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13. ABSTRACT (Maximum 200 words)

The emergence of optical signal processing in communications, image analysis, information storage and transfer, and high speed logic and computation has generated a great demond for optical materials with made-to-order properties. While the development of optical systems has been rapid, the development of materials and fabrication processes to make their components has been far slower. The research conducted under this grant has addressed the issue of new optical materials by investigating the relationship between fabrication processes, structural characteristics and the fundamental optical behavior of novel optoelectronic materials. In the 4 year period of this grant (3 years funed and 1 year extension), we conducted an investigation on non-linear-optical(NLO) materials which undergo a change in refractive index as a result of exposure to light. This optically induced change in optical properties makes them desirable for applications as active elements in optical circuits, and relevant to the applications listed above. Our studies have focused both on materials with large optical non-linearity and very fast optical response, and on materials with large index changes but with temporally stable optical response. The former are suitable or applications in optical gates, while the latter are suitable for memory

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SEMICONDUCTOR AND GLASS COMPOSITES FOR NON-LINEAR, GUIDED-WAVE OPTICAL APPLICATIONS

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U. S. Air Force AFOSR Grant No. F49620-93-1-0095

FINAL REPORT

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SUMMARY

The emergence of optical signal processing in communications, image analysis, information storage and transfer, and high speed logic and computation has generated a great demand for optical materials with made-to-order properties. While the development of optical systems has been rapid, the development of materials and fabrication processes to make their components has been far slower. The research conducted under this grant has addressed the issue of new optical materials by investigating the relationship between fabrication processes, structural characteristics and the fundamental optical behavior of novel optoelectronic materials. In the 4-year period of this grant (3 years funded and 1-year extension), we conducted an investigation of non-linear-optical (NLO) materials which undergo a change in refractive index as a result of exposure to light. This optically induced change in optical properties makes them desirable for applications as active elements in optical circuits, and relevant to the applications listed above. Our studies have focused both on materials with large optical non-linearity and very fast optical response, and on materials with large index changes but with temporally stable optical response. The former are suitable for applications in optical gates, while the latter are suitable for memory applications or for optically written optical circuits. Our approach has been to combine studies of (1) materials fabrication, (2) nano-structure development and (3) the fundamental processes underlying optical behavior. Materials of interest have included glasses containing isolated semiconductor nano-crystals and glasses with optically sensitive defect structures. Our results have so far observed the fastest optical index change measured in CdTe-glass, quantum-dot composites (sub-picosecond carrier relaxation times), and have determined the fundamental processes causing photosensitivity in germania-silica glass composites. These studies have led to an analysis of the mechanisms leading to photosensitivity and an understanding of the materials requirements for enhancement of this effect in novel materials.

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INTRODUCTION

Novel materials with active optical behavior have become increasingly important for communications, image processing and analysis, information storage and information transfer, and high speed logic and computation. The parallelism characteristics of optical signals have made them the number one choice for communications and complex image processing tasks since they require transmitting a multitude of simultaneous parallel signals or conducting massively parallel logic operations. These developments have required the discovery and fabrication of numerous materials with novel optical behavior. But this task has proven to be exceedingly difficult.

One of the major difficulties has been engineering materials for specific active optical applications which require the generation, detection and optical rerouting of optical signals. The parallelism characteristic of optical signals which has made them important in signal transfer and image analysis and computing is the reason why optimized materials have been difficult to develop. Parallelism arises from the ability of optical signals to propagate through materials without changing the materials characteristics. Most materials are highly linear optically, thus allowing a lack of cross-coupling between signals. However, the formation of optical gates, logic gates, writable memories, etc. requires that there be materials in which the cross-coupling processes are enhanced by non-linear optical (NLO) behavior. Many of the materials used today have been discovered by long and intense development efforts, or by chance. At present, developments are slow and are not keeping up with design requirements and industrial demand. This problem, in general, results from the lack of a fundamental base in processing and understanding the behavior of optical materials. The problem can be traced to a lack of established interdisciplinary educational programs in *optical materials science* in Universities. While optical engineering, optical physics and materials science have flourished in past years, the focus on optical materials (considered to be at the bottom of the food chain in optoelectronics) has been slow to achieve.

Our research efforts at the University of Florida have long been in the area of optical materials. Our programs have always emphasized the relationship between the materials fabrication, the structural development and the optical behavior aspects of all our materials development efforts. Our students have been intensely trained and educated in the three areas of (a) fabrication, (b) structural development and characterization, and (3) optical behavior measurement, characterization and modeling. Consequently, they have obtained successful positions at various industrial and national laboratories, including Sandia Labs, Xerox Corporation, AT&T Bell Labs, Bellcore, etc. in areas of optical materials development. Our research has been instrumental in understanding the relationship of materials synthesis and structure to optical behavior. We have so far examined a variety of optical thin film materials, including tailored optical glass stacks, semiconductor nano-clusters, glass composites, and photosensitive glass composites. Our objective in general has been to molecularly engineer materials for specific applications in optics by studying and understanding the principal mechanisms underlying the desired optical processes and then developing a relationship between materials fabrication and structure with optical behavior.

Our AFOSR research has consisted principally of investigating methods of fabricating active optical composite materials which use the composite nature of their structures to develop desired optical behavior. Specifically, we have studied RF sputtering, sol-gel processing with porous glass infiltration, and pulsed laser deposition for the fabrication of optical waveguide films tailored to either contain semiconductor nano-crystals or other oxide materials as part of the composite structure in order to develop optical activity associated with photo-induced, non-linear changes in refractive index.

Our research has focused on (1) transient changes in refractive index, with particular attention to very fast (sub-picosecond) optical non-linearity, and (2) steady-state changes in refractive index which can be written and erased optically (photosensitivity). These properties are useful in communications, image analysis, information transfer and management, and in logic and computer operations. The fast changes have been sought for optical interconnects, optical switches, optical multiplexers and optical gates. These components form the heart of any information management system, and will combine massively parallel processing with high-speed logic when the proper materials become available. The optically written, steady-state index changes have been sought for optical memory applications, optically written film and fiber gratings, graded index optical components in integrated optical circuits, and digital lenses for the rapid processing of massive information and image data.

The results of the past AFOSR research have scoped the capabilities of the three processing methods and have shown how each one can be tailored to desired materials engineering goals for active optical waveguide applications. For example, we have demonstrated the advantage of RF sputtering over conventional melting methods for the fabrication of semiconductors with very fast optical processes. The quantum dots fabricated by RF sputtering and tested under the AFOSR research effort have demonstrated the fastest observed carrier relaxation processes, through optical bleaching of the exciton absorption spectrum. While previous work on melt-derived, semiconductor quantum-dot-glass composites have only achieved switching times of the order of hundreds of picoseconds, our RF sputtered waveguides have exhibited carrier decay times of a few hundred femtoseconds. Our current studies of pulsed laser deposited films show an unprecedented control over film microstructure and stoichiometry, with the facility to deposit crystal or amorphous structures of the same composition, as desired. This approach has led to the formation of silicon and germanium quantum crystals of *controlled microstructure and size* that exhibit direct gap behavior, making possible a wide range of applications in optical detectors and sources. Furthermore, our approach of controlled materials synthesis has allowed the investigation of the underlying processes and structures which affect the optical behavior of photosensitive materials, thus making possible a better understanding of the controlling mechanisms and leading to a better selection of new material components and structures.

LIST OF RESULTS AND ACHIEVEMENTS OF THE GRANT

- Silica glass films with nano-clusters of CdTe were produced and tested using a pump-probe facility at MIT to exhibit sub-picosecond carrier relaxation times in the exciton bleaching process. The composite films promise to have the fastest observed carrier relaxation behavior in any semiconductor material.

- Silica glass films were fabricated with isolated Si nano-clusters. These films exhibited direct gap behavior for small size clusters and a blue-shift in the absorption edge up to the near UV region.

