

Two-photon absorption of matrix-free Ge nanocrystals

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The authors demonstrate that solution synthesized Ge nanocrystals (NCs) display a highly nonlinear optical absorption. The Ge NCs with an average diameter of 5 ± 2 nm are synthesized from germanium(II) bis(trimethylsilyl)amide with hexadecylamine surfactants at 300 °C and 1 atm in argon atmosphere. The resulting Ge NCs in a powder form are then dispersed on a silica glass substrate. Femtosecond pulses at 820 nm wavelength from a mode-locked Ti:sapphire laser are used to measure a two-photon absorption coefficient of the deposited Ge NCs. The calculated coefficient ranges from 1190 to 1940 cm/GW. © 2006 American Institute of Physics.

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Nonlinear optical semiconductor materials have been a focus of many investigations as a key element of optical switches and modulators in telecommunication systems.¹⁻³ One important nonlinear phenomenon observed in semiconductor materials is two-photon absorption (TPA). In a typical case, two photons, whose energy (E_{ph}) is near the half-band-gap energy ($1/2E_g$), are absorbed to cause an excitonic transition from valence band to conduction band.⁴ The TPA has been observed in a variety of zero-dimensional (0D) to two-dimensional (2D) III-V quantum structures.^{5,6} Among these structures, both linear and nonlinear absorptions are comparatively more enhanced in 0D systems than in higher dimensional systems.⁷ The reason stems from the concentration of oscillator strengths in fewer allowed transitions. With the increased optical nonlinearity, these 0D structures possess a strong potential to be used in optical devices, such as long-wavelength TPA photodetectors that would surpass electrical devices in speed and performance. One candidate material for this type of application is Ge, which has a direct band gap transition $\Gamma'_{25} \rightarrow \Gamma'_2$ with E_g of 0.8 eV as well as $\Gamma'_{25} \rightarrow \Gamma'_{15}$ transition with E_g of 3.4 eV.^{8,9} Herein, we focus on the TPA of matrix-free 0D Ge nanocrystals (NCs).

The Ge NCs are typically synthesized via radio frequency cosputtering of Ge and SiO₂,^{10,11} hydrothermal reduction of Si_xGe_{1-x}O₂,¹² and Ge ion implantation followed by rapid thermal annealing.¹³ All of these processes result in Ge NCs incorporated in a matrix, typically SiO₂ (Refs. 14-16) or Al₂O₃,¹⁷ followed by high-temperature (>800 °C) annealing to achieve full conversion of GeO₂

into Ge NCs.^{15,18} However, the presence of the oxide matrix around the NCs induces the formation of GeO_x around the Ge NC core. The interfacial stress between the oxide matrix and Ge NCs contributes to the creation of surface defects that affect the optical and electrical properties of the Ge NCs.¹⁹ Since the surface-to-volume ratio in 0D materials is significantly greater than that in bulk materials, the surface defects created during material processing affect the carrier lifetime and the optical properties of 0D materials more pronouncedly than for high dimensional materials.

An investigation of TPA property of NCs embedded in different types of matrix materials has shown that the nature of the matrix influences the optical nonlinearity.²⁰ However, the effect of the matrix as well as the influence of processing conditions on the optical properties are not clearly delineated from the inherent physical properties of Ge NCs. With Ge NCs embedded in a silica matrix, Dowd *et al.* used picosecond laser pulses to obtain a TPA coefficient (β) of 30 cm/GW at 2.9 μ m wavelength (λ),¹⁵ while Jie *et al.* obtained a range of $\beta=190-760$ cm/GW at $\lambda=532$ nm.²¹ In a similar experiment using femtosecond pulses, Li *et al.* reported a range of $\beta=180-680$ cm/GW at $\lambda=780$ nm depending on the concentration of Ge NCs embedded in a silica matrix,¹⁴ while Wan *et al.* reported $\beta=(0.95-1.43) \times 10^4$ cm/GW at $\lambda=532$ nm for Ge NCs embedded in Al₂O₃.¹⁷ These results show a variation of the TPA coefficient depending on the host matrix and experimental conditions, especially the wavelength used for the measurement. Characterizing the optical properties of 0D materials, decoupled from their surrounding matrices and potential surface defects, remains a challenge. Hence, studying the nonlinear

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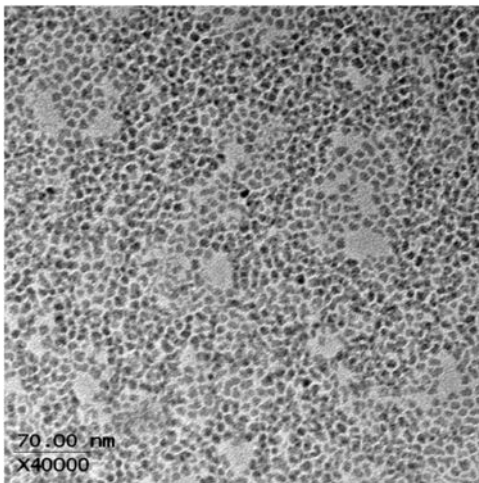


FIG. 1. TEM image showing Ge NCs with an average size of 5 ± 2 nm. The NCs are solution synthesized at 300°C and 1 atm of Ar.

response in matrix-free Ge NCs could help isolate the inherent optical properties of 0D Ge.

