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Structural transformations induced by direct UV writing in MDECRC-PECVD silica layer exhibiting negative index change

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Abstract:

Using 244 nm CW laser for direct UV writing, we obtained negative index changes in H:Ge:SiO₂ layers deposited by MDECRC-PECVD, a method allowing to include a large amount of hydrogen in the structure. The amplitude of the index change is of the order of -10^{-2} with a UV speed as large as 1 mm/s. The investigation of topography, UV and IR absorption and Raman scattering bring information on the photosensitivity mechanisms. For low laser power (<15-20 mW) whatever the beam velocity, the change of glass structure is moderate occurring just on OH/H₂O and UV absorbing defect population. The change of index is moderate. For larger laser power and large velocity, the glass structure changes are deeper, induced by the large laser power density deposited. In that case, Raman spectra show that the glass connectivity decreases producing a larger expansion and index decrease in the Ge doped silica layer. For large power and small velocity, the heating effect is so large that all effect is erased in the same time it is produced. The expansion disappears and the glass could eventually decompose. The domain with large laser power and velocity is thus the most suitable for an efficient direct UV writing.

PACS: 42.70.-a; 42.70.Nq; 42.70.Ce; 42.70.Gi; 42.82.Cr; 42.88.+h; 71.55.Jv

1. Introduction

We were successful in achieving, using 244 nm CW laser for direct UV writing, negative index change in H, Ge co-doped silica layer elaborated by Matrix Distributed Electron Cyclotron Resonance (MDECRC-PECVD), an improvement of PECVD method¹. The amplitude of the index change is of the order of -10^{-2} at a UV beam speed as large as 1 mm/s. We have therefore a material that can be potentially used for new application achievements because it exhibits strong negative index changes^{2,3}.

The starting idea was to use an elaboration procedure that allows including hydrogen in the layer at a level of a few mol % i.e. larger than it can be achieved by high pressure loading for getting a large positive index change, or even larger one without any post-deposition treatment. But, finally, we obtained not positive index change but strong negative one. As for such an index change amplitude, a volume change is expected, we have measured the surface topography (Figure 1 a). We have found two domains according to UV light power P and writing speed v when the UV absorbing layer is coated with a H:SiO₂ layer (Figure 1 c). In the first domain, the effect increasing with the laser power and $1/v$, in the second the effect intensity decreases with $1/v$.

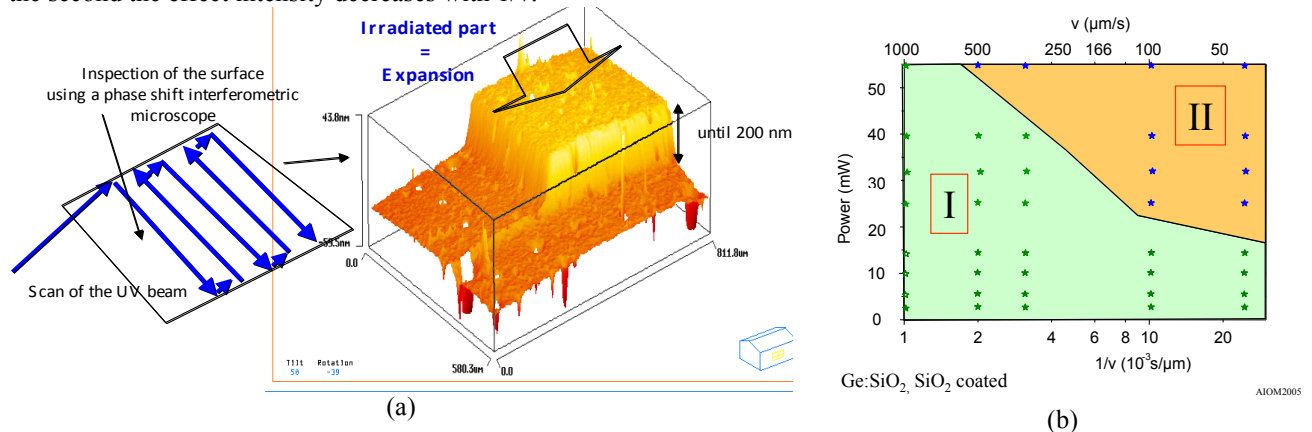


Figure 1: Topography results obtained on MDECRC H:Ge:SiO₂ coated layer after 244 nm-CW-through-microscope irradiation. (a) example of UV induced surface swelling, (b) the domains in the (P , $1/v$) plane based on the results.

