Synthesis and Characterization of Germanium Nanoparticles Prepared By Laser Ablation in Liquid Media

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Abstract:

Germanium (Ge) nanoparticles (NPs) are synthesized by means of pulsed laser (Nd-Yag) ablation of bulk germanium target immersed in ethanol with nanosecond laser pulses at fixed pulse energy at wavelength (532 nm). The fabricated nanoparticles are characterized by employing different diagnostics such as UV-Vissible absorption spectroscopy, atomic force microscopy.

The results of preparation and optical characterization of the Ge nanoparticle suspensions are presented. The considerable shift of the band gap energy of the nanoparticles compared to the bulk semiconductors was observed, and the estimated optical gap was about 3.75eV.

Keywords: pulsed laser ablation, semiconductors, germanium nanoparticles.

الخلاصة:

حضرت جسيمات الجيرمانيوم النانوية بتقنية الاستئصال بالليزر من مادة الجيرمانيوم الموضوعة في محلول الايثانول. سلطت نبضات ليزر النيدميوم-ياك النانوثانية على الجيرمانيوم المغطس بطاقة ثابتة وامد نبضة قصير وطول موجة (532 nm).

تم فحص العينات المحضرة بالمطياف المرئي – الاشعة فوق البنفسجية ومجهر القوة الذري. بينت نتائج التحضير والخصائص البصرية لجسيمات الجيرمانيوم النانوية التغير الكبير بين قيمة فجوة الطاقة البصرية لمادة الجيرمانيوم الاساس وجسيمات الجيرمانيوم النانوية فكانت بحدود (3.75 eV).

Introduction

Up to date, huge efforts have been made for the efficient nanoparticle colloids production become of their potential use in material synthesis and optical detection [1,2]. A lot of techniques based on chemical processes have been developed for a variety of nanoparticle colloids now [3]. Pulse laser ablation in liquid media (PLAL) is recognized to be one of the promised approaches to produce pure nanoparticle colloids due to simple, environmentally friendly and exempted of additional chemically active components[4,5,6].

Nanoparticles of Germanium, as well as Silicon, have attracted significant attention for many years due to the discovery of their various quantum phenomena [7,8,9] especially the emitting of visible photoluminescence (PL) in nanostructures [10,11,12]. Moreover, compared with Si nanocrystals may be more interesting for device applications. For instance, Ge nanostructures had been trusted to be a material with a smaller band gap and have exhibited the stronger quantum confinement effect, which makes it more suitable than Si for photovoltaic applications.

In this contribution, we have reported the influence of the wavelength of laser ablation (Second Harmoning Generation Nd-Yag laser) on the preparation of the Ge nanoparticle colloids, and find that the change of wavelength affects the size of the produced nanoparticles.

1. Experimental Procedures

Germanium nanoparticles were prepared by pulsed laser ablation method. The experimental set-up is shown in Fig.(1). Ge shots (99.999% pure ~ 4 mm in diameter) are fixed on the bottom of a quartz chamber and immersed in pure ethanol. Then a second harmonic generation produced by a Q-switched Nd-Yag laser device, with wavelength 532 nm, pulse width of 10 ns, energy of laser pulse equal to 550 mJ and repetition frequency of 2 Hz is induced and focused onto the surface of the Ge target.

Note that an optical aperture is employed between the original laser beam and quartz lens, which makes the laser finely focused, and the diameter of the focus is estimated to be less than 0.5 mm. After the interaction between laser and target for about 20 min. through a series of experiments, we prepare samples in which we only change the incident power density.

Atomic force microscope (AFM) is employed to identify the morphology and structure of the prepared samples. Meanwhile, ultraviolet-visible absorption spectroscopy is operated to characterize the optical constants of samples.

