



Physical and optical characterisation of Ge-implanted silica

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Abstract

Ge nanocrystals formed in silica by implantation with 1.0 MeV Ge ions and subsequent annealing at 1100°C were characterised by transmission electron microscopy and Raman spectroscopy. The nanocrystals were found to be approximately spherical in shape and to have a structure consistent with that of bulk Ge. The average size of the crystallites increased with increasing fluence and for a fluence of 1×10^{17} Ge cm⁻² the size varied from 2.5 to 12 nm. The nonlinear optical response of the material was measured at a wavelength of 800 nm using degenerative four wave mixing and z-scan techniques. The former provided information about the magnitude and temporal response of the nonlinearity whilst the latter provided information about the operative mechanism. The magnitude of the nonlinear refractive index, $|n_2|$, was shown to be more than three-orders of magnitude larger than that of pure silica and to have a relaxation time of the order of picoseconds. The mechanism causing this nonlinear response is shown to be absorptive and to increase with increasing implant fluence as a consequence. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 42.65.-k; 78.47.+p; 81.20.-n

Keywords: Nonlinear optics; Nanocrystals; Four-wave mixing; z-scan; Ion-implantation

1. Introduction

Semiconductor-doped glasses exhibit interesting optical properties and have long been of both scientific and technological interest [1–3]. For example, the optical absorption of such glasses de-

pends strongly on the composition of the semiconductor dopant, a feature that has led to their use as high-quality optical filters [4]. However, there is also considerable interest in the nonlinear optical response of these materials [1,5,6]. This interest stems from fundamental interest in the optical properties of quantum confined semiconductors and from potential applications as devices in all optical computing and telecommunications [5].

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Ge-doped silica is commonly employed for controlling the refractive index profile of optical fibres and exhibits other useful optical properties such as photorefraction [7] and second harmonic generation [8]. In most of these applications the Ge is present as a mixed oxide ($\text{SiO}_2\text{:GeO}_2$). However, recent experiments have shown that silica containing Ge nanocrystals exhibits a significant third-order optical nonlinearity [9–11]. In this study, the physical properties of Ge implanted and annealed silica are examined together with the nonlinear optical response.

2. Experimental

Fused silica slides, 1 mm thick, were ion-implanted at -196°C with 1.0 MeV Ge ions to fluences in the range 6×10^{16} – 3×10^{17} Ge cm^{-2} . This produced an approximately Gaussian Ge distribution centred at a $0.63 \mu\text{m}$ and having a FWHM of $0.38 \mu\text{m}$. Ge nanocrystals were subsequently formed by annealing at 1100°C for 1 h in forming gas (5% H_2 /95% N_2). Physical characterisation of the samples was undertaken using Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM) and Raman spectroscopy.

The nonlinear optical response of samples was studied using degenerate four-wave mixing (DFWM) and z-scan techniques [12]. Time-resolved DFWM measurements were performed at a wavelength of 800 nm using a coherent MIRA 800-D femtosecond Ti:sapphire laser. The output of the beam was divided into three equal intensity beams (a probe beam and two pump beams) and brought to a common spatial and temporal focus on the sample. The intensities of beams diffracted by the refractive index grating induced in the sample by its nonlinear response were measured using Si photodetectors. The temporal response was determined by measuring these signals whilst delaying the probe beam relative to the pump beams. z-Scan measurements employed the same laser amplifier system and a conventional measurement geometry.

3. Results and discussion

3.1. Physical characterisation

Fig. 1(a) shows a cross-sectional TEM micrograph of a sample implanted to 1×10^{17} Ge cm^{-2} . Ge nanocrystals are clearly evident in the micrograph and their distribution is well correlated with the implanted Ge distribution shown in Fig. 1(b). The average size of the crystallites varies with depth, with larger crystallites present in the region of peak Ge concentration. For this particular implant, the crystallites vary in size from ~ 2.5 to ~ 12 nm. The inset high-resolution TEM image shows that crystallites are approximately spherical in shape, and diffraction patterns confirm that they have a bulk-like structure. The average size of crystallites is approximately constant with increasing ion fluence but accurate determination of

