CONF-970231--2 SA NO96-2917C
SAND--96-2917C

Investigation of defects in highly photosensitive germanosilicate thin films

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ABSTRACT

Germanosilicate glasses exhibit a significant photosensitive response which has been linked to the presence of oxygen-deficient germanium point defects in the glass structure. Based on this correlation, highly photosensitive thin films have been engineered which demonstrate the largest reported ultraviolet-induced refractive index perturbations (Δn) in an as-synthesized material. Our thin-film fabrication process avoids the use of hydrogen sensitizing treatments and, thus, yields stable films which retain their predisposition for large photosensitivity for over one year of storage. Understanding the nature of the defects in such films and their relationship to charge trapping and enhanced photosensitivity is of paramount importance in designing and optimizing the materials. Toward this end, our films have been studied using electron paramagnetic resonance (EPR), capacitance-voltage, and optical bleaching and absorption spectroscopies. We find experimental evidence suggesting a model in which a change in spin state and charge state of *isolated* paramagnetic neutral Ge dangling bonds form either diamagnetic positively or negatively charged Ge sites which are largely responsible for the charge trapping and photosensitivity in these thin films. We present experimental data and theoretical modeling to support our defect model and to show the relevance of the work.

Keywords: Photosensitivity, thin films, glass, germanosilicate, reactive-atmosphere sputtering

1. INTRODUCTION

Germanosilicate glasses, such as those used in optical telecommunications fibers, have been the subject of intense interest in the past several years based on their photosensitive response to both ultraviolet (UV) and visible (through a two-photon process) radiation[1,2]. In typical melt-like materials, UV illumination of the germanosilicate glass in the 240 nm wavelength range results the bleaching of a characteristic absorption band located near 240 nm with the consequent growth of another band centered at approximately 202 nm [3-5]. The band bleaching and growth processes have been ascribed to trapping photo-generated holes at pre-existing oxygen-deficient germanium ($O_3\equiv(Si,Ge)\text{-}Ge\equiv O_3$) sites ($ODC_g$)[3,4,6]; i.e., the trapping of the hole leads to the conversion of the Ge-Ge site (optical absorption ~240 nm)[7,8] to the classic Ge E' site (optical absorption ~ 202 nm)[3,6,9] ($O_3\equiv(Si,Ge)+ \ldots \cdot Ge\equiv O_3$). The bleaching/creation process can result in a significant and stable change in the refractive index which can be the basis for optically patterned structures such as Bragg gratings. While devices and operational schemes based on distributed feedback Bragg grating structures are relatively common, enhanced utilization of these materials in new applications, requiring greater refractive index modulations, can only be implemented through improved materials or materials processing strategies. Improvements based on the exploitation of material defect populations and bleaching dynamics, for example, can significantly enhance the photosensitivity of the glass.

Previous attempts to modify the photosensitive response of germanosilicate materials have focused on elevated temperature and pressure hydrogen[10,11] and deuterium[12] loading heat treatments. This processing is believed to result in chemical reduction of the glass and in the creation of the germanium-associated defect centers that lead to photosensitivity. These activating treatments, however, tend to be time consuming, hazardous, and, in the case of the high pressure exposures, require rapid optical processing after treatment to prevent significant dopant out-diffusion prior to imprinting of the desired refractive index perturbation.

In this paper we report the fabrication of novel, highly photosensitive thin films produced using a reactive atmosphere sputtering technique. These films are easily sensitized during synthesis without requiring the post-deposition high temperature and pressure defect loading techniques that are generally employed to obtain films

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with enhanced photosensitivity. Moreover, our technique allows the degree of material photosensitivity to be engineered directly during sample synthesis without requiring the introduction of hydrogen impurities or dopant sensitizers into the material composition.