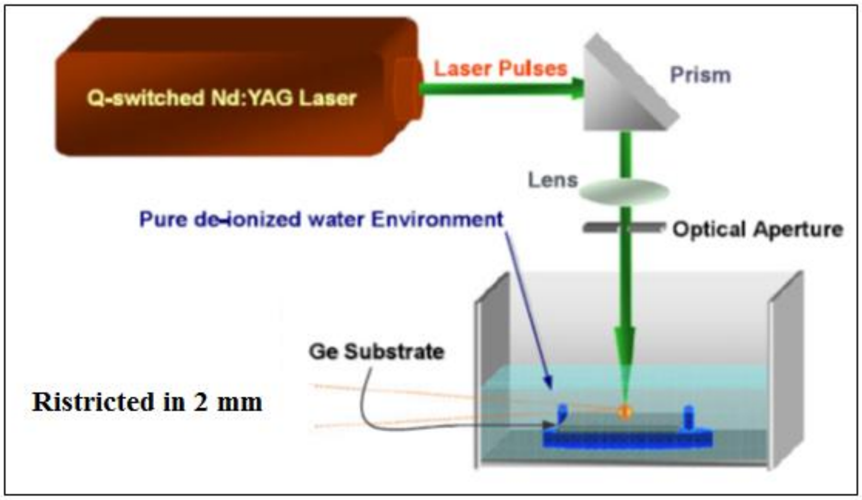


Fig.(1) Schematic of the experimental setup

Results and discussion:

Optical properties of germanium nanoparticles, fig.s(2,3) shows optical transmission and absorbance spectra of the samples as functions of wavelength. A large absorption band around 300 nm has been revealed. The Ge nanoparticles produced by PLAL method absorbs strongly in ultraviolet region. This observation allows us to suggest that Ge nanoparticles are probably quantum confined. Fig(3) we shows a broader absorption band, which indicates a broader size distribution.

The relationship between transmittance and absorbance would appear to be a simple inverse relationship, the true relationship between these two variables can be inversed and expressed with logarithmic (base 10 formula),

$A = \log(1/T)$**…………..1**

The absorbency (A) of a dissolved substance can be indexed as a linear function of its concentration, the so-called lambert-beer law [13].

Optical spectra revealed that the diameter of Ge nanoparticles is less than 20 nm, and the Bohr radius of Ge NP is around 24 nm, so quantum effects of the NPs below the Bohr radius are attributed.

From the absorption coefficient in Fig. (4), it is clear that the spectra exhibit a peak centered at around 300 nm with its tail extending to the red region (600 nm).

Fig.(5) shows the Tauc's plot derived from the UV-visible spectra of ablation samples. Tauc's plot was obtained from the folowing relation.

$$(\alpha E)^{1/2} = B\left(E - E_g\right) \ldots\ldots\ldots\ldots\ldots..2$$

Where, □= absorption coeficient (/cm), E_g= band gap of bulk Ge, B= constant and E= photon energy (eV). In Tauc's plot, the intercept on the x-axis gives a value of absorption band gap.

Fig.(6) represents extinction coefficient of nanosample Ge prepared by (PLAL) versus wavelength. Exticnction coefficient calculated from the following relation:

$$k = \frac{\alpha\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots\ldots.3$$

Refractive index decreases with increasing wavelength as it clear from fig.(7).

