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On the origin of white light emission from nanostructured silicon carbonitride thin films

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ABSTRACT

The effects of thermal annealing on the visible luminescence of hydrogenated silicon carbonitride (SiC_xN_y:H_z) thin films were investigated. Thin films of a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ were grown using electron cyclotron resonance plasma enhanced chemical vapor deposition and subsequently were annealed between 400 and 1200 °C for 1 h in nitrogen gas. The samples exhibited a broad luminescence band, covering the visible range with two dominant peaks at ~ 470 and 550 nm, which appeared "white" to the naked eye. This white light emission could be deconvoluted into four photoluminescence (PL) bands. To understand the origin of PL from this complex material, two fairly well-studied submatrices, SiC:$H_{1.3}$ and $SiN_{1.3}$:$H_{0.3}$, were also investigated. Our findings showed that the intensity of the PL emission of a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ was higher than that of the binary matrices and was achieved at an optimized annealing temperature of 500 °C. Carbon-related silicon defect centers were suggested as the sources of the luminescence of the a-SiC_xN_y:H_z thin films. The observed visible emission was strongly correlated with different Si-C bonding configurations.

1. Introduction

Silicon, the prime material of microelectronics, has seen growing interest in silicon photonics [1] and for applications in "all-silicon" tandem solar cells [2,3]. Nanoscience employed various strategies to overcome the fundamentally inefficient light emission of silicon, including through doping [4,5], developing new silicon-based structures [6], hybrid silicon-germanium nanostructures [7], and other choices of materials [8]. Each of the proposed silicon-based materials has its own disadvantages in attempting to reach commercialization, such as electrical driving problems or deficiencies in the mechanical properties. However, silicon carbonitride (SiC_xN_y) thin films exhibit a wide and tunable band gap by being combined from silicon carbide, silicon nitride, and carbonitride (a choice after diamond as a hard material) binaries [9].

Despite reports on promising mechanical properties of SiC_xN_y materials [9], they have not yet been well explored optically [10]. In effect, therefore, the understanding of the origin of photoluminescence (PL) of SiC_xN_y structures is lacking [11,12]. Existing literature on the PL mechanism of SiC_xN_y thin films reported on samples containing oxygen, i.e., $SiO_xC_yN_z$ structures [13,14], wherein oxygen-related bonds are suggested as the sources of the luminescence. In addition, to the author's best knowledge, there exists no comparative study of the visible light emission of silicon carbide, silicon nitride, and SiC_xN_y structures over a wide range of annealing temperatures (400–1200 °C).

In this contribution, the thermally induced changes of the PL of hydrogenated amorphous, N- and C-free, SiC_xN_y samples are explored. The origin of the luminescence in a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ is investigated using the correlation with the sources of the luminescence observed in submatrices of SiC:$H_{1.3}$ and $SiN_{1.3}$:$H_{0.3}$ thin films. The PL emission appeared "white" to the naked eye and showed a strong correlation with the thermally induced changes of the Si-C bond densities and hydrogen desorption.

2. Method

Samples were fabricated using electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR PECVD) with a microwave power of 500 W. A mixture of 30% SiH_4 in Ar, 10% N_2 in Ar, and pure CH_4 was fed to the reactor for a 30-min to deposit on Si (100) substrate. The temperature of 120 °C of the substrate, hydrofluoric acid etched for 1 min, resulting from a stage heater set to 350 °C. First, the precursor flow rates for the deposition of stoichiometry SiC:$H_{1.3}$ and $SiN_{1.3}$:$H_{0.3}$ were determined as 5 and 4 sccm (for SiH_4 and CH_4) and 5 and 10 sccm (for SiH_4 and N_2), respectively, where sccm denotes "cubic centimetres per minute at standard temperature and pressure". The most luminescent film, a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ was produced by 5, 10, and 8 (± 5%) sccm of SiH_4, N_2, and CH_4 gas flow rates [15]. All three classes of as-

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Table 1
The optical properties of the a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ thin films.

Temperature (°C)	E_{04} (± 0.2 eV)	E_u (eV)	D (± 0.4 nm)	n (λ = 632.8 nm)
AD	3.6	0.28	232.7	2.08
400	3.5	0.30	226.3	2.08
500	3.5	0.49	224.7	2.08
600	2.7	0.50	218.3	2.08
700	1.5	0.89	212.1	2.10
900	0.5	1.24	192.8	2.22
1100	0.8	0.94	209.0	2.59
1200	1.0	0.71	193.7	2.69

deposited (AD) thin films were further subjected to thermal annealing at temperatures of 400–1200 °C in a quartz tube furnace with nitrogen gas, sequentially in 100 °C increments, for 1 h, and cooled in nitrogen gas before extraction from the tube furnace.

The thickness and the optical band gap of the samples were determined by variable angle spectroscopic ellipsometer (VASE) measurements and J. A. Woollam's CompleteEASE software package. The hydrogen content was measured by the elastic recoil detection (ERD) technique using 2.0 MeV $^4He^+$ ion and SIMNRA code. The chemical bonds of the films were identified using a combination of X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) techniques. The details of VASE, ERD, XPS, and FTIR measurements have been discussed elsewhere [16].

The room-temperature PL spectra of the samples were measured between 350 and 1000 nm using a 325 nm He-Cd laser (E_{exc} = 3.82 eV) with an optical power of 5 mW exciting an area of 2.3 mm^2 [17]. The room-temperature PL profile broadly extends over the visible range and the PL lines are resolved through the Gaussian fitting. To minimize errors in the decomposition, especially in a broad emission band, the overlapping features of luminescence data require the conversion to energy and, consequently, the transposition of the intensity by a factor of λ^2/hc [18]. The recorded room-temperature PL data as a function of wavelength were first converted to energy, smoothed using a Savitzy-Golay function, and then fitted to Gaussian curves using Origin 9.4.1.