- A femtosecond optical pulse facility is now operational and uses a Ti-sapphire regenerative amplifier to form 200 fs white light pulses. It is being applied to the measurement of transient absorption in CdTe and Si containing films. Results are expected before the end of the year.

- A new model is being developed to explain the very fast optical switching behavior observed in past and ongoing studies of transient absorption in CdTe-glass and Si-glass composites.

- Sol-gel films of germania-silica were developed with excellent optical waveguiding properties and the conditions for optically induced photosensitivity were studied in collaboration with researchers at Sandia National Laboratories and the University of Central Florida. Published reports of these studies are listed below.

- The primary photosensitivity processes have been determined in germania-silica composite glass films. Measurements of photosensitivity revealed that UV light produces a bleaching process in an absorption band at 240 nm and a newly discovered band growth at 202 nm (reported for the first time).

- Modelling studies of the refractive index change associated with the bleaching and growth processes revealed that: (a) the film sensitization by exposure to H_2 gas forms two separate bands at 240 nm, and only one is UV bleachable, (b) it is the growth of the newly discovered 202 nm band which controls the magnitude of the writable index change in the films, and (c) the close proximity of the bands at 240 and 202 nm causes the processes of bleaching and growth to act in opposite directions on the magnitude of the index change, thus explaining its small magnitude.

- Based on our results of studies on germania-silica films, we have begun investigations of different composite materials for improved behavior (higher photo-induced index changes).

- A laser ablation chamber for pulsed laser deposition of composite films has been constructed and is being used to form CdTe, Si and GaAs films. The chamber is being equipped with a time of flight mass spectrometer for an analysis of the gas phase composition in the plume from the ablated material. This facility will enable measurements of and control over structural and compound formations in the gas phase prior to deposition. An optical spectrometer is being added to allow analysis of gas phase temperature and photo-induced reaction processes in order to better determine the dynamics of particles and compounds in the gas phase and on the substrate.

Personnel Supported

J. H. Simmons (faculty), R. Ochoa (visiting faculty), C. J. Simmons (research scientist), C. Schardt (graduate student), T. Varghese (graduate student).

Honors/Awards

A paper submitted for presentation at the American Ceramic Society Meeting in Cincinnati, May 1995, based on studies of photosensitivity of germania-silica films, conducted in collaboration with the University of Central Florida has received the Norbert J. Kreidl award for excellence. The award is given to the student who conducted the work and will present the paper (Kelly Simmons-Potter).

Interactions/Transitions

- Rome Labs: Dr. Chuck Woods. Research to develop novel bulk holographic material by using poled semiconductor-glass composites.

- Wright Labs: Dr. Michael Capano. Research to investigate the plasma formed during pulsed laser deposition, by using linear time of flight mass spectrometry and optical spectroscopy.

- AT&T Bell Labs: Dr. Allan Bruce. Research to make composite films of silica-germania at various concentrations by using RF sputtering, and to investigate the phase stability of the system using x-ray photoelectron spectroscopy.
- Sandia National Labs: Dr. Kelly Simmons-Potter. Research to test optical waveguides made from photosensitive materials for digital lens applications.
- Duke University: Richard Wells. Research to develop and test glass-GaAs composites by infiltrating GaAs quantum crystals produced at Duke University into porous sol-gel matrices prepared at the University of Florida.
- University of Pittsburgh: Dr. Sandy Asher. Research to conduct optical tests on samples of CdS crystallites on silica colloids in solution.

Publications

D. G. Chen and J. H. Simmons, "Fabrication and Characterization of GeO_2-SiO_2 Waveguides", in Glasses for Electronic Applications, Ceram. Trans. 20, R. K. Nair and D. R. Uhlmann, eds. (Am. Ceram. Soc. Westerville, OH, 1991) pp 299-307.

"Raman Scattering Investigation of $xGeO_2$-$(1-x)SiO_2$ Planar Waveguides," B. G. Potter, R. Ochoa, D. G. Chen and J. H. Simmons, Optics Lett. 17, 1349-51 (1992).

"Photosensitivity of Sol Gel Derived Germanosilicate Planar Waveguides," K. D. Simmons, G. I. Stegeman, B. G. Potter and J. H. Simmons, Optics Lett. 18, 25-27 (1993).

"GeO_2-SiO_2 Thin Films for Planar Waveguide Applications" D. G. Chen, B. G. Potter and J. H. Simmons, J. Non-Crystalline Solids 178, 135-147 (1994).

"Photosensitivity in Germano-Silicate Sol-Gel Thin Films," K. D. Simmons, G. I. Stegeman, B. G. Potter and J. H. Simmons, J. Non-Crystalline Solids 179, 254-259 (1994).

"Band Bleaching and Growth Dynamics in 45%GeO_2-55%SiO_2 Films", K. S. Potter and J. H.

Simmons, Appl. Phys. Lett. 66, 2104-6 (1995)

"Modeling of Absorption Data Complicated by Fabry-Perot Interference in Germano-Silicate Thin Film Waveguides," K. S. Potter and J, H, Simmons, J. Optical Soc. Amer. B 13, 268-272 (1996).

DETAILED DESCRIPTION OF RESEARCH

The research conducted has been aimed at fabrication and processing of optically active materials because they hold the key to enabling technology for numerous and wide-ranging applications in optical signal processing, communications, computing and image recognition. Our studies have focused on glass-based optically active materials which achieve their optical activity through their structural characteristics. These materials hold the promise for exhibiting important properties for the above-named applications and the development of those properties relies on understanding fundamental processes relating their composition and structure to their optical properties.

The two classes of materials that we have studied divide into materials that exhibit rapid optical activity and are composed of semiconductor nano-crystals isolated in a glass matrix, and materials that exhibit optically writable refractive index changes and are composed of glass-in-glass or crystal-in-glass composites. Below, we describe each topic.

Semiconductor-glass composites

The semiconductor-glass composites offer the potential for the fastest transient change in refractive index associated with an optical resonance. The latter allows the change in index to be large enough[1] to allow switching over a short device length and makes the process useful for optical integrated circuits such as those using planar waveguides. The electronic Kerr effect in glasses has been shown to have a potential for very fast optical switching as well,[2] however, the refractive index change obtained is orders of magnitude lower than that possible with the resonance processes, consequently, the Kerr effect requires the use of long optical fibers for useful optical activity.[2] Our research studies with the semiconductor-glass composites have exhibited the potential for sub-picosecond optical switching of a resonant process, yielding the fastest observed absorption bleaching effect in semiconductors. The materials were glasses containing semiconductors from columns 2-6 compounds, such as CdTe, CdS and CdSe. These 2-6 semiconductors have large excitonic oscillator strengths and have the promise for very fast optical switching which we have demonstrated.

Results of studies on two-six semiconductor-glass composites

Our studies have demonstrated a carrier relaxation process of the order of several hundred femtoseconds in CdTe-silica composites. This type of behavior holds great promise for utility in planar waveguide optical circuits. And while the required power consumption may be found to be high, the rapid optical switching behavior gives them a significant expected utility.

The optical switching process, however, is not fully understood due in part to the great difficulty of making femtosecond optical measurements. Our tests were conducted in collaboration with Dr. Fujimoto at MIT,[3] yet, the measurements were limited to a single wavelength, making it impossible for us to investigate the processes underlying the fast carrier relaxation effects observed, and to scope the utility of the carrier relaxation process for future applications. However, the data taken at 630 nm are shown in Fig. 1, and clearly demonstrate the speed with which optical bleaching of the excitonic states recovers.

In the past year, at the University of Florida, we have assembled a laser system consisting of a Ti-sapphire laser with Ti-sapphire regenerative amplifier and optical parametric oscillator for obtaining femtosecond pulses of micro-joule energies.[4] The system has the capability of forming high energy 100-femtosecond optical pulses of finely tuned wavelength (pump pulses) and synchronized 200-femtosecond pulses of white light (probe pulses). Using this setup, it is possible to investigate the dynamics of carrier relaxation from exciton bleaching processes and to determine the underlying mechanisms, thus allowing a study of materials characteristics which enhance both the magnitude of the index change and the speed of the carrier decay.

