



# Nonlinear optical properties of semiconducting nanocrystals in fused silica

A. Dowd <sup>a,b,\*</sup>, M. Samoc <sup>b</sup>, B. Luther-Davies <sup>b</sup>, R.G. Elliman <sup>a</sup>

<sup>a</sup> *Electronic Materials Engineering Department, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia*

<sup>b</sup> *Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia*

---

## Abstract

Degenerate four-wave mixing (DFWM) is used to examine the nonlinear optical response of Ge nanocrystals in a silica matrix. The nanocrystals are formed by implanting 1.0 MeV Ge ions into silica to a dose of  $3.0 \times 10^{17}$  Ge cm<sup>-2</sup> and annealing at 1100°C. The particle size is well described by a log normal distribution with a mean particle diameter of 3.0 nm and a dimensionless geometric standard deviation of 0.25. The nonlinear optical response, measured at 800 nm with pulse lengths in the range 100–1000 fs, is found to exhibit two patterns of behaviour. For short (180 fs) pulses the DFWM signal is shown to exhibit a third-order dependence on pulse energy (Kerr nonlinearity) and to have a relaxation time of  $\sim \leq 1$  ps, independent of energy. However, for long pulse lengths (600 fs) the signal exhibits a higher order ( $\sim 4$ th order) dependence on pulse energy and has a relaxation time ( $\sim 10$  ps) which increases with increasing pulse energy. Extreme pulse energies are shown to cause irreversible changes in the sample. © 1999 Elsevier Science B.V. All rights reserved.

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

Keywords: Nonlinear optics; Nanocrystals; Four-wave mixing; Ion-implantation; Quantum confinement

---

## 1. Introduction

Glasses containing a suspension of semiconductor or metallic particles can exhibit nonlinear optical behaviour, and have therefore attracted much interest as materials for all-optical logic devices [1–3]. Since the optical nonlinearity increases

with particle concentration, high particle concentrations are desirable for such applications. However, glasses prepared by conventional melt methods are limited to low particle concentrations [4] due to the low solubility of impurities in glass melts. Ion implantation, on the other hand, is free from the solubility restriction and can be employed to produce higher particle concentrations with a high degree of control over the dopant concentration. In addition, ion implantation is not restricted to a particular impurity and offers the

---

\* Corresponding author. Tel.: +61 2 62490371; fax: +61 2 62490511; e-mail: ardl09@rsphysse.anu.edu.au

ability to pattern an optical circuit using conventional microelectronic masking techniques.

Glasses containing metal particles have been widely studied because of their high third order nonlinearity [5–8]. For colloidal gold, the optical nonlinearity arises from interband electric dipole transitions, hot electron excitation and thermal effects, depending on the excitation pulse length. For femtosecond excitation, interband transitions are important, with hot-carrier and thermal effects becoming increasingly important for increasing pulse lengths (ps–ns) [9]. The nonlinear response of metal doped glasses is increased by local field enhancement and reaches a maximum at the surface plasmon resonance. However, this also leads to a high absorption which is undesirable for practical materials. Glasses containing dispersed semiconductor particles can exhibit large optical nonlinearities as well as low absorption [10–13]. In this case, however, the understanding of the material response is less well developed.

In a previous work, it was reported that glass containing Ge nanocrystals showed a large nonlinear optical response with a relaxation time of  $\sim 1$  ps [13]. In this paper we investigate the nature of this nonlinearity as a function of pulse length.

## 2. Experimental

Ge nanocrystals were formed by implanting fused-silica plates at  $-196^\circ\text{C}$  with 1.0 MeV Ge ions to doses of  $6 \times 10^{16}$ – $3 \times 10^{17}$  atom  $\text{cm}^{-2}$  and annealing to  $1100^\circ\text{C}$  for 60 min in a forming gas (5%  $\text{H}_2$ , 95%  $\text{N}_2$ ) ambient. Rutherford backscattering (RBS) measurements showed that the Ge distribution is approximately Gaussian with a projected range of 630 nm and an FWHM of 380 nm, and that the peak concentration is 10 at.% for the highest dose sample. The size distribution of Ge nanocrystals, as determined by dark-field transmission electron microscopy (TEM), is well described by a log-normal distribution with a geometric mean diameter of 3.0 nm and a dimensionless geometric standard deviation of 0.25. Such analysis also confirms that the Ge particles are crystalline with a lattice parameter consistent with that of bulk Ge.

