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※ 奈米顆粒製程之高頻矽底超音波噴嘴的研究 ※
※ **Silicon-Based High Frequency Ultrasonic Nozzles for Nanoparticles Synthesis** ※
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奈米顆粒製程之高頻矽底超音波噴嘴的研究

Silicon-Based High Frequency Ultrasonic Nozzles for Nanoparticles Synthesis

ABSTRACT

Design, simulation and fabrication of MHz silicon ultrasonic nozzles using multiple Fourier horns and actual atomization and their applications to micro/nano materials technology have been accomplished through the NSC support. Such nozzles possess a number of advantages over conventional metal-based bulk-type ultrasonic nozzles such as MEMS-based micro-fabrication technology for mass production, much higher ultrasonic frequency and thus much smaller drop diameter, much narrower drop-size distribution, and much lower electric drive power requirement. Monodisperse drops 7 µm in diameter were produced by atomization of water and gold colloid solutions using a 3-Fourier horn 0.5 MHz ultrasonic nozzle. The gold nanoparticles (17 to 30 nm in diameter) spray-coated on silicon substrates remain well dispersed.

Key words: ultrasonic nozzles, multiple-Fourier horn, ultrasonic atomization, monodisperse drops, nanoparticles, impedance, longitudinal vibration, spray pyrolysis

中文摘要

本計畫使用微機電技術在矽晶片研製高頻超音波噴嘴。已經研製成 0.5 MHz 多節喇叭型之超音波噴嘴，並且將水等液體及奈米金顆粒分散液(Gold Colloid Solution or Nanoparticle Dispersion)霧化成功。所得的水滴大小均勻，90% 以上的水滴直徑為 7.0 微米。如此霧化產生之單徑液滴(Monodisperse Drops) 是國際上之首創。

高頻率超音波噴嘴的核心在於多節喇叭型之共振子(Multiple-Fourier-Horn Resonator)。壓電片所產生之縱向超音波 (Longitudinal Mode) 在共振的條件之下、噴嘴尖端處之振幅將大為提昇。由尖端處流出之液體因而產生大振幅之微細波 (Capillary Waves)，接著霧化產生均勻液滴。另外，因為先驅液不需接觸壓電片，故可應用於各種不同先驅液之噴霧熱解而不影響噴嘴之霧化功能。

除了應用於噴霧熱解以量產奈米級顆粒之外，此類高頻率、低耗電率之超音波噴嘴亦可研製成醫藥噴霧呼吸模組或應用於蛋白質等生物奈米顆粒分散液 (Nanoparticles Dispersion) 之噴霧乾燥。

關鍵詞：陶瓷奈米顆粒，噴霧熱解，超音波噴嘴，奈米顆粒，超音波霧化

Introduction

Atomization (spray) is the breakup of a volume of liquid into drops, resulting in a dramatic increase in the amount of surface area available for heat and mass transfer in a chemical reaction. Ultrasonic atomization (liquid atomization by ultrasound alone) and two-fluid atomization (liquid atomization by high velocity air) are commonly used in industrial applications including combustion, spray coating, spray drying, and spray pyrolysis. Two-fluid atomization has the advantage of high throughput, but also has the disadvantage of broad drop-size distribution. In contrast, the drop-size distribution generated by conventional ultrasonic atomization is much narrower [1, 2]. Also, ultrasonic atomization involves Taylor-mode jet breakup of capillary waves (different from Rayleigh-mode jet breakup in ink-jet printing). Because the drop diameter resulting from Taylor-mode jet breakup is much smaller than the channel (orifice) diameter, the nozzle is less prone to channel plugging.

Conventional ultrasonic atomization utilizes either a metal-based bulk-type nozzle with a piezoelectric transducer isolated from the liquid or a nebulizer with a transducer disk in direct contact with the liquid to be atomized. Because of manufacturing difficulty, the highest frequency of the former that is commercially available is 120 kHz, which yields water sprays with a peak drop diameter (the diameter where the peak of a drop-size distribution occurs) of 55μm as shown in Figure 1(a) [1, 3]. Ultrasound-modulated two-fluid (UMTF) atomization combines ultrasonic and two-fluid atomization [1, 4], and is capable of reducing the peak drop diameter to 22-28μm depending on the air velocity (shown in Figure 1(b)).

