

Magnetic Field Controlled Nanofiber Generation For Nanoelectronic Applications

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ABSTRACT

It is important to manipulate the density of nanoparticles on a substrate subjected to laser ablation. Although there have been many advances in this area, a modern approach to controlling the nanoparticle trajectories is still required. In this paper we have summarized such an approach for changing the projected paths of nanoparticles by using a static magnetic field. This enables us to control their density in specific locations and their self assembly into nanofibers in these areas. The concentration of nanoparticles can also be redirected towards a quadrupole lens and transported into other applications. From a classical perspective we experimentally showed that the nanoparticle aggregates were concentrated at locations consistent with Lorentz force. We have also explained this phenomenon with a modern approach that gives more accurate estimate for the direction of nanoparticles and where these nanoparticles would create nanofibers. Therefore our findings can be used to understand how nanoparticles react under the influence of magnetic fields from a modern perspective and control their growth in designated areas on a two dimensional substrate.

KEYWORDS : magnetized, ablation, plasma, femtosecond, paramagnetization

1.0 INTRODUCTION

Nanoparticles have attracted much interest in the nanotechnology applications due to their huge potentials in medicine and new engineering materials. Several methods have been developed to generate nanoparticles in large quantities, among which laser ablation is desired because of simplicity in configuration and short process time. Recently, femtosecond laser ablation has been investigated for nanoparticle generation and it was observed that the nanoparticles generated by femtosecond laser ablation presents unique characteristics, compared to nanoparticles that are generated with conventional long pulsed lasers. The differences in ablation characteristics among femtosecond, picosecond and nanosecond lasers are discussed in detail in the reference [1]. Our recent research revealed that fibrous nanoparticle aggregates can be created by laser ablation of a target material in ambient atmosphere at room temperature [2] with femtosecond laser ablation.

This paper concentrates on controlling the trajectories of these particles and explaining through a modern perspective using quantum mechanics how the particle trajectories can be controlled by changing the magnetic potential energy gradients and the kinetic energy of nanoparticles. It will be shown that depending on the orientation of the magnetic moment of the nanoparticle the magnetic potential gives a positive or negative gradient for the potential energy. The highest negative gradient of potential energy is the path that the particle takes in the magnetic field.

2.0 EXPERIMENTAL SETUP

We used a femtosecond laser capable of producing variable pulse widths and pulse frequency. The laser source is an all-diode-pumped, direct-diode pumped Yb-doped fiber oscillator and 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. The samples obtained were characterized using scanning electrical microscopy (SEM, TEM and Raman Spectroscopy). In the current analysis for this paper our SEM results provided a wider aerial view of the ablated substrate which gave us enough information for characterization.