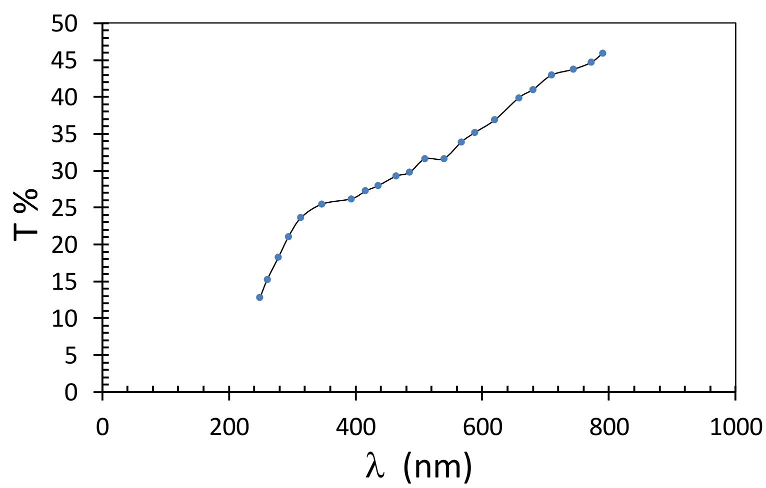


Fig.(2) transmission spectra of the Ge NP suspensions prepared by the laser ablation of bulk targets in the liquid

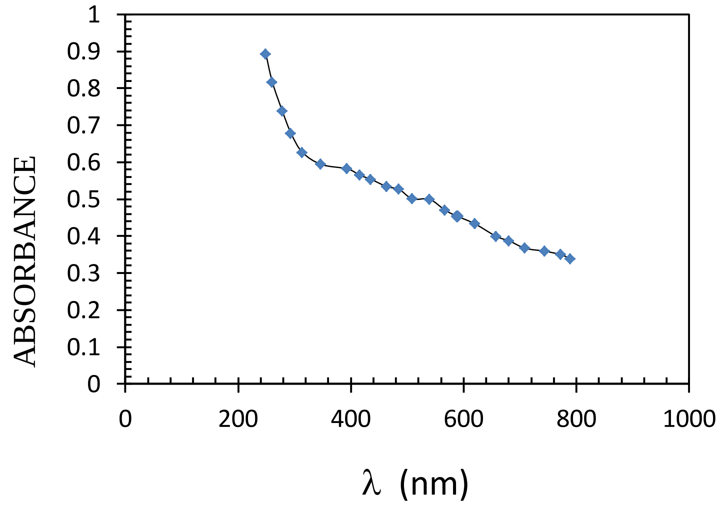


Fig.(3) UV-Visible absorption spectra of the Ge NP colloidal solutions in de-ionized water.

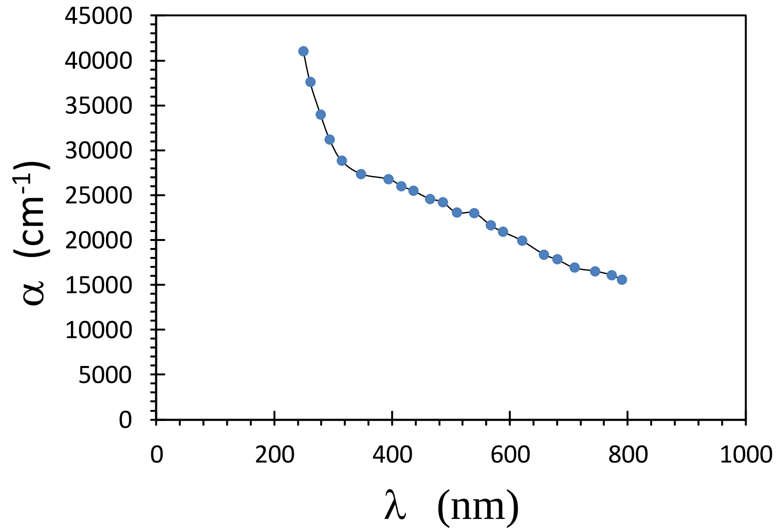


Fig.(4) Plot of absoption coefficient versus wavelength for nano Ge particles.