The amplitude measured can be as large as 200 nm but we did not know the associated microscopic change. To precise the mechanisms, we measured UV absorption since the first step of the process is obviously an absorption in the UV range by one or several photons. Then, as the most labile species in our material is the OH containing species, we measured the OH absorption in the IR range. Lastly, as the magnitude of the index change is quite large (almost 1%), we have searched for a change of structure by Raman spectroscopy.

2. Experimental details

Direct UV written areas (squares of 0.4 mm×0.4 mm) at different power (from 3 to 57 mW) and velocities (from 30 to 1000 $\mu\text{m/s}$) in a planar waveguide sample have been analyzed by IR absorption and Raman microprobe. For UV absorption, a smaller number of squares of larger dimensions (1x1 mm²) have been written. The sample consists of a 4.25±0.25 μm thick layer of H:Ge:SiO₂ silica-on-Suprasil deposited by MDEC-PECVD¹ covered by a 13.5±1.5 μm thick cladding layer of MDEC H:SiO₂. Direct UV writing was performed using a CW frequency doubled Ar-ion laser (λ at 244 nm) which was focused by an optical lens to obtain a 1/e² beam diameter of about 4. μm . UV absorption spectra were measured with a Varian Cary spectrophotometer between 190 and 300 nm with two collimated beams for a proper localization of the beams into the irradiated areas. IR absorption spectra were measured in the range 2000-4000 cm⁻¹ using a Fourier transform IR spectrometer Nicolet and an infrared microscope (Continuum), both purged with dry air. Spectra were obtained using a Globar light source, KBr beam splitter and a MCT (HgCdTe) detector. They were acquired averaging 64 scans and the spectral resolution was consistently chosen (4 cm⁻¹). The analyzed spot had a diameter of 100 μm . Raman spectra were measured at atmospheric conditions using a T 64000 Jobin Yvon confocal microRaman spectrometer, which was equipped with a liquid nitrogen-cooled CCD detector. The Argon laser beam at 514 nm wavelength was focused in the depth of the sample (50× objective) and the Raman scattering signal was collected and focused back to the detector. The confocal aperture was opened to 200 μm . The full spectra preliminarily calibrated with a silica sample, covered a wavenumber ranging from 200 to 4000 cm⁻¹. The accumulation time was 200 s. The recorded spectra were treated firstly by removing the baseline in order to eliminate the offset recorded in the spectra, i.e. by extracting the minimum intensity at an energy where no vibration is expected. Spectra were normalised by dividing each of them by their value measured at 440 cm⁻¹.

