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Effect of thermal annealing on the blue luminescence of amorphous silicon oxycarbide films

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ABSTRACT

Amorphous silicon oxycarbide (a-SiC_xO_y) films that displayed blue luminescence were fabricated using very high frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) at a temperature of 250 °C. The effects of thermal annealing on the photoluminescence (PL) were investigated. Thermal annealing at 600 °C resulted in a remarkable enhancement in the blue PL, which was clearly observed with the naked eyes in a bright room. The blue PL featured an excitation wavelength independent recombination dynamic on a nanosecond timescale. Neither Si nor SiC quantum dots were present in the annealed films as revealed by transmission electron microscopy. The PL results, combined with an analysis of the chemical bonds present in the films, revealed that the origin of the blue PL was largely due to electron–hole pair recombination through Si-related neutral oxygen vacancy defect centers.

1. Introduction

Silicon-based light-emitting materials have attracted attention over the past decade for their potential as next-generation Si photonics. Silicon-based materials, including silicon nitride (SiN_x) [1–3], silicon oxide (SiO_x) [4–10], silicon oxynitride (SiN_xO_y) [11–14], and silicon oxycarbide (SiC_xO_y) [15–18], show promise as CMOS-compatible integrated light sources. Thus, significant research efforts have been devoted to understand and optimize their structural and optical properties. SiC_xO_y generally features strong white light emission and is regarded as a promising host matrix for rare earth [16–20]. It has been reported that SiC_xO_y is more effective at enhancing the mobility and solubility of Eu^{2+} ions than SiO_x, and thus significantly increases the PL intensity of Eu^{2+} [19]. Furthermore, the effective excitation cross section of Er, in Er-doped amorphous SiC_xO_y, is four orders of magnitude larger than that when Er is excited directly. This is a result of energy transfer between the band edges or defect levels of a-SiC_xO_y and Er ions [20]. Efficient PL from SiC_xO_y systems has been studied, although progress is slow. This is, in part because of a lack of information available to correlate the PL to other influences.

Previously, we reported that the strong light emission observed from a-SiC_xO_y films can be tuned from yellow to blue by modulating the oxygen content in the films [21]. In the present work, the effect of thermal annealing on the blue luminescence of a-SiC_xO_y films was investigated. Thermal annealing at 600 °C was found to significantly enhance the blue PL. The PL featured a wavelength independent recombination dynamic on a nanosecond timescale. The origin of the blue PL was postulated by combining the PL results with an analysis of the microstructure and the chemical bonds within the films.

2. Experimental

a-SiC_xO_y films with a thickness of 450 nm were prepared using VHF-PECVD with a gas mixture of SiH_4, CH_4, and O_2 at flow rates of 2.5, 10, and 1.2 sccm, respectively. During the growth process, the radio frequency power, chamber pressure, and substrate temperature were 30 W, 20 Pa, and 250 °C respectively. The detailed experiment was described in previous work [21]. The as-deposited samples were dehydrogenated at 400 °C for 1 h. The samples were then annealed in a conventional furnace under a nitrogen atmosphere at 500, 600, or 700 °C for 1 h. The PL measurements were performed at ambient temperature using a Jobin Yvon fluorolog-3 spectrophotometer equipped with a 450 W steady Xe lamp. PL time decay measurements were recorded using an Edinburgh FLS980 spectrometer. The band gaps of the samples were determined using optical absorption measurements performed on a Shimadzu UV-3600 spectrophotometer on quartz samples. The microstructures of samples were characterized using a JEOL high-resolution transmission electron microscope (TEM). The Si, O and C elemental compositions within the samples were estimated using X-ray photoelectron spectroscopy (XPS). The local atomic environment and bonding configuration within the samples were recorded using Fourier transform infrared (FTIR) spectroscopy.

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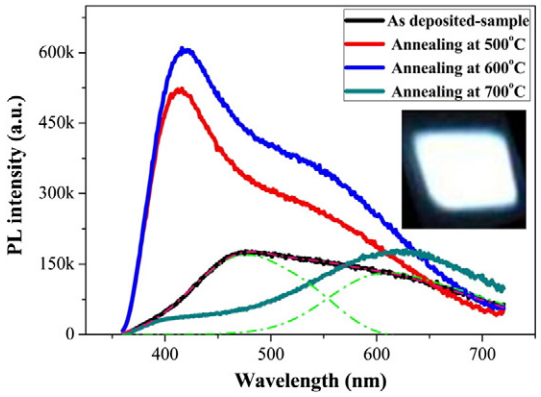

Fig. 1. PL spectra of silicon oxycarbide samples annealed at different temperatures. The spectra were deconvoluted into a strong blue Gaussian band and a weak orange Gaussian band. The inset shows a photo of the sample annealed at 600 °C emitting light following excitation at 325 nm from a Xe lamp.

