Emission-enhancement of Al and Si nanofibers using dual pulses with varying wavelengths

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Abstract: In this article we report the synthesis of Silicon and Aluminum nanofibers in air as a ambient and at room temperature. Nanofibers are generated by a process of self assembly after the conditions are met for nucleation, inside a plume of plasma created by a femtosecond laser evaporation of the material. They form as interweaving fibrous structures that show certain degree of linear aggregation at high magnification. After experimenting with pulse separation we found that by using two consecutive pulses very close together at two different wavelengths is highly effective when increasing the yield. The creation and the growth mechanism of nanofibers can be explained by the existing theories in hydrodynamics.

OCIS codes: (000.0000) General.

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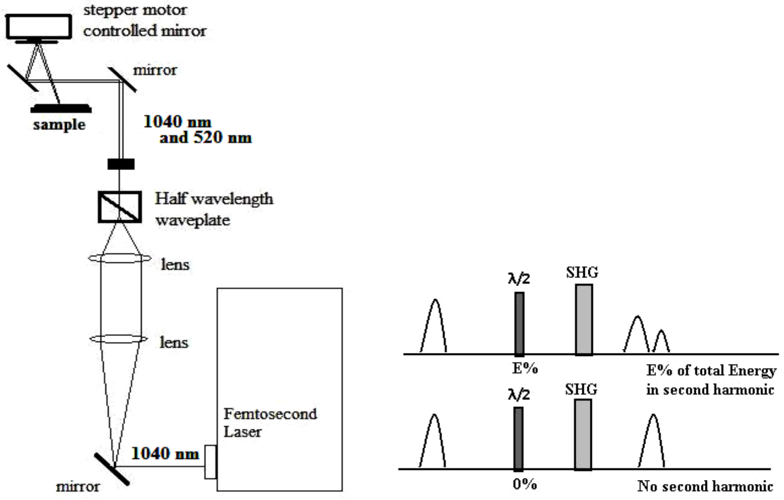
1. Introduction

Nanofibers have numerous potential applications as in nanomaterials that can be applied to microelectronics, biomedical and photonics devices. In our experimental work with nanofibers, we found that the width of nanofibers decrease with decreasing interpulse delay or increasing pulse frequency [1]. To investigate further into physical properties of nanofibers with interpulse delay we decreased the delay from about 0.5 μs to 5 ns. We found that by using two wavelengths (where the second pulse has twice the wavelength of the first) it is possible to increase the yield if the energy of the first pulse is a given integer product of the second pulse. Many of the current hydrodynamic models constructed by researchers suggest that the nanofiber aggregates form by agglomeration of nucleated nanoparticles in a highly pressurized fluid undergoing rapid quenching at a critical point during expansion of the vaporized plume in air [1,2]. The ablated material acts as a superheated fluid as the laser energy increases. It has been found that the nanofibers form by a non-equilibrium, nonthermal phase transformation [1,3] rather than by a thermal nucleation and growth process. In this paper, the process of generating higher yield has been analysed with respect to the ratio of energies in the two pulses and the results have been compared with conventional approaches to increase yield [4,5,6].

2. Experiment



(a) (b)

Fig.1. **(a)** Double pulse generating system (b) the double pulses with varying energies were created as above.

Material is evaporated by an intense laser pulse in the femtosecond regime. Because of the simplicity and low turnaround efficiency we preferred this method. It is a well known technique for thin film deposition as well as for the preparation of nanofiber aggregates and nanomaterials [8]. We used a femtosecond laser capable of producing variable pulse widths and pulse frequencies. The laser source is an all-diode-pumped, direct-diode pumped Yb-doped fiber oscillator-amplifier system capable of producing variable pulse energies up to 10 mJ at a pulse frequency between 200 kHz and 25 MHz. Average power varies between 0-20W. There is a λ/2 wave-plate and a second harmonic generator (SHG) creating two pulses. The single pulse goes through a λ/2 wave-plate that could alter the energy of the pulse created by the second harmonic generator. During the experiment arrays of microvias were drilled into a Silicon target with laser beam at various pulse frequencies and varying energies between the two pulses. The samples were then characterized using scanning electrical microscopy (SEM).

Some researchers [1,3] indicated that the presence of the background gas (air in our case) fundamentally changes the irradiation mechanism for nanofiber aggregate formation. Two phases have been observed in the collected plume material: nanofibers consisting spherical nanoparticles of crystalline Silicon ranging in diameter from 50nm to 450 nm and a highly porous network of amorphous silicon with feature sizes ranging from 1 to 10 nm.

