Photoluminescence spectra of laser-synthesized Si/C/N ultrafine powders

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Abstract. Ultrafine Si/C/N ceramic powders were synthesized by a CO_2-laser-induced reaction between silane (SiH_4), ammonia (NH_3) and acetylene (C_2H_2). The powders were characterized by infrared (IR) reflection and photoluminescence (PL) spectroscopy. From the infrared reflection spectra of Si/C/N powders, we have identified the causes of the strong photoluminescence present in these powders. The photoluminescence spectra of Si/C/N powders originate from the presence of hydroxylated and amorphous silicon (a-SiO_2) formed at the porous surface of these powders. We have shown that different chemical bonding between Si, C and N atoms, the degree of crystallinity of ternary powders and their porosity strongly influence the processes at their surface, i.e. the formation of amorphous silicon and silanole.

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Silicon nitride (Si_3N_4) is an important non-oxide-ceramic material with many modern applications because of its superior mechanical, thermal and chemical properties. Recent studies suggest that Si_3N_4 ceramic materials with improved thermomechanical properties can be obtained by incorporation of SiC particles into Si_3N_4 matrices [1]. Namely, silicon carbide–silicon nitride composites have increased hardness, creep and oxidation properties compared to pure Si_3N_4 materials [2, 3]. In the past few years a growing interest is for the production of nanosize (10–100 nm diameter) ternary, amorphous Si/C/N powders which are not a simple mixture of silicon nitride and silicon carbide, but represent new compounds with a tetrahedral atomic arrangement in which both C and N atoms are bonded together to the same central Si atom [4, 5]. The special interest for the production of ternary Si/C/N powders could be explained by their large range of properties from superplasticity to higher strength and toughness, depending on their composition. Among the innovative techniques, such as chemical vapor deposition (CVD) and arc-plasma processes, for the production of nanometric powders, laser-induced pyrolysis offers many advantages. Laser synthesis of powders starting from gaseous or volatile

mixtures [6–8] is a powerful method for growing homogeneous mixtures of pure and ultrafine Si/C/N particles. This method is based on the absorption of the infrared (IR) laser energy into vibrational modes of reaction gases, causing very high temperatures (above 1000 °C) for a short total reaction time (0.1 s or less), necessary for the initiation of a chemical reaction whose final result is the formation of powders. The grown particles have a spherical morphology, small size and narrow size distribution, and their composition and stoichiometry can be precisely controlled by adjusting the main process parameters such as laser intensity, reaction-cell pressure, reactant-flow rates and reaction-gas ratio R. Vibrational spectroscopy (Raman and IR) is a very suitable method for the characterization of Si/C/N and Si_3N_4 powders. However, the appearance of the photoluminescence (PL) is often a problem in Raman spectroscopy of Si_3N_4 powders. In fact, the silicon nitride powders, exposed to highly oxidized or ambient atmosphere for a longer period of time [9], will always be covered with an oxygen-rich layer. This layer can be either amorphous non-stoichiometric SiO_xN_y or an amorphous silica layer (a-SiO_2) or both [10]. The exact nature of this layer formed at the surface of Si_3N_4 materials depends upon various factors such as impurities and additives in the material, its porosity, stoichiometry and the composition of the ambient environment. The presence of an a-SiO_2 layer at the surface of Si_3N_4 powders could be a reason for the appearance of a strong luminescence [11], as it causes the same photoluminescence bands in systems like silica aerogel (SA) [12, 13]. In the PL spectra of SA samples [14–16], bands at $1.8 - 1.9$, 2.0 and 2.2 eV are present. The PL band at 1.8 eV originates from a non-bridging oxygen hole center defect (SiO$\cdot$H, NBOHC). The PL band at 2.0 eV originates from silane in the gel network, while non-stoichiometric SiO_x causes a PL band at 2.2 eV. We detected some of these bands in our laser-synthesized Si/C/N powders. In the PL spectra of Si/C/N samples several strong photoluminescence bands are present: at 1.8 eV, 2.0 eV and 2.2 eV. The appearance and intensity of these PL bands strongly depend on the chemical composition and the degree of crystallinity of Si/C/N powders. The presence of porosity in Si/C/N powders also can make the chemical processes at their surface more com-

plicated. Namely, at the surface of Si/C/N powders, under certain conditions, a layer of a-SiO$_2$ can be formed. When the surface of SiO$_2$ is exposed to humidity, it can be hydroxylated. The frequency of the Si−O−Si antisymmetric stretching vibration depends on the oxygen atomic composition, e.g., on x in the formula SiO$_x$. In the IR-absorption spectra the frequency of non-stoichiometric SiO$_x$ lies between 975 cm^{-1} and 1085 cm^{-1} (the frequencies of stoichiometric SiO and SiO$_2$) [17].