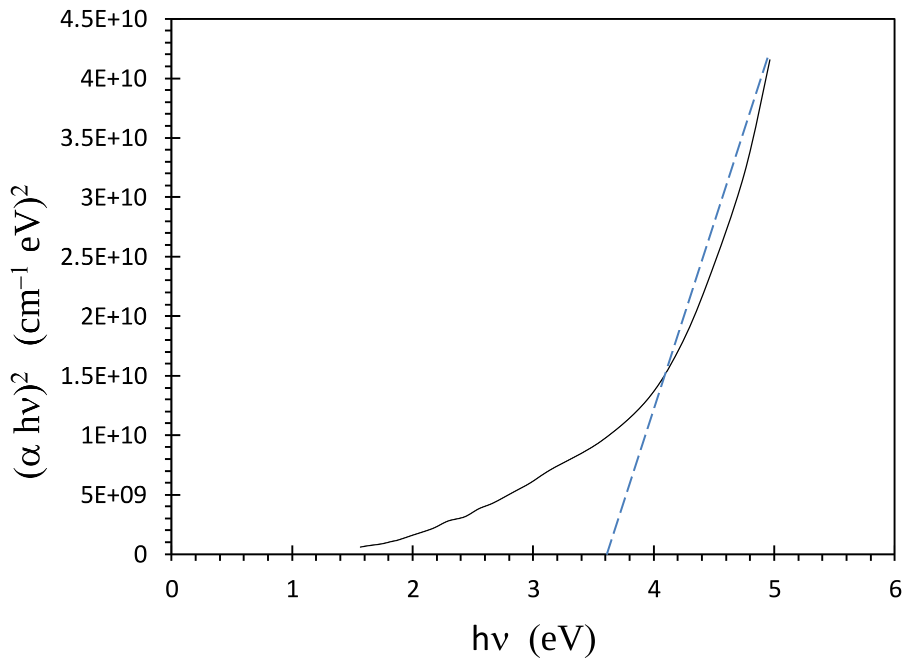


Fig.(5) plot of $(\alpha E)^{1/2}$ Vs E for nanoparticle sample.

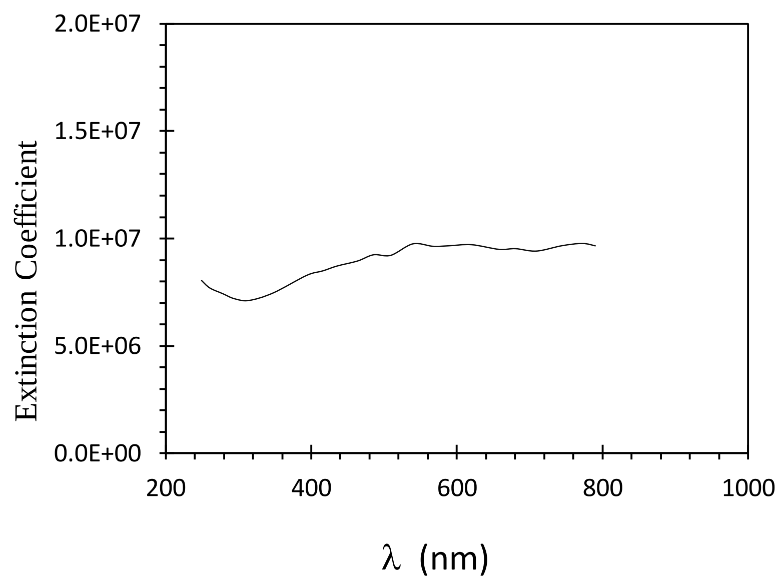


Fig.(6) represent extinction coefficient of nanosample Ge prepared by (PLAL) with wavelength.

