Optical absorption measurements of silica containing Si nanocrystals produced by ion implantation and thermal annealing

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Optical absorption spectra from silicon-implanted silica slides are shown to contain features due to optical interference. These features, which result from the modified refractive index profile produced by the implant, can readily lead to misinterpretation of absorption spectra. To demonstrate the importance of such effects, silica samples were implanted with 80, 400, and 600 keV Si ions to fluences in the range $0.6–3.0\times10^{17}$ Si.cm^{-2} and annealed at 1100 °C for 1 h to form Si nanocrystals. Optical absorption/transmittance spectra from these samples show considerable structure that is characteristic of the particular implant conditions. This structure is shown to correlate with the transmittance of the samples as calculated from the modified refractive index profile for each implant. The lack of such structure in absorption spectra measured by photodeflection spectrometry is used to confirm this interpretation. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1454217]

There is considerable interest in the optical properties of glasses containing nanometer-sized metallic and semiconducting crystallites due to the novel optical properties exhibited by these composite materials.[1–5] Such materials are commonly characterized by transmission spectroscopies as these can provide useful information about the electronic and optical properties of the nanocrystals. However, in determining the absorbance or transmittance of a sample from the intensity of light passing through it, care must be taken to correctly account for scattering losses[6] and Fabry–Perot interference effects, as both directly affect the transmitted intensity. Indeed, such effects are well known[1,7] but they continue to be rediscovered. Dowd *et al.*[6] have recently shown that scattering losses from silica samples containing Ge nanocrystals can be quite significant, particularly at shorter wavelengths where the $\sim 1/\lambda^4$ dependence characteristic of Rayleigh (Mie) scattering becomes important. Importantly, these scattering losses can be expected to distort Tauc plots and lead to erroneous band gap estimates for semiconductor nanocrystals.

Interference effects can also significantly distort absorption spectra and lead to misinterpretation of absorption features. In a recent article, Pavesi *et al.*[4] reported optical gain based on the luminescence emission of silicon nanocrystals embedded in silica. This is a particularly interesting and significant report since it raises the possibility of fabricating a laser based on the emission from Si nanaocrystals. However, the authors present optical absorption data which they claim identifies a new absorption band in the wavelength range around 800 nm and which they attribute to the O═Si defect.[8] This band coincided with the wavelength range of peak luminescence emission and was speculated to be part of a three-level system giving rise to the optical amplification process. As shown next, this band appears to result from interference effects and therefore to be an artifact of the absorption measurement.

Synthetic silica substrates (Infrasil) with dimensions of 40 mm×10 mm and 1 mm thick, were implanted at room temperature with: 80 keV Si ions to fluences of 0.6, 0.8, 1.0, and 1.2×10^{17} Si.cm^{-2}; 400 keV to a fluence of 3×10^{17} Si.cm^{-2}; and 600 keV to a fluence of 2.64×10^{17} Si.cm^{-2}. All samples were subsequently annealed for 60 min at 1100 °C in an Ar or N_2 ambient to form nanometer-sized Si crystallites. The transmittance of the samples was measured over the wavelength range 400–2500 nm (~8 nm resolution) using a Shimadzu UVPC3100 transmission spectrophotometer. The absorbance was also measured over the wavelength range 400–1600 nm using photodeflection spectroscopy.[9] In this latter technique, the sample is immersed in a suitable liquid and a probe laser used to measure the thermally induced refractive index change of the liquid in the vicinity of the sample surface. In the present case, the sample was immersed in CCl_4 ($dn/dT = -0.271$). Full field calculations show that the PDS measurements are insensitive to interference effects for the sample configurations employed in the present work.

