

Intensely Photoluminescent Pseudo-Amorphous SiliconOxyCarboNitride Polymer–Ceramic Hybrids

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SiliconOxyCarboNitrides (SiCNO), made from thermal treatments of highly cross-linked silicon, nitrogen, and oxygen containing polymers, exhibit intense luminescence that is broadly distributed over wavelengths of 500–800 nm. The intensity is sensitive to the composition, and especially to the heat-treatment temperature (T_{HT}) of these new materials. The absorbance increases, and thus the brightness of the emission dims, as T_{HT} rises. The phenomenology suggests the presence of two, spatially and energetically separated, molecular complexes: one that absorbs and another that produces photoluminescence. The SiCNO are an entirely new class of high-temperature materials that can be molecularly tailored for optical device applications.

I. Introduction

POLYMERS made from cyclic, highly cross-linked silicon–nitrogen and silicon–oxygen organics, when pyrolyzed, rearrange into novel nanostructures with myriad multifunctional properties.¹ In the organic state, these polymers remain stable to temperatures exceeding 400°C. The molecular network begins to rearrange when they are heated further. Eventually, the carbon–hydrogen bonds in the polymer begin to give way to molecular hydrogen, which is released into the atmosphere, whereas the carbon radicals left behind apparently self-assemble into graphene networks. These graphene networks form nanodomains² that contain mixed C–Si–N–O tetrahedra in the domain walls. While the C in the graphene has *sp*² character, the mixed bonds and silicon tetrahedra show *sp*³ nature. The measurements of the domain size, as well as the presence of *sp*² and *sp*³ bondings, are consistent with SAXS,^{3,4} Raman,⁵ IR,⁶ and NMR³ characterizations. The materials remain amorphous in Bragg's diffraction even when heated up to 1350°C.³

These polymer–ceramic hybrids can be classified into two groups, one which is predominantly organic, with hydrogen, and the other which is predominantly an inorganic ceramic. These extremes are obtained at heat-treatment temperature (T_{HT}) of about 400° and 1000°C, respectively.⁷

In this article we report the photoluminescence of these SiliconOxyCarboNitride materials after heat treating them over a range of temperatures and with a wide range of compositions. Measurements of the absorption optical band-gap (Tauc band-gap) are also reported.

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II. Experimental Procedure

Four series of samples with three control variables: the composition, the T_{HT} , and in bulk and powder form, were prepared. A summary is given in Fig. 1. In the SP series, T_{HT} was held at 1000°C, while the nitrogen to oxygen ratio was varied from the oxygen-rich to the nitrogen-rich end. The LP and LB series were all rich in nitrogen, but T_{HT} was changed. In the AB series the nitrogen and oxygen contents were about equal, but T_{HT} was varied from 400° to 800°C. The powders (SP and LP) had a size range of 10–30 μm, while the bulk specimens (LB and AB) were in the form of 100-μm-thick films. The procedure for sample preparation has been presented elsewhere.⁸

Photoluminescence measurements were performed with a 488 nm Argon laser with 1.5 mW power focused on a spot of 0.5 mm diameter. Emitted light was collected perpendicularly to the illuminated sample surface, by a double grating monochromator and a photomultiplier tube. Measured spectra were corrected by the instrument response. Transmittance measurements were performed with a standard spectrophotometer in the wavelength range 0.35–2.50 μm (0.50–3.54 eV).

The Tauc band-gap was estimated under the hypothesis of parabolic bands, which leads to the following equation:⁹

$$\alpha hv \propto (hv - E_{Tauc})^2 \quad (1)$$

where α is the absorption coefficient in cm^{-1} (as given by the Lambert–Beer law), hv is the energy of the incident photons, and E_{Tauc} is the Tauc band-gap. The values for E_{Tauc} were estimated by plotting the data according to Eq. (1), and taking the intercept on the hv axis. The estimation of α was limited on the long wavelength side by the instrument (2.5 μm or 0.25 eV), and on the short wavelength side by the absorption in the samples.

We also performed photoluminescence lifetime measurements by exciting the samples with the third harmonic (355 nm) of a pulsed Nd:YAG laser (pulse duration 4 ns). Luminescence lifetimes were estimated by fitting the data with a stretched exponential function;¹⁰ lifetimes of 5–10 ns were observed for all the samples.

III. Results

(I) Photoluminescence

The spectra from samples heat treated in the 800°–1200°C range (SP, LP, and LB) were insensitive to T_{HT} , but were highly sensitive to the composition. Samples in the SP series, with variable N/O ratio, showed a strong effect on the composition, as shown in Fig. 2(a). The peak intensity was highest at the nitrogen-rich end and fell continuously (except in SP-3) toward the oxygen-rich extreme. In general the emission was broad, spanning 500–850 nm. In SP-3, which contained equal moles of nitrogen and oxygen, the emission was highly peaked at 580 nm.

However, T_{HT} in the 400°–800°C range had a huge effect on the emission intensity, as shown in Fig. 2(b) for the AB samples.