The carrier decay tests have consisted of pump-probe measurements of the transient absorption associated with excitonic transitions in the films. These transitions are associated with a strong absorption peak below the bandgap energy. Saturation of the transitions (bleaching of the absorption) by band-filling occurs in a few tens of femtoseconds and cannot be measured with our present setup. However, this process is not the device speed determining step. Instead it is the carrier recombination or decay rate which controls the device speed. Generally, carrier recombination processes are very slow in semiconductors, and especially slower in quantum confined structures. However, the presence of an interface can drastically reduce recombination times by supplying effective carrier traps. This trapping is often associated with permanent photodarkening observed in melt-derived glasses.[1,5] Previous measurements on CdSe containing melt-derived glasses yielded carrier decay times of several hundred picoseconds.[6] The CdTe-silica composites have exhibited carrier decay processes as fast as 300 femtoseconds. However, a careful examination of the films has failed to exhibit any photodarkening. Due to the single frequency restriction of past tests, we were unable to distinguish between the photodarkening and possible carrier-carrier transient processes as the cause of the observed very fast carrier decay times. This restriction has been removed by the pump-continuum probe measurements reported here. Figure 2 shows the absoprtion results and confirms the bleaching of the exciton resonance. The samples were prepared routinely using a sequential RF sputtering process developed in our group.[7]

Photosensitivity Studies

Glass-based composites have long been known to exhibit photosensitivity and second harmonic generation by the formation of a permanent index grating in germano-silicate optical fibers.[8] This process has great potential for applications (1) in optical memories since the grating can be optically erased, (2) in optical integrated circuits, since the refractive index change can be used to route light along complex paths which can be written optically, (3) in active optical devices such as film or fiber lasers by allowing in-situ formation of optical gratings which can act as cavity mirrors instead of mechanical cleaving, and (4) in digital optics for image analysis because of the complex lens geometries that can be developed optically by this method.

The photosensitivity and second harmonic generation processes appear to result from self alignment of optically induced defects in the glass structure. Our past research has examined the mechanisms associated with the formation of optically induced defects. Our results, as reported in AFOSR reports and publications,[9-11] have revealed the existence of a band growth mechanism associated with Ge E' center defect formation. This defect structure, when combined with the previously known bleaching of the oxygen vacancy absorption process yields the observed effects of photo-induced index changes. In fact, our studies determined that since one process leads to absorption band bleaching and the other leads to absorption band growth, the two processes oppose each other in producing photo-induced index changes.[11] Research on novel preparation methods not available to us for the silica-germania glasses is now continuing at Sandia National Labs, based on the results of our studies. We anticipate additional collaborative efforts in the measurement of second harmonic generation with investigators at Rome Labs. (See Interactions/transitions below.)