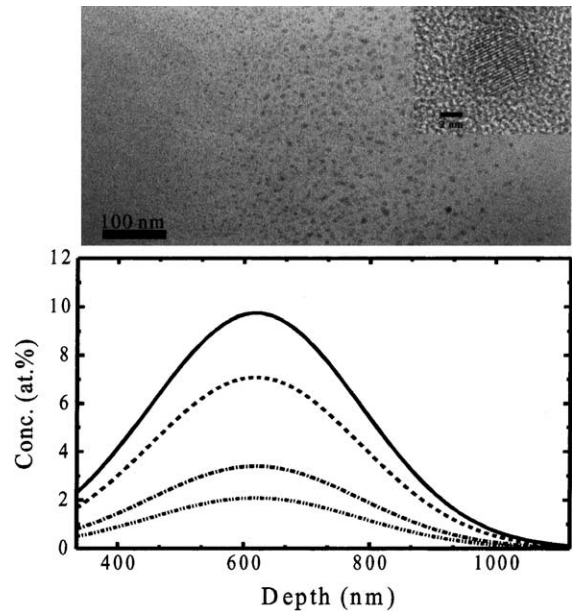


Fig. 1. (a) Cross-sectional TEM micrograph of a fused silica sample implanted with 1.0 MeV Ge ions to a fluence of 1×10^{17} Ge cm^{-2} and annealed at 1100°C for 1 h in forming gas (5% H_2 /95% N_2). Inset shows a high-resolution TEM image of a Ge crystallite. (b) Ge concentration profiles extracted from RBS analysis for sample implanted to 6×10^{16} Ge cm^{-2} (dash-double dot), 1×10^{17} Ge cm^{-2} (dash-dot), 2×10^{17} Ge cm^{-2} (dash) and 3×10^{16} Ge cm^{-2} (solid).

the particle size distribution is complicated by variations in the TEM specimen thickness and, for small crystallites, by resolution limits.

Fig. 2 shows Raman spectra for samples implanted to different fluences. The peaks observed at $\sim 300\text{ cm}^{-1}$ are attributed to Ge nanocrystals. (The inset figure shows that the integrated area of these peaks is proportional to the implanted Ge fluence, consistent with this assignment.) For comparison, the Raman line for a single crystal of Ge was centered at 299.9 cm^{-1} and had a FWHM of 4.8 cm^{-1} . All samples show a sharp Raman peak asymmetrically broadened on the low frequency side. The confinement of phonon modes in small crystallites is predicted to cause a peak shift and asymmetric broadening of the Raman line. Consistent with this prediction, measured spectra show increasing asymmetry for lower dose samples, reflecting the presence of a larger fraction of smaller crystallites. However, no significant peak shift is observed. A similar inconsistency has previously been reported for Ge nanocrystallites and was attributed to a compensating peak shift due to compressive stress in the nanocrystals [13,14]. Quantitative analysis of the Raman data is however also limited by uncertainty in the form of the

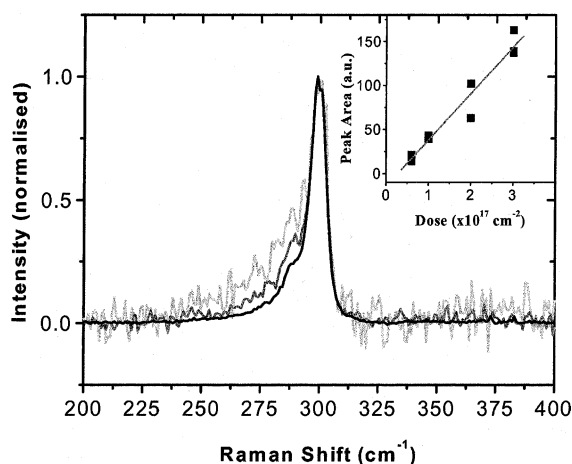


Fig. 2. Raman spectra for samples implanted with 1.0 MeV Ge ions to fluences of $6 \times 10^{16}\text{ Ge cm}^{-2}$ (light grey), $1 \times 10^{17}\text{ Ge cm}^{-2}$ (dark grey) and $3 \times 10^{17}\text{ Ge cm}^{-2}$ after annealing at 1100°C for 1 h in forming gas (5% $\text{H}_2/95\%\text{ N}_2$). Inset shows the integrated Raman intensity as a function of implant fluence.

phonon dispersion curve for Ge and by the choice of confinement function.