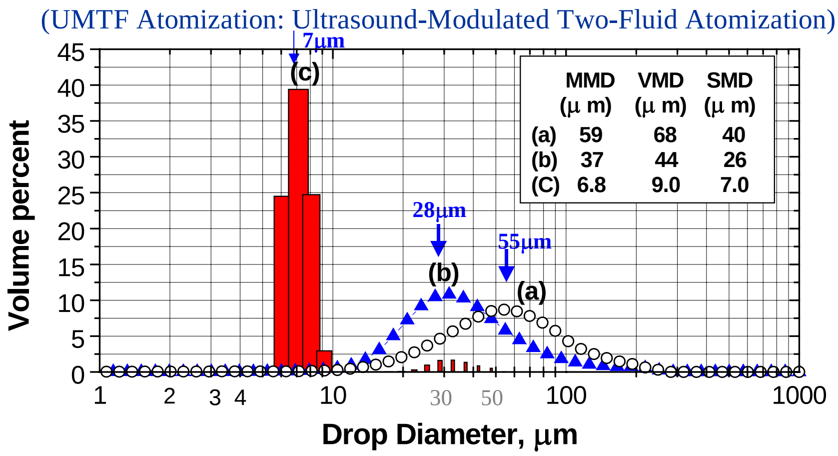


Figure 1 Drop-size distributions for (a) conventional ultrasonic atomization @ 120 kHz and 2.5W, (b) UMTF atomization @ 120kHz, 2.3W, 150m/s air, and 4.1 mA/mL, and (c) conventional nebulizer atomization @1.65 MHz, 90 V.

Ultrasonic nebulizers (basically a piezoelectric transducer disk) are commercially available at frequencies as high as 2.5 MHz. As shown in Figure 1(c), the peak drop diameter generated at 1.65 MHz is 7 μm. However, only a very small fraction of the atomized drops are produced via breakup of the capillary waves with diameters smaller than 10μm [5]. Furthermore, because the transducer is in direct contact with the liquid to be atomized, nozzle performance degrades rather quickly over time.

Silicon-based ultrasonic nozzles, first realized using MEMS technology at 74 kHz [6], possess a number of advantages over conventional metal-based bulk-type ultrasonic nozzles such as potential for mass production using MEMS technology and the ultrasonic frequency far exceeding the 120 kHz limitation of the bulk-type ultrasonic nozzles.

2 NOZZLE DESIGN, SIMULATION, AND FABRICATION

2.1 Design and Simulation of Nozzles

The MEMS-based silicon ultrasonic nozzle is made of a piezoelectric drive section and a silicon-resonator consisting of multiple Fourier horns as shown in Figure 2 [7]. Each horn is of half-wavelength design with a vibration amplitude magnification of two. 3-D simulation was carried out using the commercial ANSYS program [7]. The simulation results for the 0.5 MHz 3-Fourier-horn nozzle used in the atomization experiment are also shown in the figure. Specifically, a pure longitudinal vibration occurs at the resonance frequency of 495 kHz. At this resonance frequency, the vibration amplitude gain at the nozzle tip is equal to the theoretical value of 2^3.

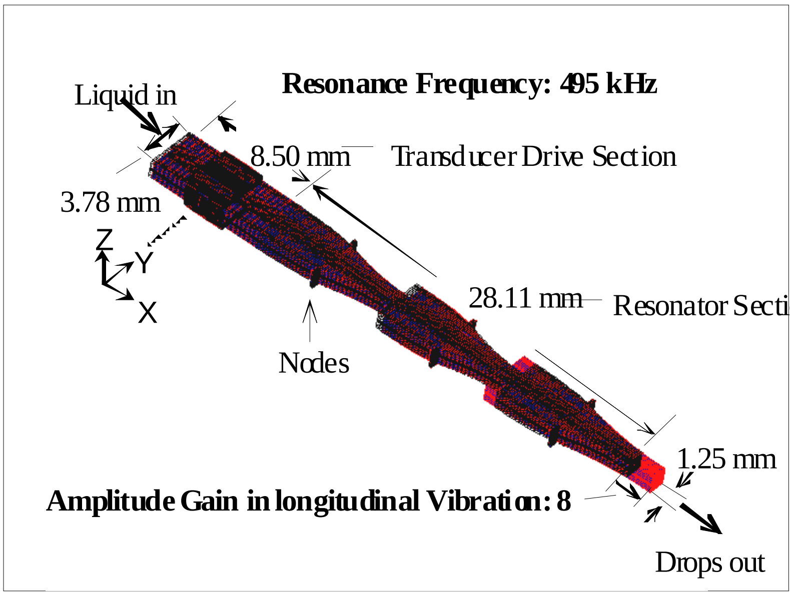


Figure 2 Dimensions and 3-D simulation results on the amplitude gain at the nozzle tip of a silicon-based 3-Fourier-horn 0.5 MHz ultrasonic nozzle.