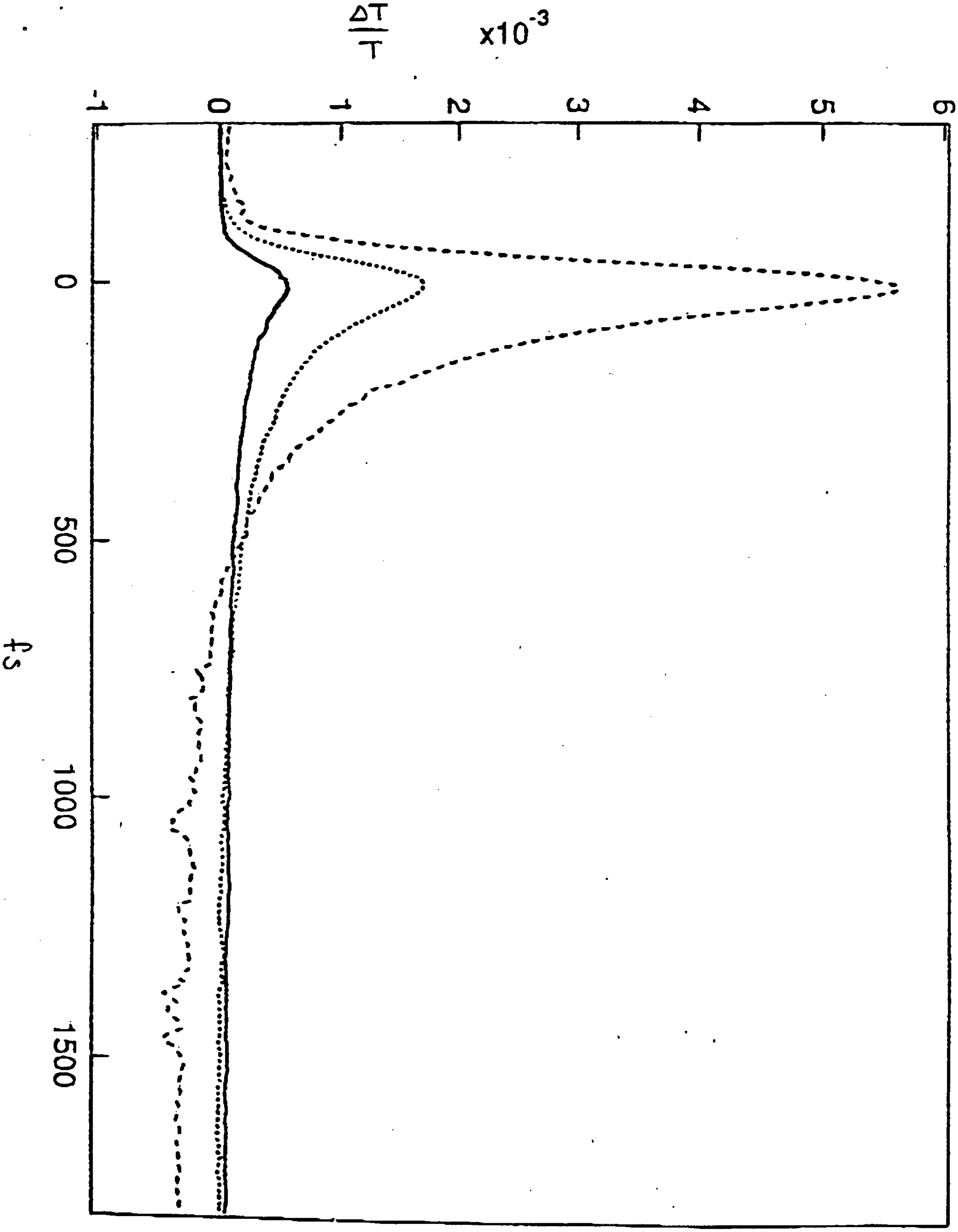

Figure 1- Absorption change with time

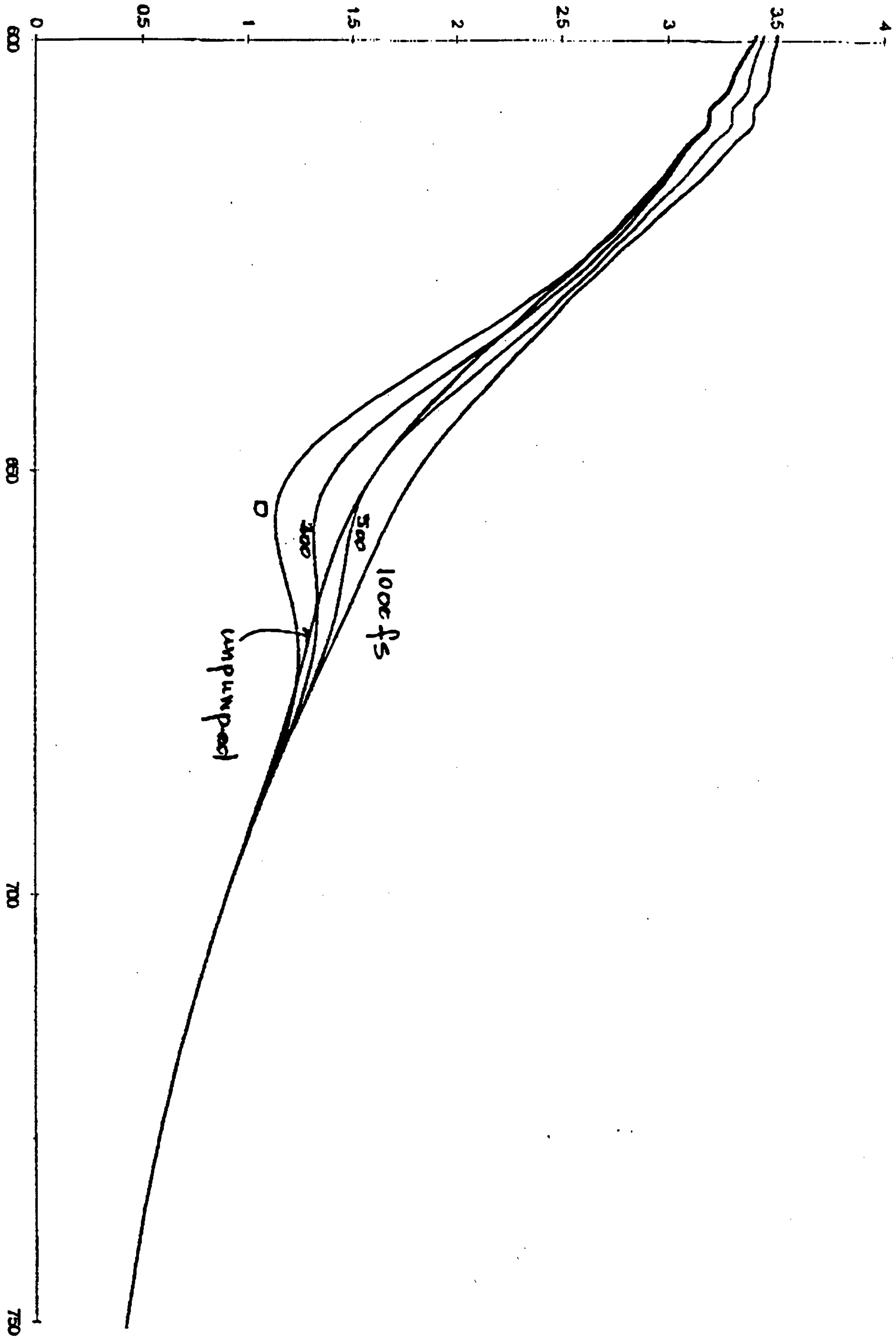

Figure 2 - Absorption change with wavelength for

The results of our research are included in Appendix A.

Interactions/Transitions

A wide range of interactions and transitions were maintained during the research period.

Rome Lab

Volume holographic plates: Continued research efforts in the area of volume holographic plates has been conducted with Dr. Chuck Woods, involves forming melt-derived glasses containing 5% CdS quantum crystals[12] and porous glasses containing polymer active media. This work involves the collaboration of Drs. Yuri Denisyuk and Nadya Reinhand from the soviet Union. Materials fabrication efforts were started at the University of Florida and optical tests were planned for Rome Labs. However the abrupt end of funding from AFOSR has stopped progress in this area. New funding sources to continue this work are being sought.

A collaborative research effort has long been in place with Mr. Mike Suscavage in the area of pulsed laser deposition of thin films.

A collaborative effort in the area of photosensitive glasses has long been ongoing with Dr. Osama El-Bayoumi.[13] This work was interrupted by his assignment to the Air Force EOARD Office in London. In anticipation of his return to Rome Labs, a new collaborative thrust will be initiated in the are of novel photosensitive materials. This collaboration will be extended to include Dr. Lee Bouthilette to measure second-harmonic generation in the newly derived films from the proposed research.

Commercial and National Lab Interactions

Dr. Allan Bruce of AT&T Bell Labs has conducted collaborative efforts to investigate the phase relationships between silica and germania using X-ray photoelectron spectroscopy (XPS). Targets of especially designed compositions are fabricated at Bell Labs and used in our PLD system to form films of interest. The XPS tests were conducted at UF.

Dr. Kelly Simmons-Potter of Sandia National Labs has conducted a collaborative research efforts by investigating the photosensitivity of films developed by PLD in our program. Papers from that collaaboration are included in the Appendix.

Other AFOSR Grant Recipients

We have interacted with Dr. Sandy Asher, University of Pittsburgh, and Dr. Richard Wells, Duke University, to conduct transient optical measurements on CdS crystals in liquid suspensions and on GaAs and other 3-5 precipitated semiconductors.

Staff and Personnel Supported

1. J. H. Simmons (faculty), R. Ochoa (visiting faculty, 20% time), C. J. Simmons (research scientist, 50% time), C. Schardt and T. Varghese (graduate students) will remain as currently supported. C. Schardt and T. Varghese are PhD candidates, having qualified at the beginning of this year. Both students have received MS degrees.

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Appendix Papers

Band bleaching and growth dynamics in 45%GeO_2–55%SiO_2 films

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Photoinduced changes in the ultraviolet absorption bands of GeO_2–SiO_2 glasses have a clear significance in photosensitive processes. In this letter, the dynamics of bleaching and growth of absorption bands in highly photosensitive germanosilicate thin films following exposure to 248 nm excimer laser radiation are discussed. Strong evidence is found in support of a single-photon process for the bleaching of a band at 238 nm and growth of a band at 202.5 nm as a source of photosensitivity. Calculated changes in refractive index are eight times greater than those found in two-photon-induced grating experiments. This suggests avenues for enhancement of photosensitive effects through proper materials conditioning. © *1995 American Institute of Physics.*

Photosensitivity in germanosilicate fiber and planar waveguides has been demonstrated following exposure of the material to both visible and ultraviolet (UV) radiation. In both instances, preexisting defects in the glass, associated with gemania-based oxygen vacancies, are excited by high intensity radiation which gradually builds a permanent index perturbation in the glass. It is generally believed that the bleaching of a Ge-associated oxygen vacancy absorption band near 240 nm is largely responsible for the photosensitivity although new studies have indicated that a shorter wavelength absorption process may also play a role.[1–4]

In this letter, photoinduced bleaching studies are carried out on sol-gel-derived germania silica thin films and the UV absorption behavior of the films is decomposed into separate bands. Analysis of the bands not only shows the previously postulated absorption band bleaching near 240 nm under UV exposure, but also clearly reveals the growth of a well-defined absorption peak near 202 nm. The 240 nm band is associated with a neutral Ge-based oxygen vacancy center[5–8] while the 202 nm band results from a Ge E' center.[8,9] Comparison of the band bleaching near 240 nm and band growth near 202 nm reveals a one-to-one correspondence as a function of fluence of 248 nm light. This correspondence identifies the photosensitive process as a direct ionization of the pre-existing neutral Ge-associated oxygen vacancy and the capture of a photoexcited hole to form a Ge E' center. Comparisons of the measured UV absorption changes with two-photon, grating-induced refractive index changes[10] and with previous ESR measurements[11] show good agreement with the proposed model.

