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Optical Properties of Germanium Nanoparticles Prepared by Laser Ablation

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***Abstract*— The synthesis of germanium nanoparticles (Ge NPs) through pulsed laser ablation in deionized water is investigated for Nanophotonics and optoelectronic applications. This study delves into the influence of laser pulse energy on Ge NP properties, specifically highlighting size control and optical characteristics. Our findings reveal a significant reduction in Ge NP size, from an initial 30 nm to 20 nm, as the laser pulse energy increases. Notably, we observed size-dependent blue luminescence from the synthesized Ge NPs. This controlled synthesis holds promise for optoelectronics and sensing applications. The study provides valuable insights into precise Ge NP synthesis and underscores their intriguing optical properties, paving the way for advanced Nanophotonic devices.**

***Keywords*—Germanium nanoparticles, Laser ablation in liquid process, PLAL, Optical properties.**

I. INTRODUCTION

The exploration of semiconductor nanoparticles (NPs) has become a focal point of scientific inquiry, driven by their pivotal role in innovative technologies. As semiconductor materials are scaled down to the nanoscale, their chemical and physical properties undergo profound transformations, giving rise to unique attributes attributed to their expanded surface area and quantum size effects. Notably, these alterations extend to the semiconductor's optical characteristics, such as refractive index and absorption coefficient, as well as its conductivity[1].

This burgeoning field of research, encompassing semiconductor devices and nanomaterials, holds immense promise across diverse domains, including but not limited to nanoscale electronics, LEDs, waveguides, solar cells, chemical and biosensors, super-absorbents, laser technology, packaging materials, automotive components, armor, and catalysts. The semiconductor industry is poised for significant advancements as nanotechnology continues to progress.

A range of semiconductor nanomaterial, including Si-Ge, Si, AlGaAs, GaAs, InGaAs, InP, AlGaN, GaN, ZnS, SiC, AlInGaP, ZnSe, CdS, CdSe, and HgCdTe, among others, has found wide-ranging applications in devices like computers, cell phones, laptops, pagers, satellite dishes, CD players, fiber networks, airbags, traffic signals, and automotive taillights [2].

The exploration of laser ablation in liquid environments has a notable history, dating back to 1987 when a pulsed ruby laser was employed to ablate an iron target in water, resulting in the formation of a metastable iron oxide phase—a pioneering experiment [3]. Although research in this area experienced a pause, it regained momentum in the early 1990s. Since then, laser ablation in liquids has been instrumental in synthesizing a diverse array of nanoparticles from various targets, including metals, semiconductors, and polymers[4]. This versatile technique has been used to synthesize materials such as carbon nitride, hydroxyapatite, germanium, gold, permalloy, and even novel combinations like germanium-gold alloys, along with hydrophilic graphite and silicon nanoparticles [5]-[6].

Laser ablation in liquid environments can also be harnessed to manipulate the structure and composition of nanoparticles, leading to intriguing findings such as the creation of gold nanoparticles with silver coatings [7]. Moreover, external electric fields have been shown to exert a remarkable influence on the composition and shape of ablated nanoparticles[8].

The laser ablation process involves the rapid heating of a solid target's surface by a high-intensity laser pulse, causing the surface and the melted layer to enter a metastable state. When the temperature approaches the Spindale point, homogeneous nucleation of the overheated liquid occurs, resulting in the release of energy, phase explosion, and the formation of an ablation plume consisting of vapor, ions, and liquid nanodroplets. Under these extreme conditions, ablated materials can undergo chemical interactions with liquid molecules, leading to the creation of novel chemical compounds [9].

The expansion of rapidly evolving nanoscale bubbles propels vapor and molten material outward, ultimately yielding nanoparticles [10]. Laser ablation in liquids stands out as an efficient method for synthesizing nano-materials

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due to its operation under high-pressure, high-temperature conditions [4].

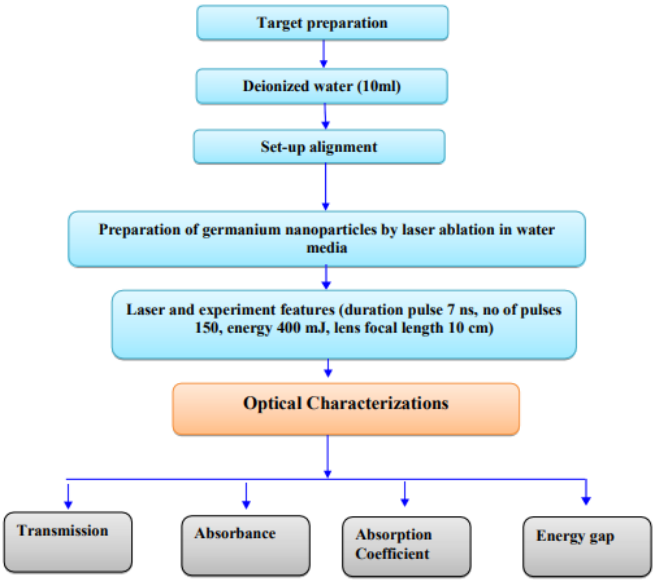
This study significantly broadens the scope of research in ablation in liquid environments by examining how externally applied electric fields influence the ablation products from germanium targets. To date, the sole previous investigation of this kind involved germanium ablation in water, resulting in the formation of germanium nanospheres without the application of external electric fields. However, in this research, it was discovered that a 9V/cm electric field magnitude gave rise to germanium nanocubes, while a 20V/cm field magnitude led to the formation of germanium oxide (GeO2) nanospindles [6].

