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Optical, structural and third order nonlinear optical properties of Ge nanoparticles prepared by laser ablation in acetone

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Dedicated to Padma Shree Prof R S Sirohi, FNAE

Here, we report on the synthesis of germanium (Ge) nanoaprticles (NPs) using pulsed laser ablation and their third order nonlinear optical properties using Z-scan and degenerate fourwave mixing (DFWM) techniques with 532 nm, picosecond laser pulses. Transmission electron microscopy (TEM) and UV-Vis absorption measurements reveal the formation of nanosized particles of Ge in acetone solution. Mircro Raman scattering experiments reveal the formation of crystalline Ge NPs and the photoluminiscence spectra show the blue emission from the Ge NPs. On the basis of TEM measurements, we estimated the average size of the Ge NPs as ~ 12nm. The nonlinear absorption coefficient (β) and the nonlinear refraction (n_2) were measured using Z-scan technique and found to be 1.75×10^{-10} cm/W and 6.8×0^{-15} cm^2/W, respectively. The third order nonlinear susceptability and temporal response of Ge NPs were measured through DFWM technique using 532 nm, picosecond laser pulses.

Keywords: Pulsed laser ablation, Germanium, nonlinear absorption, nonlinear refraction, Z-scan, degenearate fourwave mixing.

1 Introduction

Semiconductor nanoparticles and nanostructures are becoming most promising candidates in the field of photonics, optoelectronics and various inter disciplinary areas because of their size dependant optical properties and low toxicity [1-5]. Todate, various preparation methods have been implemented to realize the semiconductor nanoparticles [6-10]. In recent years, silicon (Si) and germanium (Ge) nanoparticles have received great deal of attention towards scientific research, mainly due to their good luminescence properties at the nanoscale, while their bulk form does not show any emission [11]. Besides visible emission, nanometer sized Si and Ge show greatly enhanced nonlinear optical properties owing to the quantum confinement effects due to their size [6,12,13]. These properties indicate that Si and Ge nanoparticles can become promising optical materials. The linear and nonlinear optical properties of semiconductor nanoparticles can vary with different preparation methods and experimental conditions as the preparation techniques may yield different lattices, shapes and size distribution, etc.

The quantum confinement effects in Ge nanostructures will be more prominent than Si, because of the large exciton Bohr radius for Ge (24.3 nm) [14] comapared to that for Si (4.9 nm) [15]. Therefore, appreciable quantum confinement effects can be observed for sizes less than 24 nm in Ge. The nonlinear optical response of the nanoparticles is a direct consequense of the quantum confinement effect. Thus, strong confinement effect in Ge, compared with Si will result in a large nonlinear optical response for a given size of nanoparticles. Many reports are available on the nonlinear optical properties of semiconductor nanoparticles. Ganeev *et al* studied the influence of the laser ablation parameters on the nonlinear optical properties of CdS and As_2S_3 nanoparticles [16]. Apart from this, studies have been carried out on the third order nonlinear optical properties of Si nanoparticles and the effect of surrounding matrix [6,17]. However, investigations on nonlinear optical properties of Ge nanoparticles are limited. Dowd *et al* investigated the nonlinear optical response of Ge nanocrystals embedded in silica matrix prepared by ion-implantation method [18]. Righini *et al* studied the excited state dynamics and nonlinear optical response of Ge nanocrystals embedded in silica matrix synthesized by plasmon-enhanced chemical vapor deposition method [19]. Furthermore, the dynamics of optical nonlinearity and excited carrier life time in Ge nanocrystals embedded in silica matrix were investigated using Z-scan and pump probe techniques [20]. Wan *et al* studied the third order

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nonlinear absorption of amorphous Ge nanoclusters embedded in Al_2O_3 matrix synthesized by electron-beam coevaporation method [21]. Nonlinear optical response of the Ge nanoparticles was observed thorugh the self phase modulated optical fringes [10]. However, understanding of the nonlinear optical response of Ge nanoparticles especially when they are in colloidal solutions is still not well established. In this paper, we reoprt a pulsed laser ablation technique to synthesize Ge NPs in acetone and study their third order nonlinear optical properties using Z-scan and DFWM techniques with 532 nm, picosecond laser pulses. We have also reported the Raman and photoluminescence (PL) measurements of these NPs in acetone.

