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# Synthesis of Nanoscale Tips Using Femtosecond Laser Radiation under Ambient Condition

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**Abstract** We report a unique growth of platelet-shaped nanoscale tips of transparent dielectric using femtosecond laser radiation at MHz pulse repetition rate with nitrogen background gas flow under ambient condition. The tips grew with sharp nanoscale apex while their base and lengths are of the order of few hundred nanometers. In the absence of nitrogen, the irradiation leads to nanofibrous structure formation. The collision between the nitrogen gas atoms and the vapor species slows down plume expansion and lead to an increase of nanoparticles size. This prevents the fibrous structure formation and provides appropriate condition for nanoscale tips growth.

**Keywords** Femtosecond laser ablation · Nanoscale tips · Nanostructuring

## Introduction

Nanoscale tips, wires, tubes and rods of semiconductor, ceramic and dielectric materials have been investigated for applications such as probes for scanning probe microscopy, emitters for field-emission-based devices and solar cells [1]. Also there is a significant amount of ongoing research on selective and sensitive optical nanosensors of biological agents. In this context, the current emerging trend in nanoscale research is: controlled synthesis with well-defined sizes and geometries; unravelling their fundamental physical properties and assembly of these nanoscale building blocks into functional devices. The growth of nanoscale tips by conventional vapor transport and condensation processes is explained by either catalyst-assisted Vapor–Liquid–Solid (VLS) or catalyst-free Vapor–Solid (VS) growth mechanisms [1–5]. Ultrafast laser nanostructuring techniques offer advantages of high resolution, high throughput, uniformity, localized heating, simplicity and reproducibility [6–9]. The time scales of heating and cooling of materials with femtosecond laser irradiation are significantly shorter than in the traditional thermal processes [10]. The rapid absorption of energy leads to efficient material removal before significant heat diffusion to the substrate occurs. Femtosecond laser radiation is used to fabricate nano-sized spikes of semiconductor [11], metallic [12, 13] and dielectric surfaces [14], glass nanofibers [15] and nanorods, nanocones of ZnO [16] at KHz pulse repetition rate in vacuum condition. In this study, we report direct synthesis of nanofibrous structure and nanotips of glass using femtosecond laser radiation at atmospheric pressure. Also we intend to discuss the growth mechanisms of nanoscale tips.

## Experimental Methods

The laser source is a direct-diode pumped Yb-doped fiber amplifier system ($\lambda = 1{,}030$ nm) capable of delivering a maximum of 15 W average power at a pulse repetition rate ranging from 200 kHz to 26 MHz. The glass specimens of size 1 cm × 2 cm × 1 mm and composition is 53 mol% $SiO_2$, 23 mol% $Na_2O$, 20 mol% CaO and 4 mol% $P_2O_5$ are used for the present experiment. The specimens are fixed in a two axis translation stage for laser irradiation. Nitrogen

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gas is made to flow the entire interaction zone in a direction perpendicular to the laser beam through nozzles. The laser radiation fluence used to irradiate the samples was 1.5 J/cm$^2$, which is calculated from laser spot size (10 μm), average power (15 W) and pulse repetition rate (13 MHz). The energy per pulse, pulse width and dwell time/interaction time used were 1.15 μJ, 214 fs and 0.1 ms, respectively. The sample is irradiated with multiple laser spots separated by 100 μm using computer-controlled galvanometer scanning system. The entire experiment is conducted under ambient condition.

## Results and Discussion

Figure 1a and b illustrates representative SEM images of self-assembled weblike nanofibrous structure formed on the surface of specimens irradiated with no background gas. The nanostructures are generated due to agglomeration of glass nanoparticles. In contrast, Fig. 1c and d shows images of the irradiated surfaces with nitrogen as background gas flow with 3.92 × 10$^{-5}$ m$^3$/s. For the radiation fluence (1.5 J/cm$^2$) used in the present experiment, the nanoscale tips are formed around the laser-irradiated spots along with resolidified particles. It is evident from SEM images that the tips grow from the redeposited molten droplets and pointing randomly. They have a very sharp apex of the order of few nanometers while their base and lengths are of few hundred nanometers. Further when compared to nanotips, the agglomerated nanoparticles in nanofibrous structure are much smaller in size. EDX analysis of the irradiated surface shows a significant change in the weight percentage of O, Na, Si and Ca (Fig. 2).