In this paper we present PL and IR reflection spectra of ternary Si/C/N powders that differ from each other depending on their chemical composition and crystallinity. Comparing the PL spectra of ternary Si/C/N powders with PL spectra of laser-synthesized Si$_3$N$_4$ and silica aerogel samples we show that the PL spectra of Si/C/N, Si$_3$N$_4$ powders and SA are very similar. From IR reflection spectra we identify the causes of the bands present in the PL spectra of Si/C/N powders.

1 Experimental procedure

The Si/C/N ternary ceramic powders were synthesized from a silane (SiH$_4$), ammonia (NH$_3$) and acetylene (C$_2$H$_2$) gas mixture using a continuous-wave CO$_2$ laser. One of the main process parameters, the ammonia–silane flow ratio R, was varied from 0.5 to 2 keeping fixed the SiH$_4$ flow rate ($\Phi_{SiH_4} = 400$ cm^3/min) and the C$_2$H$_2$ flow rate ($\Phi_{C_2H_2} = 200$ cm^3/min). The cell pressure was also kept constant during the powder synthesis ($p_c = 700$ mbar). The pure Si$_3$N$_4$ powders were produced with the ammonia–silane ratio $R = 3$. The experimental device used for the synthesis of Si/C/N and Si$_3$N$_4$ powders is described elsewhere [18]. The laser source (Rofin Sinar RS500) had an emitted power up to 500 W and operated in a continuous mode.

The sample of silica aerogel with a bulk density of 0.21 g/cm^3 was produced by mixing tetra-ethylorthosilicate (TEOS), water and ethyl alcohol with a TEOS:H$_2$O:ethanol molar ratio 1 : 2 : 6. A two-step catalysis method was used. The sample was neutral (pH= 7) and dried by supercritical extraction in cylindrical Teflon tubes (critical parameters for ethyl alcohol are $T_c = 243.1$ °C and $p_c = 62 \times 10^5$ Pa). Bulk density was determined from the mass and dimensions of the cylindrical monolithic samples.

IR reflection spectra of Si/C/N and Si$_3$N$_4$ powders were measured using a BOMEM DA8 spectrometer in the spectral range between 400 and 2000 cm^{-1}, while the sample of silica aerogel was measured using a Perkin-Elmer model-983G spectrometer in the same spectral range.

PL spectra were excited by a 488 nm (2.54 eV) line of an Ar-ion laser and measured using a Jobin-Ivon U-1000 monochromator with a photomultiplier tube as detector. The measurements were performed in air at room temperature (where the samples are in equilibrium with humidity from the atmosphere).