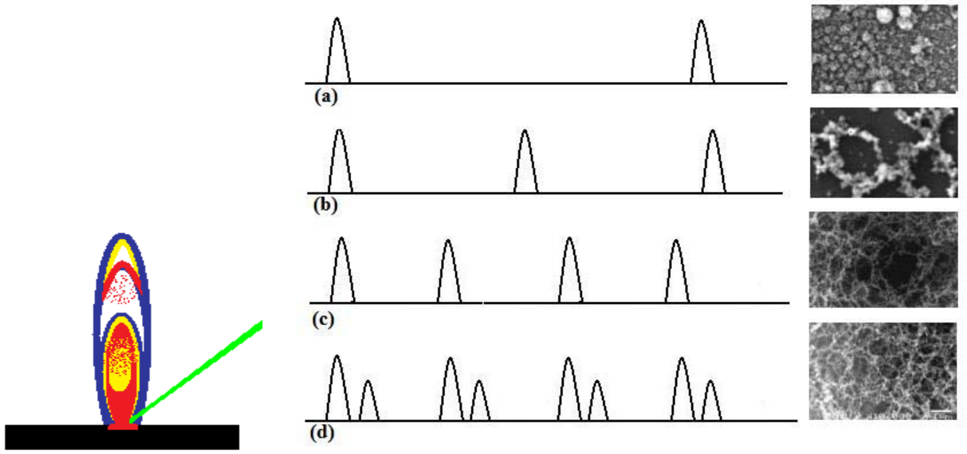


Fig.2. *left*- Evaporation of a solid target into a plume by a femtosecond laser *Right*- (a) long pulse separation results in highly porous amorphous Silicon (b) short pulse separation or high frequency results in a crystalline Silicon structure made up of individual nanoparticles (c) Further increasing of frequency generates nanofibers (d) If a second pulse is added with it's energy equal to a known fraction of the first pulse the yield can be increased (see Figure [5])

At the later stages of the plume formation of two fronts nanoparticle aggregates and atomic constituents of the plume [9,10] are depicted by a schematic drawing in Figure [2]. Characterizing experimental results with an SEM we observed that individual nanoparticle clusters are bonded with each other to form longer nanofiber aggregates (see Figure [4]).

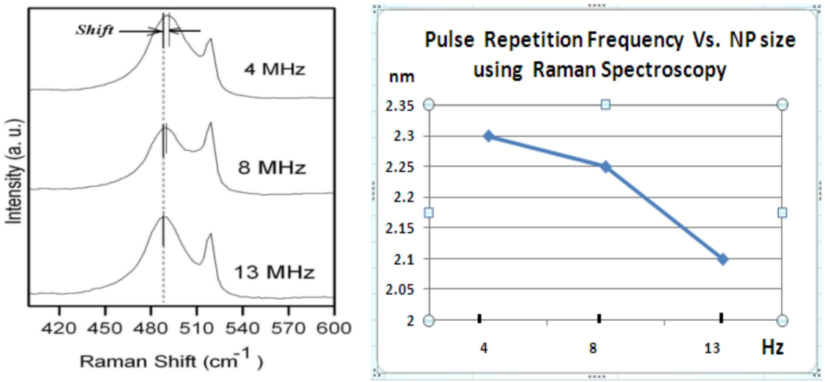
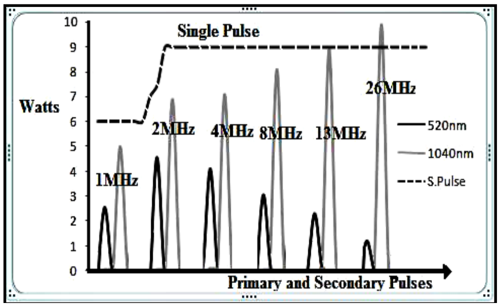


Fig.3. Raman shift of decreasing particle size – will be replaced….

3. Experimental Results

In Figure [4-a], the primary pulses (in grey) and secondary pulses (in black) are drawn next to each other with their repetition rates used by the laser. In Figure [4-b] their Energy ratios are given.