Investigation of the optical absorption characteristics of these materials indicates fundamental differences in the bleaching dynamics of the sputtered films as compared to "typical" GeO_2/SiO_2 thin films formed by sol-gel[4] or vapor deposition routes. Such differences suggest significant disparity between the participating defects responsible for the intrinsic material photosensitivity. In the following text, we explore the microscopic defect structure responsible for these differences by coupling electron paramagnetic resonance (EPR) with optical spectroscopy and various charge injection scenarios. We find that the photosensitivity of our reactive-ion sputtered thin films appear to results from a different type of Ge defect precursor structure. Specifically, both the photosensitivity and the charge trapping properties involve changes in spin state and charge state of *isolated* paramagnetic neutral Ge dangling bonds ($\cdot Ge \equiv O_3$) to form either diamagnetic positively ($+Ge \equiv O_3$) or negatively ($-Ge \equiv O_3$) charged Ge sites. By isolated we mean that the spin-active site ($\cdot Ge \equiv O_3$) does not have an ancillary charged component associated with it as does the classic Ge E' center ($O_3 \equiv Ge\cdot \ldots\ldots +(Si,Ge) \equiv O_3$)[6,7,9].

2. SAMPLE FABRICATION

Samples were fabricated via reactive atmosphere RF-sputtering in a Unifilm PVD-300 Multisource Sputtering System. The films were sputtered in an Ar/O_2 atmosphere from a 3 inch diameter hot-pressed Si/Ge (50 wt%/50 wt%) alloy target at an RF power of 118 W. Ar gas flow during deposition was 100 sccm. Oxygen flow rates were varied from 4 to 12 sccm to produce different oxidation levels in the deposited films. The chamber pressure during deposition was 10 mT with a base pressure of $<2 \times 10^{-7}$ T. The SiOx-GeOx films were deposited at ambient temperature onto either fused silica substrates or onto Si substrates with a 20 nm thermal oxide layer. For the former case, films thicknesses were 2 microns, as determined by stylus profilometry, and samples were used in all optical and magnetic spectroscopic analyses. For the latter case, film thicknesses were on the order of 1.5 microns and films were utilized in charge-injection studies. The thin tunnel oxide on the Si substrates made the electrical measurements more reliable since charge injection from the Si substrate is suppressed at moderate electric fields. In either case, substrates were attached to planetary stages to improve thickness uniformity.

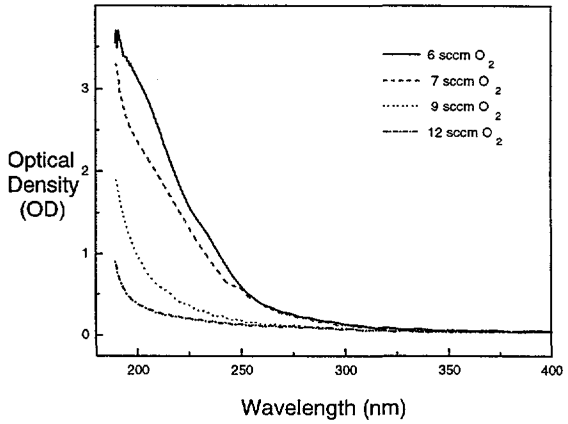

Figure 1: UV absorption spectra for reactive atmosphere RF sputtered germanosilicate films.

Manipulation of O_2 partial pressure during deposition enabled the oxidation extent of the films to be carefully controlled such that films ranging from fully metallic to fully oxidized were produced. Numerous depositions were performed to evaluate the effect of oxygen partial pressure on film optical properties and to check reproducibility[13]. Within the higher oxygen partial pressure range (in films exhibiting transparency in the visible) a significant variation in the density of germanium-associated oxygen-deficient defects was readily induced in the films, as evidenced by the intensity of the associated UV absorption features. In Fig. 1 four representative optical spectra are shown for samples deposited under varying oxidation conditions. Clearly, reduction of the oxygen flow rate has resulted in an overall increase in the UV optical absorbance of the films. Thus we have demonstrated that by controlling the deposition environment in the reactive atmosphere sputtering cell, we can engineer the extent of film oxidation and consequently the density of absorbing defects in the film. The implication is that the film photosensitivity, which is intrinsically reliant on defect densities, has also been engineered during film synthesis.

Interestingly, the well-defined absorption features which correspond to specific point defect structures in sol-gel planar waveguides[3] and optical fibers[14] are not distinct in the sputtered films. This suggests that these films may contain a greater variety and density of structural defect types compared to films prepared by other methods. Such a result is consistent with sputter-deposition processing, the ambient temperature substrate conditions employed, and the absence of a post-deposition thermal anneal in these samples.