Under femtosecond laser irradiation, the energy is delivered into the material in a short time scale that absorption occurs at nearly solid-state density. The energy is first deposited in the electronic subsystem within a layer of thickness of tens of nanometer. In dielectrics, multiphoton ionization and avalanche ionization are considered as the sources during the generation of free electrons [17]. When the density of the free electrons exceeds a certain threshold, enough energy is absorbed to produce macroscopic ablation. The ionized material is removed away from the surface in the form of expanding high pressure plasma. The plasma remains confined close to the specimen surface at atmospheric pressure. Condensation of vapor in the plume lead to the generation of nanoparticles and their aggregate and will be deposited on the surface of the specimen [8]. The laser pulse repetition rate plays a critical role in the formation of nanofibrous like structure. Since at MHz pulse repetition rate, the initial surface temperature is above the melting point, the plume is generated from liquid phase rather solid phase [8]. Vapor condensation starts with nucleation, proceeds with growth of supercritical nucleus and come to a halt due to quenching. For nanoparticles to aggregate and form fibrous structure, a continuous supply of vapor is required to the expanding plume to maintain the nucleus density. The plume generated by successive laser pulses must arrive before the critical time of nucleation. In the present experiment, this condition is met with MHz pulse repetition rate. The cooling time of the nanoparticles generated from the condensation process have been estimated to be about few hundred μs [18]. This time is much higher than the pulse separation time, which is 77 ns for 13 MHz repetition rate. Hence nanoparticles generated from the successive laser pulse are fused to the particles created from the previous laser pulse that are still above the melting temperature and grow as nanofibrous like structure (Fig. 1a, b).

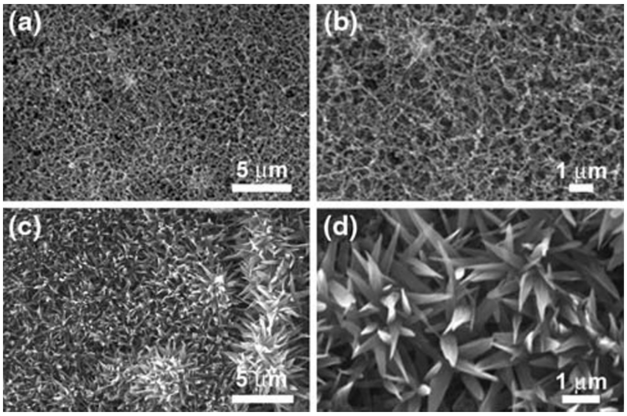

**Fig. 1** SEM micrographs of nanofibrous structure and platelet-shaped nanotips on femtosecond laser-irradiated glass. **a** and **b** without background gas, **c** and **d** with nitrogen background gas

It is evident from the SEM micrographs (Fig. 1c, d) that nitrogen background gas flow at atmospheric pressure influences the surface nanostructuring in two ways. First, it prevents the formation of weblike nanofibrous structure. Further, it helps the growth of nanoscale tips on the irradiated surface. The size of these tips is much higher than the agglomerated nanoparticles size of nanofibrous structure. Generally, during femtosecond irradiation in a reactive background gas such as air or nitrogen, the high temperature and pressure in the plasma plume form gas molecule radicals [19]. The reaction between these gas radicals and ablated products can promote condensation and faster structure growth. The atomic mass of background gas plays a significant role in the plume confinement and the size of nanostructures.

In the present experiment with nitrogen as background gas flow at atmospheric pressure, the plume expansion will be slowed down due to collisions between ablated vapor species and gas atoms and results a delay in vapor