3. Results

The as-grown a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$, SiC:$H_{1.3}$, and $SiN_{1.3}$:$H_{0.3}$ thin films were 263, 364, and 139 nm thick with optical band gaps of 3.6, 3.9, and 3.0 eV, respectively (see Table 1), and contained 32, 40, and 9 at% hydrogen. The concentration of the constituent elements is listed in Table 2. In Fig. 1(a), the Si 2p core levels of annealed a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ films with the corresponding chemical bonds are shown. The weak signal of Si–O is related to the negligible oxygen contamination and the surface oxide layer formed during the annealing. Fig. 1(b) shows the mid-infrared absorption spectra of the as-deposited and several annealed $SiC_{1.2}N_{0.7}$:$H_{1.4}$ samples, along with a-$SiN_{1.3}H_{0.3}$ and a-SiC:$H_{1.3}$ references, baseline-subtracted and normalized to the film thickness. More details can be found in [16], where we studied annealed a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ thin films from the structural and compositional point of view.

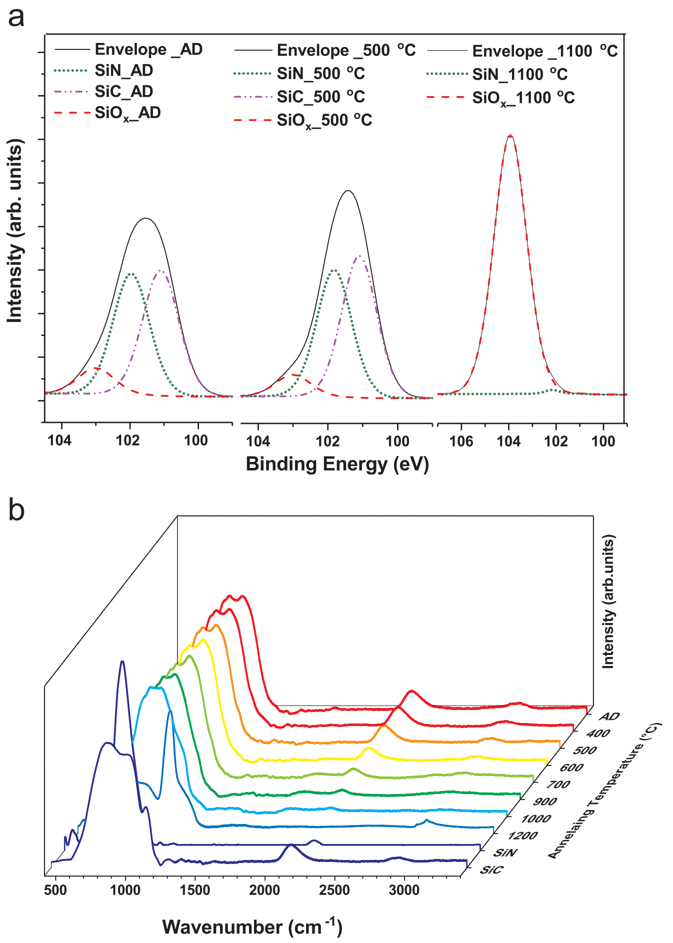

Fig. 1. Comparison of Si 2p core levels of the annealed a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ films with the corresponding chemical bonds. The relative concentration of Si-C to Si-N bonds is higher at 500 °C. The small signal of the Si-N bond is, still, detected at higher temperatures while the Si-C feature entirely disappears; (b) Infrared absorption spectra of a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ as a function of annealing temperature along with a-$SiN_{1.3}H_{0.3}$ and a-SiC:$H_{1.3}$ reference samples.

Fig. 2(a) shows PL spectra of untreated a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ and thermally annealed samples covering the entire visible range. The broadening of the PL originates from the long-range structural disorders, present in the amorphous materials introducing localized states into the band gap (“antiparallel band-edge fluctuations”) [19]. The width of the band tail due to the localized states is indicated by the Urbach energy (E_u) given in Table 1. Upon annealing to 500 and 900 °C, E_u increases while the optical band gap (E_{04}) narrows from 3.6 to 2.7 eV and from 2.7 to 0.5 eV, respectively. ERD measurements show that the majority of the hydrogen content effuses beyond annealing at 500 °C and is entirely depleted at 900 °C. The hydrogen desorption from the film layer results in an increase of unsaturated bonds. This leads to an increase of the mid-gap states in the band structure (an increase of E_u), and in turn, a decrease of the E_{04} gap. Fig. 2(a) shows that the PL intensity increases upon annealing and reaches a maximum at 500 °C,

Table 2
The elemental composition of annealed a-$SiC_{1.2}N_{0.7}$:$H_{1.4}$ thin films and as-deposited SiC:$H_{1.3}$ and a-$SiN_{1.3}$:$H_{0.3}$ thin films.

Temperature (°C)	([Si] ± 0.8) at%	([C] ± 2.5) at%	([N] ± 1.8) at%	([O] ± 1.4) at%	([H] ± 2.0) at%
AD-SiCN	22.7	28	15	2	32
500	23.2	33	13	3	27
900	34.2	37	19	5	5
1200	36.6	32	20	8	3
AD-SiN	38.4	0	49	3	9
AD-SiC	28.3	29.4	0	3	39