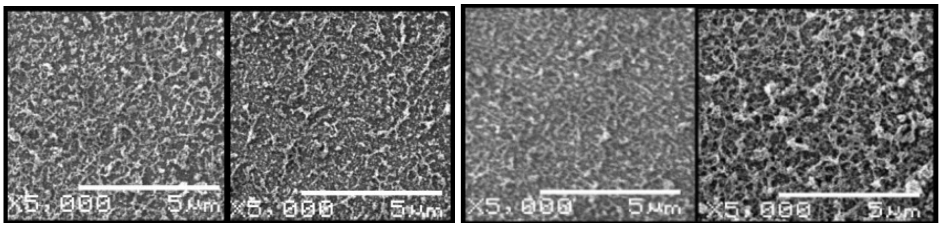


Repetion Rate of Laser	Power of First Pulse (watts)	Power of Second Pulse (watts)	Ratio	Power of Single pulse (watts)
1 MHz	2.5	5	2	7.5
2 MHz	4.5	6.9	1.5333	11.4
4 MHz	4	7.1	1.775	11.1
8 MHz	3	8.1	2.7	11.1
13 MHz	2.2	8.9	4.045	11.1
26 MHz	1.2	9.9	8.25	11.1

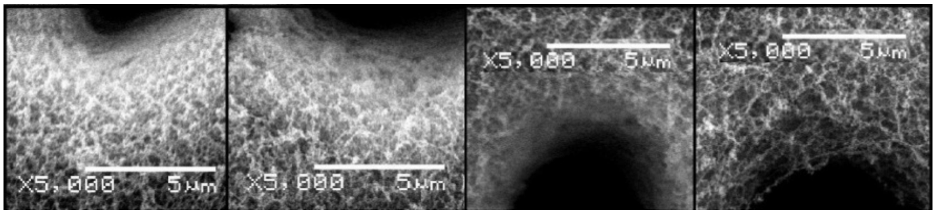
(a) (b)

Fig.3. (a) At six different repetition rates, the double pulse profiles can be shown as above with different energies in pulses. The experiment was repeated for the single-pulse ablation for comparison. The average time delay between pulses is 5-10 picoseconds. (b) Ratios of power (in Watts) in the DPVW at different laser repetition rates and the power (in Watts) of single pulse laser at the same repetition rates

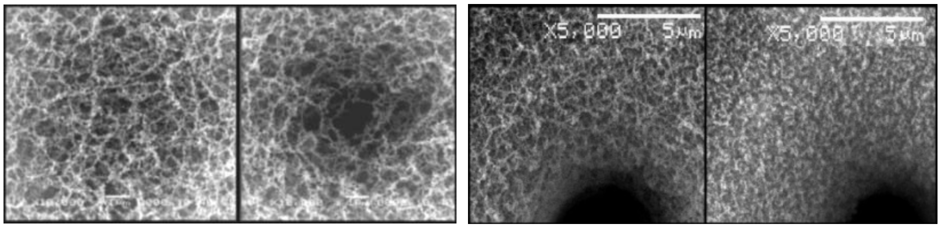
Fig.4. [below] : The following pictures shows the contrast in nanofiber aggregate formation for different pulse ratios for double (on left) and single (on right) pulses.



W1/W2 = 2 W1/W2 = 1.53



W1/W2 = 1.775 W1/W2 = 2.7



W1/W2 = 4.045 W1/W2 = 8.25

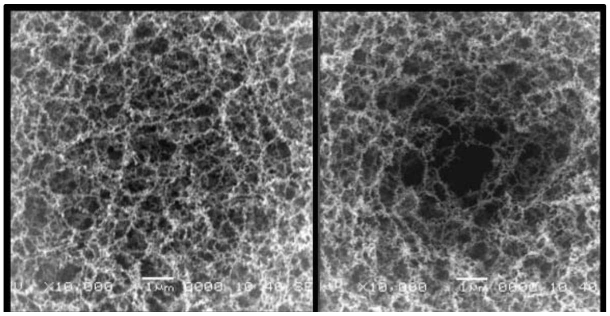


Fig.5. : Enlarged figure of W1/W2 = 4.045 showing higher yield of nanofibers produced by DPVW

4. Discussion

4.1 Pulse energy ratios

Among the various explanations for emission enhancement, several authors have suggested that it occurs mainly due to a combination of increased material emission and increased plasma volume [4]. Rai et al. [5] reported the possibility of droplets and large clusters entering the plasma after impact of the first laser pulse on a liquid jet target and thus increasing the effective density of emitting species in the plasma. Mukherjee et al. [6] suggested that the main factor responsible for the increased expansion of the dual pulse plume is the enhanced plasma temperature. Angel et al. [7] indicated that the increased emission intensity is mainly the result of a larger plasma, which is evident from a comparison of single pulse and double pulse images of plasmas. In spite of what all the previous researchers have done using double pulses, our main goal in this paper is to introduce a enhancement effect for the nanofibers using wavelengths that are different in each of the pulses with a fixed interpulse delay and different energies in each pulse. Therefore we prefer to call them “dual pulses with varying wavelengths”

We will show how a simple analogy between the energy of the bandgaps, and the ratio of pulse energy contributions to the lattice can lead to a formula that can predict the energy ratios for increasing emission in Si and Al. This formula, is derived through an inductive argument. Therefore it is not a generally acceptable formula for all materials except for Al and Si. In our case we are confident about the validity of the conclusive result since it agrees with the work done by other researchers to increase yield using classical arguments for Si and Al [4,7]. We have used the wavelength of primary pulse as 520 nm and the secondary pulse as 1040 nm.