3. Results

3.1. UV absorption

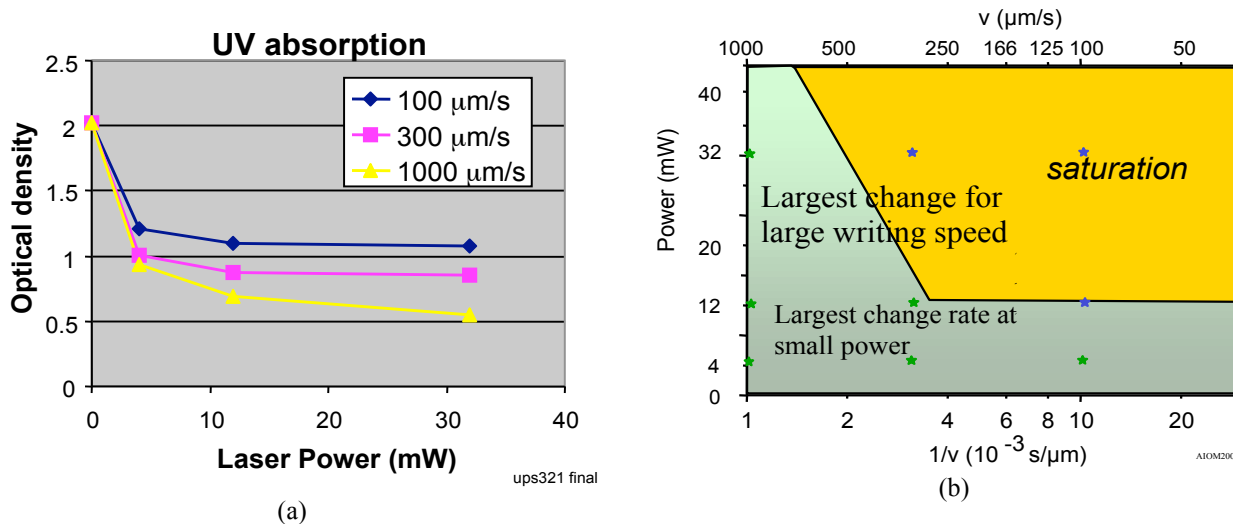
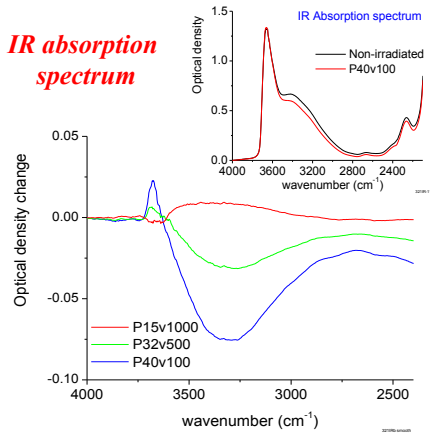


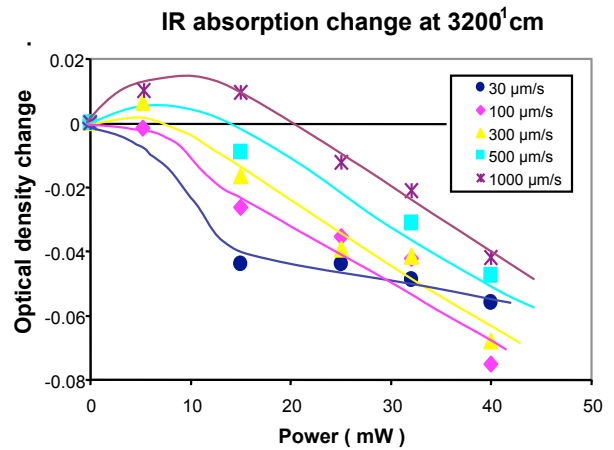
Figure 2: UV absorption change before and after irradiation. (a) the optical density change at 200 nm according to laser power and laser velocity. (b) the domains in the (P, 1/v) plane based on these results.

The UV absorption intensity is quite strong for this kind of sample. It is currently around 6000 cm⁻¹ at 200 nm i.e. the absorption length is of the order of 2 μm and is located in the H:Ge:SiO₂ layer. The UV absorption in the cladding has been measured negligible. Under UV irradiation, UV absorption decreases rapidly and proportionally over the UV range by 50%, even at laser power as low as 10 mW (see Figure 2 a). This observation does not depend much on the writing speed. Beyond 4 mW, the absorption decrease saturates. This saturation is reached for lower writing speed at lower power. The effect appears to be stronger for large power and also large speed as it was observed for topography. These results are collected in Figure 2 b and seems coincide approximately with topography observations (see Figure 1 b) i.e. the domain extension are similar.