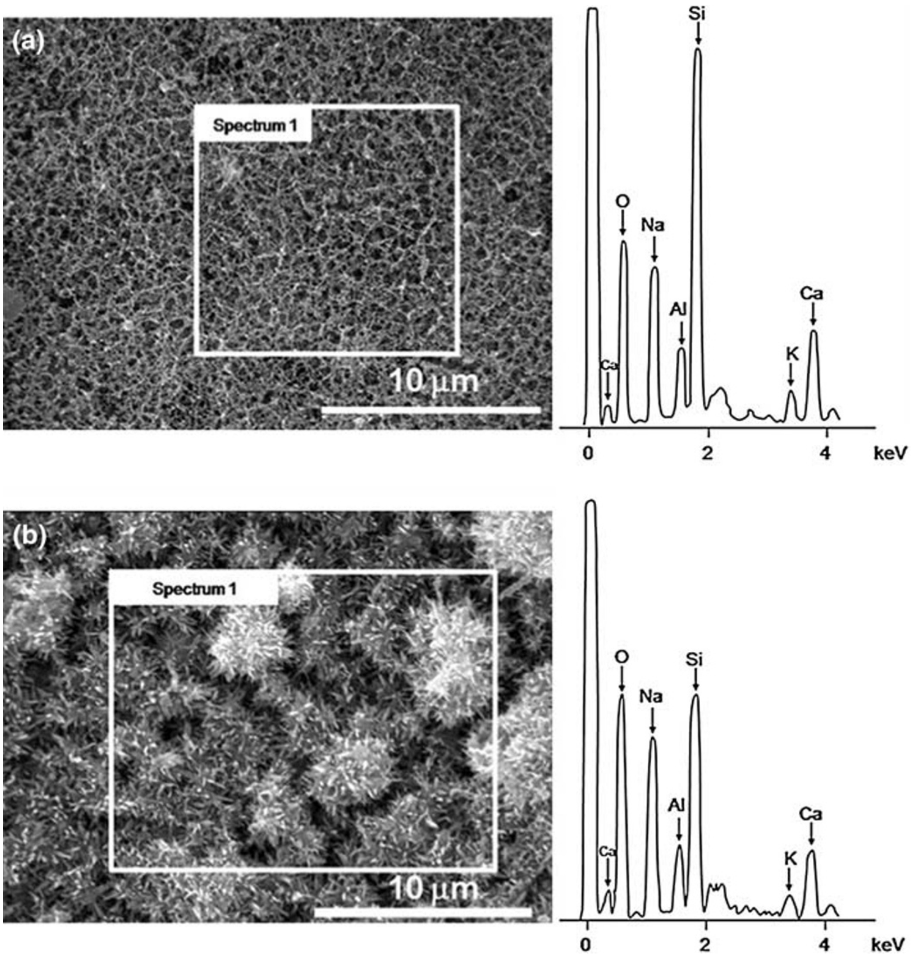

**Fig. 2** EDX analysis of nanofibrous structure and platelet-shaped nanotips **a** nanofibrous structure, **b** nanotips

condensation [18, 20]. This in turn leads to coalescence of several nuclei formed during condensation thereby increasing the nanostrutures size as evidenced from SEM images (Fig. 1). The property of background gas and its pressure influences the cooling rate of nanostructures [18, 19, 21]. In addition, the size of fully grown nanoscale tips when compared to agglomerated nanoparticles suggested that nitrogen gas flow have significant influence on the cooling rate of redeposited molten droplets.

During the expansion of vapor into the background gas, the condensation process is terminated due to mixing of vapor with gas [18]. The characteristic mixing time depends on type of gas and its pressure. The channels for the cooling of formed structures are radiation cooling, heat loss due to evaporation, heat exchange with background gas and heat release due to crystallization. In the present case at atmospheric pressure with background gas flow, heat exchange plays a dominant role in cooling. Since both experiments are conducted at atmospheric pressure, the cooling can be explained considering thermal conductivities of air and nitrogen (26.3 and 25.8 $\mathrm{mWm^{-1}K^{-1}}$, respectively). Since the cooling rate is more without the background gas, the size of the particles is much smaller. In the presence of nitrogen gas, the size of molten droplets was increased due to collisions between vapor species and gas radicals. Hence, these droplets cool by convection and radiation at a slower rate than smaller droplets formed without gas. The slow rate allows the droplets to grow into tip like structures. Though nitrogen influences the cooling rate, its role in the growth of nanoscale tips is still unclear [16]. Further studies are underway to determine the composition of tips, role of nitrogen and the influence of laser processing parameters on the formation of nanoscale tips.

## Conclusions

In summary, a unique technique for the synthesis of nanoscale tips using femtosecond laser radiation with nitrogen as background gas at atmospheric pressure is reported. The tips are oriented randomly with nanoscale apex and their base and lengths are of the order of few hundred nanometers. Irradiation without background gas forms weblike nanofibrous structure. Further studies are required to find composition, control parameters and formation mechanism of these nanostructures.

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