2 Experimental methods

Commercially available p-type Ge (100) wafer with 0-30 ohm-cm resistivity was used for the ablation process to get the NPs. The germanium target was ultrasonically cleaned with distilled water and then with acetone for 20 min before the ablation. The Q-switched Nd: YAG pulsed laser delivering 6 ns pulse duration, 1064 nm wavelength at 10 Hz repetition rate was used for the laser ablation of Ge. The cleaned Ge wafer was placed at the bottom of the beaker and filled with 10 ml of acetone and the laser pulses were allowed to focus normally on the substrates for 30 min. The laser pulses were attenuated to 60 mJ energy before focusing. During the laser ablation, the target was moved using a rotation system so that the laser always irradiates a new surface. Detailed experimental arrangement and the procedure is given in our earlier work [22,23]. After 30 min irradiation, the solution became light brown in color indicating the formation of Ge NPs. The ablated solution was then used for all the characterizations.

The linear absorption spectrum of Ge NPs in acetone was measured using UV-Vis spectrophotometer (JASCO V-670). The micro Raman scattering measurements were carried out with HR 800 Horiba Jobin Yvon Raman spectrometer with 632 nm of a He-Ne laser as the excitation wavelength at room temperature. The photoluminescence measurements were completed in the visible region with Horiba-Jobin PL-Fluorolog spectrometer using excitation wavelength of 355 nm to observe the emission characteristics of Ge NPs in acetone solution. The structural characteristics of Ge NPs have been studied with advanced TEM (Tecnai 20 G2 STwin) by drop casting the Ge NPs solution on a carbon coated copper TEM grid. The third order nonlinear optical properties were measured using Z-scan technique [24] for Ge NPs solution with picosecond (ps) laser pulses. The ps laser is a frequency doubled, Q-switched Nd: YAG (Ekspla-2143A) laser, delivering 30 ps pulses at 532 nm with a repetition rate of 10 Hz. The popular Z-scan technique, which involves a focussed single beam method and translating the sample across the focal point, was used for measuring both nonlinear refraction and nonlinear absorption. A lens with focal length of 12 cm was used to focus the Gaussian beam and the sample is moved through the beam waist of the laser beam over the length of 60 mm. At the focal point, the sample experiences maximum laser intensity and gradually decreases in either direction from the focus. The sample solution taken in 1mm cuvette, which is smaller than the Rayleigh range of the focussed beam calculated to be ~ 4 mm. Degenerate four wave mixing technique (DFWM) was used to measure the third order nonlinear susceptibility of Ge NPs in acetone.

3 Results and Discussion

Optical absorption measurements are carried out in the range of UV to visible region. Figure 1 shows the linear absorption spectrum of Ge NPs in acetone solution synthesized by pulsed laser ablation. From the absorption spectrum it is observed that it has a continuous band with a peak at 335 nm. Due to the quantum confinement effect, the absorption edge of the Ge NPs in acetone solution is significantly blue shifted relative to the bulk Ge bandgap [25]. The PL spectrum of the Ge NPs in acetone is shown in Fig 2. The PL spectra have a peak emission in the blue region with a peak centred at 422 nm. More details about this emission and the tuning of the emission with different laser parameters was discussed in our earlier papers [22, 23]. Figure 3 shows the comparative Raman spectra of the Ge NPs formed in acetone in comparison with that of the bulk Ge. The crystalline Ge wafer sample exhibits a Raman peak centred around 300 cm^{-1} with FWHM of 3 cm^{-1}, which corresponds to optical phonon vibrations of Ge-