Degenerate four-wave mixing (DFWM) measurements were performed at room temperature using the forward scattering geometry depicted in Fig. 1 [14]. Laser pulses had a wavelength of 800 nm, a pulse duration of 100–1000 fs and a repetition rate of 30 Hz. The phase-matched signal generated predominantly by the silica substrate and one of the non-phase-matched signals generated predominantly by the thin implanted layer, were recorded simultaneously. A comparison of these two signals enabled the relative contribution of the silica substrate and the implanted layer to be determined. The intensity dependent refractive index  $|n_2|$  was calculated using the equation

$$|n_2^{\text{Ge}}|^2 = k \left( \frac{I^{\text{Ge}}}{I^{\text{silica}}} \right) \left( \frac{I_{\text{ref}}^{\text{silica}}}{I_{\text{ref}}^{\text{Ge}}} \right)^3 \left( \frac{L^{\text{silica}}}{L^{\text{Ge}}} \right) |n_2^{\text{silica}}|^2, \quad (1)$$

where  $|n_2^{\text{Ge}}|$  is the nonlinear refractive index of the Ge implanted layer,  $I^{\text{Ge}}$  is the measured non-phase-matched DFWM signal,  $I^{\text{silica}}$  is the phase-matched DFWM signal from a reference sample (unimplanted silica),  $L^{\text{Ge}}$  is the effective sampling length for the Ge implanted layer, taken to be the FWHM of the highest dose Ge distribution, 380 nm, and  $L^{\text{silica}}$  is the effective sampling length in the

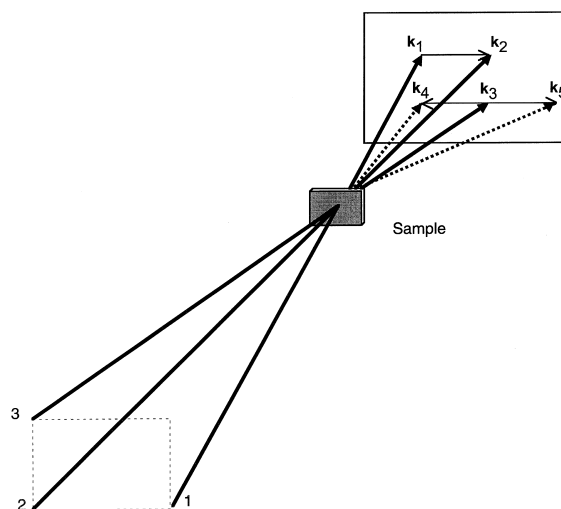


Fig. 1. Geometry of the DFWM experiment. Three beams are coincident on the sample the phase-matched and non-phase-matched signals measured are indicated with the wave vectors  $k_4$  and  $k_5$ , respectively.

silica substrate, determined to be 700  $\mu\text{m}$ .  $I_{\text{ref}}^{\text{Ge}}$  and  $I_{\text{ref}}^{\text{silica}}$  are measured reference signals proportional to the intensity incident on the Ge- and unimplanted samples, respectively.  $k$  is an experimentally determined calibration factor that allows for variations in detector responses and beam intensities, and accounts for the fact that the phase-matched and non-phase-matched signals derive from different contributions. The laser pulses were in the range 2–25  $\mu\text{J}/\text{pulse}$  with the duration (FWHM) of 100–1000 fs and the beams were focused which resulted in a spot size about  $3 \times 10^{-4} \text{ cm}^2$  and a peak light intensity of 0.3 TW  $\text{cm}^{-2}$ .

### 3. Results and discussion

Fig. 2 shows time resolved non-phase-matched DFWM signals for a sample implanted with  $3 \times 10^{17} \text{ Ge cm}^{-2}$ . These data highlight the fact that the measured nonlinear response depends on the experimental parameters employed for the measurement. For example, the magnitude of  $|n_2|$  was found to be  $1.4 \times 10^{-13} \text{ cm}^2/\text{W}$  when measured with 200 fs pulses and  $3.0 \times 10^{-13} \text{ cm}^2/\text{W}$  when measured with 600 fs pulses, showing that the magnitude of the nonlinear response depends on laser pulse

length. Analysis of the temporal response of the nonlinearity, determined by fitting the curves assuming a  $\text{sech}^2$  laser pulse and an instantaneous and delayed response, showed relaxation times of 0.7 ps (200 fs pulse) and 10 ps (600 fs pulse). Clearly, the relaxation time observed also depends on pulse duration.

