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Structural Defect Control and Photosensitivity in Reactively Sputtered Germanosilicate Glass Films

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ABSTRACT

The optical performance of refractive index structures induced in photosensitive (PS) glasses ultimately depends on the index modulation depth attainable. In germanosilicate materials, the photosensitive response is linked to the presence of oxygen-deficient germanium point defect centers. Prior efforts to increase PS in these materials, e.g., hydrogen loading, rely on a chemical reduction of the glass structure to enhance the population of oxygen deficient centers and thus increase the saturated refractive index change. We have previously reported the development of highly photosensitive, as-deposited germanosilicate glass films through reactive atmosphere (O_2/Ar) sputtering from a Ge/Si alloy target. The present work details our investigation of the effect of substrate temperature during deposition on the material structure and propensity for photosensitivity. Using optical absorption/bleaching, Raman, electron paramagnetic resonance (EPR) and selective charge injection techniques we show that the predominate defect states responsible for the PS response can be varied through substrate temperature control. We find that two regimes of photosensitive behavior can be accessed which exhibit dramatically different uv-bleaching characteristics. Thus, the corresponding dispersion of the refractive index change as well as its magnitude can be controlled using our synthesis technique. Tentative defect models for the photosensitive process in materials deposited at both ambient temperature and at elevated substrate temperatures will be presented.

Keywords: photosensitivity, germanosilicate, thin film, glass, point defects, reactive atmosphere sputtering

1. INTRODUCTION

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Photosensitivity (PS) in germanium-doped silica glass fibers and films allows the formation of stable, optically patterned refractive index structures through exposure to ultraviolet radiation. A variety of index patterns have been used both to mimic the performance of bulk optical elements and to provide novel optical functionality. The germanosilicate system exhibits a photosensitive response in the ultraviolet spectral region which has been linked, at moderate exposure intensities, to the presence of oxygen deficient germanium point defect centers.¹⁻³ Specifically, absorption of optical energy by a precursor defect is postulated to result in the ejection of an electron which, in turn, is trapped elsewhere in the glass structure. After electron ejection (or hole trapping) the precursor exhibits an unpaired spin state and has been identified using EPR analysis as a Ge E' center.^{2,3} The corresponding optical absorption spectrum exhibits a bleaching of the precursor uv absorption band (at approx. 240 nm) and the growth of a band at approximately 200 nm which has been ascribed to the Ge E' center.⁴ These changes in the absorption spectrum cause a corresponding change in the material refractive index, n , which is described by the Kramers-Kronig relations.

It is important to note that the range of optical functionality attainable in photo-patterned refractive index structures is ultimately linked to the maximum refractive index modulation available in the material. Given the direct correlation between the PS response and the material structure, efforts to improve the PS effect have focused on modification of the glass structure, through either the incorporation of additional dopant atoms (to change the wavelength response and/or increase photosensitivity) or the use of post-fabrication reducing atmosphere thermal treatments (to increase the population of oxygen deficient defect centers).⁵⁻⁷ The present work details our use of a reactive atmosphere sputtering approach for the synthesis of highly photosensitive germanosilicate thin films. In this case, a Si/Ge alloy target is sputtered in an O_2/Ar environment. Control of the oxygen partial pressure used during deposition allows the total oxygen content of the film to be varied over a broad range. This novel route to the formation of these materials thus enables the degree of photosensitivity (arising from oxygen deficient structural centers in the

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film) to be dictated during processing, without resorting to post-deposition thermal treatments. Variation of oxygen partial pressure on the optical response of the films⁸ and initial studies of defect charge state and EPR-activity has been published previously.⁹ In this paper, we discuss our efforts to evaluate the effect of the deposition substrate temperature on the film structure and, hence, the photosensitive response. We find that substrate temperature can, in fact, be used to tune the *type* of defect states dominating the optical behavior of the film, allowing modification of both the magnitude and dispersion of the refractive index change observed. The results of a range of spectroscopic probes are discussed and used to develop a structural model describing the phenomena.