3.2. IR absorption spectrum



(a)

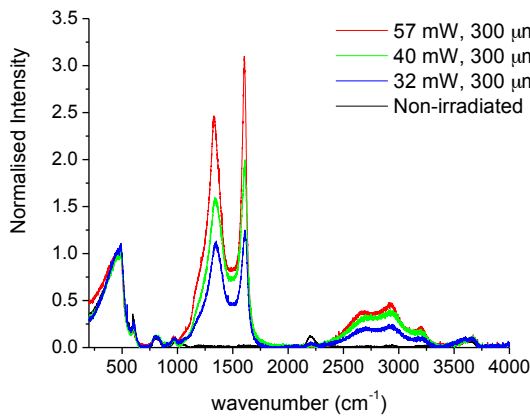


(b)

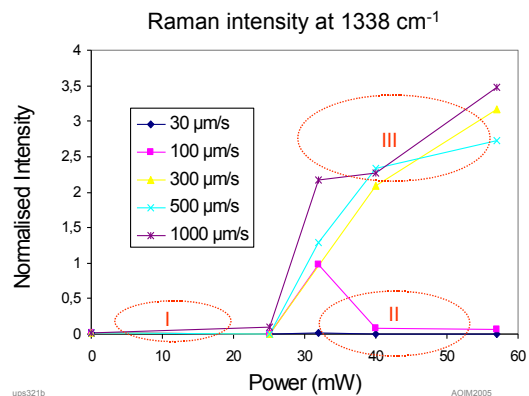
Figure 3: Infrared absorption of direct UV written areas (a) absorption change in the OH/H₂O absorption range for three couples of power and beam velocity. The inset shows the absorption spectrum before and after irradiation for P=40 mW and v=100 μm/s (b) intensity change at 3200 cm⁻¹ in the H₂O absorption range at large powers (>15 mW) with velocities from 30 to 1000 μm/s. Lines, here, are just guides for the eye.

The OH, H₂O content is similar either in the pure silica layer and in the Ge doped layer i.e. giving rise to an absorption of 250 cm⁻¹. Changes of IR absorption spectra after irradiation are plotted in the Figure 3 a. The main change is located around 3200-3300 cm⁻¹ for laser power larger than 15 mW (H₂O absorption), it is a decrease. Below this power, and for large speed, the change is a small increase (maximum 0.02 in optical density). The effect of laser power and writing speed on the absorption at 3200 cm⁻¹ are presented in the Figure 3 b. The change remains small, even at large power, the change is smaller than 10% on the initial H₂O content.

3.3. Raman spectrum



(a)



(b)

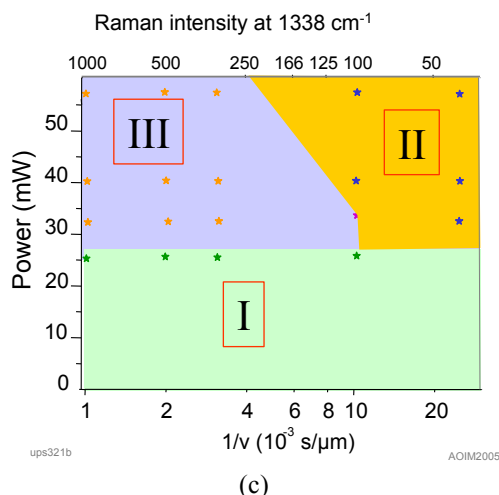


Figure 4: Raman scattering in directly UV written areas (a) normalised spectra until 4000 cm^{-1} for power level from 32 to 57 mW with writing velocity of $300\text{ }\mu\text{m/s}$. (b) plot of Raman intensity at 1338 cm^{-1} for laser power from 0 to 57 mW and writing velocity from 30 to $1000\text{ }\mu\text{m/s}$. (c) scheme of the different domains based on these results.