Ge. This peak is symmetrical around its central position. Raman spectra of the Ge NPs formed due to laser ablation of Ge in acetone show a shift in the peak position and an asymmetrical broadening on the lower frequency side when compared with the spectrum of the bulk Ge sample/wafer. Only major peak corresponding to Ge-Ge optical phonon mode at 300 cm^{-1} with lower shift and broadening is observed in the Raman spectra. Hence it is concluded that the size dependent Ge NPs have formed due to laser ablation of Ge wafer in acetone. A broad peak centred at 270 cm^{-1} is also not observed, so there is no formation of amorphous Ge NPs. Thus pure Ge NPs which are crystalline innature have been observed due to pulsed laser ablation of Ge in acetone. The ablated solution was drop casted on TEM grid to image the NPs using TEM. Figure 4 (a) shows the TEM image of the as prepared Ge NPs. It is clearly observed that the Ge NPs have good dispersion and the particles are free from agglomeration. According to the size distribution histogram of the Ge NPs, shown in Fig 4 (e), it is observed that the average size of Ge NPs is 12 nm with a standard deviation of 2.5 nm. Figure 4 (b) shows the high resolution TEM image of the Ge NPs which clearly shows the formation of highly oriented crystalline planes of the Ge (111). The respective selective area electron diffraction (SAED) pattern of Ge NPs is shown in Fig 4 (c) which indicates that there was no GeO_2 NPs formation". However the EDS spectrum shown in Fig 4 (d) indicates the presence of a noticeable oxygen, but most of the NPs are pure Ge only.

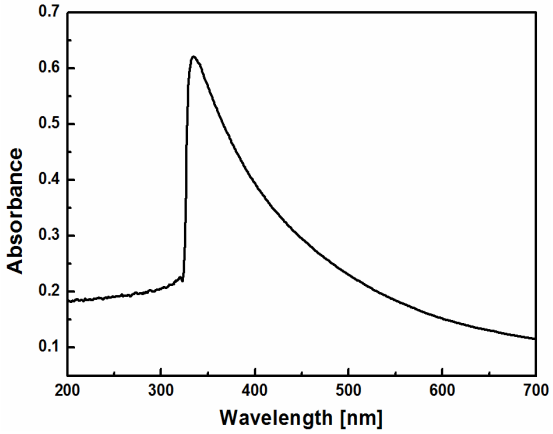

Fig 1. UV-Vis absorption spectrum of Ge NPs in acetone.

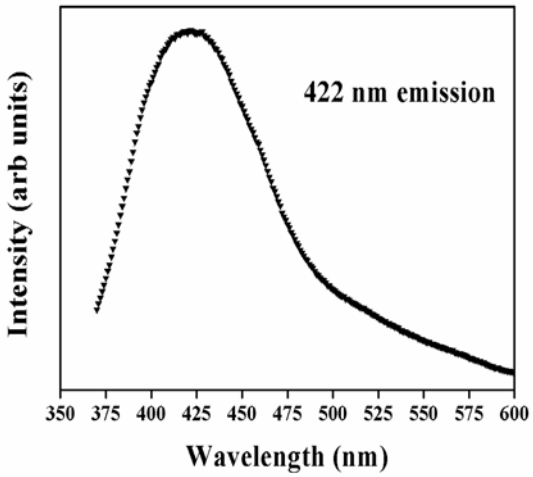

Fig 2. Photoluminiscence emission spectrum of Ge NPs in acetone.

