



Tuning Hybrid Nano-semiconductor-glass Via High Intensity Laser

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Abstract

Conceptually, the high intensity laser represents the simplest thin film deposition techniques that consists of both a target and a substrate holders housed in a vacuum chamber with a high powered pulsed laser as the external energy source for evaporation of target material (Semiconductor Glass). Using deposit thin laser films three ranges of frequencies were produced: (0-15,000 mJ/cm²) as a result tuning of semiconductor was satisfying condition, while the second, 0-33,000 mJ/cm² as a result tuning of semiconductor had a stable condition and the last 0-100,000 mJ/cm² as a result tuning of semiconductor was unstable condition. The results demonstrate a decrease in resistance due to charging the semiconductor glass by high intensity laser as well as a superior charge efficiency and lifetime of semiconductor glass coated cells compared to high intensity laser. The current increase in the charge appeared proportional with extra energy stored of the semiconductor glass coated electrodes at 2Co (>23%) in comparison with control. It is concluded that an increase in the capacity of semiconductor glass may address the main difficulty for utilizing the high intensity laser chemistry for future demands.

Key Words: High Intensity Laser (HIL), Hybrid Nano-semiconductors, Laser Processing, Tuning.

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Introduction

The high intensity laser pulses have several characteristics that make them useful for a plethora of applications i.e. fast time resolution, high spatial resolution, high bandwidth and the potential for high intensities (Stoica, *et al.*, 2018; Greetham, *et al.*, 2010). Common applications include pump-probe experiments to study electronic and vibrational dynamics in solids ultrafast spectroscopy time-resolved spectroscopy which benefits from the high temporal resolution provided by femtosecond (fs) laser pulses to probe characteristics and material processes (Sarger and Oberlé, 2005). Intensities in excess of 1022 W/cm² have been achieved in laboratory extreme physics lasers with 1013 W/cm² and above, directed onto solid targets, allow the study of physics at extreme conditions i.e. probing non-linear quantum electrostatics on a table top (Lee, *et al.*, 2015).

Biomedical applications ultrafast lasers have become important in ophthalmological applications on account of their reduced collateral tissue damage during surgical procedures i.e. LASIK (Lubatschowski and Heisterkamp, 2003). Moreover, ultrafast lasers have also been demonstrated to produce nano-materials i.e. laser induced periodic structures (LIPS) and nanoparticles. Materials processing ultrafast lasers are widely used for micromachining, exhibiting superior performance, due again to causing less damage to surrounding material (Yang, *et al.*, 2019).

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Amplification is required to achieve higher intensities, which is limited by the damage threshold of the internal optics of the laser. The enabling step for extremely high-power ultrafast lasers to achieve intensities beyond 10^{13} W/cm² is Chirped Pulse Amplification (CPA) developed by Gérard Mourou and co-workers in the 1980's (Cerami, *et al.*, 2017).

High intensity laser (HIL) conceptually is amongst the simplest thin-film deposition techniques which consists of a target holder and a substrate holder housed in a vacuum chamber with a high powered pulsed laser as the external energy source to vaporize the target material and deposit thin films. Excimer lasers are the primary source for laser, with a pulse duration on the order of a nanosecond and a pulse energy on the order of a joule. Deposition can be done under vacuum or with a gas atmosphere of choice. The basis of HIL is to replace the nanosecond excimer laser with a much shorter pulse (ultrafast) laser (Morou, *et al.*, 1998). In contrast to an excimer laser, which vaporizes or "ablates" material from a deep (~micron) region below the irradiated target surface, the HIL has been demonstrated to produce nanoparticles under vacuum. One of the aims of this paper is to tune hybrid semiconductors nanoparticle with HIL. The HIL band, known as the disorder band, represents a ring breathing mode as well as an in-plane vibrational mode in the graphene sheets which is sensitive to the amount of graphitically bonded layers present. The HIL, also is a deposition technique which involves an ultrafast laser to ablate a target of any given material to produce a thin film. With HIL, instead of having a continuous thin film, the deposited films consist of a large number of nanoparticles that are generated in the ultrafast laser ablation plume and are collected and tightly packed on a substrate (Huang, *et al.*, 2019). The HIL's beam passes through a set of condensers to focus down onto the target of choice using germanium, semiconductor glass, and graphite. Measuring the height profiles with laser revealed another interesting observation that the semiconductor nanoparticles are not spherical when deposited on the substrate, but rather shaped more like platelets. This type of oblate spheroid shapes has been seen in semiconductor glass and nickel in other works. They may therefore be attributed to particles that have not completely cooled and are slightly molten when reaching the substrate, akin to the pattern a raindrop makes when it splashes on a car windshield.