3. EXPERIMENTAL RESULTS

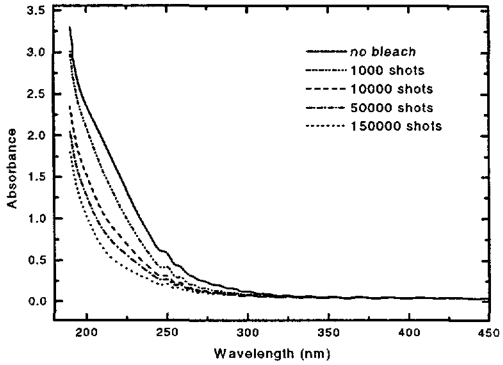

Figure 2: Absorbance spectra of representative film following various exposures to 248 nm UV radiation.

Following sample fabrication, the films were exposed to UV radiation from a Lambda Physik KrF excimer laser operating at 248 nm with up to 25 mJ/cm^2, 25 nsec pulses at a rep. rate of 15 Hz. Intermittent UV absorption and room temperature EPR spectra were taken in order to observe the possible bleaching effects of the UV radiation. EPR measurements were made on an X-band spectrometer (Bruker ESP-300E). Spin concentrations were determined by comparing the double integrated spectra of the samples with that of a Bruker weak-pitch standard. As can be seen in Fig. 2, exposure of the film to UV laser light resulted in an overall bleaching of the UV absorption bands. Similar behavior was observed in all of the films and no effect was seen to result from irradiation of bare fused silica substrates. In contrast to the usual observations for photosensitive germanosilicate films[3,4,14,15], we did not observe any growth in the Ge E' associated absorption band at 200 nm as a result of the UV exposure and bleaching. This indicates that the defect dynamics of bleaching in these films differs significantly from that of samples fabricated using more traditional techniques. This statement is substantiated by EPR data taken on the same sample. As can be seen in Fig. 3, our films contain an initially high density of Ge E' centers which are eliminated through the series of UV exposures. This is in sharp contrast to typical photosensitive materials in which an initially low Ge E' center density increases with UV exposure as the ODC$_g$ precursor to the Ge E' is ionized leaving the Ge E' center behind.

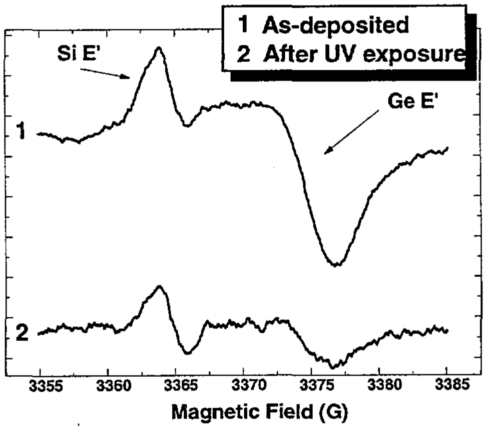

Figure 3: EPR spectra before (1) and after (2) UV irradiation of film.

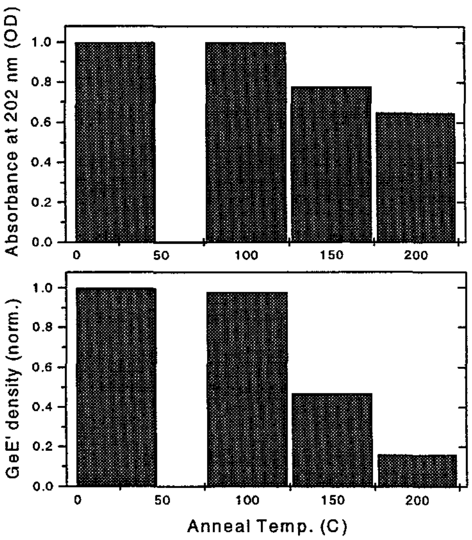

Figure 4: Optical absorbance at 202 nm and Ge E' center density following isochronal anneal on as-deposited sample.