2. SAMPLE FABRICATION

Samples were fabricated using reactive atmosphere RF-sputtering from a 3 inch diameter hot-pressed Si/Ge (50/50 wt%) alloy target in a Unifilm PVD-300 sputtering system. An Ar/O₂ atmosphere was used during deposition. Total chamber pressure was held at 10 mTorr with oxygen partial pressure varied (0.14 - 0.18 mTorr) so as to yield high uv absorption while maintaining visible transparency (to allow visible light spectroscopy). Films were deposited onto both Si wafers (with a 20 nm thermal oxide layer) and fused silica substrates. The substrate temperature was varied using a resistive heating element monitored with an embedded thermocouple. Films were formed on ambient temperature substrates (180°C due to energy dissipation from the sputtering plasma) and substrates held at 600°C. All samples for optical evaluation were deposited onto the fused silica substrates with an approximate thickness of 2 μm. Electrical measurements were performed on 1.5μm thick films deposited onto Si. The thin tunnel oxide on the Si substrates made electrical measurements more reliable since charge injection from the Si substrate is suppressed at moderate electric fields.

3. OPTICAL/STRUCTURAL ANALYSIS

After film synthesis, the optical samples were examined using Raman, EPR and optical absorption spectroscopies. Raman spectroscopy was performed using a waveguide geometry in which the 514.5 nm beam from a Ar ion laser was prism coupled into a waveguide mode of the film. The beam power was held at 100 mW before the input prism. The resulting streak was then imaged normal to the film plane into the slit of a Spex Triplemate spectrometer equipped with a Peltier-cooled Si photodiode array controlled by an EG&G PARC OMA III system. Spectral resolution for the system was 0.5 cm⁻¹. Spectra were collected at room temperature under unpolarized conditions. Optical absorption was performed using a Perkin-Elmer Lambda 900 system from 185 to 1600nm. Spectra were collected in the as-deposited state and iteratively during the course of optical bleaching studies.

Electron paramagnetic resonance (EPR) studies were made on an X-band Bruker ESP-300E spectrometer to evaluate the presence and development of paramagnetic structural defects in the films. Spin concentrations were determined by comparing the double integrated spectra of the samples with that of a weak-pitch standard.

Propensity for photosensitivity and insight into the mechanisms responsible were obtained through optical irradiation of the samples using a Lambda-Physik KrF excimer laser operating at 248nm with up to 10mJ, 25 ns pulses at a repetition rate of 15Hz. The energy density at the sample was approximately 7 mJ/cm²/pulse. Optical absorption measurements, coupled with EPR data, were collected after each exposure cycle from specimens that had been simultaneously exposed to the excimer beam. Changes in optical absorption were analyzed using standard Kramers-Kronig formalism to provide the dispersion of the change in refractive index, Δn.

Characterization of operable point defect states was also aided using a selective charge injection technique in conjunction with capacitance-voltage (CV) measurements and EPR. A full description of the technique is given in Ref. 9 in which it was used to investigate structural defects in reactively sputtered germanosilicate films deposited onto 180°C substrates. In the present work, this technique is also used to compliment optical bleaching results obtained from materials deposited onto 600°C substrates thus

providing further insight into the influence of substrate temperature on film defect structure. Briefly, the technique allows selective injection of either positive or negative charge carriers into the glass thin film. Both EPR spectra and net space charge in the material can be monitored after carrier injection to evaluate the propensity of the material to trap charge and the corresponding influence this process has on the identity and/or population of paramagnetic defect states.

4. RESULTS AND DISCUSSION

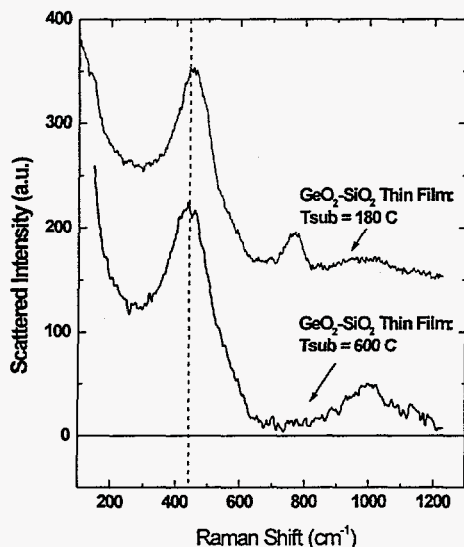


Figure 1: Unpolarized Raman spectra collected from low (top) and high (bottom) substrate temperature samples. The dotted vertical line corresponds to 435 cm^{-1} .

annealed structure. Prior work evaluating Raman spectra in silica and germania under high applied stresses, in fact, also shows significant shifts in the symmetric stretch bands^{12,13}, consistent with the spectra obtained in the present samples. Using a similar argument, the energy of asymmetric stretch bands in the