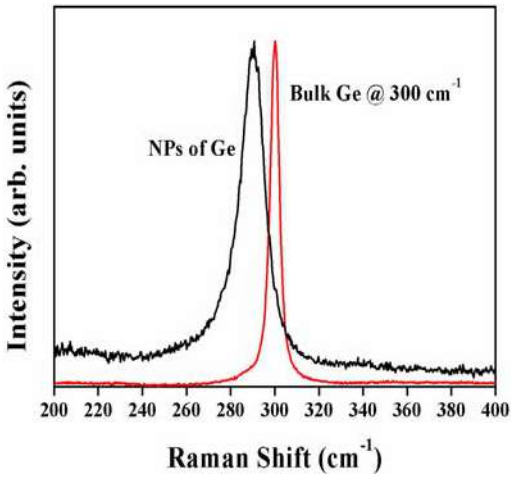

Fig 3.Comparative micro Raman spectra of Ge NPs in acetone and the bulk Ge

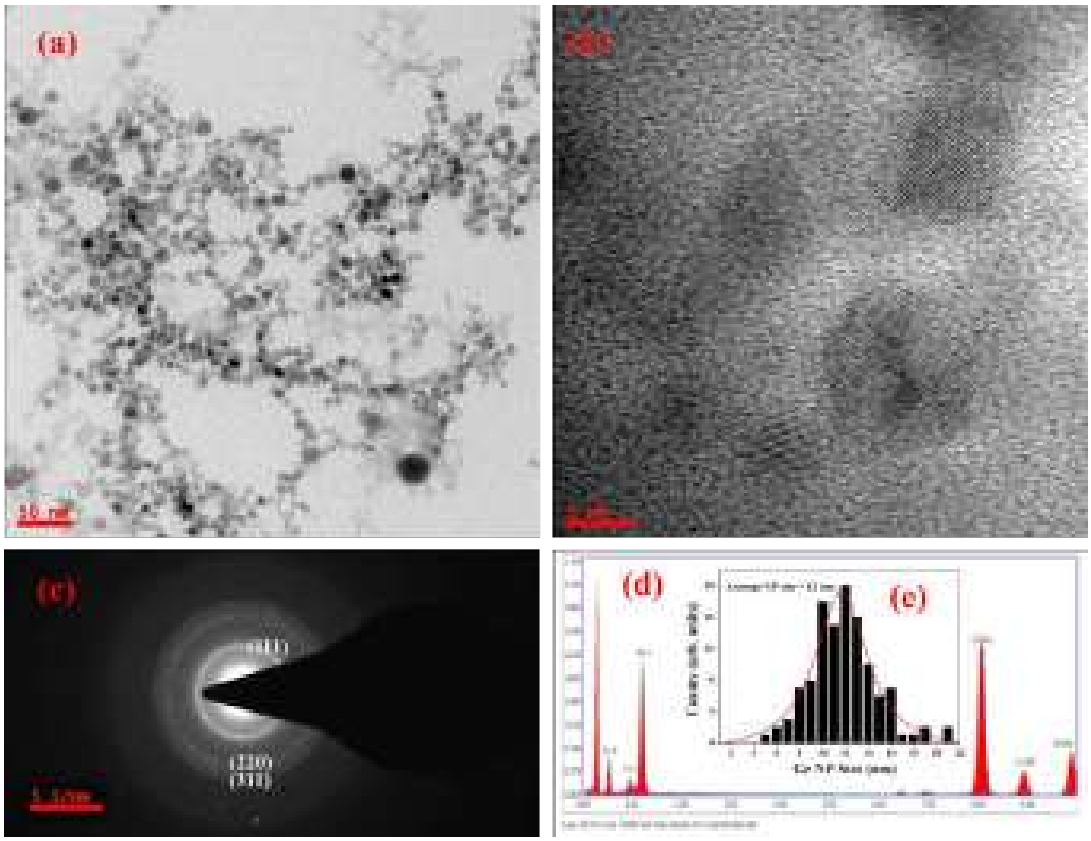

Fig 4. (a) TEM image of Ge NPs obtained by laser ablation of Ge wafer in acetone, (b) High resolution TEM image showing clearly the crystalline planes of (111) Ge, (c) the respective SAED pattern, (d) shows the elemental composition from the Ge NPs recorded using EDS associated with TEM and (e) gives the size distribution histogram of Ge NPs.