2 Results and discussion

Figure 1 represents PL spectra of Si/C/N samples obtained varying only the ammonia–silane ratio R ($R = 0.5, 1.5, 2$) while the other process parameters were kept fixed. On the
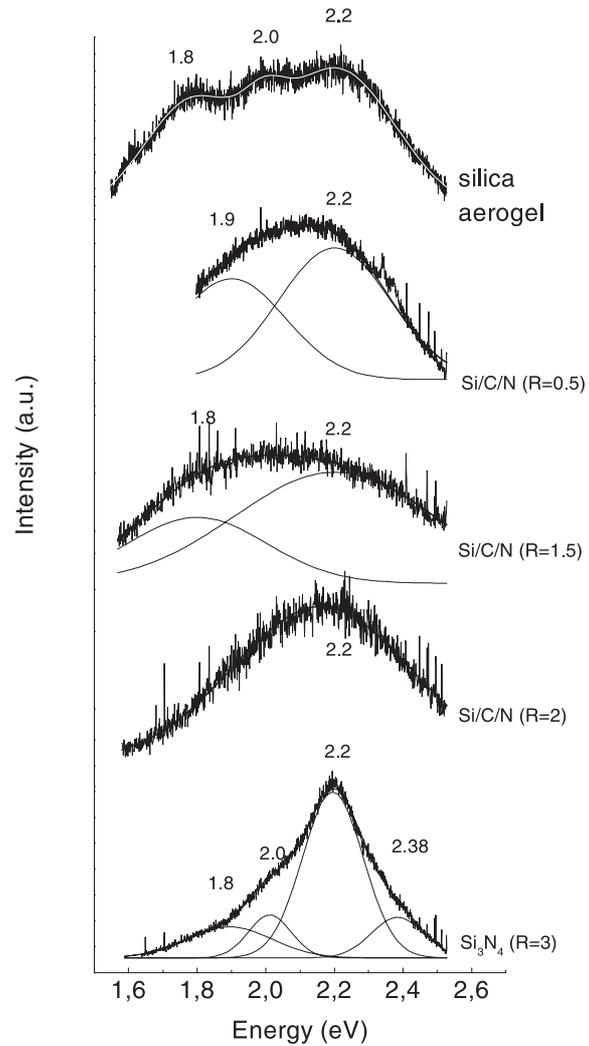

Fig. 1. PL spectra of Si/C/N samples obtained on varying the ratio R ($R = 0.5, 1.5, 2$). On the *top* and *bottom* of the figure are shown the PL spectra of SA and Si$_3$N$_4$ samples as references

top and bottom of Fig. 1 are represented the PL spectra of SA and Si$_3$N$_4$ samples as references. Each PL band was fitted by an individual Gaussian and the spectra have been modeled by the sum of Gaussians shown with a full line. The fitting procedure gives maximum position (ω_{max}), half-width (w), area below the band (A) and intensity of the PL band (I).

In the PL spectra of Si/C/N powders the mode at 2.2 eV is present in all Si/C/N samples. In the Si/C/N sample produced with $R = 2$ this mode only is present. So this sample is well fitted with a single Gaussian. In the case of Si/C/N samples produced with $R = 1.5$ and 0.5 there are two modes. The more prominent mode is at 2.2 eV while the mode at 1.8 eV is also present, but is much weaker. The spectra of these samples are fitted with two Gaussians whose sum is shown with a full line in Fig. 1. The mode at 2.2 eV can be ascribed to the existence of non-stoichiometric SiO$_x$ ($1 < x < 2$) formed at the surface of these powders, while the weaker mode at 1.8 eV originates from the NBOHC-type defect. The existence of this mode indicates that the silanole sites are also formed at the surface of Si/C/N powders. In the PL spectra of Si$_3$N$_4$ powder three modes are present. The most prominent mode is at 2.2 eV. The less intense mode is at 2.0 eV and can be re-

lated to the existence of silane (SiH_2) captured in the pores. This mode is not evidenced in the PL spectra of ternary compounds. The mode of silanole is the weakest mode located at 1.8 eV. Comparing the PL spectra of ternary Si/C/N and Si_3N_4 powders with a PL spectrum of a SA sample it is evident that the positions of the PL bands coincide.

The IR reflection spectra of Si/C/N (with $R = 0.5, 1.5, 2$) and Si_3N_4 powders are given in Fig. 2. Experimental data are shown with circles while the calculated spectra are shown with full lines. These spectra are well fitted with six oscillators whose TO (LO) mode frequencies are presented in Table 1. The frequencies of the TO and LO modes were deduced from the infrared reflection spectra using a fitting procedure based on a dielectric function model of the form [19]:

$$\varepsilon = \varepsilon_\infty \prod_j \frac{\omega_{LO_j}^2 - \omega^2 + i\gamma_{LO_j}\omega}{\omega_{TO_j}^2 - \omega^2 + i\gamma_{TO_j}\omega} \qquad (1)$$