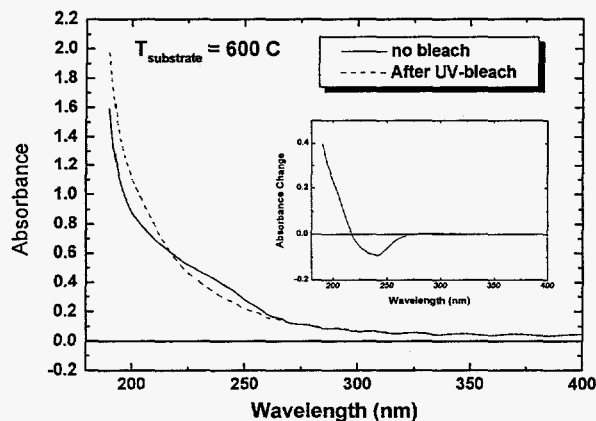


Figure 2: Optical absorption exhibited before and after UV-exposure for the high substrate temperature material. The difference spectrum is depicted in the insert.

bulk materials, typically located from 850 to 1100 cm^{-1} should also shift, possibly explaining the 769 cm^{-1} band. However, the general spectral features are not consistent with this explanation. Raman spectra of alkali-modified germanosilicate glasses have exhibited a band in this energy range associated with non-bridging oxygen (NBO) species¹⁴. Given the highly strained structure of these films, it is reasonable to expect the presence of NBO's. The 768 cm^{-1} band is thus tentatively assigned to a non-bridging oxygen vibration.

These results contrast the Raman behavior of the film deposited at a 600°C substrate temperature. In this case, the spectrum is most consistent with those published previously in melt and sol-gel-

derived materials^{10,11} with similar stoichiometry. This spectrum exhibits the symmetric stretch vibration at approximately 435 cm^{-1} with no obvious band observed in the $750\text{ to }800\text{ cm}^{-1}$ range. These observations indicate a film structure that contains significantly fewer atomic defects. This is expected as the elevated substrate temperature should provide additional energy for structural rearrangement to promote lower energy configurations during deposition, resulting in a structure more closely related to that obtained using a high temperature processing strategy.

Differences between the two substrate temperature materials are also observed in the representative, as-deposited (no uv-bleach) optical absorption spectra given in Figures 2 and 3 taken from samples deposited onto fused silica substrates.

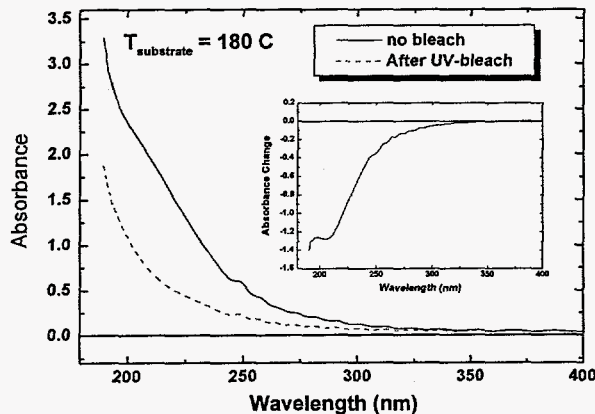


Figure 3: Optical absorption exhibited before and after UV-exposure for the low substrate temperature material. The difference spectrum is depicted in the insert.

changed by the deposition conditions used. Corresponding EPR studies of the same samples (Figures 4 and 5) also supports this view. These results reveal a dramatic difference in the population of EPR active Ge centers between the high and low substrate temperature materials.

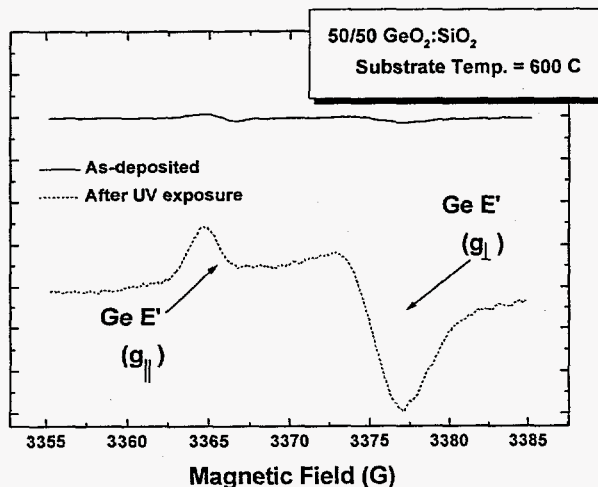


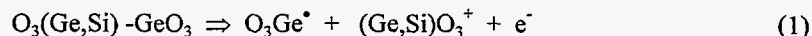
Figure 4: EPR spectra from the high substrate temperature material collected before and after UV-exposure.