Samples with thin-film geometry were chosen instead of core-clad fibers because thin films lend themselves directly to successive UV exposures with interspersed absorption measurements. The ability to control oxygen-deficient-germania (ODC_g) defect concentrations through direct exposure of the film surface to reducing heat treatments, and to produce any desired $xGeO_2$–$(1-x)SiO_2$ composition in thin-film form made these samples uniquely useful. In this letter, we examine the behavior of 45%GeO_2–55%SiO_2 films subjected to a reducing heat treatment of 0.5 h at 550 °C in a 5%H_2–95%N_2 flowing-gas atmosphere. The films, deposited on fused silica substrates, were formed by an alkoxide sol-gel process[12] and had thicknesses of 0.6 μm. Following sample fabrication and prior to any UV exposure, absorbance of the films over an apertured area 4×8 mm was measured over a wavelength range of 180 nm–1.5 μm. The apertured sample area was then repeatedly exposed to 248 nm laser radiation pulsed at 10 Hz with an energy of 0.45 mJ/pulse on one half of the sample and 1.02 mJ/pulse on the other half of the sample. Pulse widths were 20–25 ns and the period of exposure was increased for each subsequent exposure. Absorbance measurements were made after each exposure period. Films produced under identical conditions, but not subjected to the UV exposures, were tested for growth of photosensitivity using counterpropagating 488 nm beams as reported elsewhere.[10]

The film absorbance data, before and after heat treatment, and after exposure to radiation, showed sizable Fabry–Pérot (FP) oscillations. A method described elsewhere[13] was developed for calculating the period and intensity of the FP oscillations in the film absorbance spectra and for extracting absorption bands from the data. Modeling the total absorbance of the films with four absorption bands resulted in an excellent fit of the data over the entire measurement range. Approximate absorption band peak positions and widths were determined based upon previous measurements conducted in bulk germania and in germanosilicate fiber preforms.[5–9,14] The peak positions and widths (FWHM values in parentheses) are 181.0 nm (30.0 nm), 202.5 nm (36.0 nm), 238.0 nm (36.0 nm), and 264.0 nm (46.0 nm). The bands are attributed, respectively, to the GeO_2 molecular defect,[7] The Ge E' defect,[8,9] the ODC_x center,[5–8] and a band which is similar to the Ge(1) band reported in Ref. 6. The effect of UV exposure on the absorption bands is shown in Fig. 1 for the sample which was irradiated with pulses of 0.45 mJ/pulse. No change was observed in the bands at 181.0 and 264.8 nm, however, bleaching of the band at 238.0 nm and growth of the band at 202.5 nm were observed with

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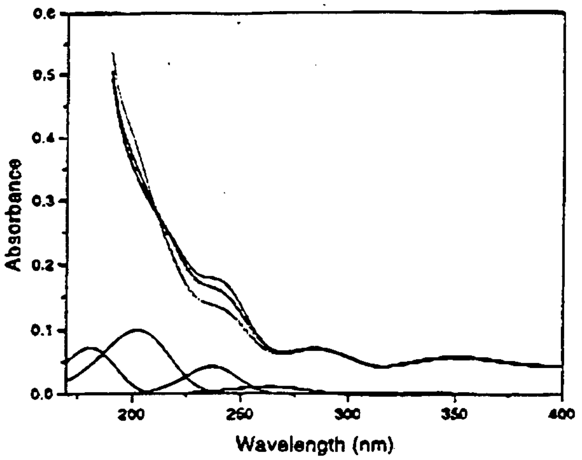

FIG. 1. Effects of UV exposure on the absorption spectrum of a 45 mol % GeO_2–55 mol %SiO_2 sol-gel thin film which received a 30 min postdeposition H_2 reducing treatment. The UV exposure was done at 248 nm with 0.45 mJ/pulse. The solid line denotes the spectrum prior to UV irradiation, the long dashed line follows an exposure to 3700 pulses and the dotted line follows an exposure to 110 000 pulses. Dot/dash curves under the absorption spectra indicate widths and peak positions of absorption bands used to fit the data. The bands are located at 181.0, 202.5, 238.0, and 264.0 nm.

increasing UV exposure. A slight improvement to the fits could be achieved by the inclusion of an additional weak band near 214 nm, attributed to the Ge(2) oxygen paramagnetic center.[6] Such a band, if present, is very small compared to the other, more distinct, absorption features, and did not exhibit a change with UV exposure. It was, therefore, excluded from the subsequent analysis. The unbleachable 240 nm defect reported by Hosono *et al.*[14,15] was observed as a remnant loss after bleaching of the 238 nm band. Comparison of these results with similar measurements on uncoated fused silica substrates and on substrates coated with $(0.1)GeO_2$–$(0.9)SiO_2$ films showed little effect due to UV irradiation. This indicates that the bleaching and growth processes can be attributed to GeO_2 associated defects in the glass rather than to silica-based defect structures.

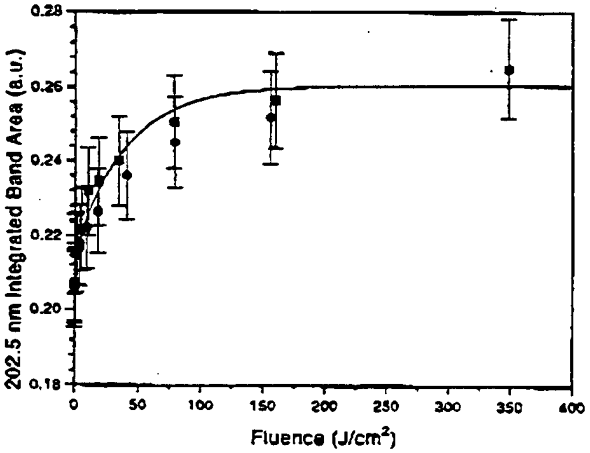

FIG. 2. Growth of the 202.5 nm integrated absorption band area with increasing UV exposure. Circles and squares represent data from samples exposed to 0.45 and 1.02 mJ/pulse, respectively, at 248.0 nm. The solid line denotes an exponential fit to the data given by: $I=0.2604-0.0443 \times \exp(-f/41000)$, where f=fluence.

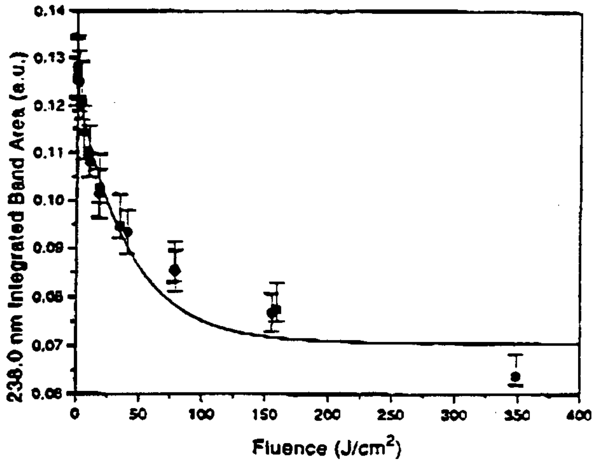

FIG. 3. Bleaching of the 238.0 nm integrated absorption band area with increasing UV exposure. Circles and squares represent data from samples exposed to 0.45 and 1.02 mJ/pulse, respectively, at 248.0 nm. The solid line denotes an exponential fit to the data given by: $I=0.0706+0.0527 \times \exp(-f/41000)$, where f=fluence.

The growth of the integrated area of the 202.5 nm band and bleaching of the 238 nm band with UV exposure for the two different pulse energy values are shown in Figs. 2 and 3, respectively. Each plot combines data from both energy values in terms of total fluence and demonstrates a linear dependence of both the band growth and bleaching on pulse energy. The lack of nonlinear dependence of the band dynamics on pulse power identifies this as a direct-ionization, single-photon process. The dependence of band growth and bleaching on fluence were fit with a single exponential function (solid line) which yields an accurate description of the data. The coefficients of the exponential growth and bleaching processes are given in Table I and correspond to the equation: $I=A\ \exp(-f/B)+C$, where I=the integrated band intensity, and f=fluence in mJ/cm^2.