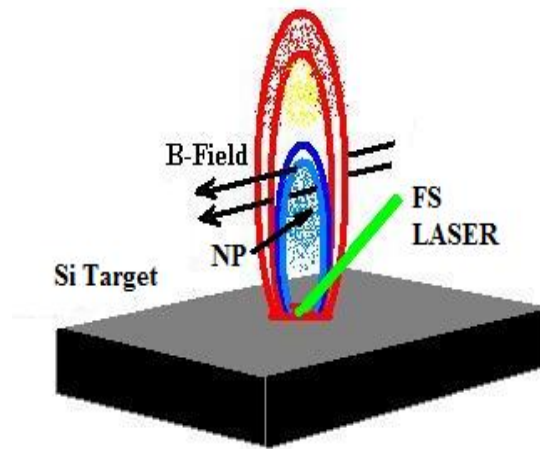
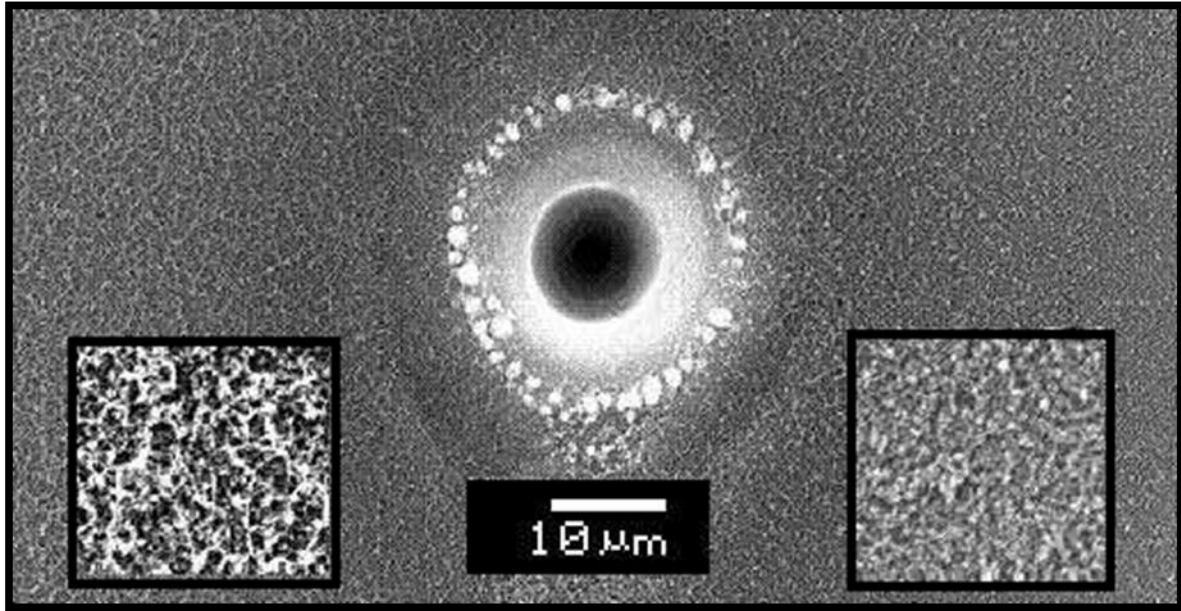


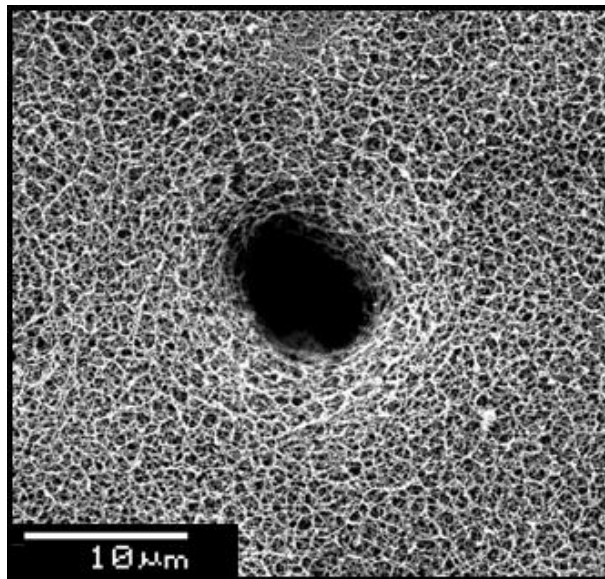
Figure [1] : Setup for investigating the magnetic effects on the sample.

3.0 EXPERIMENTAL RESULTS

We observed that the formation of nanofiber aggregates in Silicon were deviated to either the left or the right half around the ablated area if the magnetic field is directed upward or downward showing a clear difference between the two sides. When the Lorentz force law is applied to Figure[.], direction of the higher concentration of fibers on the substrate depended on the of velocity of the plasma and the magnetic field direction.



(a) *To be replaced by a better picture*



(b)

Figure [2] : Femtosecond laser ablation under the influence of magnetic field. Large amounts of fibrous nanostructures were observed, as shown in Figure [2] left hand side. (b) Femtosecond laser ablation without the influence of magnetic field. Fibrous structures have formed uniformly.