As can be seen from Fig. 2 all the spectra of Si/C/N powders exhibit an amorphous structure very similar to Si_3N_4. The first two modes, around $500\,\mathrm{cm^{-1}}$ and $950\,\mathrm{cm^{-1}}$, are ascribed to the symmetrical and antisymmetrical Si−N−Si stretching modes [20]. In all the spectra there are also present a mode at $800\,\mathrm{cm^{-1}}$ and two well-defined modes of a-SiO_2 centered about $1070\,\mathrm{cm^{-1}}$ and $1200\,\mathrm{cm^{-1}}$. These modes are ascribed to the symmetric and antisymmetric stretching modes of Si−O−Si, which are known in the literature as S, AS_1 and AS_2 modes [21]. The presence of these modes shows that at the surface of the Si/C/N and Si_3N_4 samples an a-SiO_2 layer is formed. The intensity of these three modes changes with the ratio R. For the Si/C/N sample produced with the lowest R value ($R = 0.5$), modes at $800\,\mathrm{cm^{-1}}$, $1070\,\mathrm{cm^{-1}}$ and
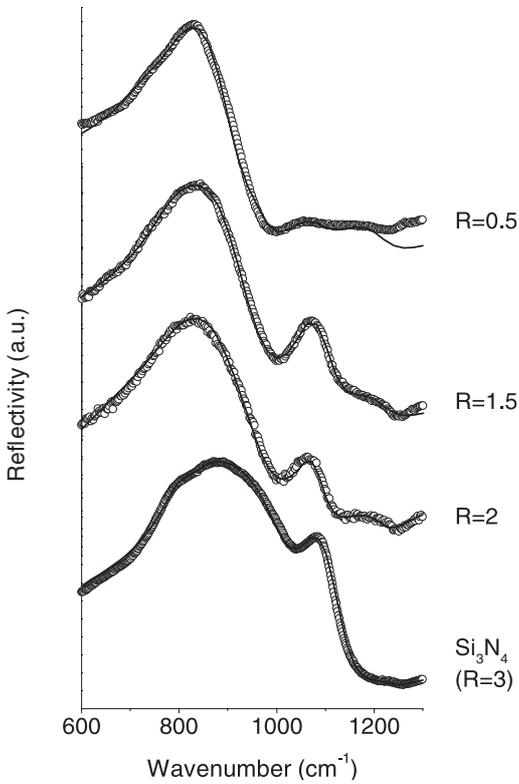
Table 1. Phonon parameters (in cm^{-1}) of Si/C/N and Si_3N_4 powders

R	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}
0.5	458	60	469	60
	821	97	921	111
	955	97	970	90
	796	90	810	93
	1076	119	1097	116
	1187	115	1213	115
1.5	463	70	486	70
	824	123	950	122
	966	120	979	120
	790	110	810	110
	1065	87	1114	90
	1190	124	1219	122
2	450	150	500	100
	833	169	948	169
	952	140	970	142
	808	120	812	120
	1072	70	1094	73
	1212	110	1222	90
Si_3N_4	465	68	500	68
	830	100	1032	145
	960	130	964	135
	796	69	814	76
	1064	90	1137	73
	1232	82	1236	70

$1200\,\mathrm{cm^{-1}}$ are barely visible. As the flow ratio R changes to higher values ($R = 1.5, 2$) the AS_1 and AS_2 modes become more intense. In a pure Si_3N_4 sample the most prominent modes of a-SiO_2 are the S and AS_1 modes. The mode of silanole around $970\,\mathrm{cm^{-1}}$ is also present in the spectra of Si_3N_4 and Si/C/N samples, but as R varies from 0.5 to 2 it becomes more damped.

In Fig. 3 there is presented the dependence of the area below the main Si−O−Si band at 2.2 eV on the ratio R. The area below the band at 2.2 eV changes with the ratio R. It has its lowest value for lowest R, increases with R and for a Si/C/N sample ($R = 2$) that is very similar to Si_3N_4, approaches the value of pure Si_3N_4.