The nature of the nonlinear response can be inferred from its dependence on pulse intensity. Since silica is known to exhibit a third order (Kerr) nonlinearity over the intensity range measured, the DFWM signal measured from silica is proportional to the cube of the incident laser intensity (cf. Eq. (1)). A constant value of  $|n_2|$  for the implanted layer as a function of pulse energy therefore implies a similar cubic dependence of the DFWM signal (see Eq. (1)). Fig. 3 shows the magnitude of  $|n_2|$  determined as a function of pulse energy, for two different pulse lengths. For a pulse length of 180 fs,  $|n_2|$  is independent of pulse energy, consistent with a third order (Kerr) nonlinear response. Similar results were observed for pulse lengths in the range 100–250 fs. In contrast, data measured with 600 fs pulses show that  $|n_2|$  increases with increasing pulse energy. In this case, the non-phase-matched DFWM signal increased with approximately the fourth power of the input light

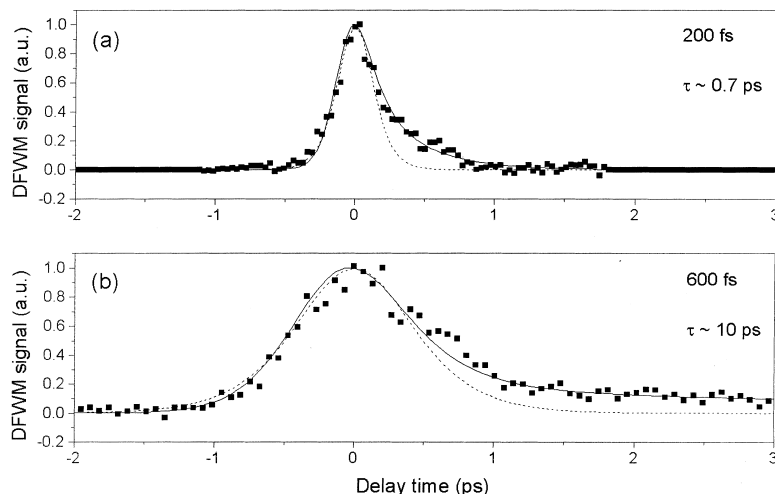


Fig. 2. Non-phase-matched DFWM signals excited by (a) 200 fs and (b) 600 fs pulses, using a pulse energy of 4  $\mu\text{J}$ . The solid lines show fits to the signals assuming decay times of 0.7 and 9 ps, respectively. The dashed lines indicate the response of an unimplanted fused silica slide. The signals have been normalised to the same height.

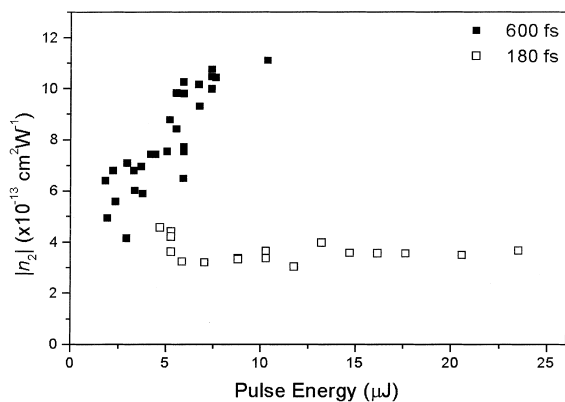


Fig. 3. The absolute value of the refractive index change as a function of input energy for two different pulse lengths.

intensity. Similar results are observed for pulse lengths in the range 400–600 fs.

The apparent 4th order dependence may arise from such contributions as two-photon absorption (5th order) or thermal effects. Further evidence that an additional mechanism contributes to long pulse-length measurements comes from the relaxation time. It has already been shown (see Fig. 2) that the dominant relaxation time depends on pulse duration for a fixed pulse energy. However, whilst the relaxation time for short pulses ( $\leq 250$  fs) remains constant at approximately 1 ps as a function of pulse energy, the value for longer pulse lengths ( $\geq 400$  fs), is almost an order of magnitude higher ( $\sim 10$  ps) and increases with increasing energy. Thus, both the magnitude and the relaxation time of the nonlinearity increase with increasing pulse energy for long pulse length (400–600 fs) measurements.

Fig. 4 shows another aspect of higher pulse-energy measurements, namely: samples can undergo an irreversible change when the pulse energy exceeds a critical value. The first stage of this process is characterised by an apparent increase in the relaxation time (by up to an order of magnitude). On repeating the measurement with reduced intensity, the relaxation time does not return to its low-intensity value. In addition, the power dependence of the DFWM signal changes in this energy region: for short pulses it increases with increasing power whereas for long pulses it de-