The asymmetric result seen in figure 2 can be explained using a classical viewpoint. The Lorentz force can be written as $\mathbf{F} = +nq (\mathbf{V} \times \mathbf{B})$ where v is the velocity toward the top of the page. Where \mathbf{V} is the upward velocity of the plume, perpendicular to the substrate. Taken the vector product with \mathbf{B} (towards top of the page as in Figures 2 and 3) gives the force \mathbf{F} to the left for a single ion in the plasma. The outward ejection pattern of nanoparticles are further evident when the ablated points are zoomed outward as below in Figure [3].

4.0 Discussion

4.1. Basic phenomenology of bulk magnetism

By using quantum mechanics, it is possible to explain how magnetic fields can control nanofiber generation through crystal-field interaction, exchange interaction and spin-orbit coupling [3]. When a material is exposed to a magnetic field \mathbf{H} , a magnetization $\mathbf{M} = \chi \mathbf{H}$ is induced. The susceptibility χ , defining the response of the system, depends on the nature of the atoms and the field they are exposed to. In order to explain in a qualitative way the magnetic behavior of matter, it is sufficient, in first approximation, to treat each atom as a single, independent magnetic dipole moments. This dipole moment can be induced by an external field.

The atoms that do not possess a ferromagnetic moment e.g. as Si in our case, the effect of an applied magnetic field \mathbf{H} will be the generation of an induced moment \mathbf{M} . This effect is encountered in many materials. However due to its small absolute value, it is often hidden by other stronger magnetic responses and it is observable only in those materials in which all electronic shells are filled. If the atoms consists of intrinsic magnetic moments, they will be randomly oriented if $\mathbf{H} = 0$, but they will align when an external field is applied. This paramagnetic response will be positive and relatively stronger ($\chi \sim 1/1000$) with respect to the

diamagnetic component ($\chi \sim 1/100,000$). The magnetization from a small field H to absolute temperature T ratio is given by the susceptibility, described by Curie's law :

$$\chi \propto \frac{H}{T}$$

If the intrinsic magnetic moments interact with each other, their energy is minimized for parallel (ferromagnet) or antiparallel (antiferromagnet) alignment. However, in the ferromagnetic case a complete alignment of all magnetic moments would produce too high a total magnetostatic energy for it to be the equilibrium configuration. As a consequence, magnetic domains are created: in each domain all moments are rigidly coupled but different domains can be oriented in different directions. The total magnetization can thus average zero. When a magnetic field is applied, in each domain, all moments start to align parallel to it until a saturation magnetization is obtained.

Until now, an assumption has been made that every atom behaves as if it were isolated. This condition is not satisfied in metals and semiconductors, where the conduction electrons are delocalized over the whole crystal during laser ablation. The origin of magnetic behavior in this case is more complex and strongly related to the quantum mechanical features of the constituent atoms. In order to understand the development of magnetism in bulk metals, it is, necessary to understand the origin of the atomic magnetic moment.

4.2 The origin of atomic magnetic moment

First let us look at the origin of magnetism in bulk matter, first let us look at the formation of magnetic moments in atoms. Let us consider an atom in a homogeneous magnetic field \mathbf{H} . The Hamiltonian for the Z electrons, each having an intrinsic spin magnetic moment $\mathbf{m} = 2\mu_B \mathbf{S}$ and a momentum \mathbf{l} , is : $H = H^{(0)} + H^{(1)}$. Where all the terms containing the magnetic field have

been grouped in $H^{(1)}$, that can be treated as a perturbation of $H^{(0)}$. Hence the energy of the ground state, in 2nd order perturbation theory [3]:

$$E_0 = E_0^{(0)} + \langle 0 | \mathcal{H}^{(1)} | 0 \rangle$$

$$E^{(p)} = \mu_B \vec{H} \langle 0 | (\vec{L} + 2\vec{S}) | 0 \rangle = -\vec{H} \vec{M}_0$$

