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UV absorption and luminescence in silicon oxynitride prepared by hydrogen-free SPCVD-process

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Abstract

UV absorption and luminescence are investigated in bulk samples of silicon oxynitride prepared by a hydrogen-free SPCVD-process (surface plasma chemical vapour deposition). The UV absorption spectra, apart from the well-known silicon oxygen-deficient centre (Si-ODC), exhibit two unknown absorption bands with maxima at 5.77 and 4.54 eV and two unknown luminescence bands at 3.55 and 3.03 eV under laser excitation at 257 nm (4.83 eV). These new bands are supposed to be due to a nitrogen-modified silicon oxygen-deficient centre.

1. Introduction

Up to date, silicon oxynitride has been studied in connection with its application in integrated optics and microelectronics [1–3]. Nitrogen doping efficiently increases the refractive index of silica; therefore, silicon oxynitride is used as the core material in planar optical waveguides. However, until recently silicon oxynitride was not used as a material for fibre optics. This is due to a high hydrogen content in the glass inherent in most silicon oxynitride fabrication technologies. The exception is provided only by some unique thin film technologies [4].

In Ref. [5] a surface plasma chemical vapour deposition (SPCVD) [6] that does not employ hydrogen-containing reagents and is conducted under reduced pressure was applied for the first time to the fabrication of silicon oxynitride optical fibre preforms. The resultant optical fibres showed an unexpectedly low loss in the near-IR region (about 1 dB/km at the wavelength of 1.6 μm). Further research resulted in silicon oxynitride fibres with a loss of 0.5 dB/km at the wavelength of 1.3 μm and 0.3 dB/km at the wavelength of 1.55 μm [7].

In this paper, to supplement the optical loss measurements in the visible and near-IR regions presented in Refs. [5,7], we investigate the optical properties of the silicon oxynitride prepared by the hydrogen-free SPCVD-process in the UV spectral region. Colour centres that manifest themselves in the UV absorption and luminescence spectra are an important property of a glass. In particular, second-harmonic generation [8] and Bragg-grating writing [9] in optical fibres as well as fibre radiation resistance [10] are intimately related to such colour centres.

Lastly, the microstructure and optical properties of a glass are technology-dependent. Therefore, silicon oxynitride prepared by the hydrogen-free SPCVD-process should be considered as a new optical material.

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2. Sample preparation

In the SPCVD-process, the raw materials, $SiCl_4 + O_2 + N_2$ gas mixture, are fed into a silica substrate tube at a pressure of about 1 Torr toward the plasma column excited inside the substrate tube by a microwave power source. Silicon oxynitride is deposited layer by layer on the inner surface of the substrate tube kept at a temperature of 1200°C. By varying the O_2 and N_2 gas flow ratio it is possible to vary the nitrogen content in the glass. It is significant that nitrogen enters into the glass more readily under oxygen deficient conditions with respect to the stoichiometric relation $SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2$. Hence the presence of oxygen-deficient centres in the glass is preset already at the stage of synthesis. On completion of the deposition process the tube is collapsed into a cylindrical glass rod (preform) by heating the glass up to 2000°C with the help of an external torch. Such a heat treatment leads to nitrogen burn-off from the last-deposited layers adjacent to the inner surface of the synthesized structure.

The diameter of the final preforms was 12–15 mm, silicon oxynitride occupying the central region 1–4 mm in diameter. Refractive index profiles of all the preforms had a central dip (nitrogen burn-off), its diameter being 0.2–0.3 mm. The experimental samples were transverse preform slices, 0.5–5 mm thick, shaped to the square form in the cross section plane. The shaping was necessary for the luminescence measurements. The face and lateral sides of the samples were well polished. In addition, to reveal the effect of the collapsing process, longitudinal slices were made out of an uncollapsed tube before and after deposition.

