Linear optical properties of Ge nanocrystals in silica

Annette Dowd, Robert G. Elliman, and Barry Luther-Davies

View online: http://dx.doi.org/10.1063/1.1409591
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/79/15?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Light absorption enhancement in closely packed Ge quantum dots
Appl. Phys. Lett. 102, 193105 (2013); 10.1063/1.4805356

Optical absorption and emission of silicon nanocrystals: From single to collective response
J. Appl. Phys. 113, 143505 (2013); 10.1063/1.4799394

Influence of the embedding matrix on optical properties of Ge nanocrystals-based nanocomposite
J. Appl. Phys. 113, 053512 (2013); 10.1063/1.4789959

Influence of nanocrystal size on optical properties of Si nanocrystals embedded in Si O 2 synthesized by Si ion implantation

Linear optical properties of a Ti-SiO 2 nanoparticle composite
J. Appl. Phys. 93, 566 (2003); 10.1063/1.1528308

Model PS-100
Tabletop Cryogenic Probe Station
An affordable solution for a wide range of research
Linear optical properties of Ge nanocrystals in silica

Annette Dowd and Robert G. Elliman
Electronic Materials Engineering Department, Research School of Physical Sciences, Australian National University, Canberra 0200 Australia

Barry Luther-Davies
Laser Physics Centre, Research School of Physical Sciences, Australian National University, Canberra 0200 Australia

(Received 28 June 2001; accepted for publication 7 August 2001)

The absorption and extinction spectra of Ge nanocrystals in silica formed by ion implantation are studied using photothermal deflection and transmission spectroscopies. It is found that scattering makes a significant contribution to the extinction spectrum, damping the spectral features and resulting in a Rayleigh scattering-like \( \omega^4 \) dependence. In contrast, the spectra measured by photothermal deflection clearly show features such as the \( E_1/E_1 + \Delta_1 \) transitions. The Tauc gap is extracted to be \( \sim 0.7 \pm 0.1 \) eV. © 2001 American Institute of Physics. [DOI: 10.1063/1.1409591]

The physical properties of small nanometer-sized particles have received considerable attention in recent years, driven by both fundamental and technological interests. The optical properties of semiconductor crystallites embedded in insulating matrices have been of particular interest in this regard. Such structures are usually prepared by the formation of a supersaturated solid solution of impurities in the glass followed by the addition of energy which promotes the precipitation of the insoluble component(s) into nanometer-sized clusters. Ion implantation is a commonly used technique for the addition of dopants to glass because it offers possibilities of a local concentration higher than that obtainable by sol–gel methods, as well as the fact that almost any element can be introduced. The optical properties of the glass, such as absorption, photoluminescence, and nonlinear optical properties are significantly affected by the presence of nanocrystals.

In order to understand better the physics of the nanocrystals or to make use of them in practical devices, more detailed information on the electronic properties of the nanocrystal ensemble is needed. Optical measurements are very popular due to the simple experimental procedure and relative ease of interpretation of results. Transmission spectroscopy, which gives a measure of extinction, is the conventional technique and has provided useful information on the size-dependent quantization of electronic levels in direct-gap nanocrystals such as CdS, Se, Te, and CdSe. However, researchers often report featureless absorption spectra especially for indirect-gap semiconductor nanocrystals such as Ge, which is generally attributed to inhomogeneous line broadening as a result of the wide nanocrystal size distribution.

Nanocrystals are much smaller than the wavelengths of visible light, resulting in a complicated interaction with the incident electric field. The extinction spectrum, as measured in conventional spectrometers, contains contributions from scattering as well as absorption, which leads to the dampening of the absorption structures. The resulting spectrum cannot be directly compared with the bulk absorption spectrum. While it is possible to correct the transmission measurements to take into account scattering from nanometer-sized Ge clusters by effective medium considerations or by doing an additional reflectance measurement, a direct measurement of absorption is preferable to obtain information on the electronic structure without the scattering contribution from the small nanocrystals. In this letter, we focus on the effective absorption coefficient \( \alpha \) deduced from the conversion into heat of a monochromatic light beam propagating in Ge-doped silica. Photothermal deflection spectroscopy (PDS) takes advantage of this mechanism to yield an excitation spectrum of the nonradiative recombination of photoexcited carrier pairs. This spectroscopic method is especially suitable for measuring absorption in highly scattering samples but has had only limited use in studying the optical properties of nanocrystals.