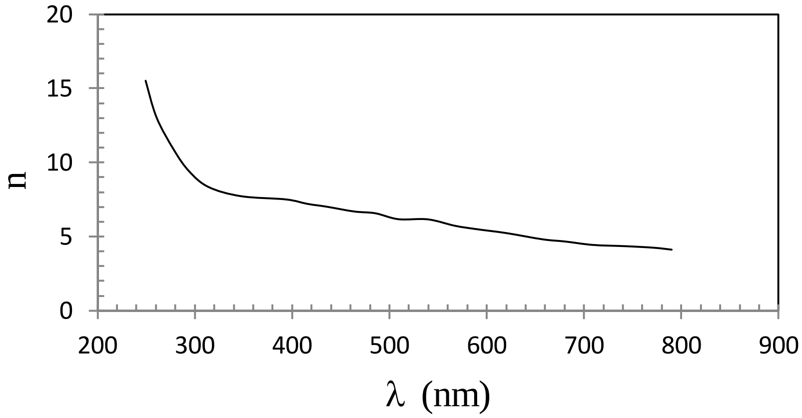
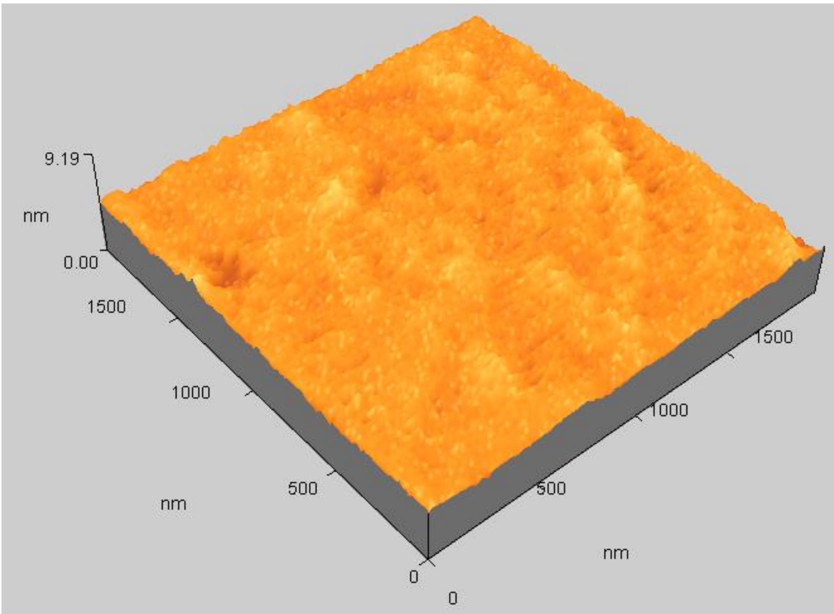


Fig.(7) Shows refractive index of Ge nanoparticles versus wavelength.

2. **Structural properties (Atomic Force Microscopy)**

To see the smaller nanoscale structures, the AFM studies are carried out. Fig (8) shows the AFM images of the nanopaterned Ge surface ablated by Nd-Yag laser (532 nm wavelength). Fig.s (8 A,B) and (9 A,B) are the three dimentional (3D) and the histogram view for ablated Ge. It is observed that the base diameters of the Ge nanoparticles are in the range of (20) – (50) nm. These patterns have pyramidal shape nanoparticles with large density of nanoparticles and the shapes having average height of (10) nm.