temperature substrate samples, a more "classic" bleaching behavior (representative of MCVD or sol-gel-synthesized materials) is exhibited in which the band forming the shoulder at approx. 240 nm decreases

samples deposited onto fused silica substrates. Figure 2, for the high temperature substrate samples, exhibits a spectrum which is very similar to prior results obtained from fiber preforms, fibers and sol-gel derived thin films. A shoulder in the 240 nm range is observed which has been previously associated with the oxygen-deficient Ge precursor center which plays a role in the photosensitive process. In contrast, Figure 3, which depicts data from the ambient substrate temperature sample, does not show this feature but does show a rather broad shoulder in the 200 to 225 nm range which is superimposed on the absorption edge for the film. These results suggest that the optically active defect structure of the two materials has been changed by the deposition conditions used. Corresponding EPR studies of the same samples (Figures 4 and 5) also supports this view. These results reveal a dramatic difference in the population of EPR active Ge centers between the high and low substrate temperature materials. For low substrate temperature samples, much higher spin concentrations, corresponding, to Ge dangling bonds, were observed compared to the high substrate temperature specimens.

Bleaching effects after exposure to 248 nm excimer radiation were subsequently followed using both the optical absorption and EPR analyses. A summary of optical bleaching results is also given in Figures 2 and 3 which depicts both spectra collected from as-deposited samples and those obtained after a total uv-exposure of approximately 3.22 kJ/cm^2 . The difference spectra are also included. Immediately evident is a significant difference in bleaching spectral behavior between high and low substrate temperature samples. In the high

while absorption increases in the 200 nm range. Such an effect has been previously observed by several researchers and has been attributed to an optical defect interaction described by the following equation:



Thus, the effect of this mechanism is to increase the concentration of Ge E' centers. This is supported by the optical absorption increase in the 200 nm range, which has been associated with this structural entity.⁴ Further support of this model for the high substrate temperature material is also found in the EPR studies which show an increasing Ge E' center spin density with uv-exposure (Figure 4).

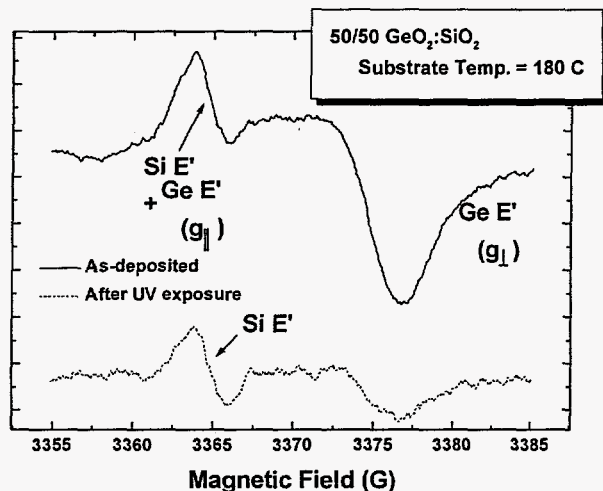


Figure 5: EPR spectra from the low substrate temperature material collected before and after UV-exposure.

These results are contrasted by bleaching behavior observed in samples deposited under low substrate temperature conditions. As shown in Figure 3, optical bleaching of the material occurs over the entire uv range with no competing increase in absorption observed. The difference spectra indicate, however, a preferential absorption decrease in the 200-210 nm wavelength range. The EPR also shows a significantly different behavior with regard to the paramagnetic Ge center in the low substrate temperature material. In this case, uv bleaching actually results in a decrease in the spin density of this center (see Figure 5).

Selective charge injection in these materials also indicated a significant difference in the participating defect species between the high and low substrate temperature samples. In the high substrate temperature case, the results of this measurement technique lended support for the traditional defect model. Here, the EPR Ge E' center density was influenced only through injection of holes (increased EPR center density). Electron injection, however, produced no effect. This is consistent with the inability of the diamagnetic, oxygen deficient defect center to function as an effective electron trap. It can, however, trap holes to form the Ge E' center as previous depicted in Eqn. (1). These results dramatically contrast those previously reported for the lower substrate temperature materials in which an initially high paramagnetic Ge center density was consistently reduced through charge injection of either polarity.⁹ In that case, neutral, isolated dangling Ge bonds were hypothesized to serve as the precursor defect state. This structure is able to accept either electrons or holes to form diamagnetic, charged species as depicted in Eqn (2) below:



It is apparent that the predominate precursor defects interacting with the uv radiation in the low substrate temperature films are different from those discussed for the high substrate temperature samples. In the low substrate temperature material there is a correlation between uv-absorption bleaching and EPR-active center density changes thus giving insight into the identity of one defect type which could contribute to the absorption changes observed. It is important to note that with the highly strained nature of the low substrate temperature films and the relatively broad band character of the uv-absorption spectrum, other, EPR-inactive, defect species might also be participating. This issue is now under investigation.

