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Scattering induced optical limiting in Si/SiO_2 nanostructure dispersions

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Abstract

We present evidence for scattering induced optical limiting in a suspension of Si/SiO_2 nanostructures in an isopropanol solution. The structures were studied by open and closed aperture z-scan with 6 ns Gaussian pulses at 532 nm from a frequency doubled, Q switched Nd:YAG laser. The linear absorption of the nanostructures displayed evidence of quantum confinement. An intensity dependent scattering study illustrated the contribution to optical limiting from scattering mechanisms. We propose that optical limiting is occurring at scattering centres, most likely plasmas, which are formed through ionisation of the SiO_2 outer shells.

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Materials that display optical limiting properties are required for the production of photonic devices that control amplitude gain or extinction, polarisation, phase, reflection and refraction of light [1]. Materials that display good optical limiting capabilities include VO_x nanotubes [2], phthalocyanine nanoparticles [3], gold nanoparticles [4], silicon nanowires [5] and carbon nanotubes [6]. Carbon nanotubes have been extensively studied due to their broad-band optical limiting capabilities and have been lauded as the benchmark optical limiting material [6]. Nanoscale silicon has also been extensively studied, due to its CMOS compatibility and the enhancement of its non-linear effects due to quantum confinement [7]. The self-healing ability of solution based optical limiters makes them auspicious materials for real world applications, such as the protection of optical sensors from intense laser sources.

Optical limiting is usually attributed to effects such as reverse saturable absorption, non-linear refraction and thermal non-linearities or scattering. In the case of silicon, the non-linearities are usually attributed to 2 photon related absorption and $\chi^{(3)}$ variation related to quantum confinement effects [7–11]. The objectives of the work presented in this report are; to investigate the contribution to optical limiting that can be attributed to scattering for the silicon nanostructures under study and; to identify the most likely source of the scattering.

Carbon black suspensions optically limit by a scattering process [12]. One proposed mechanism is that the carbon particles heat up as they absorb light, which causes them to ionise and produce microplasmas when the vaporisation temperature is reached. The microplasmas then scatter the light [13–16]. Another mechanism may involve the carbon particles transferring the absorbed heat to the surrounding solvent, creating bubbles which scatter the light. This occurs below the vaporisation temperature of carbon [17–19].

Laser induced breakdown in SiO_2 with pulse widths from 7 ns to 150 fs has been reported [20]. In this report

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we propose that optical limiting is occurring in suspensions of Si/SiO_2 nanostructures due to a scattering process. The scattering centres are most likely plasmas which are formed through ionisation of the SiO_2 outer shells.

It should be noted that Joudrier et al. attributed non-linear scattering in colloidal suspensions of silica particles to a photoinduced refractive index mismatch [21]. They used a mixture of toluene (refractive index 1.372) and hexane (refractive index 1.494) in the ratio 1:0.8 to closely match the refractive index of the solvent to that of silica (refractive index 1.455). We do not believe that this mechanism is occurring in our system as we used spectroscopic grade isopropanol as the solvent, (refractive index 1.377) which is not close enough to the refractive index of the SiO_2 (refractive index 1.455) for this mechanism to be relevant.

1. Sample characterisation

1.1. Sample morphology and preparation

The sample was produced by an oxide assisted growth process [22]. Fig. 1 is a TEM image displaying the sample morphology. The sample consisted of chain-like structures. Crystalline silicon spheres were surrounded and connected by SiO_2 shells. The average sphere diameter was 31 nm including the oxide shell, and the average wire length was 2.36 μm. The sample was dispersed in spectroscopic grade isopropanol (IPA) under agitation by a sonic tip, at a concentration of .03 g/L. The sedimentation profile of the sample was studied and the sedimentation life-time of the unstable component was calculated, as per the method described by Nicolosi et al. [23]. The sample was then left to stand while the unstable phases separated out, and the relatively stable components of the suspension were then pipetted off. The 'stable' phase was in fact a very good dispersion which would eventually undergo sedimentation if left to stand for weeks or months. Optical characterisation was carried out on the stable phase. The stability of the dispersion ensured that the concentration of the solution was not changing during the investigation process.