The laser-synthesized Si/C/N materials were exposed to a room atmosphere for a longer period of time under the same conditions. In the Si/C/N sample produced with a low
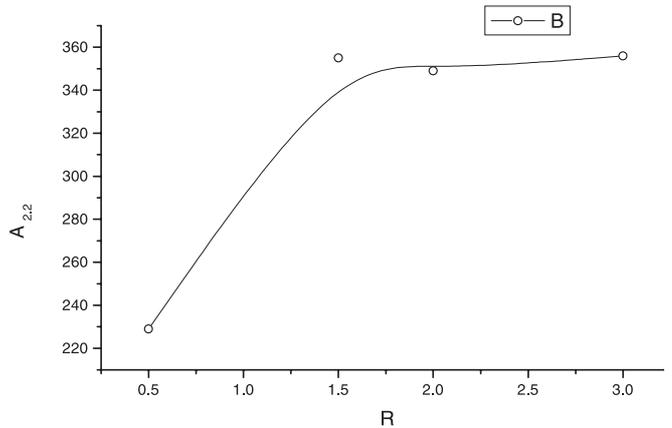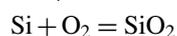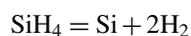

Fig. 2. The IR reflection spectra of Si/C/N and Si_3N_4 powders

Fig. 3. The dependence of the area below the main Si−O−Si band at 2.2 eV (circles B) on the ammonia–silane flow ratio R

R value ($R = 0.5$), the formation of Si−C bonds is favored to the formation of Si−N bonds, giving rise to a ternary compound where most Si atoms have the local structure C_{4-x}−Si−N_x. Varying the ratio R from 0.5 to 2, the nitrogen content in Si/C/N powders increases, but with a higher reactant flow the temperature of the reaction decreases. Ternary Si/C/N powders become more amorphous in structure (as can be seen from the IR spectra) and more similar to Si_3N_4. Therefore they are more subject to surface oxidation. According to this, we concluded that the formation of an a-SiO_2 surface layer depends on the chemical composition and the degree of crystallinity of Si/C/N powders. The stoichiometry of ternary Si/C/N powders could also influence the formation of an a-SiO_2 surface layer. Although the nitrogen content rises with the ratio R our powders do not have stoichiometric composition. The reason for this is the dissociation efficiency of NH_3, which cannot exceed 30% even at the temperature of the laser induced reactions higher than 2000 °C. In that case, an excess of Si−H bonds could exist in Si/C/N powders. The Si−H bonds are very unstable in the presence of water and O_2 even at room temperature. These bonds tend to hydrolyze when exposed to ambient air according to the reaction:

$$SiH_4 = Si + 2H_2$$
$$Si + O_2 = SiO_2$$

The layer of a-SiO_2 could be formed at the surface of Si/C/N powders. The layer of a-SiO_2 in equilibrium with humidity from the atmosphere becomes hydrolyzed and, in Si/C/N and Si_3N_4 samples, except for the Si/C/N sample produced with the ratio $R = 2$, silanol sites have been formed. The porosity could also influence the processes at the surface of Si/C/N powders. Our nanometer-sized powders have relatively high specific surface areas ($> 100 \, m^2/g$) and hence absorb oxygen and H_2O in the air easily. The presence of a silica layer (a-SiO_2) and silanole at the surface of our powders causes a strong photoluminescence of Si/C/N powders.

3 Conclusions

The PL and IR reflection spectra of Si/C/N samples with $R = 0.5, 1.5, 2$ were examined and compared with Si_3N_4 and SA samples. This study reveals the following:

1. The chemical composition and the degree of crystallinity of Si/C/N ultrafine powders depend on the ammonia–silane flow ratio R. The powders produced with the ratio $R > 0.5$ contain more Si−N than Si−C bonds, become more amorphous and are very similar to pure Si_3N_4 powders.

2. The formation of an a-SiO_2 layer at the surface of the Si/C/N samples strongly depends on their chemical composition, their crystallinity, stoichiometry and their porosity. The Si/C/N powders which contain more Si−C than Si−N bonds are less subject to surface oxidation than the Si/C/N samples where the Si−N bonds are dominant.

3. The a-SiO_2 layer in equilibrium with humidity from the atmosphere becomes hydrolyzed and the silanole sites have been formed in all the Si/C/N samples, except the sample produced with the ratio $R = 2$.

4. The existence of silanole sites and the a-SiO_2 layer at the surface of Si/C/N powders causes the appearance of PL spectra very similar to PL spectra of the Si_3N_4 and SA samples. Therefore, we concluded that the PL bands at 1.8 eV, 2.0 eV and 2.2 eV of Si/C/N powders are caused by the same kind of defects that are present in Si_3N_4 and SA samples.

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