance (ECR) chemical vapor deposition (CVD). Song et al. proposed the intense UV photoluminescence centered at 370 nm, which was emitted from the magnetron-sputtered silicon oxide films. However, controllability of strong luminescence in the range from UV to red has been lacking and the mechanism of the observed emission is still not clear. In this work, we demonstrate intense and stable light emission over a wide range of wavelengths from UV to the red region from hydrogenated amorphous silicon-rich oxide (SiO$_x$:N:H, 0<x<2) thin films.

Hydrogenated amorphous silicon-rich oxide thin films were deposited by the plasma-enhanced chemical-vapor deposition (PECVD) technique, from appropriated gaseous mixtures of 5% argon-diluted silane and nitrous oxide, in a capacitively coupled reactor with 50 mTorr deposition pressure. The substrate temperature was 300 °C and the rf (13.56 MHz) power density was 200 mW/cm$^2$. The dependence of the PL on the structural composition was investigated by varying the flow rate ratio $\Gamma$ ($=\frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi} \frac{\gamma}{\xi}$). The substrates were phosphorous-doped Si(100) wafers with resistivities of 3.5–5.5 Ω cm. Before loading into the chamber, RCA purification was performed.

FIG. 1. PL spectra of the hydrogenated amorphous silicon-rich oxide (SiO$_x$:H) thin films prepared at various [SiH$_4$][N$_2$O] flow rate ratios.
cleaning and HF dip procedures were applied to clean the silicon surface. An in situ hydrogen plasma pretreatment was carried out for surface cleaning and passivation. For the PL measurements, excitation was performed with 325 nm laser light (He–Cd laser) of, typically, 1 mW focused to a spot of 100 μm. The emitted light was collected by a 50 mm f/1.4 lens in the direction normal to the illuminated surface, and focused on a SPEX 500M monochromator with a thermal electrically cooled GaAs photomultiplier and standard lock-in technique was used for the spectral analysis. The ratio of the silicon to oxygen contents was determined by secondary ion mass spectrometry (SIMS). Furnace-grown oxide film was used as the calibration standard. The FTIR transmittance spectra for samples deposited with various flow rate ratios. Due to the lack of standard calibration samples for off-stoichiometric silicon dioxide films, the SIMS data can only provide the relative compositions of the major elements, but they cannot give the precise incorporated impurity concentration data. The FTIR transmittance spectra for samples deposited with various x values are shown in Table I. Cross-sectional transmission electron diffraction patterns of these thin films did not exhibit any crystalline phase. An intense PL centered at approximately 375 nm (3.3 eV) was observed for the samples deposited with x = 0.4. Furthermore, two weak PL bands centered at 415 nm (2.99 eV, B band) and 520 nm (2.4 eV, G band) can be seen in the spectrum of this film. With further increase of the SiH₄ flow rate, the intensity of the UV band decreased, and the other two bands became more intense. The luminescence intensities of these three bands were comparable while the samples were deposited at the x = 0.6 condition. Further study revealed that a new weak band peaking at 730 nm (1.7 eV, R band) appeared. This weak band may also exist in those samples with x < 0.6, but it is hard to differentiate it from the second-order signal of the strong UV band. The UV band in the PL spectrum for samples with x = 0.7 are split into two bands (U1 and U2 bands), considering the intensity evolved with increasing the SiH₄ flow rate. The intensity of the UV band which peaked at 398 nm (3.11 eV, U1 band) decreased dramatically and a new band centered around 448 nm (2.77 eV, U2 band) appeared. Moreover, the energy position of the R band did not change, but the intensity increased and the band became broadened. The PL spectra of samples prepared at the x = 1.0 condition exhibited broad, weaker, and unstable characteristics, which make up those of porous silicon.

Figure 2 shows the evolution of the PL emission energy as a function of the x values. The denoted data as shown in the parenthesis are the FWHM in eV. These bands are labeled according to their FWHM and the intensity variation. The corresponding x values determined from SIMS data could be used to represent the degree of silicon richness. The smaller x values represent higher silicon content. As depicted in Fig. 1, the whole PL spectrum was shifted from the UV region toward the red region with increasing the x values. The measured redshift of the PL spectra with the increasing degree of silicon richness indicates that the quantum confinement effect could possibly play some key role in the luminescence process.