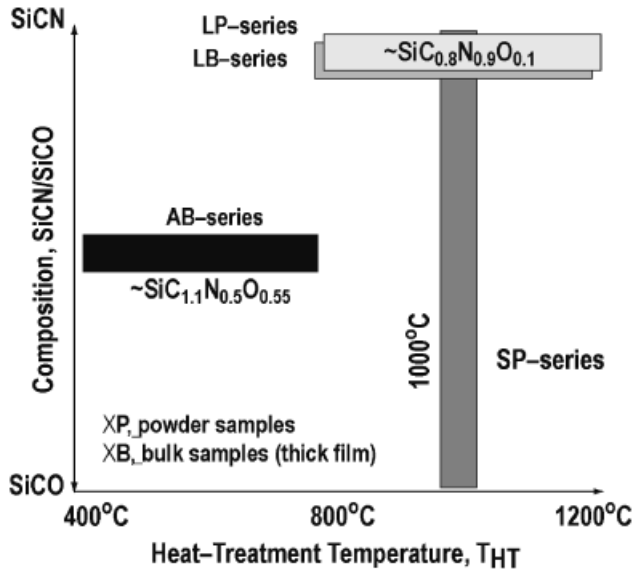


Fig. 1. The compositions and the heat-treatment temperature (T_{HT}) for the four sets of samples.

The emission intensity is low for the 400°C sample, but rises quickly to a maximum at $T_{HT} = 500^\circ\text{C}$ and then again falls at higher T_{HT} .

The peak intensities for all four sets of data, relative to each other, are plotted in Fig. 3. The plot shows that the emission peak from the $T_{HT} = 500^\circ\text{C}$ sample is three to five orders of magnitude more intense than the results from SP, LP, and LB series. Data from Si-nanocrystals (nc) are included as a benchmark.^{11,12} The results from the SP, LP, and LB series are in the same range as this benchmark.

(2) Absorption

While the intensity of emission varies greatly with the T_{HT} , the wavelength at emission peak did not show a significant change, varying from about 2.0 to 2.5 eV (Fig. 4(b)). This suggested a dichotomy between the mechanism for absorption and for emission (usually emission energy is lower than the absorption edge). Therefore the absorption spectra were measured. These results are shown in Fig. 4. The graph on the left shows the transmittance as a function of the wavelength. The sharp absorption peaks, in the 1–2.5 μm range, in the samples annealed at low temperatures are attributed to CH, NH, and CH_2 vibrational modes.¹³ These hydrogen-related bands tend to disappear with the increase of the annealing temperature.

The Tauc band-gap, E_{Tauc} , was determined by plotting the data according to Eq. (1). The results are shown in Fig. 5. The extrapolated threshold is equated to the band-gap. The values for this band-gap are plotted on the right in Fig. 4(b). Note that although the Tauc band-gap decreases rapidly with higher

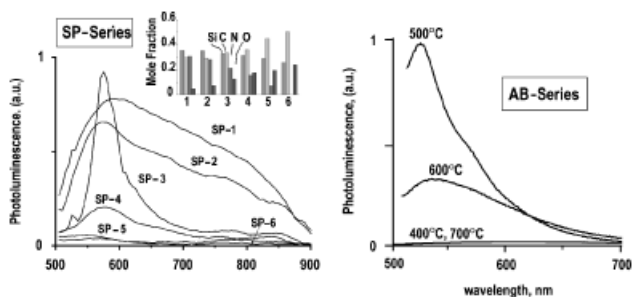


Fig. 2. Photoluminescence spectra from the SP-series (left) and the AB-series (right).

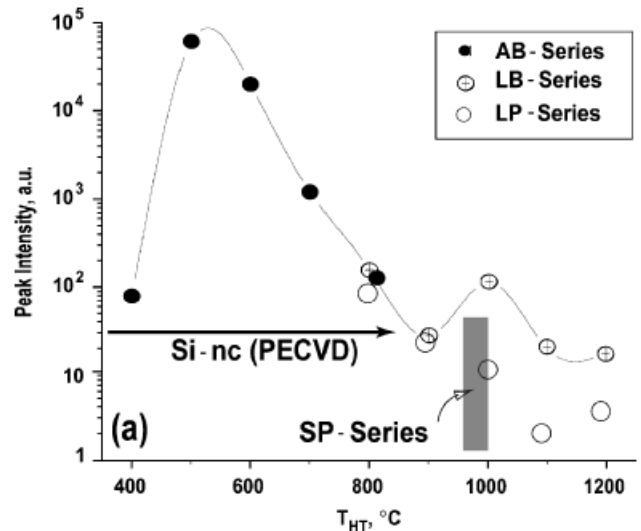


Fig. 3. The change in the peak intensity with the heat-treatment temperature (T_{HT}).

annealing temperature, the emission energy remains essentially unchanged.

IV. Discussion

A principal observation from the data presented above is that polymer-derived ceramics can be intensely luminescent, and that the luminescence is quenched by high absorption in the samples annealed at higher temperatures (Fig. 4(b)). This result is the opposite of the measurements of photoluminescence in various amorphous materials constituted from Si, C, N, O, and H (a-SiN_x:H, a-SiC_x:H, a-C:H, and a-CN_x:H),^{14–18} where the photoluminescence peak energy is lower than the Tauc band-gap for absorption. This observation can be explained in two ways.