The nonlinear optical measurements of Ge NPs in acetone were investigated by performing the Z-scan measurements with 532 nm, ps laser pulses. The nonlinear absorption coefficient (β) was measured by performing the open aperture Z-scan measurements in which the intensity at the sample is varied by translating the sample. The measurements were carried out at an input intensity of 34 GW/cm^2 at the focal point. The normalized change in open aperture transmittance is given by the expression [24].

$$T_{OA(2PA)} = 1 - \frac{\beta I_0 L_{eff}}{(1+(z/z_0)^2)\,2^{3/2}}$$

where z is the sample position and $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range; ω_0 is the beam waist at the focal point ($z = 0$), λ is wavelength of the laser beam, I_0 is the peak intensity on the sample at the focus; L_{eff} is the effective thickness of the sample defined by the expression $L_{eff} = 1 - e^{-\alpha_0 L}/\alpha_0$, with α_0 and L being the linear absorption coefficient and sample length of the cell filled with Ge NPs, respectively. Figure 5 (a) represents the open aperture data obtained at input intensity of 34 GW/cm^2. The open circles are the experimental data and the solid lines are theoretical fittings. The closed aperture data was fitted using the theoretical equation [24],

$$T_{CA} = 1 - \frac{4\Delta\Phi(z/z_0)}{[1 + (z/z_0)^2]\,[9 + (z/z_0)^2]}$$

where ΔØ is the phase change of the laser beam due to nonlinear refraction which is 0.58. ΔØ value was estimated from the theoretical fits to experimental data. For an optical beam with wavelength λ, the light induced nonlinear refractive index n_2 is related to the nonlinear phase shift (ΔØ) through the relation,

$$n_2(\text{cm}^2\,\text{W}^{-1}) = \frac{|\Delta\varphi|\lambda}{2\pi I_0 L_{eff}}$$ .Thus the sign of n_2 is determined by ΔØ.

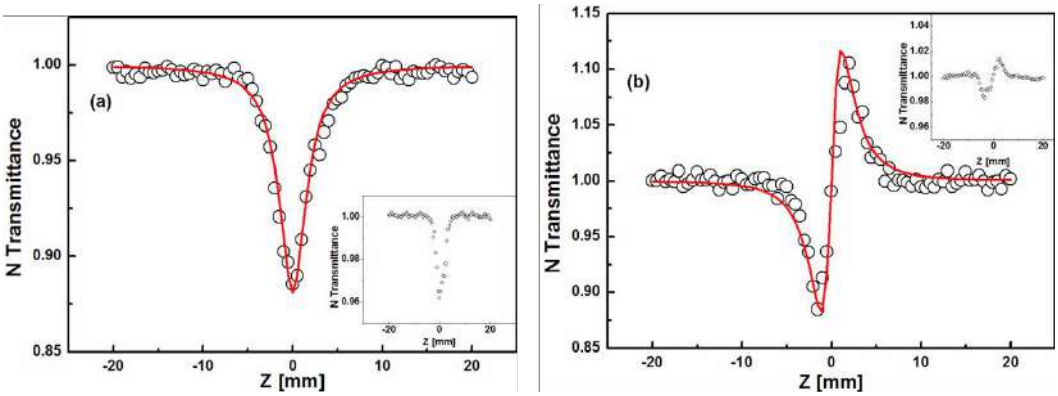

Fig 5. (a) represents the Z-scan open aperture data for Ge NPs in acetone at input intensity of 34 GW/cm^2 and the inset graph shows the open aperture data for acetone (b) represents the Z-scan closed aperture data for Ge NPs in acetone at input intensity of 8.9 GW/cm^2 and the inset graph shows the closed aperture data for acetone.