The literature provides contradictory data on the refractive index dependence on the silicon oxynitride composition [4,11,12]. So, we characterized the samples by the difference of the refractive indices of pure and nitrogen-doped silica Δn, assuming that it is linear with respect to the nitrogen content.

3. Experimental set-ups

Absorption spectra and their distribution over the sample cross section were measured on a set-up depicted in Fig. 1a. Deuterium lamp radiation was focused by a lens on the monochromator entrance slit

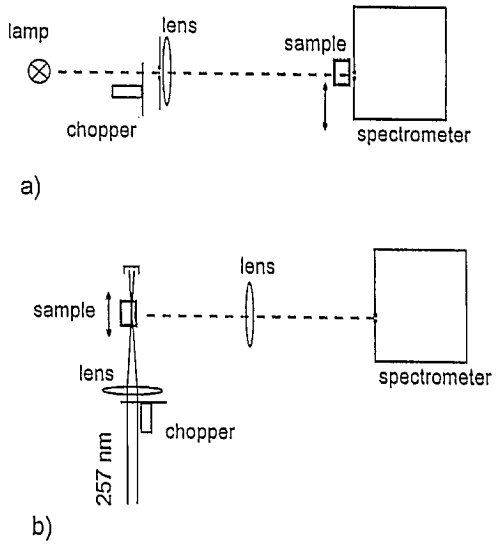

Fig. 1. Experimental set-ups for measuring UV absorption (a) and luminescence (b).

0.1 by 0.1 mm in size. A sample was mounted on a micropositioner immediately in front of the entrance slit perpendicular to the beam axis. A diaphragm installed in front of the lens provided a practically constant beam diameter over the sample thickness. By moving the sample perpendicular to the beam, we could measure the absorption at different points of the sample cross section, the spatial resolution being preset by the entrance slit size. The spectrometer was home-made and consisted of a monochromator, a photomultiplier tube, a lock-in amplifier, and a computer.

Luminescence spectra were measured on a similar set-up (Fig. 1b). The sample cross section was imaged on the monochromator entrance slit by a lens. Luminescence was excited at the wavelength of 257 nm by the argon-ion-laser second harmonic introduced into the sample through the lateral side. The absorption at 257 nm being sufficiently small, this experimental scheme provided uniform excitation over the sample cross section. As in measuring absorption, by moving the sample the luminescence distribution of over the cross section was measured.

4. Results and discussion

Fig. 2 shows a typical silicon oxynitride UV absorption spectrum with three bands of different intensity. The spectrum is well approximated by a sum of four

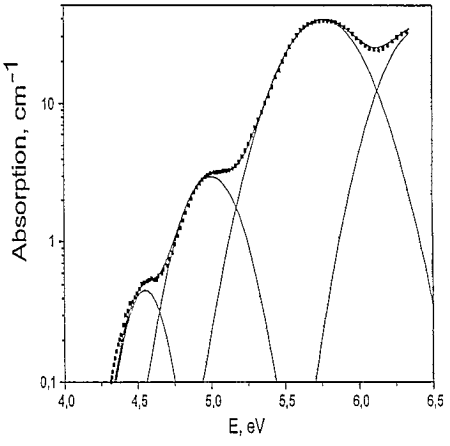

Fig. 2. A typical experimental UV absorption spectrum in silicon oxynitride (dots). Solid lines show four Gaussian components and their sum.

Gaussian components, if one assumes that there is one more band in the region 6.5–7 eV. The exact position and width of the fourth band have not been determined; however, this fact does not affect the accuracy of the parameters of the other three bands. Gaussian resolution yields the following values for the peaks (full widths at half-maximum) of the three bands: 4.54 ± 0.08 (0.4 ± 0.02), 5.00 ± 0.02 (0.4 ± 0.1) and 5.77 ± 0.02 (0.6 ± 0.1) eV.