Magnetic term

The above equation gives the paramagnetic energy of the atom in motion. The paramagnetic polarization term describes the magnetic polarization induced by the magnetic field and give no contribution to the permanent magnetic moment [4]. Consequently the magnetic moment of the atom can be written as :

$$\begin{aligned} \vec{M} &= -\frac{\partial E_0(\vec{H})}{\partial \vec{H}} \simeq \\ &\simeq -\mu_B \langle 0 | (\vec{L} + 2\vec{S}) | 0 \rangle \end{aligned} \quad [A]$$

A differential volume element has an energy of :

$$U = -\mu_o \int_V \vec{M} \cdot \vec{H} dV \quad [B]$$

The force on a differential volume element is :

$$F_i = \mu_o \int_V \vec{M} \cdot \frac{\partial \vec{H}}{\partial x_i} dV \quad [C]$$

4.3 Magnetism in Clusters

We have reviewed the basic concepts of atomic and bulk magnetism. However the system under study (which is made of nanoparticles) does not belong to either of these two classes. When the characteristic lengths of a magnetic system are reduced to the nanometric scale, both extrinsic and intrinsic properties are affected and, furthermore, surface and finite size

effects need to be considered. A comprehensive discussion of all the phenomena that originate from reducing the dimension and the dimensionality of a magnet is beyond the scope of this paper.

The fact that magnetism, as other cluster properties, is very sensitive to the geometrical arrangement has the consequence that every atom will give, depending on the number and distance of its nearest neighbors, a different contribution to the total magnetic moment. The atomic magnetic moment is in fact determined by the spin orbit coupling and the contribution that each atom will give to the total moment will be determined by its coordination number. This topic will be discussed further since super-paramagnetism is the starting point for the interpretation of the magnetic behavior of cluster assembled materials.

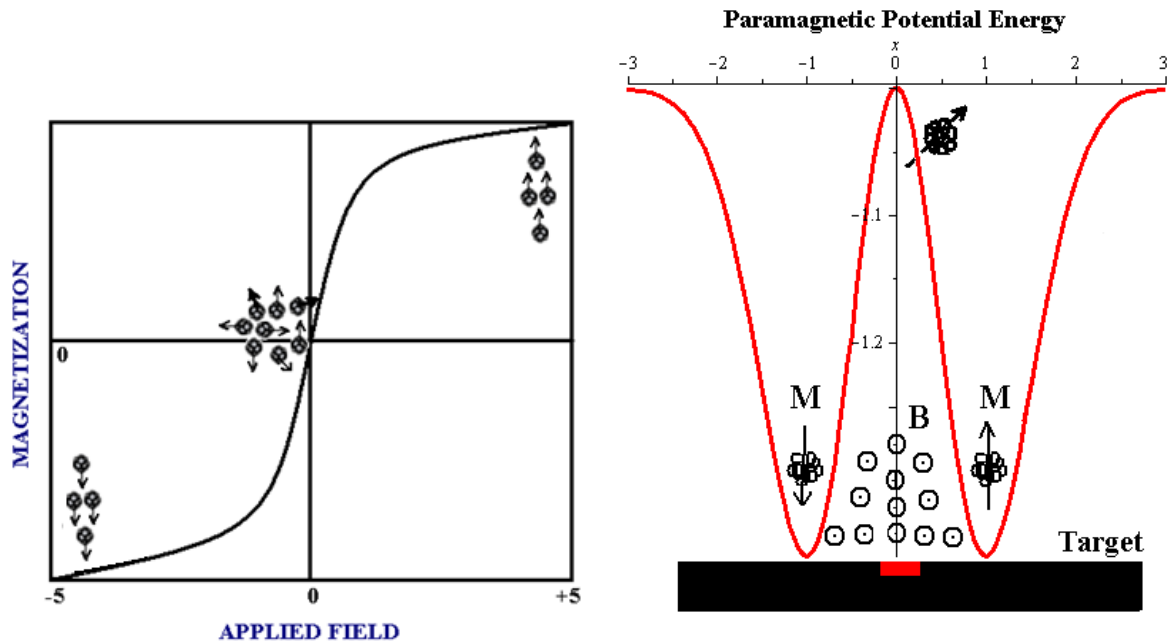


Figure [4] (a) Langevin Function describing the magnetization (b) Equivalent of a double well potential function. Higher the energy of the nanoparticle ensemble more chaotic is the system. Lower energies become stable and magnetic moments uni-directional.