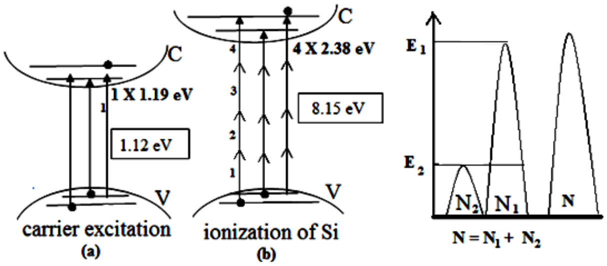


Fig.6. : It takes one photon for a single carrier to overcome the bandgap of secondary pulse 1.12 eV in Si Fig.5-(a) and simultaneous absorption of four photons to ionize Si to Si+ by primary pulse Fig.5-(b).

For both pulses. $E = h\nu = hc/\lambda = (1240\ eV.nm)/\lambda$

$E_{520\ nm} = 2.38$ eV and $E_{1040\ nm} = 1.19$ eV - h is Planck's constant and c is the speed of light

If (N_1/N_{Total}) is the fraction of photons in the 1st pulse and N_2 / N_{total} is the fraction of photons in the 2nd pulse. The number of photons that does Si+ ionizations by the first pulse is equal to (4 x 2.38 x N_1/ N_{total}) eV. Carrier excitations from valence to conduction band from second pulse = (1 x 1.19 x N_2/ N_{total}) eV. Taking the ratio of the first pulse to the second pulse :

$$\frac{[E_{520\,nm}]}{[E_{1040\,nm}]} = \frac{4\,x\,2.38\left[\frac{N1}{N_{total}}\right]}{1.19\left[\frac{N2}{N_{total}}\right]} = \frac{4 \text{ x } 2.38\,[N_1]}{1.19\,[N_2]} \qquad \text{Eqn.(1)}$$

Only 1/3 of the incoming photons go towards ionizing Si into Si+[11]. Remaining 2/3 of the incoming photon energy goes into phonon excitation [11]. Using this information in the above equation [1] gives a theoretical estimate ;

$$N_1 + N_2 = N_{total}$$

1/3 N_{total} (photons that ionize) + 2/3 N_{total} (photons that go into carrier excitation) = N_{total}

$$\frac{4 \text{ x } 2.38\,[N_1]}{1.19\ [N_2]} = \frac{4 \text{ x } 2.38\,[1/3]}{1.19\ [2/3]} = 4.0 \qquad \text{Eqn.(2)}$$

In Al, 2/3 of the carriers go into phonon excitation. Or in other words only 1/3 of the absorbed energy goes into ionization. This information is used in equation [2]. Al has a bangap of ~ 7 eV.

Our theoretical estimate gives ; $\frac{3 \text{ x } 2.38\,[N_1]}{1.19\ [N_2]} = \frac{3 \text{ x } 2.38\,[1/3]}{1.19\ [2/3]} = 3.0$

These results for Silicon and Aluminum agrees with the energy ratios for the two pulses in the double pulse experiment done by Babushok et al.[4] and Rai et al [5]. The significant difference in our experiments is that we have used two different wavelengths in the primary and the secondary pulse.

5. Conclusion

In this work our focus has been on synthesis and emission-enhancement of nanofibers. Much of the current research using double pulses have been done to study pulse separation effects on nanoparticle sizes and to study their size distribution curves. Our research introduces a few parameters to the previous work that changes the results significantly. When we started to increase the pulse frequency, changes in the nanoparticle texture becomes evident. The result was a fiber like agglomeration due to self assembly. Next we brought the pulses 5ps apart and their wavelengths changed to have the primary wavelength, half the secondary wavelength. The experiment was repeated for different power ratios (or energy ratios). We observed a new phenomena that has not been seen before while producing nanofibers at energy ratios unique to each of the materials Si and Al. This effect can be seen in the images characterized by the SEM. We saw a significant increase in emission. Therefore we conclude that when the pulses are very close to eachother as similar to the double pulse approach (5 picoseconds in our work) and their energy and wavelengths are altered to agree with a given ratio for each material, the yield is enhanced significantly for Si and Al.