NONLINEAR OPTICAL PROPERTIES OF SEMICONDUCTOR NANOCRYSTALS IN SILICA MATRICES

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Introduction:

In recent years, there have been many studies into the optical nonlinearities of composite materials containing metallic and semiconducting nanocrystals. This interest stems from the rapid temporal response and large nonlinearity exhibited by these materials, which make them potential candidates for new technologies based around optical information processing. Several techniques exist for producing such nanocrystals in dielectric matrices including sputtering\textsuperscript{1,2}, chemical vapour deposition\textsuperscript{3,4} and ion implantation\textsuperscript{5,6}. This latter technique is attractive because of its simplicity and compatibility with planar waveguide technology.

Previous work has concentrated on metallic nanocrystals. Such systems exhibit resonant absorption associated with a surface plasmon resonance, at which the nonlinearity is greatly increased above the bulk value. However, these samples display relatively long response times in addition to the high absorption at this wavelength, suggesting that they may not be practical nonlinear materials. On the other hand, semiconductor systems show a much faster response time, much reduced absorption, and nonlinearities of the same magnitude as the metallic nanocrystals. In this letter, we report the measurements of the optical nonlinearities of Ge and Si implanted glasses.

Experimental:

The Ge and Si nanocrystals were formed by ion implantation of 1 mm thick fused silica substrates followed by thermal annealing. During implantation of Ge ions (1000 keV) or Si ions (400 keV) to a dose of $3 \times 10^{17}$ cm$^{-2}$, the substrate was held at 77 K. Subsequent annealing of the samples was at 1100 °C under a reducing ambient (5% H$_2$, 95% N$_2$) for 60 minutes, during which time the nanocrystals formed.

Analytic techniques employed included Rutherford backscattering (RBS) using 2.0 MeV He ions, optical absorption and transmission electron microscopy (TEM) on a Philips 430 operating at 300 keV. Cross sectional samples for TEM were prepared by the usual ion beam thinning method.

Optical nonlinearity measurements were undertaken using time resolved degenerate four wave mixing technique (DFWM)\textsuperscript{7}. Samples were characterized with 800 nm amplified pulses from a mode-locked Ti-sapphire laser to a maximum power of 20 µJ. The profile of the beam at the sample surface was analysed using a CCD array and focussed to a spot size of 130 μm. Measurements were taken at 300 K. The repetition rate was 30 Hz, and the pulse width was 600 fs. This low repetition rate forms an important part of this measurement...
system because it reduces the effect of beam heating. Nonlinearities reported in the literature may be overestimated due to such effects.

**Results and Discussion:**

A fit to the RBS data showing the distribution of Ge in the sample is shown in figure 1. This distribution is characterized by a Gaussian function, the FWHM of which is ~0.5 μm. Figure 2 shows a typical cross section view from a Ge implanted sample after annealing. The average nanocrystal size is 3.5 nm in diameter.

![Figure 1. Ge profile following 3×10^{17} cm^{-2} implant derived from RBS measurement.](image1)

![Figure 2. Cross-sectional TEM image of the matrix exhibiting a large number of Ge nanocrystals in a precipitation layer.](image2)

The presence of the implanted species changed the absorption spectra of the silica matrices (see figure 3). The spectra exhibit a broad featureless absorption in the visible that tails off by 700 nm. This band is quite broad, owing to the inhomogeneity of the particle sizes, so we have made no attempt to estimate an effective band gap for these samples.

![Figure 3. Absorption spectra for Ge (solid line) and Si (dotted line) nanocrystals in SiO_2.](image3)

![Figure 4. Nonphase matched DFWM signal for samples implanted with Ge (solid line) and Si (dotted line).](image4)

Figure 4 shows DFWM signals for the Ge and Si doped samples (at a laser power density of ~100 GWcm^{-2}. In the equation as follows:

\[ |n_s|^2 = \left\{ n_s^{SOI} \right\}^2 \left( \frac{I_s}{I_m} \right)^2 \]
where $\ln_2^{SiO_2}$ is the nonlinearity of silica ($= 2.5 \times 10^{-16}$ cm$^2$W$^{-1}$); $I$ is the effective thickness of silica sampled ($= 700$ µm); $l$ is the thickness of the implanted layer; $I_{pm}$ is the intensity of the nonphase matched signal from the sample and $I_{pm}$ is the phase matched signal. The nonlinearities are $ln, l = 6.5 \times 10^{-13}$ and $2.6 \times 10^{-13}$ cm$^2$W$^{-1}$ for Ge and Si samples respectively.

The nonlinearity for both samples shows rapid relaxation. Over the time range measured, the Ge doped glass has two time constants, an instantaneous component ($\tau < 100$ fs) and a slower component ($\tau \sim 1$ ps). These decay times are approximately an order of magnitude faster than those measured for metallic nanocrystals. However, the magnitudes of the nonlinearities for Ge and Si samples are quite different. $ln, l$ for Ge is greater by a factor of approximately 5. Since both glasses were ion implanted to the same high dose, defects due to ion implantation should be saturated for both. Thus, the difference in nonlinearity between the two glasses must be attributed to another mechanism.

Preliminary Z-scan measurements suggest that the nonlinearity is absorptive, and for bulk material the absorption coefficient of Ge at 800 nm is about 50 times larger than that of Si (a photon of this wavelength is indirectly absorbed in Si; in contrast, it has sufficient energy to be directly absorbed in Ge). This may explain the difference in nonlinear response of these materials. However, quantum confinement causes the indirect energy gaps of the Ge and Si nanocrystals to increase as the particle size decreases and effective mass calculations suggest the energy gap for Ge and Si increases to around 1.55 eV (the photon energy used in DFWM experiment) for particles of diameter \~ 5-6 nm. Moreover, Si diffuses more slowly in SiO$_2$ than does Ge, leading to smaller nanocrystals. The fraction of nanocrystals with diameter \> 6 nm will therefore be less for Si than for Ge. Therefore, a possible explanation of the absorption difference is that there are a greater number of Ge nanocrystals which absorb a photon of 1.55 eV than there are Si.

**Conclusions:**

In conclusion, semiconductor nanocrystals were formed in silica matrices by ion implantation and subsequent annealing. The nonlinearity of each of the two systems was measured at 800 nm using DFWM and was found to have values as high as $ln, l_{Ge} \sim 7.8 \times 10^{-13}$ and $ln, l_{Si} \sim 2.6 \times 10^{-13}$ cm$^2$W$^{-1}$. It is proposed that this difference is attributable to the difference in absorption coefficient and this may be exacerbated by quantum confinement effects.

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