Figure 5 (b) represents the closed aperture data at the input intensity of 8.9 GW/cm^2. The open circles are the experimental data and the solid lines are theoretical fittings. The valley followed by the peak in the closed aperture trace is the signature for positive nonlinearity of the sample. Note that we also carried out the Z-scan measurements on solvent (acetone) and found that the solvent shows a significant nonlinearity

at this intensity. The inset graph in Fig 5(a) and 5(b) represents the open and the closed aperture data for acetone, respectively. The solvent contribution was then removed from the open and closed aperture data of the samples by dividing of the sample data with the corresponding pure solvent data. The best theoretical fits (in Fig 5, solid lines), which were defined using the above equations, allowed calculating the nonlinear optical parameters to be $\beta = 1.75\times10^{-10}$ cm/W and $n_2 = 6.8\times10^{-15}$ cm^2/W. The nonlinear absorption and the nonlinear refraction observed for the Ge NPs is attributed to the two photon absorption (TPA) effect and electronic polarization, respectively. Since the studies are carried out with a picosecond laser, the nonlinearities can be attributed to be real rather than due to thermal contribution, which dominates at longer pulse duration. However, we cannot completely rule out the thermal contribution. The nonlinear absorption coefficient and nonlinear refraction values of Ge NPs in acetone are comparable with the values reported for Ge NPs in the literature [13].

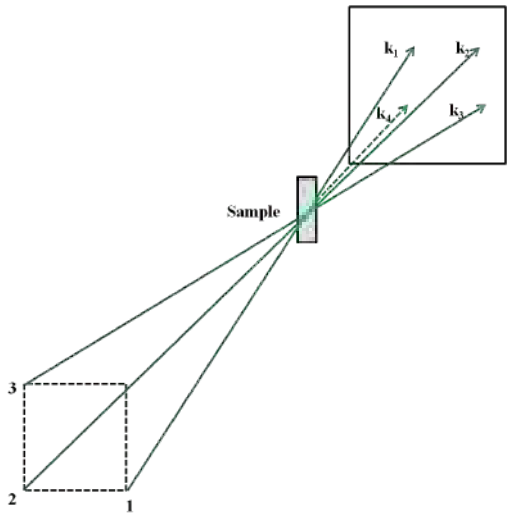

Fig 6. Geometry of the DFWM experiment. Beams 1-3 are coincident on the sample. The resultant fourth beam (dashed line) is the DFWM signal that occurs because of the in $k_4 = k_3 - k_2 + k_1$.

The third order nonlinear optical susceptibility measurements of Ge NPs were carried out by using degenerate four wave mixing (DFWM) technique in a boxcar geometry [26] using 532 nm, picosecond laser pulses. Figure 6 represents the geometry of the DFWM technique. In boxcar arrangement, the fundamental beam is divided into three nearly equal intensity beams in such a way that the three beams form three corners of a square box and are focussed into the nonlinear medium both spatially and temporally. The resultant DFWM signal that comes along the fourth corner of the box is generated as a result of the phase matched interaction, $k_4 = k_3 - k_2 + k_1$ of the three incident beams. The sample is taken in the form of solution filled in a 1 mm quartz cuvette. Care is taken to reduce the contribution of the cuvette towards the overall DFWM signal by choosing suitable focussing conditions. All the three incident beams have the same linear polarization. The transient DFWM profile for Ge NPs solution was obtained by delaying the beam 3 with respect to other two incident beams. By performing the nonlinear transmission experiments on the sample, the input intensity for all three input pulses were chosen such that the effect of nonlinear absorption can be neglected and hence the obtained DFWM signal contains purely instantaneous response of the Ge NPs. The obtained third order nonlinear susceptibility is purely real in nature without any contribution of the imaginary components due to two photon absorption. Choice of low input powers allowed us to neglect the contribution of higher order nonlinearities.

The third order nonlinear optical susceptibility $\chi^{(3)}_{sample}$ of Ge NPs was measured by comparing the DFWM signal of the sample with that of acetone as reference ($\chi^{(3)}_{reference} = 2.05\times10^{-13}$ esu [26]) for picosecond pulses which is in turn was deduced by comparing it with signals from CS_2 ($\chi^{(3)}_{CS_2}$) = 76.2 × 10^{-13} esu [27]). The following relationship is used to determine the sample $\chi^{(3)}_{sample}$ [28],