II. METHODOLOGY

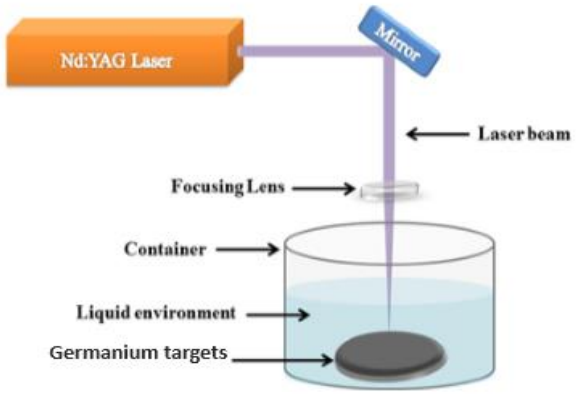
Fig. 1a provides an overview of the experimental procedures utilized in our study, while Fig. 1b offers a detailed depiction of the synthesis of Germanium nanoparticles (Ge NPs) using the laser ablation in liquid technique. This process involved focusing laser pulses onto segments of Germanium semiconductor plates submerged in a plastic container filled with deionized water. The laser source employed was a pulsed Nd-YAG laser operating in Q-switched mode (HUAFGI), emitting pulses at a wavelength of 1060 nm, with pulse durations of 7 ns, repetition frequencies of 1 Hz, and energies of 400 mg.

For the experimental setup, we utilized a plastic tube measuring 5 cm in diameter and 10 cm in length as a reaction cell, which was filled with 10 ml of deionized water. Prior to use, the Germanium targets underwent a series of preparations, including polishing, ethanol cleaning, and deionized water washing.

To assess the optical absorption spectra of the resulting Germanium colloidal nanoparticles, we employed a double-beam UV-vis210A Shimadzu spectrophotometer, covering a spectral range from 200 to 800 nm.



(a)



(b)

Fig. 1. a) Germanium nanoparticles preparation flow chart, and b) laser ablation in liquid process

III. RESULTS AND DISCUSSION

In Fig. 2, absorbance spectra and optical transmission of samples are shown as functions of wavelength, illustrating the optical characteristics of germanium NPs. Around 250 nm, a broad absorption band was observed. Ge NPs synthesized using the PLAL approach exhibit significant absorption of UV light. This observation suggests the potential for quantum confinement in the Ge NPs due to their size-dependent behavior, as often observed in nanoparticles below the Bohr radius. Notably, the optical absorption spectra (Fig. 4) reveal a distinct peak at around 250 nm with a tail extending into the red region (600 nm). This optical behavior aligns with quantum effects and indicates the unique characteristics of the synthesized Ge NPs. Furthermore, Fig. 5 presents the extinction coefficient of the Ge nanosample prepared through pulsed laser ablation (PLAL), illustrating its relationship with wavelength through the specified equation [14]:

$$\kappa = \frac{\alpha\lambda}{4\pi} \qquad (1)$$

Meanwhile, Fig. 6 displays the Tauc's plot derived from UV-visible spectra of ablation samples, incorporating the relationship [15]:

$$(\alpha\ \eta\nu)2 = \boldsymbol{B}\ (\boldsymbol{E} - \boldsymbol{Eg}) \qquad (2)$$

Where, α represents absorption coefficient (cm-1), Eg represents bulk Ge band gap, B is a constant and E represents photon energy (eV). In Tauc's plot, intercept on the x_axis gives an absorption band gap value.

Our study revealed distinct outcomes in the ablation of germanium targets under externally applied electric fields. Notably, a 9V/cm electric field led to the formation of germanium nanocubes, while a 20V/cm field resulted in the generation of germanium oxide (GeO2) nanospindles. These findings contrast with the sole prior investigation involving germanium ablation in water without electric fields, which produced germanium nanospheres. The data highlights the significant impact of electric field magnitude on ablation product morphology and composition, providing valuable

insights into the manipulation of germanium nanostructures for diverse applications.