3.2. Nonlinear optical response

Fig. 3(a) shows time-resolved DFWM signals for a sample implanted with $3 \times 10^{17}\text{ Ge cm}^{-2}$. The measurement was performed with 200 fs laser pulses with an intensity of $4\text{ }\mu\text{J}$. (Note that the magnitude of the nonlinear response varies with laser intensity and pulse length [10].) The phase-matched signal is dominated by the response of the silica substrate whereas the nonphase-matched signal is characteristic of the implanted layer. The nonlinear refractive index ($|n_2|$) can be calculated from the maximum height of the DFWM signal and for this particular sample was estimated to be $|n_2| = 1.4 \times 10^{-13}\text{ cm}^2\text{ W}^{-1}$. (Higher values were measured for longer pulse lengths [9].) This is three orders of magnitude greater than the nonlinear response of unimplanted silica ($|n_2| \sim 3 \times 10^{-16}\text{ cm}^2\text{ W}$). Analysis of the temporal response revealed two components, an instantaneous response ($\tau < 200\text{ fs}$) and a delayed response ($\tau \sim 0.7\text{ ps}$).

Fig. 3(b) shows closed and open-aperture z-scan signals for a sample implanted with $2 \times 10^{17}\text{ Ge cm}^{-2}$. The closed aperture signal is asymmetric and a clear dip is evident in the open aperture

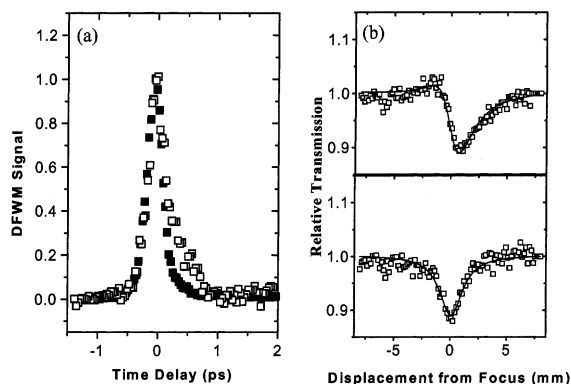


Fig. 3. (a) Phase-matched (filled squares) and nonphase-matched (open squares) DFWM signals from a sample implanted with $3 \times 10^{17}\text{ Ge cm}^{-2}$; (b) closed aperture (top) and open aperture (bottom) z-scan signals for a sample implanted with $2 \times 10^{17}\text{ Ge cm}^{-2}$.

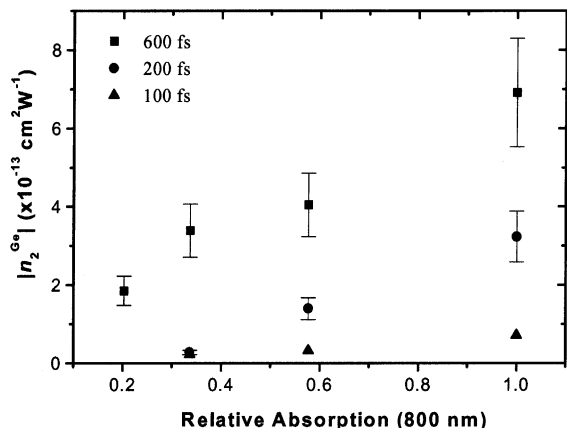


Fig. 4. Magnitude of the nonlinear refractive index, $|n_2|$, from DFWM measurements as a function of relative absorption at 800 nm for different pulse lengths.

signal. Analysis of these signals and comparison of implanted and unimplanted samples shows that the nonlinear response of Ge-implanted silica is dominated by an absorptive process. The real component of $|n_2|$ is unchanged by implantation, within experimental uncertainty, whereas the imaginary component increases with increasing implant fluence due to the increasing absorbance. This is shown in Fig. 4 which shows the magnitude of the nonlinear refractive index $|n_2|$ as a function of sample absorption at 800 nm.

4. Conclusions

Ge nanocrystals were produced in silica by implantation and annealing. The average size of nanocrystals was shown to vary with depth for a given implant fluence and to be approximately constant with increasing implant fluence. The

magnitude of the nonlinear refractive index, $|n_2|$, was measured and found to have a magnitude of 3–4 orders on magnitude higher than that of unimplanted silica. The nonlinear response was shown to be absorptive and to relax on a time scale of 1–3 ps.

Acknowledgements

The authors would like to acknowledge Dr. Terry Mernagh of AGSO for access to the Raman facility.

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