To produce freestanding Ge NCs, we have developed a high-yield solution synthesis route using germanium(II) precursors.^{22,23} These precursors require benign synthesis conditions without the use of metal catalyst and without the formation of salt by-products. The synthesis entails reduction of germanium(II) bis(trimethylsilyl)amide by hexadecylamine at 300°C under 1 atm argon atmosphere for 5 min to obtain Ge NCs in a powder form. The Ge NCs are dissolved in chloroform followed by centrifugation at 25 000 rpm for 20 min to remove undissolved large particles. The supernatant is subsequently separated, and an equal volumetric amount of methanol is added, followed by another round of centrifugation to precipitate Ge NCs as fine dark powder. To cast Ge NCs on a silica glass substrate, the Ge NC powder is redissolved in chloroform. For TPA measurements, a substrate of silica glass slide is cleaned with piranha solution (95 wt % H_2SO_4 : 30 wt % H_2O_2 in 3:1 volumetric ratio). The chloroform solution containing Ge NCs is dispersed on the substrate and then dried completely before the TPA measurement. The average NC layer thickness varies from 10 to $50\ \mu\text{m}$. Siemens 5200 x-ray diffractometer (XRD) and JEOL 2100 transmission electron microscope (TEM) are additionally used for crystallographic and structural characterizations of the nanocrystals.

The average diameter of the Ge NCs based on TEM images (Fig. 1) is 5 ± 2 nm. Each particle is encapsulated by amine surfactant,²² which prevents spontaneous aggregation and oxidation of the particles. The crystallinity of the Ge NCs characterized by XRD is shown in Fig. 2. Since the particle size is small, XRD peaks are broadened and overlapped. Deconvolution yields peaks at 27° , 45° , and 53° , which correspond to characteristic {111}, {220}, and {311} planes of cubic-phase Ge NCs. The results from TEM and XRD support that the Ge NCs are crystalline and in cubic phase.

Single-beam direct transmission (T) measurements have been a primary method for determining TPA coefficients (β) in semiconductors.²⁴ This method has been widely used for many bulk semiconductors, such as GaAs, CdTe, ZnTe, and CdSe.⁵ Transmission (T) is related to irradiance (I) by

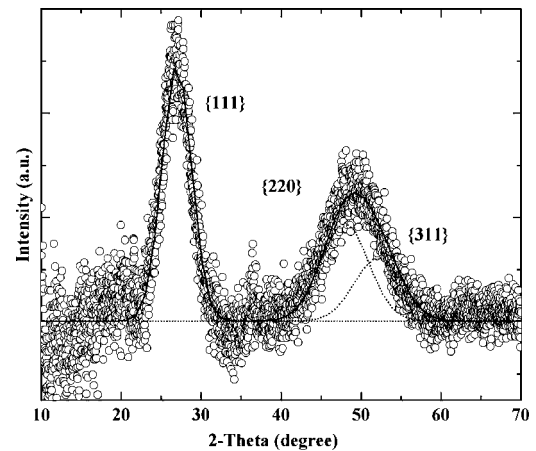


FIG. 2. Typical XRD pattern, with the presence of {111}, {220}, and {311} planes, indicates that the Ge NCs are in cubic phase.

$$T = \frac{\alpha_0 T_0}{\beta \sqrt{\pi l} [1 - \exp(-\alpha_0 l)]} \int_{-\infty}^{\infty} \ln \left(1 + \frac{\beta}{\alpha_0} I(1-R) [1 - \exp(-\alpha_0 l)] \exp(-x^2) \right) dx, \quad (1)$$

where l is the sample thickness, R is the reflectivity of the sample, α_0 is the linear absorption coefficient, and β is the TPA coefficient.²⁵ T_0 is the transmission when $I=0$ and is defined as

$$T_0 = (1 - R_{12})(1 - R_{23})(1 - R_{31}) \exp(-\alpha_0 l), \quad (2)$$

where R_{12} is the reflectivity of the air-germanium interface, R_{23} is the reflectivity of germanium-glass interface, and R_{31} is the reflectivity of glass-air interface. Surface reflection is taken into account since Ge has a high refractive index. At low irradiation intensity, Eq. (1) can be simplified to calculate β from the following equation:

$$\beta = \frac{2\sqrt{2}\alpha_0 \exp(-\alpha_0 l) \sqrt{(1 - R_{12})(1 - R_{23})(1 - R_{31})} d(1/T)}{[1 - \exp(-\alpha_0 l)] d(I)}. \quad (3)$$

Linear regression on $1/T$ vs I yields the linear and nonlinear absorption coefficients of the Ge NCs.