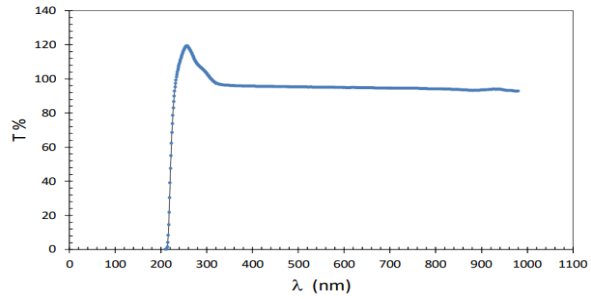


Fig. 2. Spectra of the transmission of GeNP suspensions that have been prepared by bulk targets' laser ablation in the De-ionized water

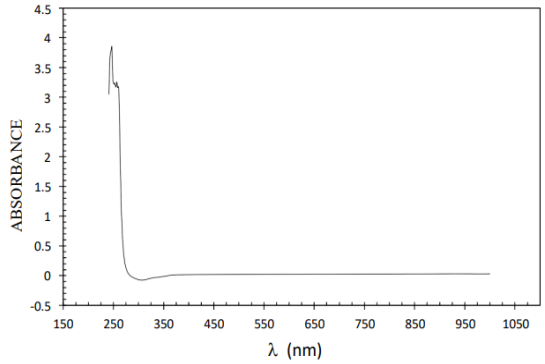


Fig. 3. Spectra of the UV-Vis. absorption of GeNP colloidal solutions in the Deionized water.

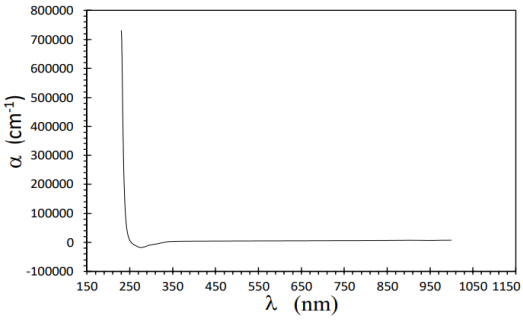


Fig. 4. Plot of absorption coefficient Vs. wave-length for nanoparticles of Ge.

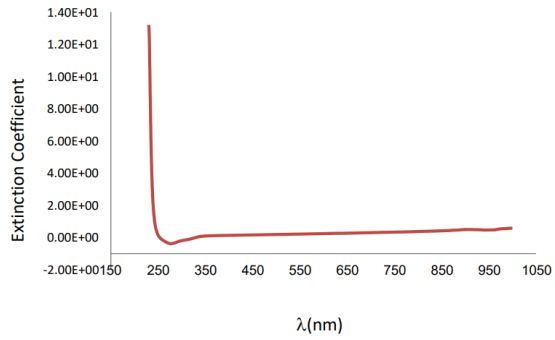


Fig. 5. Extinction coefficient of Nano-sample of Ge that has been prepared by (PLAL) with wave-length.

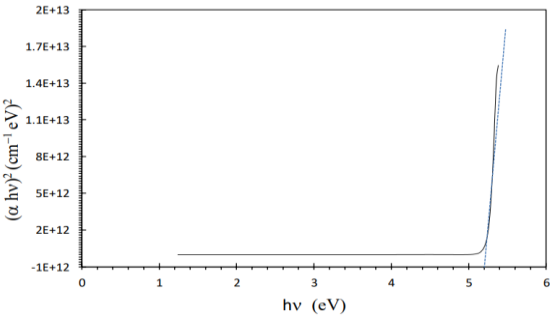


Fig. 6. (αE)1/2 Vs E plot for nano-particle sample.

IV. Conclusions

In conclusion, our study has effectively achieved the synthesis of Germanium nanoparticles (Ge NPs) in deionized water through the utilization of pulsed laser ablation. Notably, we have observed several noteworthy outcomes in the course of our research. Firstly, we have found that as the energy of the laser pulse increases, there is a corresponding decrease in the average size of the Ge NPs, illustrating the feasibility of controlling their size through modulation of energy input. Secondly, we have demonstrated that higher ablation pulse energies result in a heightened number density of Ge NPs, suggesting the potential for more efficient production processes. Most significantly, our work has revealed that the Ge NPs produced in this manner exhibit size-dependent blue luminescence, a feature with exciting implications for their utilization in optoelectronic devices and sensing applications. Overall, these findings underscore the adaptability of pulsed laser ablation as a precise method for tailoring Ge NP characteristics and highlight their promising optical properties, which could significantly impact advancements in a wide array of technological domains.

Conflict of Interest

Authors declare that they have no conflict of interest.

V. References

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