To illustrate the significance of interference effects, Figs. 1(a)–1(c) show transmittance spectra for silica samples implanted with Si ions of different energies. For these measurements, the reference cell of the spectrophotometer was empty. In each case the measured transmittance exhibits a complex dependence on wavelength with clear evidence for interference effects. Also included in Fig. 1 is the transmittance calculated by thin-film matrix methods[7] using the refractive index profiles shown in the inset. The refractive in-

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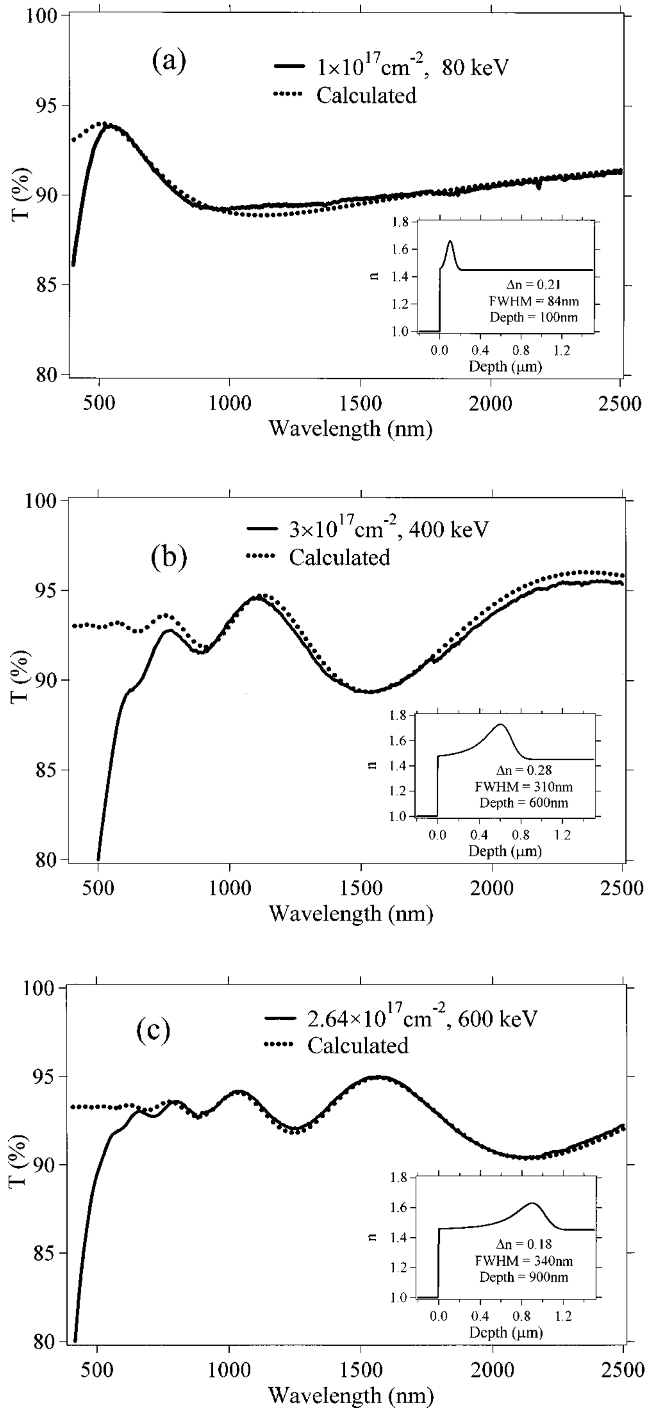

FIG. 1. Optical transmittance as a function of wavelength for samples implanted with (a) 80 keV Si ions to a fluence of 1×10^{17} $Si.cm^{-2}$, [corresponding to the conditions employed by Pavesi *et al.* (see Ref. 4)], (b) 400 keV Si ions to a fluence of 3×10^{17} $Si.cm^{-2}$, and (c) 600 keV Si ions to a fluence of 2.64×10^{17} $Si.cm^{-2}$. All samples were annealed to 1100 °C for 1 h in argon to produce Si nanocrystals. The resulting refractive index profiles are shown inset. The dotted lines show theoretical estimates of the transmittance calculated on the assumption of reflective losses only.

dex profiles were determined from the calculated Si distribution[10] with the maximum Δn adjusted for best fit. Note that the resulting Δn values are in good agreement with the predictions from the Maxwell–Garnett approximation.[1] These data show that reflective losses alone are able to account for most of the structure apparent in the measurements. [It should be noted that absorptive and scattering losses are expected to account for deviations between the experimental and calculated curves at short wavelengths but have not been taken into account for the present purposes.] The structure is very different for the different energy implants, reflecting the different refractive index profiles.