In the future, clarification of the emission origins would be our top priority. However, the detailed molecular bonding configuration of the deposited films should be first explored. Due to the lack of standard calibration samples for off-stoichiometric silicon dioxide films, the SIMS data can only provide the relative compositions of the major elements, but they cannot give the precise incorporated impurity concentration data. The FTIR transmittance spectra for samples deposited with various x values are shown in Fig. 3. The corresponding structure change of the deposited silicon-rich oxide films as a function of x can be described by separating the whole spectrum into three regions.

The first region is the O–H stretching mode located at 3385 cm⁻¹ for samples deposited with x = 0.4, which slowly shifted to 3370 cm⁻¹ as x increased to 0.7. The decrease of the integrated intensity with increasing the [SiH₄] gas-phase
composition indicates that the relative composition of oxygen decreased. The shift to the lower-energy side also reveals that the microstructure of the oxide films degraded while the [SiH₄] gas-phase composition was increased. Another peak located at approximately 3490 cm⁻¹ is identified as the NH₂ bending mode.⁹

The second region is the H–SiO₃ stretching mode mode peaked around 2245 cm⁻¹. It is clear from Fig. 3(c) that this stretching mode appeared when Γ ≥ 0.5 and increased with further increasing the [SiH₄] gas-phase composition.

The third region contains the stretching mode (1050 cm⁻¹) and bending mode (800 cm⁻¹) of the Si–O–Si bond, the bending and wagging mode of the polysilane chain (SiH₂)n, H–SiO₃ stretching-mode absorption (830–890 cm⁻¹), or Si–N stretching vibration (850–870 cm⁻¹).

The vibration frequency of the Si–O–Si stretching mode shifted from 1065 to 1024 cm⁻¹ as the [SiH₄] gas-phase composition was increased. The thermally grown stoichiometric SiO₂ has a stretching-mode frequency of 1073.8 cm⁻¹. This shift is similar to the results of the amorphous SiOₓ: H (0<r<2) alloy films proposed by Tsu, Lucovsky, and Davidson⁹ and lower the stretching vibration frequency means worse oxide quality. Their samples were deposited by using remote PECVD with an O₂–He mixture as the upstream plasma gas and 10% argon-diluted silane gas as the downstream gas. However, no evidence of obvious high nitrogen incorporation was measured from the FTIR spectra, the strong Si–O–Si IR absorption band and the lower refractive index (1.56<n<1.66), as determined from reflectance spectra, revealed that SiO₄ instead of SiO₃Nₓ is the dominant phase.

Considering our PL, SIMS, reflectance, and FTIR results, we find that the emission energy and intensity evolutions are strongly correlated to the [O]/[Si] composition. Furthermore, the luminescence energy evolution as a function of the Γ values, as shown in Fig. 2, exhibits some trends. Therefore, the UV bands could possibly be associated with the combination of oxygen-related defects and the quantum size effect. That is, due to excess silicon atoms incorporated into the films, silicon clusters would possibly be formed in the films. Because of the difference in the bonding configuration between the silicon clusters and the SiOₓ network, there might exist an oxygen-deficient transition layer between them to act as a recombination center. Moreover, the quantum confinement effect of the fine silicon clusters could enhance the quantum efficiency. When the grain sizes of these fine silicon clusters are too small, the energy levels in these clusters could be higher, and the photogenerated carriers cannot diffuse into these clusters. Instead, they would recombine through these oxygen-related species. For samples with larger clusters size, the energy levels could be comparable to the defect levels, and the transition energies of these two recombination mechanisms could be almost the same. With further increasing the cluster size, the energy levels of the clusters could be lower than the defect levels. Then, these two peaks are separated. Moreover, the energy redshifts of PL bands with respect to Γ could possibly result from the quantum size effect of the embedded silicon clusters. In comparison to the proposed theoretical results,¹⁰ the cluster size could be in the range of 1.5 to 3.5 nm. The cluster size of our silicon-rich oxide films could be increased with increasing the [SiH₄] gas-phase composition, and the PL energy shifted to the red region. However, further studies are necessitated before conclusions could be made.

In summary, an adjustable, intense PL at room temperature was observed from plasma-enhanced chemical-vapor-deposited hydrogenated amorphous silicon-rich oxide (SiOₓ:N:H, 0<x<2) thin films in the ranges from UV to red.

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