The absorption band at 5.00 eV (248 nm) is due to the singlet-to-singlet absorption of the silicon oxygen-deficient centres (Si-ODC), which are typical of certain types of silica. Si-ODC owe their presence to the oxygen-deficient conditions of the glass synthesis. Despite the intensive studies, the Si-ODC microscopic structure is yet to be clarified. The most plausible models for Si-ODC are two-fold-coordinated silicon atom = Si: [13] and oxygen mono-vacancy ≡Si–Si≡ [14]. High concentrations of Si-ODC in the tested samples of up to 1.5×10^{17} cm^{-3} are noteworthy. This value is about one order of magnitude higher than those of pure silica fabricated by non-plasma technologies.

The 5.77 eV absorption band resembles that of the paramagnetic E′-centre that arises in silica after UV- or γ-irradiation [10]. If the 5.77 eV band defect were the E′-centre, than it would produce a considerable ESR signal, three orders of magnitude greater than the ESR sensitivity which corresponded to $\approx 2 \times 10^{15}$ cm^{-3}. However, no ESR signal was observed. A lower limit to the concentration of the defects responsible for this band as follows from the Smakulla equation for the collapsed glass with $\Delta n = 0.03$ is $\approx 2 \times 10^{17}$ cm^{-3}. Consequently, this is a diamagnetic centre. An interesting fact that can be helpful in interpreting this centre is a three-fold growth of the 5.77 eV band after collapsing (Fig. 3).

The luminescence spectra reveals 4 bands (Fig. 4, solid curve). The 4.45 eV band (lifetime $t \approx 10$ ns) and the 2.70 eV band ($t \approx 10$ ms) are due to the Si-ODC radiative relaxation [15]. The luminescence bands at 3.55 and 3.03 eV are excited, apparently, in the 4.54 eV absorption band (Fig. 2) and, to our knowledge, have been unknown up to now. The 3.03 eV luminescence lifetime, as for the Si-ODC triplet-to-singlet luminescence, is $t \approx 10$ ms, while the 3.55 eV luminescence is, apparently, a singlet-to-singlet one with $t < 20$ ns. This value was estimated with the help

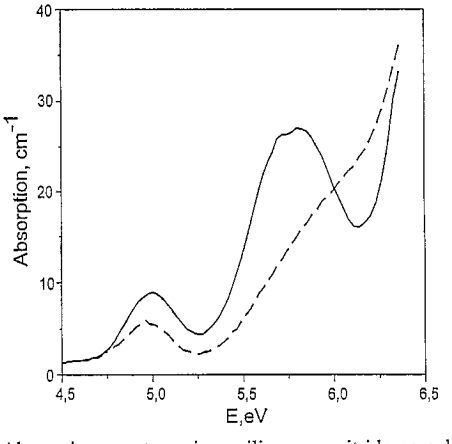

Fig. 3. Absorption spectrum in a silicon oxynitride sample with $\Delta n = 0.012$ before (dashed line) and after (solid line) collapsing.

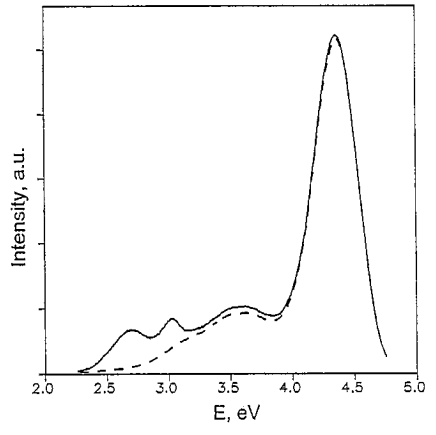

Fig. 4. Luminescence spectra excited at 4.83 eV in a silicon oxynitride sample with $\Delta n = 0.03$. The modulation frequency of the exciting light is 10 Hz (solid line) and 300 Hz (dashed line).