1.2. Linear absorption

Fig. 2 shows the linear absorption curve for the sample. The observations were made using a Shimatzu absorption spectrometer. The sample absorbed in the UV–Vis range. Absorption shoulders occurred close to the direct band-gap energies of crystalline silicon [24,25]. A blue shift was recorded in the first direct transition at Γ–X, with the absorption onset being blue shifted from 1.2 eV to 1.6 eV. Blue shifting of the Γ–X transition has been attributed to quantum confinement effects [26]. Due to the large distribution of the sizes within the sample batch it is possible that this contribution is arising from very small crystallites. Also, small, isolated crystalline grains form close to the oxide interface due to nucleation kinetics, which gives rise to quantum confined effects.

At energies above the Γ–X point, the absorption is dominated by direct transitions. The Γ_{25}–Γ_{15} (3.4 eV) transition is clearly observable. The X_4–X_1 (4.3 eV) transition was blue shifted to approximately 4.5 eV. Similar blue shifting was reported by Holmes et al. [26] and attributed to quantum confinement. The sample therefore displayed absorption dominated by direct transitions and evidence of quantum confinement.

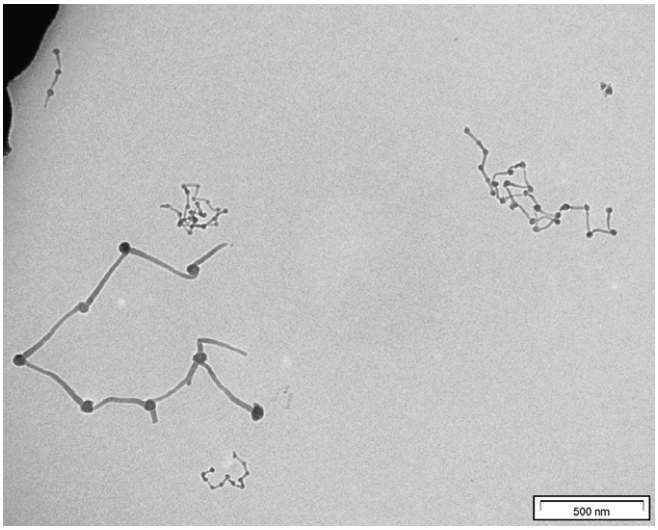

Fig. 1. TEM image showing sample morphology. The sample contained chain-like structures of crystalline silicon spheres (average diameter = 31 nm including the oxide shell) surrounded and connected by SiO_2 shells.

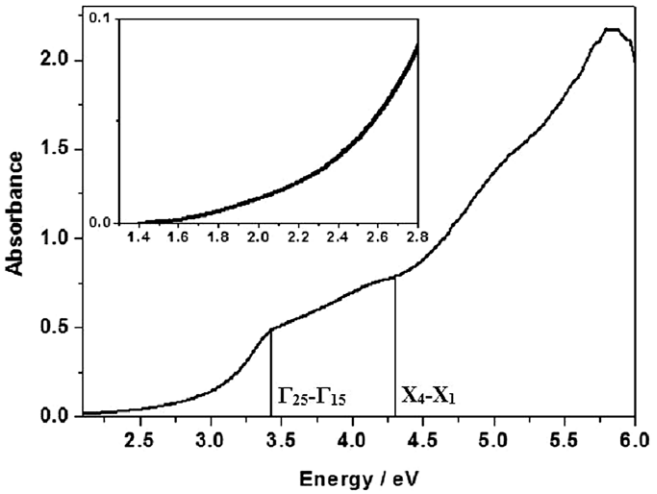

Fig. 2. Linear absorption of the sample in the UV–Vis range. The sample displayed absorption dominated by direct transitions and evidence of quantum confinement.

2. Optical limiting

2.1. The z-scan technique

The non-linear optical properties were investigated by open and closed aperture z-scan with 6 ns Gaussian pulses at 532 nm from a frequency doubled, Q switched Nd:YAG laser. The beam waist radius was 20 μm, and the pulse repetition rate was 10 Hz. The sample was held in a 1 cm cuvette. Fig. 3 shows the normalised non-linear transmission as a function of incident pulse energy density, as measured by open aperture z-scan. The normalised transmission is plotted against the energy density in a single pulse. The pulse energy density is defined as $F_{\text{pulse}} = E_{\text{pulse}}/[\pi\omega(z)^2]$, where E_{pulse} is the energy in a single pulse, and $\omega(z)$ is the radius of the propagating Gaussian pulse as a function of position z [1]. The sample clearly exhibits optical limiting, with linear absorption dominating until a threshold limit is reached, at which point the sample starts to display non-linear extinction. Closed aperture z-scan produced bell shaped curves for normalised transmission against z position. Therefore there is no evidence of a strong contribution to the limiting effect from non-linear refraction. The system appears to be dominated by non-linear losses.