One possible explanation is multiphoton absorption, where visible luminescence can be excited by infrared radiation.¹⁹ This explanation is considered to be unlikely because multiphoton absorption is observed when high-intensity pulsed laser sources are used to excite the samples; in the present experiments, low-power continuous wave sources were used.

A second explanation is that the samples contain two band-gaps, one of low energy that absorbs and the other of high energy that luminesces. These band-gaps are assumed to arise from two different, spatially separated, molecular complexes. This explanation is consistent with a nanodomain model for these materials.² The model consists of a network of graphene-like, two dimensional structures that form nanodomains. The walls of this network contain mixed bonds of Si–C–N–O tetrahedra. The photoluminescence is assumed to arise from the mixed-bond tetrahedra, whereas the absorption is assumed to occur in the graphene network. The relative concentration of these Si-centered sites and the C-sites in the graphene can be calculated from the model² (they are about equal), which can explain the correlation between emission and absorption. The unusual finding from the current work is the continuous evolution of the absorptive structure with increasing annealing temperature. It is usually assumed that the carbon network develops above about 800°C, but apparently it begins to evolve at about 600°C.

The second unusual result is the narrowly peaked photoluminescence from sample SP-3, shown in Fig. 2(a). We suspect that nanoclusters or nanocrystals of stoichiometric silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) are forming in this specimen. High-temperature calorimetric studies of these materials also show this anomalous behavior when the N/O molar ratio is approximately equal to two.⁹

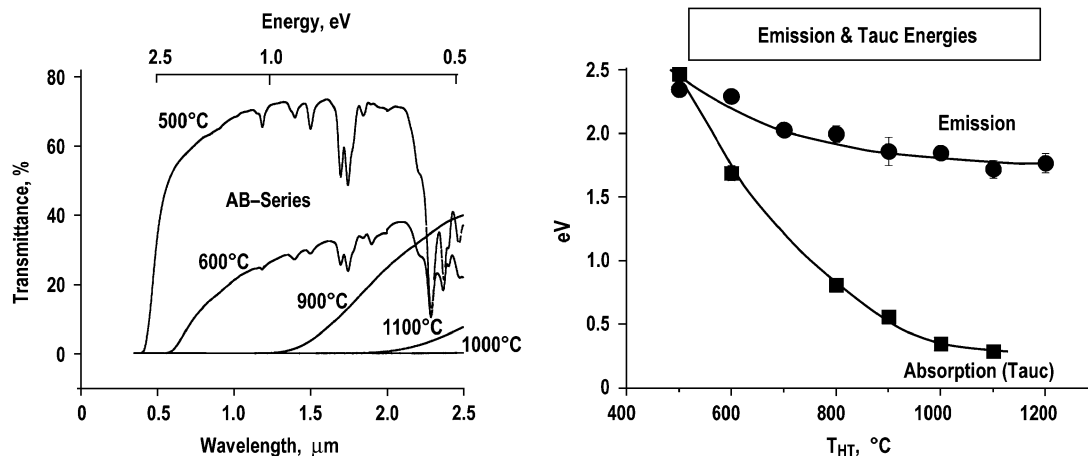


Fig. 4. Absorption spectra for the measurement of the Tauc optical band-gap (left), and a comparison of the emission energy with the absorption band-gap (right).

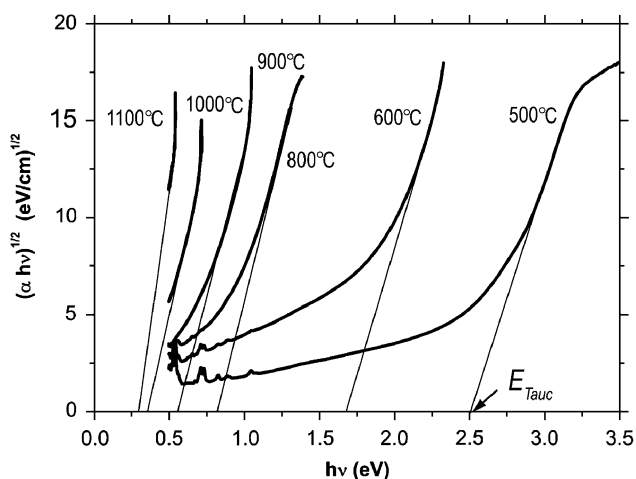


Fig. 5. The plot of the absorption data, according to Eq. (1), for determination of the Tauc band-gap.

V. Conclusions

The intensity of the photoluminescence from polymer-ceramic hybrids of Si, C, N, and O depends on their compositions and the T_{HT} . The highest intensity, which is four orders of magnitude greater than benchmark silicon nanocrystals, is obtained for a T_{HT} of 500°C. The emission band-gap and the Tauc absorption band-gap appear to be uncoupled because they change very differently with the T_{HT} .

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