The most informative coefficient in the above equation is B, which represents the rate of the fluence-dependent bleaching and/or growth process. The same value is obtained for both pulse energies and for the separate band growth and bleaching data indicating direct correspondence between bleaching and growth processes. This is strong evidence of a physical model for the formation of a photosensitive index perturbation in which absorption band changes result from ionization of existing ODC_g centers and subsequent trapping of a hole at an oxygen vacancy to form Ge E' centers. Thus, as the Ge E' center population grows the neutral oxygen vacancy center population decays proportionally. Based on our data, a comparison of the pre-exponential terms (A) used in the fits indicates that the ratio of oscillator strengths of the

TABLE I. Parameters for single exponential fit to UV absorption data.

45%GeO_2 films (0.5 h/550 °C)	Peak (nm)	A	B	C
0.45 and 1.02 mJ/pulse	238.0	0.0527	4.1×10^4	0.0706
0.45 and 1.02 mJ/pulse	202.5	−0.0443	4.1×10^4	0.2604

Ge E' band to the ODC_g band is 0.84. The magnitude of the oscillator strength of the Ge E' band may therefore be calculated to be ~0.34, assuming Hosono's value of 0.4 for the oscillator strength of the ODC_g band.[15]

The change in absorption at saturation resulting from the measured band bleaching and growth processes can be used in a Kramers–Kronig (KK) transformation to calculate the associated change in refractive index. The Maclaurin method for transformation of discrete, finite data sets described by Ohta[16] was used to produce a numerical integration routine which yielded the change in refractive index at 488 nm. The bleaching and growth processes alter the refractive index at 488 nm in opposite directions and subtract from each other. The KK analysis yields an index change of -3.1×10^{-5}. This is ~8 times the value calculated from saturation in the two-photon, photosensitive grating experiments ($|\Delta n|=4.6\times10^{-6}$).[11] Additional fluence-dependent absorption features below 190 nm, while not measurable due to instrument limitations, are not expected to have a significant effect at 488 nm.[4] The difference observed in the calculations between the single-photon and the two-photon measurements may result from incomplete ionization of the defects by the two-photon excitation and from the subtractive effect of bleaching and growth of the two adjacent bands. The subtractive effect is, in fact, responsible for differences in the sign of the calculated refractive index perturbation in other measurements and indicates a direction for device improvements. Materials may be found in which the difference in magnitude of the oscillator strengths of the oxygen deficient center and the E' center transitions may be large. Then, the subtraction effect may be drastically reduced, yielding a much larger range of index changes associated with the photosensitivity process.

In conclusion, measurements of the dynamics of single-photon band bleaching and band growth processes were conducted on 45%GeO_2–55%SiO_2 glass films prepared by a sol-gel process and subsequent hydrogen-atmosphere reducing treatment. The data show a significant growth of the 202.5 nm band and a significant bleaching of the 238 nm band upon exposure of the films to 248 nm excimer KrF laser radiation. The lack of dependence of the growth and bleaching processes on pulse energy indicates that the excitation mechanisms result from a direct-ionization process. The growth and bleaching processes are attributed to the trapping of photoexcited positive charges at preexisting oxygen deficient centers around the germanium ion to form Ge E' centers. The latter have been directly correlated with the appearance of photosensitivity in the same glasses.[11] The identity of the rate of band growth and band bleaching indicates that the two processes are directly linked, supporting the proposed physical mechanism of single hole trapping. The refractive index change at 488 nm resulting from the application of Kramers–Kronig calculations to the observed single photon, band bleaching, and growth processes is about 8 times greater than the absolute value of index change measured by two-photon photosensitivity grating experiments. The difference may be due to incomplete ionization of the ODC_g defects by the two-photon process. The KK transformations reveal that the band bleaching and growth processes subtract from each other in inducing the index change at long wavelengths. Therefore, it is clear that enhancement of the photosensitivity phenomenon will require the development of materials and/or heat treatments which alter the relative magnitudes of the oscillator strengths of the bleaching and growth processes in order to allow one or the other of them to dominate.

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Modeling of absorption data complicated by Fabry–Perot interference in germanosilicate thin-film waveguides

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Complex absorption spectra obtained from thin films at normal incidence can be difficult to interpret owing to the appearance of Fabry–Perot interference fringes in the data. We describe a technique for modeling such spectra so that true absorption features can be identified and evaluated separately from the overlying fringes. The technique is used to interpret data obtained from photosensitive germanosilicate solgel films on fused-silica substrates but may be easily extended to analysis in other material systems. © 1996 Optical Society of America

1. INTRODUCTION

The analysis of normal-incidence absorption data obtained in transmission from thin-film samples is generally complicated by the presence of Fabry–Perot (FP) interference fringes arising from interference of the spectrophotometer beam within the plane of the films. These fringes are easily identified and differentiated from real absorption features because they change position with the angle of incidence of the beam on the sample. To interpret absorption or transmission data accurately, however, one must evaluate the fringes and employ a curve-fitting analysis so that the features of the relevant absorption bands can be studied. This is not a simple process because the periodicity of the fringe pattern changes as a function of wavelength and is strongly affected by both the refractive-index dispersion and the extinction coefficient dispersion of the material.

Previous researchers have developed techniques for evaluating film thickness and complex optical constants from an analysis of the periodicity of the observed fringe patterns in transmission and reflection spectra. These studies have generally relied on the use of adjacent fringe extrema for the determination of fringe orders in the spectra[1-7] or on the use of multiple spectra,[7] which further complicates the process. In addition, such techniques, although they are useful in the visible and the infrared, falter in regions [such as the ultraviolet (UV)] where strong absorption occurs and dampens the observed interference. Alternative techniques that use off-normal incidence (e.g., Brewster's angle)[8] to decouple absorption and index dispersion simplify the problem but are appropriate only for a narrow spectral range and for limited sample configurations. Furthermore, in cases in which the film and the substrate indices are similar, the interpretation of fringe data by the above methods becomes difficult. We describe in detail a fitting technique for normal-incidence optical absorption data that yields an accurate evaluation of spectral features of dielectric films upon dielectric substrates. The process involves modeling FP fringes across the entire spectral range of the data while introducing absorption features in the propagation constant of the FP equations. This requires some prior knowledge of both the index dispersion and the shape of absorption features in the material. We apply the technique to the analysis of absorption data obtained in photosensitive germanosilicate thin films[9] upon fused-silica substrates to demonstrate the utility of the method.

2. MODELING FABRY–PEROT INTERFERENCE

The first necessary task in eliminating FP fringes in the data is to determine the index dispersion of the waveguides. For the photosensitive germanosilicate materials that are discussed in this paper, researchers have produced Sellmeier expressions for the refractive-index dispersion in pure silica[10] and pure germania[11] as well for the $x\mathrm{GeO_2}:(1-x)\mathrm{SiO_2}$ system[11] based on measurements in bulk glasses. The mixed Sellmeier expression is given in Eq. (1), in which SA, SL and GA, GL are the Sellmeier coefficients for SiO_2 and GeO_2 glasses, respectively, and X is the mol fraction of GeO_2 in the material:

$$n^2 - 1 = \sum_{i=1}^{3} \frac{[\mathrm{SA}_i + X(\mathrm{GA}_i - \mathrm{SA}_i)]\lambda^2}{\lambda^2 - [\mathrm{SL}_i + X(\mathrm{GL}_i - \mathrm{SL}_i)]^2}. \qquad (1)$$

Using the above expression, we modeled the index dispersion for the film. An ellipsometric measurement found good agreement between the film and the bulk glass indices at 632.8 nm.