The Raman spectrum does not change after irradiation with low laser power whatever the writing speed. It seems to be also unchanged under large power and low speed. For large power and large speed, drastic changes are detected around 1500 cm^{-1} and 2800 cm^{-1} (see Figure 4 a). The change appearing at 2800 cm^{-1} seems to be roughly proportional to the one around 1500 cm^{-1} . The energy shift of these features does not change when excitation line is changed indicating that they are Raman scattering not fluorescence. The variation of their intensity with laser power and writing velocity is shown in Figure 4 b. From that one, we can define three domains, although two domains (I and II) looks similar without exhibiting change on the Raman spectrum but we think that they exist compared to the other optical properties. As a matter of fact, for $100\text{ }\mu\text{m/s}$, the two domains are separated by a change on the Raman spectrum.

The group at 1500 cm^{-1} is composed by two lines: one at 1338 and another one at 1598 cm^{-1} . The group at 2800 cm^{-1} is composed by three lines: 2667 , 2910 , 3200 cm^{-1} . Other structures are detected at 2208 cm^{-1} disappearing under irradiation, and two at 3570 and 3670 cm^{-1} exhibiting a constant intensity. The bands at 490 nm and 606 cm^{-1} called defect bands are also decreasing after irradiation.

4. Discussion

4.1. Change in UV absorption

The first step in the photosensitivity mechanisms is clearly the absorption in the H:Ge:SiO₂ since the absorption intensity is very strong (several 1000 cm^{-1}) in this layer. The spectral diffusion of the excitation leads to strong bleaching of the whole UV spectrum at least between 190 and 300 nm but it saturates rapidly. The change of UV spectrum could have been related to a bleaching of SiE' centers absorbing at 195 nm and known as related to UV induced positive index change but using ESR we will show in another paper that this is not the case, actually.

4.2. Change in IR absorption spectrum in the range of OH linkages

The OH and H₂O contents in this kind of material are almost the same. They reach each of them 2 mol % either in the core or in the cladding material. Nevertheless, the change is small (a few % of the total absorption) showing a slight increase of H₂O for low power and an increase of OH and a decrease of H₂O for larger power.

4.3. Change in Raman spectrum

The sharp bands at 490 cm^{-1} and at 606 cm^{-1} called defect bands generally, which are specific of the pure silica Raman spectra are due to intermediate range order in the form of highly regular rings of bonds. They have been attributed to the uncoupled symmetric oxygen breathing motion in the puckered four- and planar three- membered rings respectively⁴. This attribution has been confirmed recently by DFT vibrational frequency calculation⁵. We observe, that irradiation of sample induce a decrease of the intensity of the defect bands, interpreted as a reduction of the four- and three-membered ring units⁶. These changes vary with increasing fluence. This is consistent with a decrease of the glass density. In the spectral region between 1000 cm^{-1} and 1500 cm^{-1} drastic changes are induced by irradiation. The dominant bands located at 1338 cm^{-1} have been assigned to the symmetric vibration of silanone =Si=O⁷ having two oxygen atoms in the back bonds⁸. The band at 1598 cm^{-1} could be comparable to the one mentioned by Skuja et al.⁹ about interstitial oxygen, but here it is Raman line and not luminescence. It is possible that it is a symmetric vibration of another kind of silanone bonds weakened by a hydrogen bonds. The band at around 2208 cm^{-1} has been previously detected in the Raman spectra of H₂ – bearing silica glass⁹ and was attributed to Si or Ge hydrides stretching vibrations. It disappears under irradiation. The intensity of the bands observed in the spectral region between 2500 cm^{-1} and 3250 cm^{-1} increase almost

proportionally to the previous lines around 1000-1500 cm^{-1} . Composed by three bands (2667, 2910, 3200 cm^{-1}), the two first bands could be assigned to vibration of unusual H containing species (numerical investigations are still in progress). The last band contains a contribution from H_2O symmetric stretching vibration mode¹⁰. Vibrations of Ge-OH and Si-OH groups are located at around 3570 cm^{-1} and 3670 cm^{-1} , respectively. Their constancy is consistent with the ones in IR absorption spectrum.