From a technological standpoint, this demonstrated ability to modify the optically active structural defect states in these materials enables the corresponding photosensitive response to be tailored through *in-situ* control of thin film deposition conditions. Returning to Figure 2, the large difference in uv-bleaching behavior observed between the high and low substrate temperature samples will necessarily produce a concomitant variation in the refractive index changes observed in each material. Figure 6 depicts the results of a Kramers-Kronig transformation of the absorbance change data exhibited by each sample. Note the contrast in the dispersion in the refractive index change exhibited by each material, a direct result of the

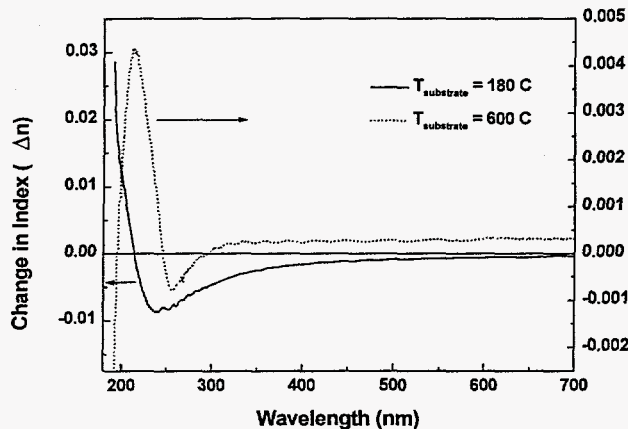


Figure 6: UV-induced refractive index changes for high and low substrate temperature materials.

different structural defect states contributing to correspondingly different uv-bleaching responses. Competing absorption band bleaching and growth processes in the high temperature sample produces a characteristic oscillation in the sign of the refractive index change with a net positive refractive index change obtained at wavelengths in the visible and near-infrared (NIR). With UV-exposure resulting in optical bleaching across the entire UV spectrum, the low substrate temperature sample approaches the zero-change point from below, exhibiting a negative refractive index change in the visible and NIR wavelength range. Thus, through materials synthesis control, both the dispersion and sign of the photo-induced refractive index change can be

tailored in these materials. Moreover, for similar oxygen-deficient defect densities, we anticipate that the low substrate temperature material will exhibit a larger absolute refractive index change since there is no competition between band growth and bleaching processes. In this case, all of the absorption strength modification contributes in the same sense to the negative index change.

5. CONCLUSION

We have demonstrated the successful synthesis of germanosilicate glass thin films possessing enhanced uv photosensitivity using reactive atmosphere, RF-magnetron sputtering from fully reduced Si/Ge alloy targets. This innovative technique for the fabrication of these materials allows control of both the population and characteristics of oxygen-deficient structural defect centers known to participate in the photosensitive response of the material. Control of substrate temperature during deposition produces a dramatic change in the precursor defects interacting with the uv beam, producing concurrent differences in the optical bleaching behavior of the materials. Optical and EPR evaluations of uv-bleached high and low substrate temperature materials, coupled with selective charge injection techniques, have enabled tentative structural defect models to be developed to describe the photosensitive response of both materials. Films produced under high substrate temperature conditions exhibit behavior consistent with a defect picture previously used to explain photosensitivity in MCVD and sol-gel derived germanosilicate glasses. In this case, a diamagnetic, oxygen deficient germanium center serves as the predominate precursor defect structure. Film deposition onto low temperature substrates results in a material response indicating the involvement of a neutral, paramagnetic, germanium dangling bond state as the precursor.⁹ The dramatic differences between the optical bleaching behaviors resulting from the interaction of these precursors with the uv beam resulted in a concurrent variation in the dispersion of the refractive index change. This study thus illustrates our ability to tailor the magnitude, sign and characteristics of the photosensitive response in these glasses through appropriate control of synthesis conditions. Through our synthesis strategy, it is possible to control the defect structure and corresponding photosensitivity *in-situ*, during film fabrication, without resorting to reducing atmosphere treatments (under elevated temperatures and pressures) typically used to enhance photosensitivity in germanosilicate glass.

6. ACKNOWLEDGEMENTS

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