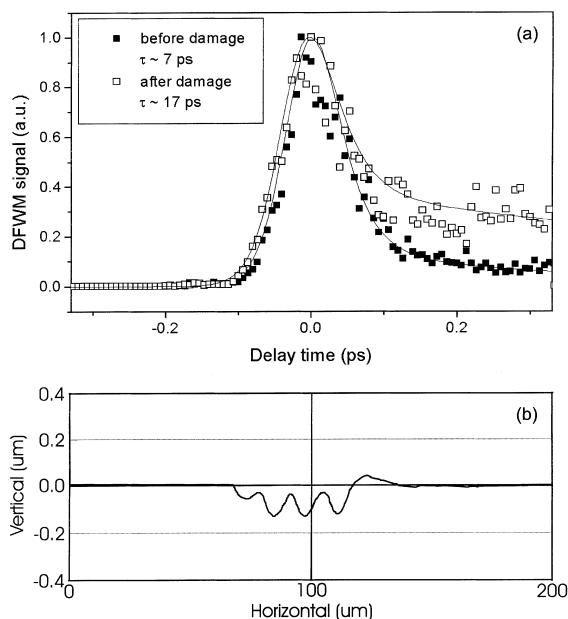


Fig. 4. (a) DFWM response to an 8  $\mu\text{J}$  600 fs pulse before and after damage. (b) Profilometer scan of sample showing ablation after exposure to 15  $\mu\text{J}$  600 fs pulses.

creases with increasing power. This is accompanied by permanent darkening of the irradiated region of the sample. On increasing the intensity still further, the sample is catastrophically damaged and a permanent grating is written in the sample. This results from physical damage of the sample, as shown in the profilometer scan in Fig. 4(b). In this case the surface of the glass has been ablated, resulting in a sinusoidal pattern in the surface of the silica of period approximately 10  $\mu\text{m}$  which corresponds to the pitch of the refractive index grating formed on the sample during the DFWM measurement.

#### 4. Conclusions

Ge nanocrystals were produced in silica by ion implantation and annealing. The nonlinear refractive index of such samples was found to exhibit distinct behaviour depending on the excitation pulse length. For short pulse lengths, 100–250 fs, the magnitude of the nonlinear refractive index is in-

dependent of the pulse energy (Kerr-like behaviour) and exhibited a relaxation time of  $\leq 1$  ps, independent of pulse energy for pulse energies less than 20  $\mu\text{J}$ . For long pulse lengths (400–600 fs), the nonlinear refractive index increased with the pulse energy. In this case, the relaxation time was approximately an order of magnitude larger,  $\sim 10$  ps, and increased with increasing pulse energy. At extreme pulse energies, irreversible changes in the sample were noted. These varied from changes in the colour of the sample to physical damage of the silica.

### Acknowledgements

We would like to thank David Llewellyn for his valuable help in preparation of samples and subsequent TEM analysis.

### References

- [1] Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu, Y. Masumoto, *Appl. Phys. Lett.* 59 (1991) 3168.
- [2] F.Z. Henari, K. Morgenstern, W.J. Blau, V.A. Karavanskii, V.S. Dneprovskii, *Appl. Phys. Lett.* 67 (1995) 323.
- [3] T. Matsumoto, N. Hasegawa, T. Tamaki, K. Ueda, T. Futagi, H. Mimura, Y. Kanemitsu, *Jap. J. Appl. Phys. Lett.* 33 (1994) L35.
- [4] F. Hache, D. Ricard, C. Flytzanis, U. Kreibig, *Appl. Phys. A* 47 (1988) 347.
- [5] M.Y. Lee, T.S. Kim, Y.S. Choi, *J. Non-Cryst. Solids* 211 (1997) 143.
- [6] D. Ricard, P. Roussignol, C. Flytzanis, *Opt. Lett.* 10 (1985) 511.
- [7] J.M. Ballesteros, R. Serna, J. Solis, C.N. Afonso, A.K. Petford-Long, D.H. Osborne, R.F. Haglund, *Appl. Phys. Lett.* 71 (1997) 2445.
- [8] W. Schrof, S. Rozouvan, E. Van Keuren, D. Horn, J. Schmitt, G. Decher, *Adv. Mater.* 3 (1998) 338.
- [9] H.B. Liao, R.F. Xiao, J.S. Fu, H. Wang, K.S. Wong, G.K.L. Wong, *Opt. Lett.* 23 (1998) 388.
- [10] S. Vijayalakshmi, M.A. George, H. Grebel, *Appl. Phys. Lett.* 70 (1997) 708.
- [11] E. Vanagas, J. Moniatte, M. Mazilu, P. Riblet, B. Honerlage, S. Juodkazis, F. Paille, J.C. Plenet, J.G. Dumas, M. Petrauskas, *J. Appl. Phys.* 81 (1997) 3586.
- [12] R.G. Elliman, B. Luther-Davies, M. Samoc, A. Dowd, in: *Materials Modification and Synthesis by Ion Beam Processing 1996*, Materials Research Society Symposium Proceedings, vol. 438, 1997, p. 423.
- [13] A. Dowd, M. Samoc, B. Luther-Davies, R.G. Elliman, in press.
- [14] M. Samoc, A. Samoc, B. Luther-Davies, Z. Bao, L.P. Yu, B. Hsieh, U. Scherf, *J. Opt. Soc. Am. B* 15 (1998) 817.