Defect stability has been investigated in these samples. Preliminary isochronal anneals were conducted in an atmosphere of flowing helium (to avoid atmospheric film reduction or oxidation) for temperatures starting at 50°C and continuing up to 350°C in steps of 50°C for durations of 30 minutes each. The data indicate that both the optical absorption and Ge E' center density measured in the as-deposited samples decrease with increasing temperature. At a temperature of 250°C the Ge E' density has dropped to approximately 15% of its original value. In samples which have already been bleached we see a steady recovery in the UV absorbance with increasing anneal temperature such that 60% of the original signal has recovered following the 250°C anneal. Data on the as-deposited sample is represented in Fig. 4. It can be noted that the Ge E' density decreases more rapidly than the 202 nm optical absorbance signal. This gives further credence to the supposition that the defect bands in these samples originate from a broad variety and density of structural defect types but that at least part of the 202 nm absorption in the samples is associated with the Ge E' center

The lack of growth of the high energy absorption band enables the development of large index perturbations in these materials since we avoid the negative consequence of subtractive competing processes in the band bleaching dynamics[3,13]. Fig. 5 shows the saturated induced refractive index obtained following UV bleaching of one of our films fabricated under low O_2 partial pressure conditions (highly defected, large UV absorbance). The induced Δn was calculated using a standard Kramers-Kronig formalism. It is seen that the Δn in these films is as high as $4x10^{-3}$ in the visible and $4x10^{-4}$ at 1.5 microns. This is competitive with numbers given for films that have been pre-sensitized using post-fabrication hydrogen loading[11], and it is orders of magnitude better than typical values of Δn obtained in as-synthesized materials[4].

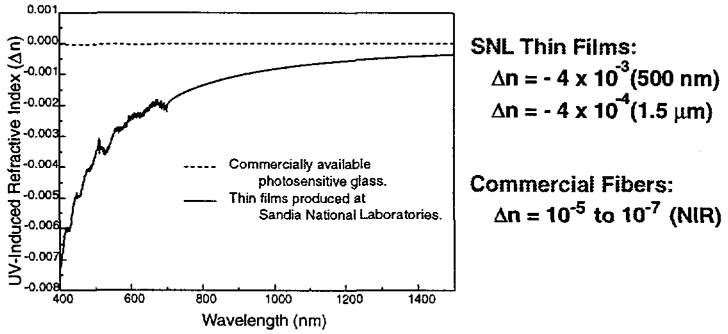

Figure 5: Induced refractive index in photosensitive thin films. The dotted line was obtained from data taken from sol-gel thin films[4] and resembles typical numbers for as-synthesized germanosilicate optical fibers.

In addition to the spectroscopic studies outlined above, electrical measurements were made to determine the charge state of the relevant defects in the sputtered photosensitive films[16,17]. In these studies the germanosilicate films deposited to thermal-oxide-coated silicon were injected with charge (electrons or holes) and capacitance voltage measurements were made to evaluate the change in space charge polarity of the films. Associated Ge E' center densities were simultaneously monitored. To make the measurement, positive or negative corona ions were deposited to the top surface of the films[18]. The corona ions resulted in a relatively uniform applied potential of +300V (-350V) across the oxide. The samples were then placed in a vacuum (10^{-4} Torr) and exposed to 10.2 eV photons from a 50 W deuterium lamp. Since the bandgap of the germanosilicate thin films is roughly 8 eV for this 50:50 (Si/Ge) composition, these photons create electron/hole pairs in the top 10 nm or so of the oxide. Under the action of the positive (negative) corona ion bias, the holes (electrons) are driven to the Si/SiO$_2$ interface while the electrons (holes) simply recombine with the positively (negatively) charged corona ions. Standard 1 MHz capacitance-voltage (CV) measurements were made using a Hg probe to form a temporary "gate". The mid-gap CV voltage shifts (ΔV_{mg}), defined as the voltage shift from the

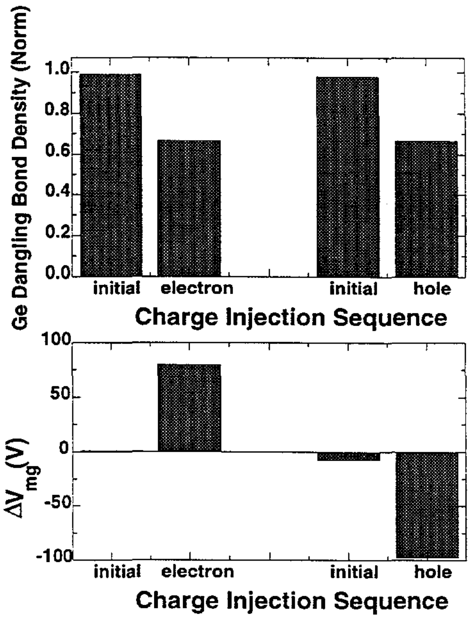

Figure 6: EPR and charge injection sequence.