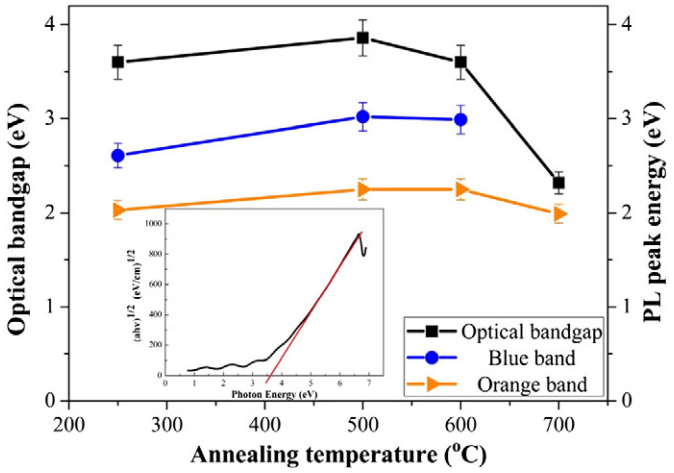

Fig. 2. Optical band gap and PL peak energy of the deconvoluted bands in a-SiC_xO_y as a function of annealing temperature. Inset shows the Tauc plot of the as-deposited sample.

3. Result and discussion

The PL spectra of the as-deposited and annealed samples are shown in Fig. 1. The spectrum of the as-deposited sample displayed a broad band centered at approximately 475 nm. This broad band can be deconvoluted into a strong blue Gaussian band and a weak orange Gaussian band. The integrated intensity and the full wide at half of maximum (FWHM) of the decomposed blue and orange Gaussian bands were summarized in Table 1. From Fig. 1, one can see that the blue band was found to gradually shift from 475 nm to 420 nm as the annealing temperature was increased to 600 °C. This blueshift was accompanied by a significant enhancement of the PL intensity. Thermal annealing of the films at 600 °C was found to significantly enhance the integrated PL intensity I_{PL} of the blue PL by more than two times when compared with the as-deposited sample, as shown in Table 1. Notably, the strong white light emission from the sample annealed at 600 °C could be clearly observed with the naked eye in a bright room when excited with a wavelength of 325 nm from Xe lamp, Fig. 1 (inset). However, as the annealing temperature was increased to 700 °C, the intensity of the blue PL dropped dramatically, while the orange band centered at approximately 625 nm become dominant. From Table 1, one can also see that the FWHM of the blue band decreased sharply with the increase of annealing temperature, while that of the orange band increased and saturated at the annealing temperature of 500 °C.

The optical band gap energies (E_{opt}) of the samples were determined using the absorption profiles and the Tauc equation $(\alpha h\nu)^{1/2} = B(h\nu - E_{opt})$, where α is the absorption coefficient and $h\nu$ is the photon energy [22], Fig. 2 (inset). The energy of the PL peaks, and the corresponding E_{opt} values, for the films annealed at different temperatures are shown in Fig. 2. From Fig. 2, one can see that the behavior of the PL peak energy for both deconvoluted bands with the annealing temperature exhibits a similar tendency to the E_{opt}. The energy of the PL peak was lower than the corresponding E_{opt} value, indicating that the PL of the samples did not originate from band to band recombination. This conclusion was supported by the absence of any Si or SiC nanocrystals within the sample annealed at 700 °C, when observed using cross-sectional high-resolution TEM (Fig. 3). To understand the origins of PL emission, the samples were excited at different wavelengths, as displayed in Fig. 4. The PL peak position observed for all samples was independent of the excitation wavelengths. This PL behavior was similar to that of the defect-related PL in which the PL peak position is independent of the excitation wavelength because of a narrow distribution of defect-related localized states [23]. This result suggested that the PL may originate from defect-related luminescence centers.

To elucidate the nature of the blue light emission in the a-SiC_xO_y films, the PL lifetime of the samples were measured. The blue PL decay traces from the as-deposited and annealed samples are shown in Fig. 5. The decay traces fit the double exponential decay function:

$$I(t) = I_0 + I_1 * \exp(-t/\tau_1) + I_2 * \exp(-t/\tau_2),$$

where I_0 is the background level, I_i and τ_i ($i = 1, 2$) are the amplitude and lifetime of each exponential decay component, respectively [23]. Fig. 5 shows that the blue luminescence lifetime τ of all samples contained both a fast decay component τ_1 (1.27 ns) and a long decay component τ_2 (in the range of 6.53–5.48 ns depending on the annealing temperature). The dynamic behavior of the luminescence was consistent with that observed in defect-related Si-based materials such as

Table 1
The integrated intensity and the full wide at half of maximum (FWHM) of the decomposed blue and orange Gaussian bands for a-SiC_xO_y films annealed at different temperatures.

Samples	Blue band		Orange band	
	I_{PL} (a.u.)	PL spectrum FWHM (nm)	I_{PL} (a.u.)	PL spectrum FWHM (nm)
As-deposited sample	2.2×10^7	129	2.0×10^7	166
Annealing at 500 °C	4.2×10^7	75	5.4×10^7	199
Annealing at 600 °C	4.5×10^7	77	6.9×10^7	196
Annealing at 700 °C	…	…	3.6×10^7	190

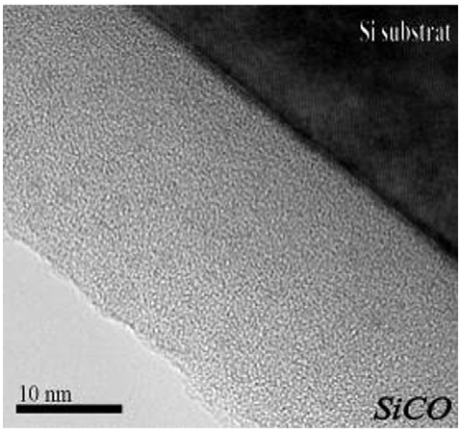

Fig. 3. The cross-sectional high-resolution TEM image of the sample annealed at 700 °C.