As the index dispersion functions for the films may be reasonably modeled by the mixed Sellmeier expression discussed above, the next task in eliminating the FP fringes from the data is to model the interference fringes produced in the air–film–substrate system. By use of a standard summation technique for multiple-beam fringes[12] it is possible to develop an expression for the

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transmittance of such a structure that utilizes an imaginary (phase) component. Equation (2) gives the ratio of the transmitted electric field amplitude (A_t) to the incident electric field amplitude (A_i) in which t_0, r_0 and t_1, r_1, respectively, are the transmission and the reflection coefficients for the air–film and film–substrate interfaces and where δ is the phase shift acquired after two passes through the film with thickness d, refractive index n_f, and extinction coefficient k_f. The phase shift is given by $\delta = 4\pi d n_f(1 + ik_f)/\lambda_0$:

$$\frac{A_t}{A_i} = \frac{t_0 t_1 \exp(i\delta/2)}{1 - r_0 r_1 \exp(i\delta)}. \tag{2}$$

We may now determine the total transmitted light intensity by multiplying Eq. (2) by its complex conjugate, keeping in mind that the function δ is itself complex. The simplified expression is given in Eq. (3), where a represents the real index portion and b represents the imaginary loss portion of the phase-term delta [$\delta = (a + ib)$]:

$$T_1 = \frac{t_0^2 t_1^2 \exp(-b)}{1 - 2r_0 r_1(\cos a)\exp(-b) + r_0^2 r_1^2 \exp(-2b)}. \tag{3}$$

Finally, inasmuch as the sample described in this paper was fabricated by a standard solgel dip-coating process, which necessarily results in the formation of a thin film on both sides of the substrate, we must repeat the above process for the substrate–film–air structure on the back side of the sample to determine the total transmission of light through the sample. Note that the coating on the second side of the substrate does not increase the number of interference layers in the FP structure because of the interposed substrate, which acts incoherently on the beam. Rather, the transmission of the first film appears as a simple input intensity distribution to the second film. Any coherence effect between the two layers is negligible. Hence the final expression for transmitted light intensity through the entire sample is given in Eq. (4), in which t_0', r_0' and t_1' and r_1' are the new transmission and reflection coefficients for the substrate–film and film–air interfaces and in which the new incident electric field is determined from Eq. (3). Because the rear film originates from the same coating bath and experiences the same atmospheric exposures as the front film, it is taken to have identical thickness and optical properties, and hence all other variables in Eq. (4) are defined as in Eq. (3):

$$T_2 = \frac{t_0'^2 t_1'^2 \exp(-b)}{1 - 2r_0' r_1'(\cos a)\exp(-b) + r_0'^2 r_1'^2 \exp(-2b)} T_1. \tag{4}$$

From Eq. (4) and realizing that the absorbance (Abs) data given by the spectrophotometer relate to transmittance through Abs = $\log_{10}(1/T)$, it is now possible to model the fringes observed in the UV–visible absorption spectra taken from the thin-film samples. The above expression is, thus far, exact. The only assumption made is that the incident radiation is a plane wave at normal incidence to the film. However, approximations are made in our implementation of Eq. (4). First, we assume zero loss in the substrate, and second, the reflection and transmission coefficients are assumed to be real so that loss is included only in the phase term of Eq. (4). For the case in which substrate losses are nonzero it would be necessary to include an expression for background loss in k_f in the absorbance function to model the data correctly. The assumption of real transmission and reflection coefficients is not always accurate. However, a calculation of the effect of loss on the coefficients for normal-incidence radiation results in an estimated transmittance error of $\pm 2 \times 10^{-4}$ when loss values representative of the germanosilicate samples are utilized. For samples demonstrating large substrate or film extinction coefficients it would be necessary to make both the reflection and the transmission coefficients in Eq. (4) complex.

Here we compare two optical spectra from a 55 mol. % SiO_2–45 mol. % GeO_2 sample. The sample was first evaluated in its as-prepared, oxidized condition. It was then examined following exposure to an additional, reducing-atmosphere thermal treatment whose purpose was to develop large absorption bands in the UV region. Figure 1 shows a comparison of the FP interference model derived above [curve (c)] with the absorbance data for the sample in both its oxidized and reduced states [curves (b) and (a), respectively]. In this case the loss value used in the phase term was modeled to be a constant, $k_f = 0.0001$. It can be seen that the fit provides an excellent estimate of the FP oscillations. At wavelengths shorter than ~320 nm, the onset of absorption in the film separates the three curves; however, the period of the FP oscillations in the data is still accurately described by the modeled function. This additional short-wavelength loss can be investigated by inclusion in Eq. (4) of terms corresponding to characteristic absorption in the material. In the case of glass, the UV absorption in this region is made up of multiple bands with Gaussian band shapes, whereas in semiconductors the absorption follows the usual $(\omega - \omega_g)^{1/2}$ dependence. Similarly, the Urbach tail from the fundamental UV absorption edge of the material may be modeled. The application of this approach to an analysis of the absorption bands in the absorbance data from the reduced film is discussed below.

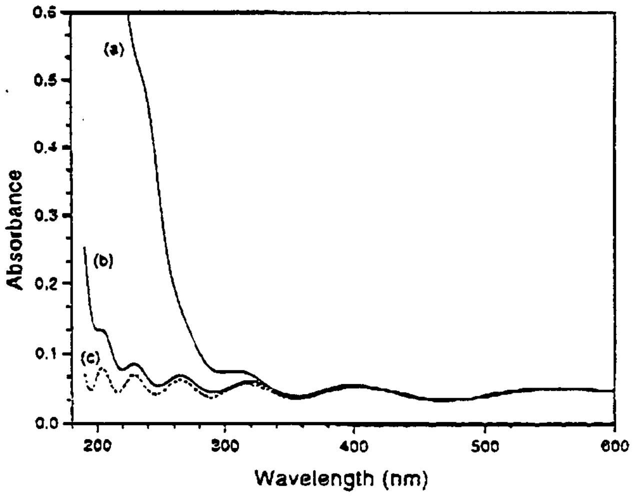

Fig. 1. Comparison of UV absorption data taken from a 45-mol. % GeO_2 thin-film sample in (a) its reduced and (b) its oxidized states with (c) a theoretically generated FP fringe fit.

3. MODELING GAUSSIAN ABSORPTION BANDS

Several possible approaches exist for the analysis of the absorption data obtained from the germanosilicate films. Section 2 demonstrated that the FP fringes seen in the data may be adequately modeled, and, therefore, one might be tempted simply to subtract the fringes from the data without further modification to observe the absorption behavior of the films. However, as the UV absorption increases in the films, the magnitude of the FP oscillations in the absorbing region becomes damped. Therefore a simple subtraction of the fringes would inevitably lead to oversubtraction in the absorbing region and would result in an underestimate of absorption band strengths. In addition, such oversubtraction could impose erroneous structural features on the spectra.

The effect of absorption on fringe visibility is demonstrated in Fig. 2. Here a series of curves generated from the fringe analysis presented above in Eq. (4) is plotted, along with the optical loss spectrum from a 45 mol. % GeO_2 sample that had been subjected to a 2-h, postdeposition reducing-atmosphere thermal treatment at 550 °C. As in Fig. 1, the optical loss in the generated spectra has been modeled as a constant defined by $k_f = 0.0001, 0.005, 0.015, 0.03$. It is clear from Fig. 2 that, although the FP fringe intensity decreases as the film absorbance increases, even at an absorbance of 0.8 in the film the effect of FP interference on the spectrum is nonzero. At larger absorbance values, however, the effective path length of the material has increased to the point that the effect of such interference is negligible.

It is evident, therefore, that either ignoring the fringe effects or simply subtracting the undamped fringes from the data would lead to a misinterpretation of the results. Correct data analysis requires that the formulas for the absorption band functions present in the material be included in the expression for the extinction coefficient in the FP equations. In this way the FP fringes will be appropriately damped with increasing absorption in the film, and an accurate evaluation of the absorption band widths and intensities can be made.

In implementing this approach it is convenient to use a fitting procedure that decouples the variations in absorption from index dispersion. In terms of the FP oscillations, a small increase in the extinction coefficient simply leads to a decrease in amplitude, as shown in Fig. 2. At large values of absorption the FP oscillations essentially disappear. In the region of high transmission and in the presence of absorption peaks we first assume the index and the extinction coefficient to be decoupled in order to calculate the first-order characteristics of the absorption peaks. Then, using Ohta's numerical Maclaurin method,[13] we calculate the corresponding Kramers–Kronig-induced fluctuations in index dispersion for each peak. Here we have calculated the magnitude of the largest fluctuation to produce an index change of less than 10^{-3}, and, therefore, decoupling was assumed in the fitting procedure. However, the reader should be cautioned that this test is always necessary because larger absorption features (as in resonant processes) may cause significant variations in the refractive-index dispersion and will require some iterative modification.