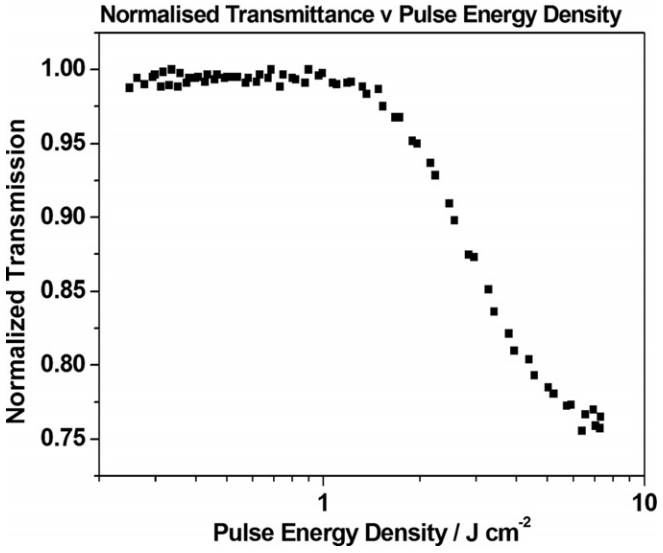

Fig. 3. Normalised non-linear transmission as a function of incident pulse energy density, as measured by open aperture z-scan. The sample clearly behaves as an optical limiter.

2.2. Scattering

The sample was placed at the focus of the z-scan beam. The incident laser beam was kept at constant intensity. The intensity of the scattered light was measured as a function of angular position around the sample, as outlined in Fig. 4. The scattering profile obtained was characteristic of Mie scattering, with a pronounced front lobe and a diminutive rear lobe. A polar plot of angular dependent intensity is displayed in Fig. 5.

Intensity dependent scattering was carried out to observe the onset of non-linear behaviour. The detector and scattering arm were moved to 50° off the horizontal axis, so that the detector was clearly out of the linear regime. The intensity of the scattered light was recorded

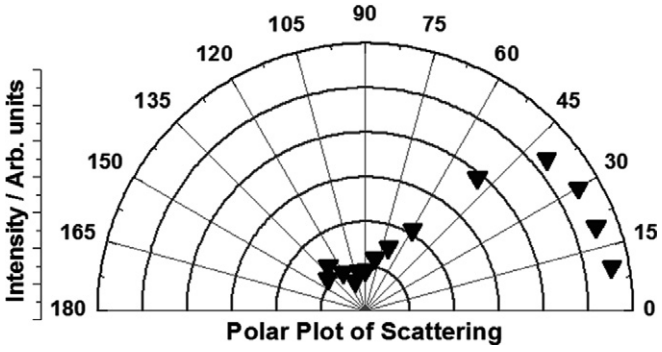

Fig. 5. Polar plot of the angular profile of scattered light. The sample displays Mie scattering characteristics.

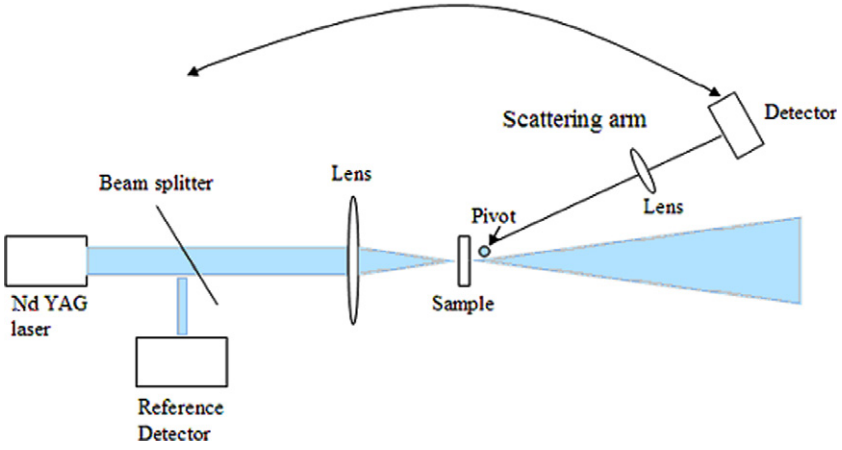

Fig. 4. Scattering experiment set-up. The scattering arm could be rotated around its pivot, giving the detector a range of 160°.