The nanocrystal/silica composite samples were formed by ion implantation followed by high-temperature annealing. Fused silica (Infrasil) substrates, of 1 mm thickness, were implanted at 77 K with 1.0 MeV Ge ions to fluences of 0.6, 1.0, 2.0, and 3.0 \( \times \) \( 10^{17} \) Ge cm\(^{-2} \). This resulted in a layer of Ge within the silica characterized by a Gaussian concentration profile centered at \( \sim 650 \) nm from the surface and with a full width at half maximum of \( \sim 400 \) nm. The peak Ge concentration was less than 10 at. % in all cases. The two highest dose as-implanted samples contained small amorphous clusters of Ge atoms (<2.0 nm diam). The samples were annealed at 1100 °C for 60 min in a forming gas (5% H\(_2\), 95% N\(_2\)) atmosphere, which resulted in the formation of Ge nanocrystals. The size distribution of the nanocrystals determined from transmission electron microscopy was described by a log–normal function with a mean diameter of 5–6 nm and geometric standard deviation of 1.5, independent of dose.

Optical characterization of the samples was undertaken using transmission spectroscopy and PDS. Optical transmission measurements were carried out on a Shimadzu UVPC3100 transmission spectrophotometer. An unimplanted silica substrate was used as a reference. The extinction spectra were calculated from the transmission spectra using

\[ v_0 = \frac{1}{x} \]
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions.

index change in the CCl₄. The beam was detected with a and was periodically deflected according to the refractive

laser beam passed parallel and close to the sample surface,

lated the refractive index of the liquid. A continuous He–Ne

scattering-like samples, shown in Fig. 1. The spectra show a Rayleigh

trated in the extinction spectra obtained for the as-implanted

nealed samples are relatively featureless and are dominated

by a background that increases with photon energy and is

nealed in the visible range showing that scattering contributes significantly to

the extinction. Additionally, spectral features at ~2.5 and 3.0 eV are observed in the annealed samples despite the expected inhomogeneous broadening from the nanocrystal size distribution. The absorption does not scale with dose in the case of the as-implanted samples because the presence of Ge clusters in some samples increases the optical absorption.

The peak at ~2.5 eV is identified as the $E_1/\Delta_1$ spectral structure, as also observed by other groups studying the absorption spectra of Ge nanocrystals in Al₂O₃. This structure originates from transitions between parallel bands in the Γ-L direction in the Brillouin zone and the transition energy is not expected to have a strong dependence on size.

The position of the peak agrees with the results obtained by Tognini et al. for truncated spherical nanocrystals in the size range 2.5–12.5 nm. In contrast with their results and those of semiempirical Mie calculations the peak in the absorption in Fig. 2 is more pronounced and resembles more closely the spectra measured by Teng et al. for Ge islands ~26 nm in size. The increase in peak prominence may be due to a shift of oscillator strength from lower to higher transitions or overlap with other transitions (e.g., $E_0'$).

Since the mean nanocrystal size for our samples remains approximately constant with implanted dose, we could not study the spectra as a function of nanocrystal size. However, the fact that the features are clearly seen (such as the large peak at 2.5 eV) even for samples containing a peak concentration of Ge as low as a few at. % demonstrates that the PDS technique is an attractive alternative to RT transmission spectroscopy.

A useful parameter for comparing nanocrystal composites is the Tauc optical gap. Amorphous and indirect-band-gap semiconductors have often been analyzed with the Tauc relation:

$$ (\alpha E)^{\gamma} = B(h\omega - E_T) $$

where $\alpha$ is the absorption coefficient, $\gamma$ equals $\frac{1}{2}$, $B$ is a constant, and $E_T$ is the Tauc gap. Equation (1) has been used by some authors to determine from the extinction spectrum $E_T$ and the nature of the material. However, if the wavelength-dependent scattering contribution is not taken

A(h\omega) = 2 - \log_{10}[T(h\omega)], where $h\omega$ is the photon energy, $A(h\omega)$ is the extinction spectrum, and $T(h\omega)$ is the trans-

mission spectrum.

PDS was used to give true absorption measurements over the photon energy range 0.7 $\leq$ $h\omega$ $\leq$ 3.1 eV. The sample was placed in a glass windowed stainless-steel cell containing CCl₄ and was irradiated with chopped monochromatic light. Absorption in the sample caused a periodic local heating in the sample. The thermal wave generated in the absorbing nanocrystal layer propagated into the CCl₄ and modulated the refractive index of the liquid. A continuous He–Ne laser beam passed parallel and close to the sample surface, and was periodically deflected according to the refractive index change in the CCl₄. The beam was detected with a position-sensitive photodiode. For these experimental conditions the beam deflection was taken to be proportional to the temperature change. The raw PDS spectra were matched with the extinction values obtained by transmission measurements over the range 1.6 $\leq$ $h\omega$ $\leq$ 2.1 eV (600–800 nm). All optical measurements were performed at room temperature (RT).