4.4 Superparamagnetism

In a cluster every atom has a magnetic moment of the order of μ_B and all atomic moments are aligned, giving rise to a total magnetic moment μ . Because of quantization, the projection of μ along a fixed arbitrary direction, can assume only discrete values but, if μ is sufficiently big, these values can be considered continuous and a semiclassical treatment is justified. The cluster magnetic moment can, in this approximation, point in any direction of space. Let us now consider an ensemble of identical particles; the total magnetization of the system \mathbf{M} , is given by the vectorial sum of all single magnetic moments. As for the atomic magnetic moments in a paramagnet, the average magnetization will be zero in the absence of magnetic field since all magnetic moments are randomly directed in space. When a magnetic field \mathbf{H} is applied, the magnetic moments will orient in the direction of the field and give rise to a net magnetization. The Hamiltonian of a single macro-spin can then be written as : $H = -\mu H \cos\theta$ where θ is the angle between the magnetic moment and the axis of the magnetic field, that is assumed to be z. The total magnetization can be found averaging over the ensemble:

5.0 On the substrate – controlling the direction of nanoparticles.

The nanoparticles move in the direction where the paramagnetization potential energy given by equation [Eqn B] is minimized. It can be seen from Figure [2] that nanoparticles travelled perpendicular to the direction of the magnetic field. Since $\mathbf{M} \cdot \mathbf{H} = |\mathbf{M}| |\mathbf{H}| \cos(\theta)$ when \mathbf{M} is antiparallel to \mathbf{H} ($\theta \sim \pi$) and gives a minimum value for U . This reasoning explains why the nanoparticle would travel in the direction where the paramagnetic potential energy is minimized and the direction where the force is maximized for the same

conditions. It can be seen from the equation below that increasing flux of the magnetic field \mathbf{H} will also increase the Paramagnetic potential energy $U[\mathbf{x},\mathbf{y}]$.

$$U = -\mu_o \int_V \vec{M} \cdot \vec{H} dV$$

Or in other words the location of the nanoparticles can be expressed as moving in a coordinate system as in Figure [5]. It was explained before in Figure [1] that the most stable direction for nanoparticles is to have unidirectional magnetic moments. In the above equation \mathbf{M} is the magnetization of a nanoparticle and \mathbf{H} is the magnetic field through the ablated vapor. And the force on a differential volume element of nanoparticles is given by :