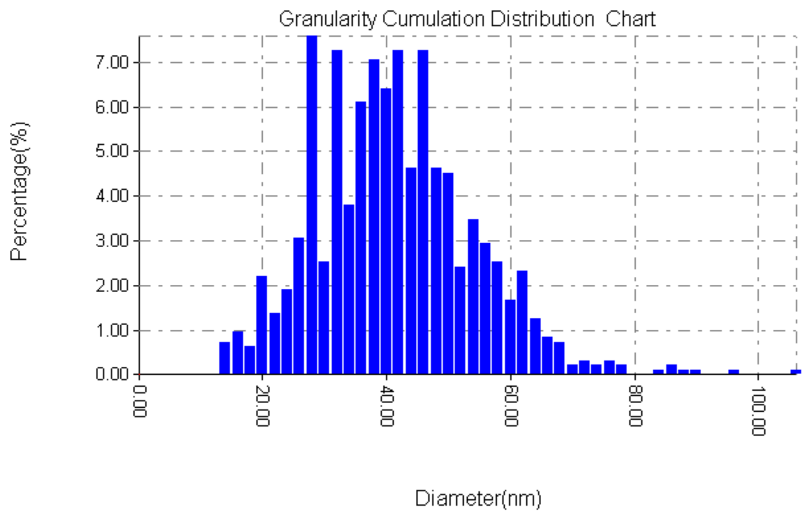
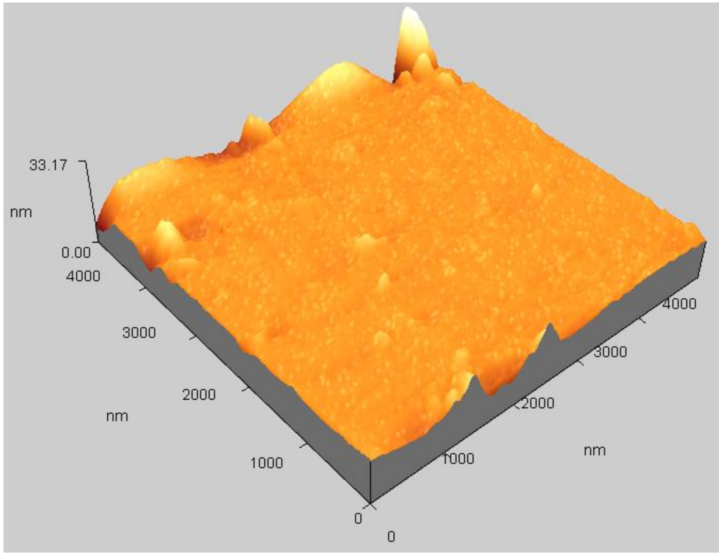


Fig.(8) (A) Shows three dimensional (3D) atomic force images of laser ablated nanoparticles Ge, (B) shows normalized particle abundance versus nanoparticle diameter (histogram of Ge nanoparticles) .



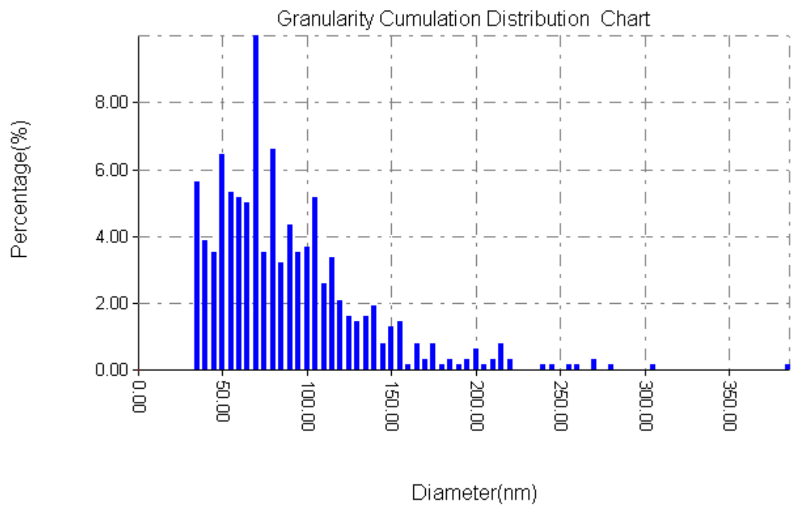


Fig.(9) (A) Shows three dimensional (3D) atomic force images of laser ablated nanoparticles Ge, (B) shows normalized particle abundance versus nanoparticle diameter (histogram of Ge nanoparticles) .

Conclusions:

In summary, we have prepared Ge nanoparticles colloids by laser ablation in liquid media (LAL). Also we reported the results of investigation of the optical and structural characteristics of Ge nanoparticles suspensions. The considerable shift of the absorption edge of Ge nanoparticles suspensions compared to the bulk germanium was demonstrated and attributed to the quantum confinement effects.

Moreover, we presented the results of the measurements of the refractive indices and absorption coefficients of these semiconductor nanoparticle suspensions.

The atomic force microscopy images reveal that there is formation of inhomogeneous size nanoparticle. This indicates that wide range of size distribution.

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