Objectives

To investigate the properties of hybrid semiconductor nanoparticle (HSCNP) thin glass produced by high intensity laser (HIL) to develop tuning system for hybrid semiconductor-glass using nanoparticle thin films produced.

Materials and Methods

The color of the plume would change whenever the laser is sufficiently out of focus. To study how the plume changes spectrally as a function of focus spot size, which effects the intensity and influence at the target, the laser-focusing lens was moved at various distances from best focus. The particle size distributions, examined for semiconductor glass and germanium nanoparticles are produced with HIL. The nanoparticles are deposited directly on holey carbon coated copper TEM grids at 30s for germanium, and 45s for semiconductor glass in a chamber background pressure of 4×10^{-7} Torr. Two samples of each material are prepared, one at best focus another with the focusing lens 4.5 cm out of focus.

The nanoparticles generated are collected on a substrate of either glass or holey carbon coated laser grids. Since the laser beam is incident at 45° from the target normal, the peak intensity and fluency for the first set of optics have 6.5×10^{14} W/cm² and 98 J/cm², respectively. The second set of optics, with a single lens for focusing, provides a peak intensity and fluency of 2.6×10^{13} W/cm² and 3.9 J/cm². The deposition process is housed a vacuum chamber operating with a background pressure of about 4×10^{-7} Torr. The substrate holder contains a quartz-halogen filament heater capable of heating the substrate up to 800°C whenever necessary. The glass substrates used were either borosilicate glass or quartz of dimensions 2x50 mm in size and 1 mm thickness. The plasma plume produced in this set up for semiconductor glass, germanium, and aluminum Optical spectroscopy of thin film semiconductors can give insight towards their electronic structure by measuring their wavelengths transparent or opaque i.e. a broadband light source (quartz halogen lamp with a blackbody spectrum of 3,200 K). The latter was used to aluminate light through a sample and the spectrometer used to measure the optical transmission spectrum is the Control Development 2D model with a spectral range of 305-1,000 nm.

To determine whether or not the HIL nanoparticle films could act as an electrically continuous thin film two germanium nanoparticle film samples



were prepared by HIL i.e. one deposited at a substrate temperature of 450°C another at 550°C at a fluency of 98 J/cm² and an intensity of 6.5x10¹⁴ W/cm². An increase from 450°-550°C resulted in an increase of almost 5 folds at 5.2K and almost 3 folds larger at 269K. A combination of further crystallization and sintering of the nanoparticles can explain this. The majority carriers are holes, with a positive 2D Hall coefficient. This mobility is considered small compared to the bulk value for Ge of 1900 cm²/Vs for holes (**Brus, 2017**) but is competitive with other thin film technologies i.e. amorphous semiconductor glass with a hole mobility of around 5x10⁻⁴ cm²/Vs (**Zhigilei, (2018)**); Cadmium telluride thin films with a hole mobility of about 30 cm²/Vs organic semiconducting thin films with a mobility of about 9x10⁻² cm²/Vs, and orders of magnitude higher than colloidal quantum dot thin films (**Brownson and Banks, 2015**).

The sample set included several HIL germanium nanoparticle thin films grown at various substrate temperatures and at two different fluencies with a bulk laser and a polycrystalline thin film grown on quartz using sputtering (substrate heated to 500°C) as a reference signal. The two main fluencies used for nanoparticle deposition are 3.94 and 98 J/cm² and substrate temperature ranges from room temperature to 500°C. The characterization of Group (semiconductor glass and germanium) semiconductor nanoparticle thin films produced using HIL, treated as continuous thin films, with a borosilicate substrates and SiO₂ glass 1 mm thick. These films are grown at different substrate temperatures using the sample heater in the vacuum chamber. The ultrafast laser wavelength is 780nm with 800 μJ/pulse at a repetition rate of 1 kHz focused using a fused silica lens with a focal length of 681mm at the laser wavelength (**Amoruso, et al., 2016**); **Ausanio, et al., (2016)**.