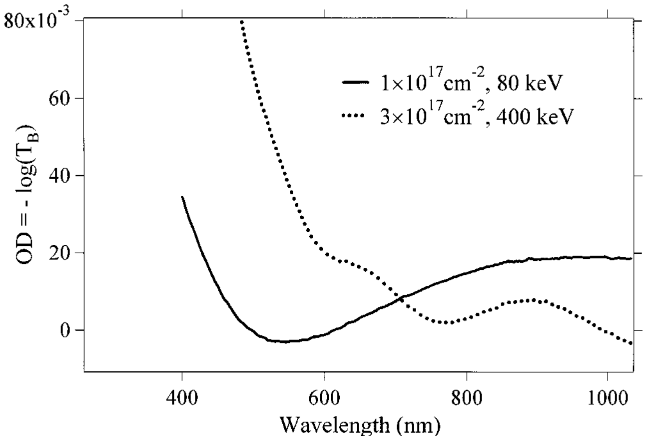

FIG. 2. OD as a function of wavelength extracted from a balanced transmittance measurement for samples implanted with 80 keV (solid) and 400 keV (dashed) Si ions.

Figure 2 shows the optical density (OD) extracted from experimental transmittance data, as measured in a balanced spectrophotometer (i.e., with an unimplanted sample in the reference cell). The form of the curve for the sample implanted with 80 keV Si ions is almost identical to that reported by Pavesi *et al.*[4] However, that for the sample implanted with 400 keV ions is completely different, as expected from the transmittance data of Fig. 1. This confirms that the apparent absorption band around 800 nm is not intrinsic to the presence of Si nanocrystals but is in fact due to reflective losses associated with the particular refractive index profile corresponding to the 80 keV implant. Interestingly, the OD is observed to fall below zero on this logarithmic plot for wavelengths around 550 nm. Again, this is clear evidence for interference effects, arising from the fact that the transmittance of the implanted sample exceeds that of an unimplanted reference sample within certain wavelength ranges.

Further support for the aforementioned arguments comes from photodeflection spectrometry[9] results shown in Fig. 3.

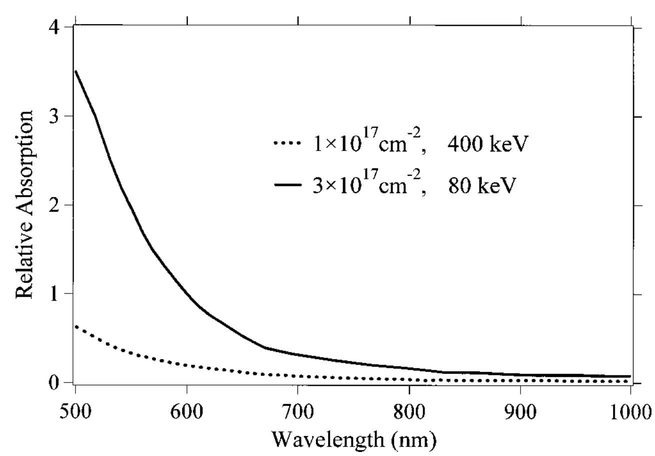

FIG. 3. Relative absorbance as a function of wavelength measured by photodeflection spectrometry for samples implanted with 80 keV (solid) and 400 keV (dashed) Si ions.

These spectra show that the absorbance decreases monotonically with increasing wavelength over the range 400–1600 nm. No characteristic absorption features are evident over this range.

In conclusion, detailed optical absorption measurements of ion-implanted silica samples containing Si nanocrystals have shown that features previously attributed to defect absorption[4] are in fact experimental artifacts resulting from optical interference effects. This was confirmed by comparing transmittance spectra for samples implanted under different conditions and by showing that the structure evident in these spectra was consistent with that from calculated spectra in the absence of any absorption. Photodeflection spectroscopy was used to confirm that the features observed in the transmittance measurements were associated with the measurement technique.

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