The extinction spectra for both the as-implanted and annealed samples are relatively featureless and are dominated by a background that increases with photon energy and is well described by a power law. This is most clearly illustrated in the extinction spectra obtained for the as-implanted samples, shown in Fig. 1. The spectra show a Rayleigh scattering-like $\omega^3$ dependence. In general, the significant part of the extinction spectrum of silica glass in the visible range is due to Rayleigh scattering from random inhomogeneities in the refractive index. Ion implantation results in randomly dispersed Ge atoms or even very small Ge clusters in the silica, which will similarly act as scattering centers and result in additional attenuation, also approximately proportional to $\omega^3$. In these samples, extinction scales with implanted dose.

The PDS spectra, for which the effect of scattering is much less significant, appear quite different. Figure 2 shows the comparison between the extinction spectra for the highest dose annealed sample measured by transmission and photothermal deflection spectroscopies. The spectra still show a general increase in absorption with photon energy, however, the absorption is much lower than the extinction at higher energies showing that scattering contributes significantly to

**FIG. 1.** Log–log plot of extinction (as measured by transmission spectroscopy) of Ge nanocrystals over the photon energy range 1–3 eV. The straight line has a slope of 4 and indicates that the extinction of these samples is dominated by Rayleigh-like scattering.

**FIG. 2.** Comparison of absorption spectra of Ge nanocrystals determined by conventional transmission spectroscopy and PDS. Since scattering essentially does not affect the PDS signal, features due to the electronic transitions in the nanocrystal composite are more clearly seen. The discontinuity in the transmission measurement at 1.5 eV is due to a detector change.
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.56.106.27 On: Mon, 12 Oct 2015 03:43:48

The nanocrystal system does not show a sharp absorption edge and has finite absorption down to $\sim 0.8$ eV, which is not far from the band gap of bulk Ge at room temperature ($\sim 0.66$ eV). However, a quantum confinement model predicts a blueshift in the indirect-band gap to $\sim 0.95$ eV for a 6 nm Ge nanocrystal.\cite{3} Figure 3 shows Tauc plots for the four doses of Ge. The spectra show that absorption behavior of an indirect-gap crystalline material or amorphous material up to 2 eV, i.e., they follow Eq. (1). (The direct $E_1 / E_1 + \Delta_1$ transitions, expected to be little affected by quantum confinement, occur above 2 eV in bulk Ge.) This result compares with that obtained by Heath, Shiang, and Alivisatos\cite{3} for 6 nm colloidal Ge nanocrystals. The Tauc gap energy here was determined to be $\sim 0.7 \pm 0.1$ eV for all four samples. We attribute the apparent absence of a quantum confinement induced blueshift of the absorption edge to the broad size distribution of the nanocrystals. The absorption spectrum is expected to be dominated by the larger nanocrystals of the ensemble (in these samples the largest nanocrystals are $\sim 10$ nm and are expected to have near bulk band structure) due to the size-dependent absorption cross section and energy gap distribution. Bulk Ge has a direct gap ($E_D$) at 0.8 eV but clearly the spectra obey the indirect transition law up to 2 eV, an observation also made by Heath, Shiang, and Alivisatos. They offered two explanations: that either quantum confinement shifted the direct transition strongly out of the energy region of interest, or that due to the strong dependence of the quantum confinement energy on nanocrystal size, the size distribution would cause a broadening of the $E_D$ oscillator strength over a wide energy range. However, it should be noted that transitions between band tails (localized states) will lead to similar behavior, so firm conclusions about the nature of the band gap cannot be drawn.

In conclusion, a comparative study of the transmission and photothermal deflection spectroscopy measurements has been carried out on Ge-doped silica formed by ion implantation. The main results are as follows: (a) the transmission spectra are dominated by scattering from the microscopic refractive index inhomogeneities within the glass, which results in the absorption features being damped; and (b) PDS is able to clearly show the spectral structure of the nanocrystal ensemble including the near-infrared band-gap region.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{PDS absorption data for Ge nanocrystals plotted in the form of a Tauc plot [see Eq. (1)]. The straight lines are least-squares fits to the region 1.5–2.0 eV of the absorption curves. The Tauc optical gap ($E_T$) is defined as the x-axis intercept.}
\end{figure}