It has been proposed and calculated, that an ultrafast laser may be able to directly photoexfoliate one graphene layer at a time, with pulses being on the order of 45 fs; longer pulses would ablate multi-layered graphene (**Maine, et al., 2019**).

Result

The fluency was held to 50 mJ/cm² at 1kHz while a scan speed was 0.1 mm/s. The observed laser induced periodic structure (LIPS) is measured to have a periodicity of 150±22 nm and a width of 140±16 nm with the laser polarization

perpendicular to the semiconductor glass direction. Sapphire laser with 125 fs pulse duration and a repetition rate of 1 kHz produced a periodicity of 170 nm. The structures are similar to those from direct laser scribing. Sheets on the order of almost a micron in lateral dimension, transparent to the electron beam were the main structural component, along with filamentary features. At a lower fluency of 57.1 mJ/cm², filament structure began to disappear, leaving behind graphene sheets, sheet agglomerates, and graphite nanoparticles. The tuning of a hybrid semiconductor-glass ranged from 1-8 with HIL using force range between 0-15,000 mJ/cm² as a result tuning of semiconductor being satisfying [Figs.1-3] (0-33,000 mJ/cm²) and was unstable condition for 0-100,000 mJ/cm².

First application of the high intensity laser attempted has improved the charge acceptance of lead acid battery cells (PbA). The cells used for testing were commercial lead acid batteries using an absorbent glass mat separator (AGM) with a capacity of 0.85 Ah at C/20 rate (42.5 mA), where the C-rate refers to the current that would fully charges/discharges a cell/hr. The electrolyte was 1.265 sg Sulfuric acid (commercial battery acid). ³⁷ The negative plates were half coated with carbon, with a graphite spray coating and semiconductor glass, scanned at a rate of 0.1 mm/s with a fluence of 70 mJ/cm². The high intensity laser is determined by first measuring the amount of charge each cell holds by discharging the cells at a slow constant current (SCC) until a cutoff voltage is reached (1.75 V) from full charge. With the total charge known, the discharge current (while using the same current the capacity measurements were taken with) can be timed to discharge a certain amount of charge and the SoC is the fraction between how much charge is left (subtracting the total capacity by what is removed) and the total capacity; coulomb counting. This method is more accurate than using open circuit voltage (Voc) since it can take a significant amount of time for the Voc to equilibrate.



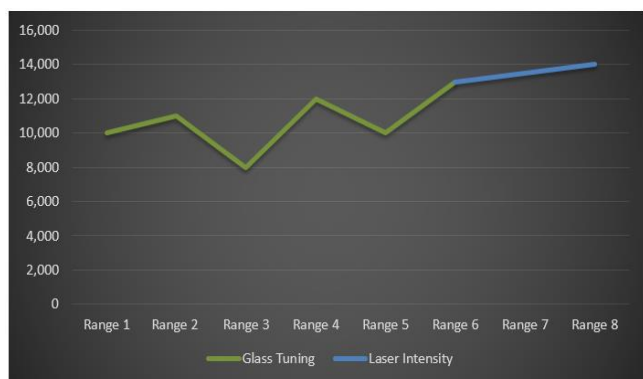


Fig. 1. The tuning of a hybrid semiconductor-glass ranges from 1-8 with HIL using force ranged between 0-15,000 mJ/cm² as a result tuning of semiconductor being satisfying.

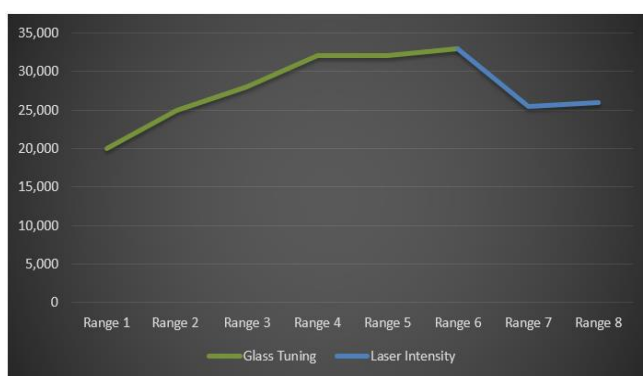


Fig. 2. The tuning of a hybrid semiconductor-glass ranges from 1-8 with HIL using force range between 0-33,000 mJ/cm² as a result tuning of semiconductor being stable.