origin (0 V), were used to monitor the sign of the net trapped charge in the dielectric. Thus, a negative (positive) ΔV is indicative of net trapped positive (negative) charge. Even though etch-back experiments were not performed to determine the spatial location of the trapped charge, we view the magnitude of ΔV_{mg} as an approximate measure of the amount of trapped charge in the dielectric. Fig. 6 shows the EPR defect densities measured in the films both before and after injection of electrons or holes along with the capacitance voltage ΔV_{mg} data. It is seen that the initial as-deposited films have a high Ge E' center spin density ($3 \times 10^{14}/cm^2$) and are virtually charge neutral. Injection of electrons results in a *decrease* in the Ge E' center density and a corresponding *increase* in ΔV (negative space charge field). Injection of holes results in a *decrease* in the Ge E' center density and a corresponding *decrease* in ΔV (positive space charge field). This means the initial neutral paramagnetic Ge defects are capable of trapping either electrons or holes to form charged diamagnetic centers.

4. DEFECT MODEL

The above results can be interpreted by assuming that the germanium defect centers of interest are isolated $\cdot Ge{\equiv}O_3$ centers and, thus, act as is charge traps in these germanosilicate thin films. For instance, upon electron injection we observe a concurrent increase in negative space charge and a decrease in the isolated $\cdot Ge{\equiv}O_3$ center density. These measurements suggest that the following reaction occurs during electron injection:

$$\cdot Ge{\equiv}O_3 + e- \rightarrow -Ge{\equiv}O_3 \qquad (1).$$

The injection of electrons causes the neutral isolated $\cdot Ge{\equiv}O_3$ center to trap an electron becoming negatively charged and diamagnetic, thereby, explaining the increase in the negative space charge and decrease in the EPR-active $\cdot Ge{\equiv}O_3$ center. Following hole injection, an increase in the positive space charge density and a concurrent decrease in the isolated $\cdot Ge{\equiv}O_3$ center density is observed. Somewhat analogously, these coordinated processes can be modeled by considering that the isolated $\cdot Ge{\equiv}O_3$ defect captures a hole, thereby, becoming positively charged and diamagnetic,

$$\cdot Ge{\equiv}O_3 + h+ \rightarrow +Ge{\equiv}O_3 \qquad (2).$$

The hole injection results cannot be explained by the classic Ge oxygen vacancy center. If this were the case, then upon injecting holes the Ge E' density should increase rather than decrease ($O_3{\equiv}Ge\text{-}(Si,Ge){\equiv}O_3 + h+ \rightarrow O_3{\equiv}Ge\cdot \ldots +(Si,Ge){\equiv}O_3$). The differentiating feature is that the classic Ge E' center is positively charged when paramagnetic, whereas, the isolated $\cdot Ge{\equiv}O_3$ is electrically neutral when paramagnetic. In essence, even though the EPR spectra of the isolated $\cdot Ge{\equiv}O_3$ center and of the classic Ge E' center are essentially indistinguishable from their electronic Zeeman interactions, we have been able to distinguish them by their different charge states by coupling EPR with charge injection sequences and capacitance-voltage measurements. (Their nuclear hyperfine interactions with the 7.8% abundant 73Ge isotope may be different; however, it is difficult to ascertain if this is the case using thin films.)

Assuming the identification of the relevant Ge defect in the films as the isolated Ge dangling bond, a model for the photosensitive optical process may be developed. It can be shown that both the optical absorbance and the isolated Ge E' center defect concentration decrease with similar responses to excimer laser irradiation dose[17]. This observation suggests a correlation between the two; i.e., the optical bleaching of this UV region is concurrent with the bleaching of the isolated, neutral, paramagnetic $\cdot Ge{\equiv}O_3$ defect center. Thus, it appears that at least part of the UV absorption band is due to optical transitions involving the isolated paramagnetic $\cdot Ge{\equiv}O_3$ center, and that at least a portion of the decrease in the UV absorbance is due to a decrease in $\cdot Ge{\equiv}O_3$ density.