2.2 Fabrication of Nozzles Using MEMS Technology

Major fabrication steps for the silicon resonator halves (including the base sections where PZT plates are to be bonded) are standard MEMS techniques [7]. Inductive Coupled Plasma (ICP) etching, instead of wet etching, was used because of its capability to produce a smooth and precision finish in cutting through the 530 µm-thick wafer to make resonator halves with a rectangular trough 100µm deep and 200µm wide. Subsequently, two resonator halves were glued together to form a central rectangular channel (200µm x 200µm) for liquid flow. Two PZT plates, one on each side, were then bonded to the resonator at the base section using silver paste.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Atomization Results

As water or Au colloid solution (nanoparticles dispersion) is pumped into the 200 µm x 200 µm channel of the nozzle by a syringe pump at a constant flow rate, ranging from 10 μl/min to 150 μl/min, a liquid drop forms at the nozzle tip but no atomization takes place when the frequency of the drive signal differs significantly from the resonance frequency (see Figure 3(a)). In contrast, a thin film of liquid forms at the nozzle tip and a 0.4 mm-wide sheet of drops is seen when the drive signal is at the actual resonance frequency of 484.5 kHz (see Figure 3(b)). Due to resonance effect of the multiple Fourier horns, the drive voltage (5.5 V) required is one order of magnitude lower than that required in atomization using conventional nebulizers. The resulting drop-size distribution measured with Malvern Particle Sizer 2600c is shown in Figure 4. Clearly, monodisperse drops (over 90%) at a diameter as small as 7 μm have been produced.

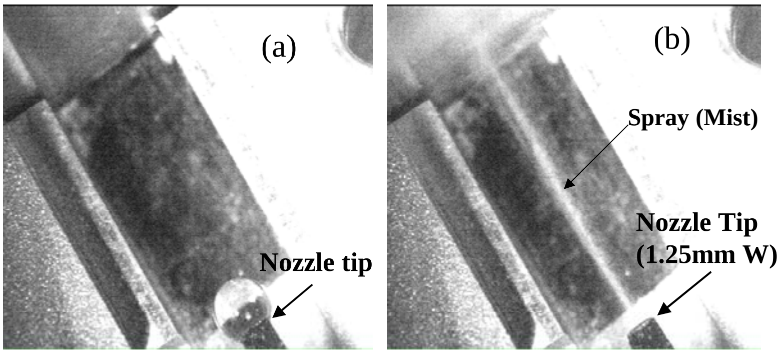


Figure 3 Atomization of water using a Si-based 3-Fourier horn nozzle (nozzle tip 1.25 mm wide and 1.06 mm thick) at the drive voltage of 5.5 V: (a) No atomization and (b) stable atomization at the frequency of 484.5 kHz.

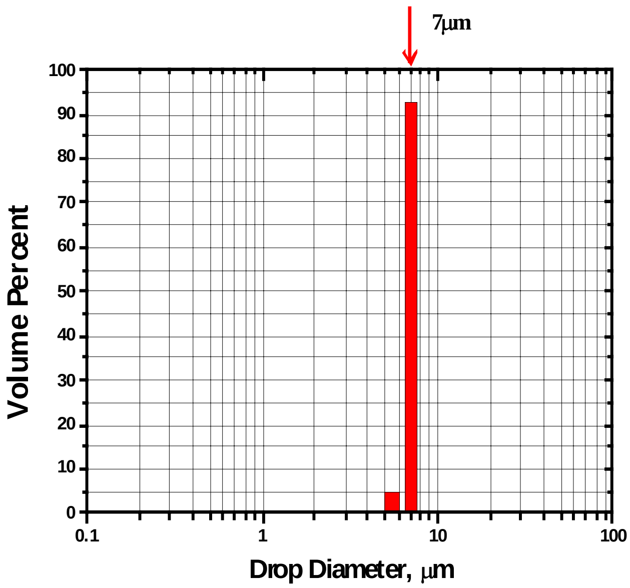


Figure 4 Drop size distribution of atomization using a 3-Fourier horn nozzle at the ultrasonic frequency of 484.5 kHz and the drive voltage of 5.5 V.

Atomization of Au colloid solutions shows that Au nanoparticles have no significant effect on the atomization conditions. The resulting drops are also similar to water drops in both mean diameters and size distributions.