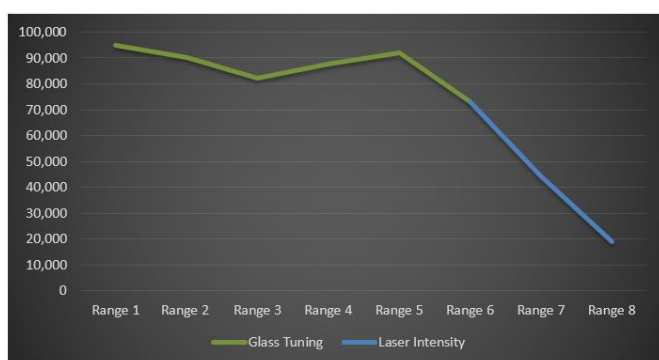


Fig. 3. The tuning of a hybrid semiconductor-glass ranges from 1-8 with HIL using force range between 0-100,000 mJ/cm² as a result tuning of semiconductor being unstable.

Discussion

Semiconductor Glass has been seen in previous works in various materials and with graphite using an 800nm ultrafast Ti: Sapphire laser with 125 fs pulse duration and a repetition rate of 1 kHz, giving a periodicity of 170nm (Ku, *et al.*, 2017; Wang, *et al.*, 2018). The conclusion from these measurements has been that when using an ultrafast laser to irradiate graphite, it may be

advantageous to use smaller particles since the particles can be exfoliated more easily (in the context of making graphene directly by scanning a graphite surface) (Liu, *et al.*, 2017). The next strategy to grow graphene from graphite nanoparticle films has been to use an ultrafast laser to irradiate the side of the film opposite to that facing the receiving substrate a graphene printing technique using ultrafast laser-induced forward transfer (Zhang, *et al.*, 2016; Wang, *et al.*, 2018; Alkaim *et al.*, 2017). Instead of using a continuous thin film and a laser focal-spot, a film of graphite particles (Aerodag G) was coated on a thin piece of optically flat glass, a coverslip (0.13-0.16 mm thick) was irradiated by a focused laser line using cylindrical optics. The coverslip was held close to the substrate by using other coverslips as spacers. The substrate of choice, polished semiconductor glass, due to its smoothness and conductivity had prevented charging effects during SEM imaging without using chemical precursors (Corrigan and Masias, 2018). Scanning rates are held constant to 0.1 mm/s, with the only variable being fluence (85.7, 57.1, and 35.7 mJ/cm²) (Oriaqat, 2016). This research investigated series of battery tests to show the semiconductor glass coating on the 38 negative plate improved the charging performance of the test cells. While the first set of results demonstrated the decrease of battery cell resistance upon charging with the use of semiconductor glass; the second test demonstrated superior charge efficiency and lifetime of semiconductor glass coated cells compared to using untreated graphite coatings on the negative electrode and the control cell. The more increased charge current, the semiconductor glass coated electrodes stored more energy (23% more than the control at the 2C charge rate). The latter addresses the main difficulty for utilizing the PbA chemistry for future demands (Szeto, *et al.*, 2013).

Each cell is charged with a constant current at various rates until 2.45 V is reached followed by a constant current discharge rate of 85 mA, which is held constant for all battery cells (Furukawa, *et al.*, 2010). The specific capacity decreased with increasing charging rate, measured by the discharge time, at all charging rates. This is due to the semiconductor glass consistently had higher capacities at the end of the discharge cycle, indicating better charging performance. For any given discharge current, the longer the cell takes to reach its cut off voltage the more capacity it has. All resultant specific capacities reported from the



discharge plots are mAh/g. A study of capacity change as a function of discharge rates, each cell is charged at a constant current of 85 mA until 2.45V have been reached, followed by a constant voltage charge of 2.5V until the charging current drops to 10 mA. Then the cell was discharged with various rates until a cut off voltage of 1.75V was reached. In this testing configuration, the graphite coatings had slightly larger overall capacities compared to semiconductor glass and the control.

Conclusion

Using an ultrafast laser to irradiate graphite, it may be advantageous to use smaller particles since the particles can be exfoliated more easily via making graphene directly by scanning a graphite surface.

Ethical Approval

There is no correlation between the nature of this research with the ethical aspects nor is there any conflict of interest between the co-authors nor any Governmental bodies regarding the contents of this research.

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