$$F_i = \mu_o \int_V \vec{M} \cdot \frac{\partial \vec{H}}{\partial x_i} dV$$

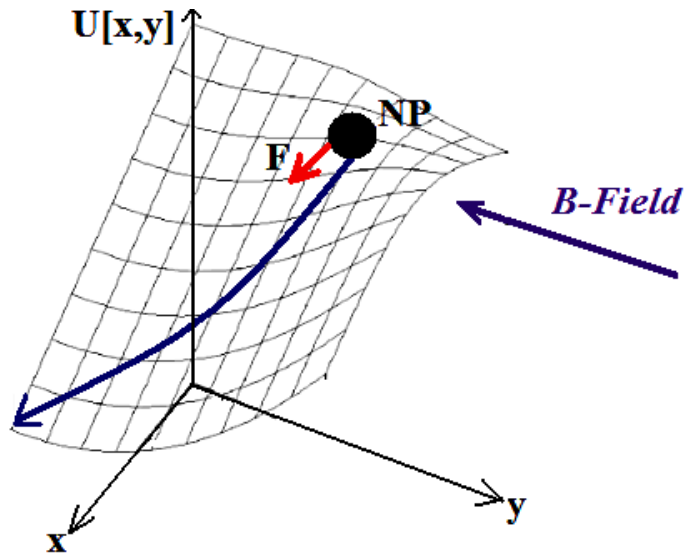
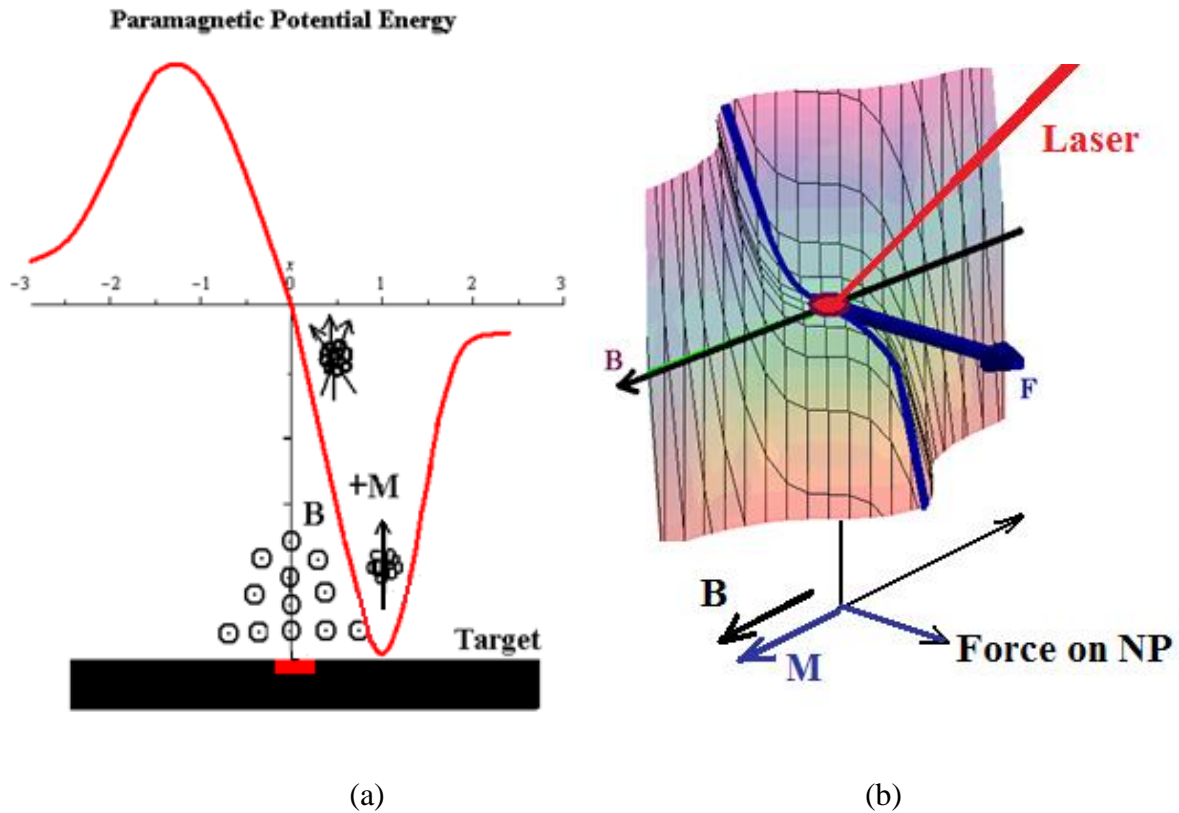
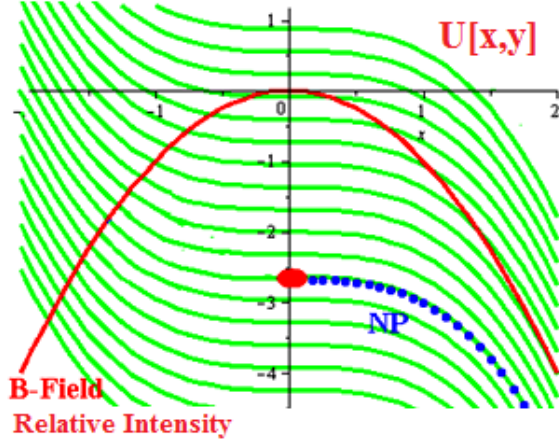


Figure [5] : The Nanoparticle will travel in the direction where the potential energy $U[\mathbf{x},\mathbf{y}]$ is minimized in the Paramagnetic potential energy contour diagram.