These observations, coupled with knowledge that decay of the $\cdot Ge{\equiv}O_3$ density can occur by charge capture to form charged diamagnetic Ge+ and/or Ge- centers, makes it possible to model the bleaching process in these germanosilicate thin films. A reasonable interpretation of these observations is that some of the bleaching of the UV bands occurs by a charge transfer mechanism involving the isolated $\cdot Ge{\equiv}O_3$ center. It is proposed that the 248 nm light photo-excites the unpaired electron from the isolated $\cdot Ge{\equiv}O_3$ to the conduction band, thus forming a positively charged diamagnetic $+Ge{\equiv}O_3$ center. The resultant photo-excited electron can then become captured by another isolated $\cdot Ge{\equiv}O_3$ center, forming a negatively charged diamagnetic $-Ge{\equiv}O_3$ center. Thus, part of the photo-bleaching process simply involves the optical rearrangement of charges in existing neutral $\cdot Ge{\equiv}O_3$ defect sites. The proposed optical bleaching mechanism is schematically illustrated in Fig. 7 and can be described by

$$2(\cdot\mathrm{Ge}\equiv\mathrm{O}_3) \rightarrow +\mathrm{Ge}\equiv\mathrm{O}_3 \;+\; -\mathrm{Ge}\equiv\mathrm{O}_3 \qquad (3).$$

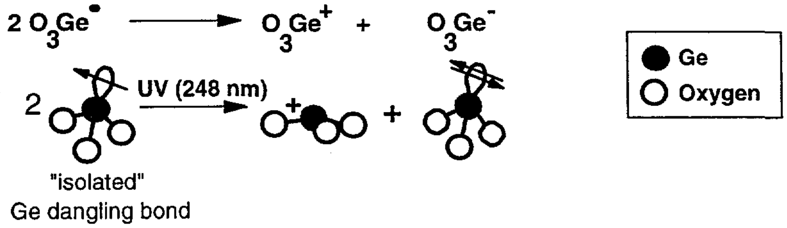

Figure 7: Defect model

The consistency of this model can be readily checked. First, it explains the co-annihilation of the UV absorption bands and isolated $\cdot\mathrm{Ge}\equiv\mathrm{O}_3$ centers. Second, the bleaching process is consistent with the observation that the isolated Ge dangling bond can exist in three different charge states (positive, neutral and negative). Third, the final bleached state incorporates overall charge neutrality of the dielectric through the formation of equal numbers of positive and negative charged Ge sites. Precise energetic positions of the three defect centers within the bandgap and the relative oscillator strengths are yet to be determined.

5. CONCLUSIONS

In summary, past efforts to increase photosensitivity in germanosilicate materials have relied on post-fabrication, high temperature and/or elevated pressure hydrogen atmosphere treatments which are intended to create the necessary point defects in the glass by chemically reducing the material. We have demonstrated the first successful synthesis of highly photosensitive germanosilicate waveguides using reactive atmosphere sputtering. Our process has enabled us to control both the thin film oxygen content and the relevant defect type and density in-situ without the use of post-fabrication treatments. Experimentally we find a good qualitative agreement between the density of isolated Ge dangling bonds measured magnetically, the density of charge trapping sites measured electrically, and the density of absorbing centers measured optically in reactive-ion sputtered germanosilicate thin films. Thus, by integrating optical and EPR spectroscopy with electrical measurements we have been able to identify a principle defect responsible for the photosensitive response in these films as the isolated Ge dangling bond. We find that both the photosensitivity and the charge trapping properties involve changes in spin state and charge state of isolated paramagnetic neutral Ge dangling bonds ($\cdot\mathrm{Ge}\equiv\mathrm{O}_3$) to form either diamagnetic positively ($+\mathrm{Ge}\equiv\mathrm{O}_3$) or negatively ($-\mathrm{Ge}\equiv\mathrm{O}_3$) charged Ge sites. We also demonstrate that the different photo-response of these sputtered thin films as compared to conventional forms of germanosilicate systems largely stems from different types of Ge defect precursors. Finally, we speculate that, because this synthesis method can produce films with a broad range of photosensitive defect densities, with successful development the enhanced versatility of this technique will allow materials optimized for numerous device applications to be readily fabricated.

6. ACKNOWLEDGMENTS

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

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