The analysis presented below is greatly helped by the availability of dispersion measurements over the entire composition range of the films of interest. In many studies, however, this dispersion information is lacking or only partially available. In such cases, trial Sellmeier coefficients may be used and modified through an iterative fitting of the FP oscillations in regions of low absorption. For this reason it is recommended that measurements be taken outside the region of interest, where no absorption features are present, to determine better the appropriate dispersion coefficients.

Generally, the existence of color-center defects in glassy materials gives rise to absorption bands at wavelengths longer than the fundamental absorption edge of the material. Because glasses contain no long-range order, the local environment of a particular absorbing defect center varies from site to site. This leads to an inhomogeneously broadened distribution in the absorption energy of the defect. Such inhomogeneous broadening is described by a Gaussian line shape in the energy of absorption for the species as gives in Eq. (5):

$$\rho(\nu) = A \exp\left[\frac{-(\nu - \langle\nu\rangle)^2}{2\Delta\nu^2}\right]. \qquad (5)$$

Here $\rho(\nu)$ is the probability of absorption at the frequency ν, A is the peak amplitude, ν is related to the energy by $E = h\nu$, $\langle\nu\rangle$ is the center frequency of the Gaussian, and $\Delta\nu$ is the Gaussian half-width. Many researchers have attempted to fit UV absorption spectra taken from photosensitive germanosilicate glasses by modeling Gaussian absorption bands in wavelength and applying such bands directly to absorbance data. This technique, although it is commonly employed, incorrectly describes the physical model for absorption within the material and can skew the bands. Therefore the Gaussian fitting method of Eq. (5) described above is used in the following analysis.

Based on the above discussions, a fitting procedure was established for analyzing the absorption data obtained from the thin-film samples. The FP oscillation equation [Eq. (4)] yielded an excellent fit of the absorbance

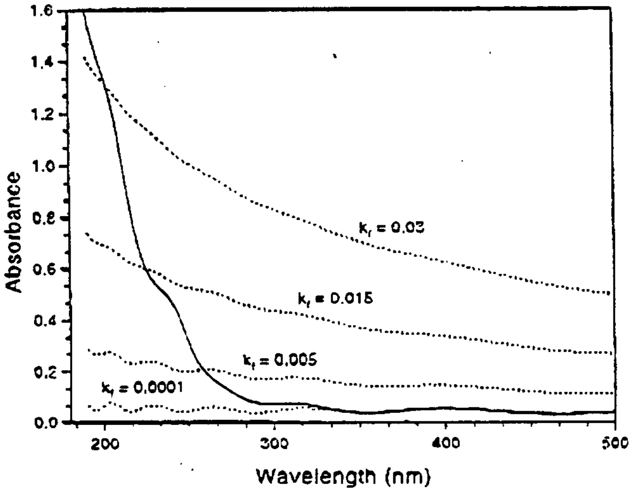

Fig. 2. Series of curves (dashed) generated from the FP fringe analysis described in Section 2 plotted along with the optical loss spectrum from a reduced, 45-mol. % GeO_2 sample (solid curve). The optical losses in the generated spectra have been modeled by constant k_f values of 0.0001, 0.005, 0.015, and 0.03.

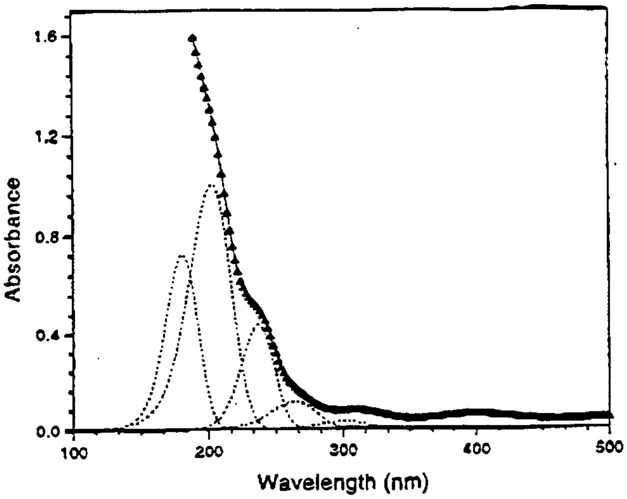

Fig. 3. Triangles represent the experimental absorbance data from a reduced, 45-mol. % GeO_2 sample. The solid curve is the theoretical fit to the data, and the dashed curves depict the five Gaussian bands used to model absorption in the sample. The bands are centered at 181.0, 202.5, 227.5, 264.8, and 300 nm.

data from the oxidized sample (see Fig. 1) at wavelengths longer than 250 nm where the slight absorption onset occurs. The data for the sample after it had been reduced, however, were more complex, as they exhibited numerous, strong absorption peaks as far away as 300 nm. Because the two spectra were obtained from the same sample, the film thickness and background absorption values derived in fitting the oxidized sample were used in fitting the data for the sample in its reduced state. Thus only a sum of Gaussian bands was added to the background extinction coefficient, k_f [Eq. (4)], in the model to describe the absorption features in the reduced film. The expression for the total loss in the film is given by $k_{f(\text{total})} = k_f + \sum_i \rho_i(\nu)$. We calculated the theoretical absorbance by varying the Gaussian parameters A, $\langle \nu \rangle$, and $\Delta \nu$ in Eq. (5) and converting the data to wavelength for a minimum number of bands necessary to fit the data. The approximate locations of the bands were determined based on past absorption measurements conducted in bulk germania and in germanosilicate fiber preforms.[14–20] We determined accuracy in the fit by minimizing the rms error between the data and the fit for each spectrum. An example of this fitting is given in Fig. 3, in which absorbance data from the 45 mol. % GeO_2 reduced sample from Fig. 2 (triangles) are compared with the calculated fit to the data by the technique described above (solid curve). Clearly, the fit is shown to be in excellent agreement with the data. Also included in the figure is the series of Gaussian bands used to model absorption in this spectrum (dashed curves). The five bands are located at 181.0, 202.5, 237.5, 264.8, and 300 nm and have halfwidths of 11.8, 15.2, 12.0, 16.6, and 16.0 nm, respectively. The uncertainty in these values is ±0.5 nm for the center of the Gaussian peaks and ±1 nm in the Gaussian halfwidths. The bandwidths and peak positions are found to be in good agreement with literature values.[14–20]

4. CONCLUSIONS

Modeling of absorption data taken in transmission through coated samples, thin-film waveguide samples, multilayer films, and significantly striated bulk samples is often complicated by the presence of FP interference in the data. Because the periodicity and the amplitude of the interference are inherently dependent on both the material refractive index and absorption function dispersions, the unambiguous removal of the interference fringes is not entirely trivial. In this paper we have outlined a versatile technique for the interpretation of absorbing features in absorption or transmission spectra that requires only prior knowledge of the refractive-index dispersion of the material and a reasonable model for the shape of the absorption features in the spectra. The method is based on the inclusion of wavelength dependent loss in the FP equations for a substrate–film–air system, and it allows for an easy iterative fitting of index dispersion coefficients and peak positions and widths. In addition, we have demonstrated the utility of our fitting routine in the analysis of absorption spectra taken from a germanosilicate film upon a fused-silica substrate, which has exhibited a strong photosensitive response. Although our example utilizes a single dielectric thin film upon a dielectric substrate, we have indicated necessary changes to our approximations in the model for alternative systems. Extension of our model to multiple-layer films is theoretically trivial but much more difficult to implement, because information concerning the dispersion of each of the layers must be known.

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