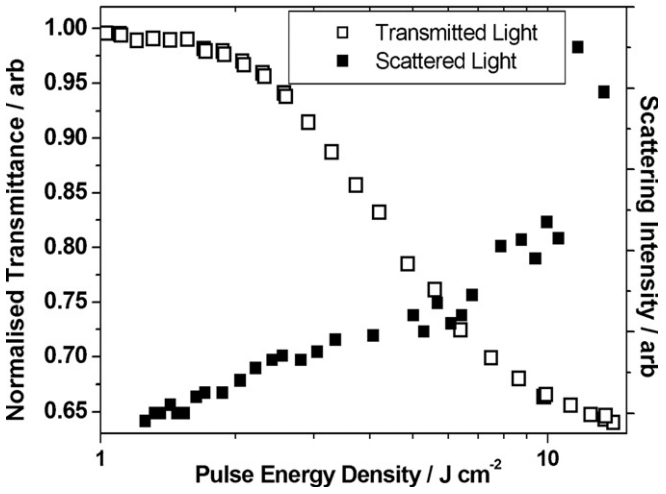

Fig. 6. The graph shows the dependence of transmitted light and scattered light on pulse energy density. The detector which collected the scattered light was positioned at an angle of 50°. The onset of non-linear dissipation also marks an increase in the intensity of the scattered signal. The scattered signal scales non-linearly to pulse energy density.

while the intensity of the incident laser beam was incrementally increased. It appears that the onset of non-linear dissipation of light also marks an increase in the intensity of the scattered signal, as demonstrated in Fig. 6. The scattered signal scaled non-linearly to pulse energy density.

3. Discussion

The optical limiting that occurs for the sample under study is unlikely to originate from a photoinduced refractive index mismatch, as reported elsewhere for colloidal suspensions of silica particles [21]. The refractive indices of the solvent and SiO_2 outer shell are too different for good matching to exist at low light intensities.

Open and closed aperture z-scan demonstrated that the optical limiting was originating from a mechanism that was dominated by non-linear losses. The suspension behaved as a Mie scatterer, with increased scattering coinciding with the onset of non-linear extinction. Further investigation is needed to determine the contribution that non-linear absorption makes to the optical limiting process. An example of both two-photon absorption and non-linear scattering contributing to effective optical limiting can be found in a report by Venkatram et al. [27].

Pan et al. observed optical limiting from silicon nanowires [5]. The silicon nanowires in the Pan report photoluminesced at 521 nm, and displayed optical limiting at 532 nm and 1064 nm. The sample under study here did not photoluminesce in the region of 521 nm (photoluminescence results are not presented in this report), and the sample did not produce optical limiting at 1064 nm. However, although the samples had very different microscopic structures, they both displayed optical limiting behaviour at 532 nm.

Du et al. demonstrated laser induced breakdown and plasma formation in bulk SiO_2. The sample was mounted on a translation stage and probed with a 7 ns–150 fs pulses from a 780 nm laser [20]. We used a 532 nm Nd:YAG laser with 6 ns pulses to probe the sample under study. It is possible that laser induced breakdown is occurring at the SiO_2 outer shell, causing plasma formation which scatters the light non-linearly at pulse energy densities above 1.5 J cm^{-2} – see Fig. 6.

4. Conclusions

Oxide coated silicon nanoclusters in an IPA suspension display good optical limiting properties. It is unlikely that the optical limiting arises from photoinduced refractive index mismatch, as reported for colloidal suspensions of silica particles. We propose that the non-linear behaviour has a strong contribution from plasmas which act as scattering centres. These plasmas are formed by laser induced breakdown of the nanostructures SiO_2 outer shells.

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