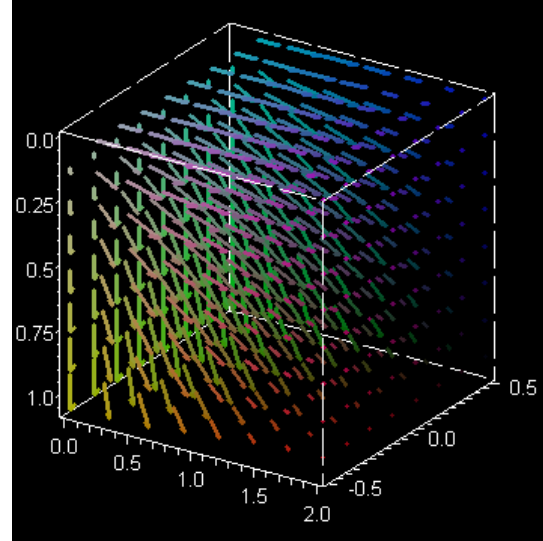
The Fundamental Theorem of Calculus for line integrals implies that $U[x,y]$ can be defined in the following way, $\mathbf{F}_i [x,y] = - \nabla U [x,y]$. Plots of potential energy functions around the ablated hole are valuable aids to visualizing the change of the force in a given region of space.

So that $U[x,y]$ is a scalar potential of the conservative force vector $\mathbf{F}_i [x,y]$ for the i th nanoparticle. In our case $U[x,y]$ is defined as a Paramagnetic potential function that depends entirely on the applied static magnetic field and the Magnetization vector. By manipulating \mathbf{M} given by Eqn[A], the magnetization direction and \mathbf{H} it is possible to find a far more accurate estimation of force \mathbf{F} than that given by the Lorentz Force $\mathbf{F} = +nq (\mathbf{V} \times \mathbf{B})$.





(c)



(d)

Figure [6] : Simulations that predict the trajectory of nanoparticles (a) assuming all the nanoparticle magnetic moment vectors \mathbf{M} , are aligned with the \mathbf{H} -field giving $\mathbf{M} \cdot \mathbf{H} \geq 0$. Therefore the lower (+x) quadrant has the lowest energy and the upper (-x) quadrant has the highest energy (b) Laser ablation, paramagnetic potential, the magnetic field and Paramagnetic moment \mathbf{M} shown by a 3D figure (c) Potential graph and the nanoparticle trajectories from the ablated point (d) concentration of nanoparticles towards lower right quadrant. The steepest slope in the potential function has the highest concentration of nanoparticles which will self assemble to make the highest concentration of nanofibers.

CONCLUSION [not required if Letters]

Through our research we mainly focused on manipulating the direction of the nanoparticles and understanding what parameters control their direction. The material manipulation was done while the vaporized material was still in a plasma stage. If the i th particle has a potential energy U_i then a collection of plasma made up of $+n_i$ ions would have the same localized potential energy. This $+n_i$ collection would move in the same direction as the other differential volume elements, would move while self assembling similar to the above fundamental principle to reduce energy. The final result would be strands of nanofibers in a location controlled by the experimental parameters such as paramagnetization \mathbf{M} , Magnetic field \mathbf{H} and the laser fluence.

Since crystallization occurs after condensation of plasma [8], we believe that the nanoparticles are arranged in fibers according to some Si paramagnetization [9] that disappears in the case of Silicon after the static magnetic field \mathbf{H} was removed. This enhancement effect in chosen locations by laser ablation along with the magnetic field gives us the ability to control their growth and collect them for other applications.

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