$$\chi^{(3)}_{sample} = \left(\frac{n_{sample}}{n_{ref}}\right)^2 \left(\frac{I_{sample}}{I_{ref}}\right)^{1/2} \left(\frac{L_{sample}}{L_{ref}}\right) \alpha L_{sample} \left(\frac{e^{\frac{\alpha L_{sample}}{2}}}{1-e^{-\alpha L_{sample}}}\right) \chi^{(3)}_{ref}$$

where I is the DFWM signal intensity, α is the linear absorption coefficient, L is sample path length, and n is the refractive index. As the sample concentration is very low, the refractive index of acetone (n = 1.359) is taken as the refractive index of solution. DFWM signals as a function of different input intensities for Ge NPs is shown in Fig 7 (a). A slope of ~ 3 obtained for Ge NPs indicating that the origin of the DFWM signal doesn't have any contribution of two photon absorption in which case the slope of the curve would have been different [28]. The origin for the DFWM signal is purely electronic contribution. DFWM signals as a function of delay time for the Ge NPs in acetone is shown in Fig 7(b). The solid circles are the experimental data and the solid line represents the theoretical fit using Gaussian function. The nonlinear response is very fast and is expected to be faster than 30 ps pulse duration employed. The calculated third order nonlinear susceptibility ($\chi^{(3)}$) of Ge NPs in acetone solution is 1.1×10^{-11} esu.

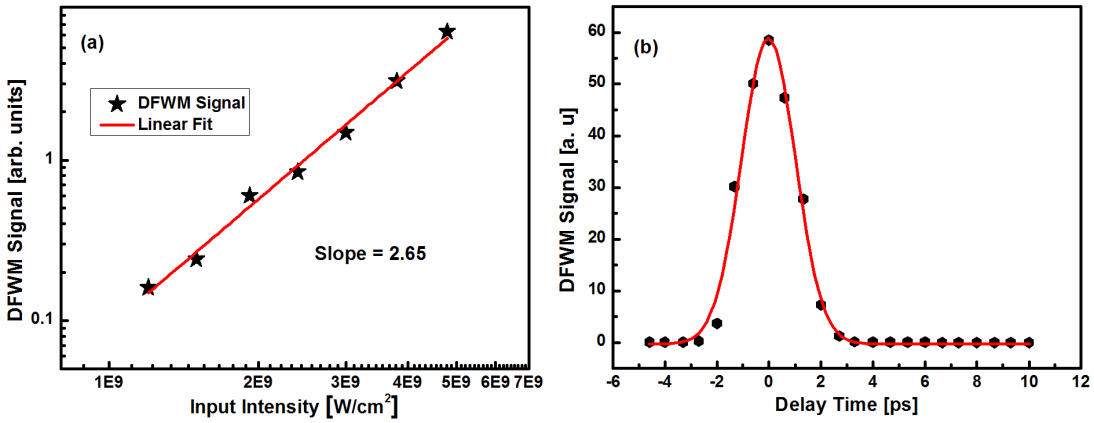

Fig 7. (a) DFWM signal recorded for Ge NPs in acetone as a function of input intensity. (b) Temporal profile of DFWM signals of Ge NPs in acetone as a function of beam 3 delay time for the parallel configuration.

Though laser ablation of Ge in water/ethanol was reported [13], no studies had been carried out on the effect of the environment on the formation of the Ge nanoparticles. Furthermore, the quantum confinement effects in Ge NPs are more predominant compared to Si, which in turn require more detailed structural, optical and nonlinear optical properties of Ge NPs.

4 Conclusions

The pulsed laser ablation technique was used to synthesize Ge NPs in acetone. Linear absorption spectra showed the absorption peak at 335 nm. TEM measurements revealed the Ge nanoparticles formation in acetone with an average NP size of 12 nm. Third order nonlinear optical properties of Ge NPs are measured at 532nm, ps laser pulses using Z-scan and DFWM techniques. The nonlinear absorption coefficient and the

nonlinear refraction are estimated to be 1.75×10^{-11} cm/W and 6.8×10^{-15} cm^2 /W, respectively. Third order nonlinear susceptibility of Ge NPs is found to be 1.1×10^{-11} esu.

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