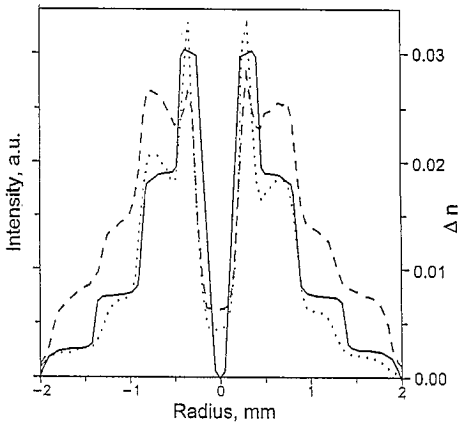

Fig. 5. Refractive index profile (solid line) of a multi-step silicon oxynitride sample and radial distributions of luminescence intensity at 3.55 (dotted line) and 4.45 eV (dashed line).

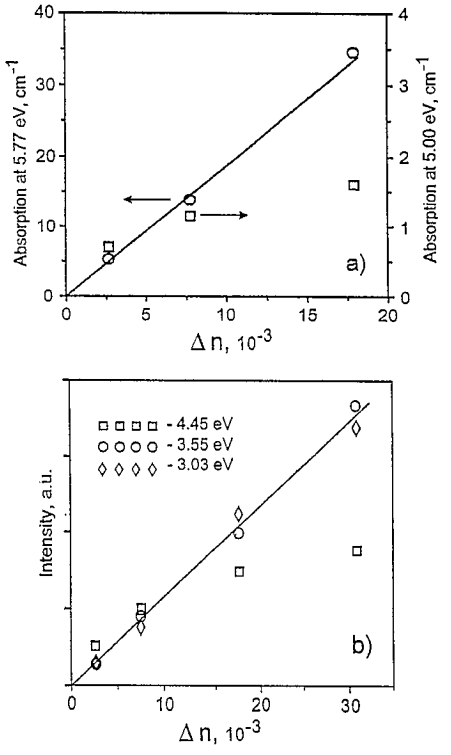

Fig. 6. Dependences of the absorption at 5.77 and 5.00 eV (a) and luminescence intensities (b) measured on a multi-step silicon oxynitride sample.

of a pulsed KrF excimer laser with a pulse duration of 20 ns.

The dependence of absorption and luminescence on nitrogen concentration was investigated on a sample with a multi-step refractive index profile. Fig. 5 shows the refractive index profile of the sample along with radial distributions of the luminescences at 4.45 and 3.55 eV. The contribution of the long-lived 3.03 and 2.70 eV luminescence bands was suppressed by increasing the chopper frequency up to 300 Hz (Fig. 4, dashed curve). It is seen from Fig. 5 that the 3.55 eV luminescence intensity is proportional to the nitrogen concentration in the glass. The discrepancy at the sample centre is probably due to insufficient spatial resolution. Contrastingly, the radial distribution of the 4.45 eV luminescence differs essentially from the refractive index profile to reveal a nonlinear dependence of the Si-ODC concentration on the nitrogen concentration.

Fig. 6 presents the absorption and luminescence band intensities as a function of Δn. The linear growth of the 5.77 eV absorption band intensity and the 3.55 and 3.03 eV luminescence band intensities with Δn testifies that the corresponding colour centre incorporates one nitrogen atom. The lifetimes of the above-said luminescence bands being close to the respective values of the Si-ODC, we believe that we are dealing with a Si-ODC neighbouring a nitrogen atom, i.e. a nitrogen-modified Si-ODC.

5. Conclusion

Silicon oxynitride prepared by the hydrogen-free SPCVD-process contains a considerable amount of colour centres detectable in the UV region. Apart from the well-known silicon oxygen-deficient centre with a concentration of up to 1.5×10^{17} cm^{-3}, there exists at least one new colour centre with absorption bands at 5.77 and 4.54 eV and luminescence bands at 3.55 and 3.03 eV. Now we are not able to determine the structure of this defect. However, the experimental results suggest that this is a nitrogen-modified silicon oxygen-deficient centre.

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