The inverse transmission measurement is conducted, using a mode-locked Ti:sapphire laser with a repetition rate of 76 MHz and pulse width of ~ 200 fs. When the laser beam at 820 nm wavelength is focused, a power density up to $3.0\ \text{GW}/\text{cm}^2$ can be obtained with a beam radius of $\sim 25\ \mu\text{m}$ at the focal point. A piece of silica glass slide, which reflects approximately 10% of the incident beam, is used for input power monitoring. The transmitted power through the sample is measured by another optical power meter behind the sample.

The presence of TPA in Ge NCs is evidenced by the decreasing transmission with increasing incident power (Fig. 3). The total absorption (α) can be represented as $\alpha = \alpha_0 + \beta I$. The linear absorption is obtained by $\alpha_0 = \ln(A)/z$, where A is the y intercept when $I=0$, and z is the sample thickness. The value of α_0 is found to vary from 353 to $382\ \text{cm}^{-1}$, while β is found to vary from 1190 to $1940\ \text{cm}/\text{GW}$ in our Ge NC samples.

As a control sample, a piece of ZnSe bulk crystal with 2 mm thickness is used. Under similar measurement condi-

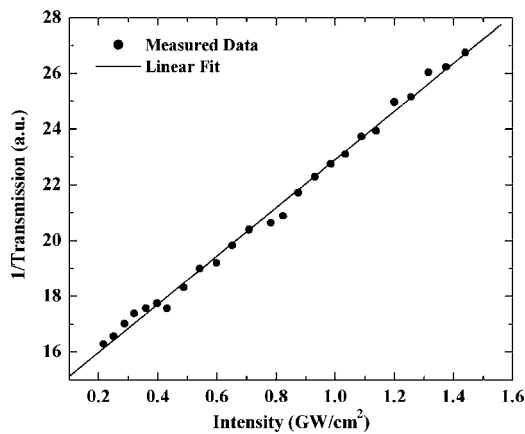


FIG. 3. Inverse transmission vs irradiance measurement of Ge NCs to extract the TPA coefficient.

tions, the inverse transmission yields $\alpha_0 = 0.07 \text{ cm}^{-1}$ and $\beta = 4.0 \text{ cm/GW}$. The calculated β is consistent with a previous result, showing the value of β to be 5.5 cm/GW at 532 nm . This β corresponds to 4.1 cm/GW at 820 nm after considering wavelength dispersion of β .²⁶

When compared to the TPA coefficient of Ge NCs embedded in a host matrix, we observe that the TPA coefficient of matrix-free Ge NCs is generally greater than the reported values.^{14,15,21} For instance, the TPA coefficient of our free-standing Ge NCs (β up to 1940 cm/GW) is higher than that in SiO_2 matrix obtained by Li *et al.*¹⁴ However, a direct comparison between our result and that of Li *et al.* must be made with caution. The reason is that different excitation wavelengths as well as different concentrations of Ge NCs in the films are used for the measurement.

The two-photon absorption at 820 nm wavelength in Ge NCs can be attributed to the $\Gamma'_{25} \rightarrow \Gamma'_{15}$ transition ($\Delta E \sim 2.7\text{--}3.6 \text{ eV}$ in bulk Ge). The linear absorption coefficient is related to the existence of $\Gamma'_{25} \rightarrow \Gamma'_2$ transition ($\Delta E \sim 0.8 \text{ eV}$ in bulk Ge).⁸ With the absence of surface defects associated with the Ge NCs incorporated in an oxide matrix,¹⁹ the origin of nonlinear absorption observed in this experiment can be assigned solely to Ge NCs. In comparison, numerous investigations on the origin of TPA in Ge NCs embedded in an oxide matrix suggest that the surface-localized defects cause carrier trapping, and the TPA process is dominated by free-carrier absorption.^{14,15,27} For instance, surface-localized states are generated during thermal annealing of Ge NCs prepared by Ge ion sputtering into an oxide matrix. During annealing, traces of oxygen from the matrix outdiffuse to form GeO_2 .¹⁹ In our experiment, Ge NCs are formed in an argon environment and chemically passivated by amine surfactant, preventing spontaneous oxidation of the surface. The chemical passivation also removes interfacial stress and surface reconstruction, which otherwise will lead to surface defects.²⁸ Future work will include time-resolved photoluminescence measurements of our Ge NCs to confirm the origin of the TPA process as well as investigate the TPA coefficient as a function of irradiance wavelength. Since we are currently capable of tailoring the surface functional groups, we also intend to put the Ge NCs in both inorganic and organic matrices and characterize their impact on optical properties.

In summary, we have measured the TPA coefficient of matrix-free Ge NCs produced via solution synthesis. The TPA coefficient β is calculated to be around $1190\text{--}1940 \text{ cm/GW}$. In the absence of oxide matrix during synthesis, the surface defects associated with the GeNCs prepared by sputtering method are eliminated, and the origin of TPA process is assigned to the $\Gamma'_{25} \rightarrow \Gamma'_{15}$ transition in Ge NCs.

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