5. Conclusion: Photosensitivity mechanisms

The index change calculated by Kramers Kronig relation from UV absorption changes using Gaussian fitting reaches $-7 \cdot 10^{-4}$. The index change from IR absorption change reaches $+10^{-4}$. So, UV is the first step of the mechanisms in any case but not the origin of refractive index change. IR absorption changes are also not responsible of the refractive index change. Topography results, instead of a densification, normally observed for usual germanium-doped silica materials and associated to a UV induced positive index change, show an expansion after UV laser irradiation. This phenomenon is at the base of the measured negative index change, as the same amplitude of the index change is roughly obtained by Lorentz-Lorenz relation and elastic calculations. Furthermore, we can distinguish, by topographic analysis, two different regions in the P-v domain, revealing distinct phenomena or processes contributing to the material expansion: a light induced expansion and an effect of laser heating. Raman spectra after UV irradiation for laser power from 4 to 60 mW and writing velocity of 30 to 1000 $\mu\text{m/s}$ shows changes at 1330, 1590, 2660 and 2920 cm^{-1} . Those ones are related to structural transformations involving a three fold co-ordinated oxygen i.e. a silanone⁷. We demonstrate that Ge acts as a light absorber due to the strong UV absorption, leading to a heating effect that can propagate also into neighboring pure $\text{H}:\text{SiO}_2$ layer. As a matter of fact, irradiation of this layer without the neighbouring $\text{H}:\text{Ge}:\text{SiOH}$ layer has no effect but the same Raman spectrum can be obtained in this material simply by heating at 600°C, 1/2 h. The Raman observations according to P, v leads to define regions in this sample that almost coincide with the ones obtained in sample that does not have a cladding². There are the followings.

Region I (low laser power, whatever the beam velocity): we observe a reorganization of H_2O population (different hydrogen bonds). On UV absorption, a large change is detected (the absorbing defect is bleached), half of the absorption disappears. On the contrary, no difference is seen on Raman scattering because, the structure change detected in IR and UV absorption represent a small contribution. Such transformation has also a small impact on the specific volume change because the glass connectivity does not change and thus the topography change is small.

Region III (large laser power, large beam velocity): The Raman spectrum shows several kinds of silanone. They can be produced by the following kind of reaction: $\text{SiOSi} \rightarrow \text{Si=O} + \text{Si}$. This reaction exhibits an energy of 3.1 eV as calculated by quantum chemical software Gaussian using small cluster. The corresponding change in polarisability is smaller than 2%. The change of index arises mainly of the change of volume. IR absorption shows that water molecules are consumed and OH groups are produced in the course of irradiation. We think about transformation of H_2O into OH: by $\text{SiOSi} + \text{H}_2\text{O} \rightarrow 2\text{SiOH}$. UV saturate (no further transformation of the UV absorbing defects), topography change shows an expansion because connectivity decreases as indicated by the silanone formation. Here, heating effect on hydrated silica glass is the driving force. GeH_2 groups also disappear and the glass is on the way to decompose by forming Si or Ge nanocrystals. We do not see nanocrystals on Raman spectrum when the sample has a cladding like the sample used in this paper but we have detected the signature at 300 cm^{-1} of Ge nanocrystals when the cladding is absent.

Region II (large laser power, small beam velocity): Raman spectrum is restored, silanone linkages are erased. Here, the heating effect is so large that the remelting and either the return of the glass to its original state (when there is a cladding) or GeO and O_2 outgassing occur similarly to the case of Nishii et al.¹¹ for which there was no cladding. These authors found in $\text{Ge}:\text{SiO}_2$ layer obtained by sputtering, a very large negative index decrease of 0.045 with an expansion of the glass of 18% but the formation of porous glass as mentioned by the authors are not detected here.

6. Acknowledgments

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