In addition, the Au colloid solution was sprayed on clean silicon substrates for 15 seconds. Since the drops were so small, the sprayed substrates were air dried rather quickly.

They are stored in a covered clean box for characterization using a Scanning Electron Microscope (SEM).

3.2 Characterization of Sprayed Au Nanoparticles on Silicon Substrates

The morphology of the Au nanoparticles on the silicon substrates was examined using a Scanning Electron Microscope (SEM, Philips Model XL 30) with an EDAX energy dispersive X-ray detector for micro analysis of elements. As shown in Figure 5, the Au nanoparticles range from 17 to 30 nm in diameter. They are larger than 15 nm reported in the literature [8], possibly due to a slightly longer reaction time and the fact that the solution has been stored for two weeks before spray on the substrates. Nevertheless, the SEM micrographs show that the nanoparticles are well dispersed on the silicon substrates with no pretreatment. Even the Au nanoparticles within a single drop remain dispersed with no agglomeration. Further study is in progress to determine the limit of such monolayer layout of Au nanoparticles on silicon substrates using such high frequency ultrasonic nozzles.

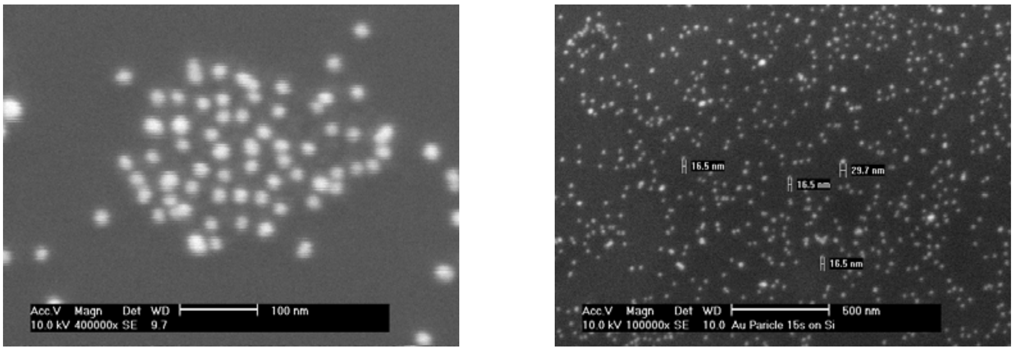
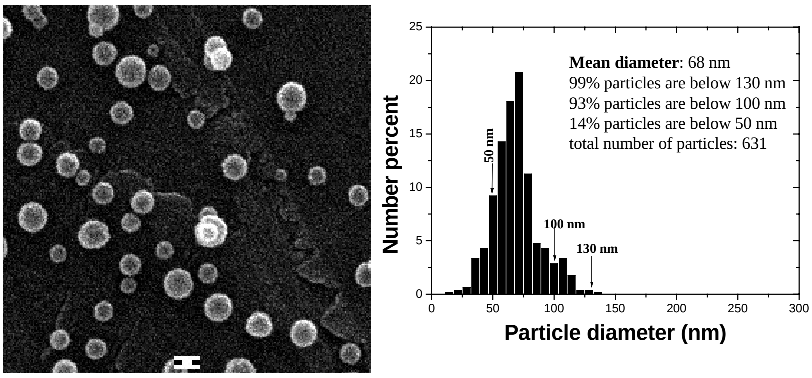


Figure 5 SEM micrographs of Au nanoparticles on silicon substrates



100 nm

Mean particle diameter: 68 nm

Figure 6 SEM micrograph and size distribution of product particles from spray pyrolysis at 800°C for 0.01wt% precursor solution drops 4-6 μm in diameters.

3.3 Application to Nanoparticles Synthesis

Uniform yttria-stabilized zirconia particles 68 nm in diameter (see Figure 6) was produced by spray pyrolysis (at 800°C) of yttrium-containing zirconium hydroxyl acetate precursor drops 4-6 μm in diameter, generated by a commercial 2.5 MHz ultrasonic nebulizer at an drive voltage of 100 V [9]. As much as 14% of the particles were smaller than 50 nm in diameter. Indium tin oxides nanoparticles 12-24 nm in diameter were obtained in salt-assisted spray pyrolysis using an ultrasonic nebulizer at 1.7 MHz; the precursor mean drop diameter was claimed to be 4.5 μm [10]. Therefore, the MEMS-based MHz ultrasonic nozzles reported here which have shown capability of producing monodisperse 7μm-diameter droplets should advance the technology of nanoparticles synthesis by spray pyrolysis.

4 CONCLUSION

Atomization using silicon-based MHz ultrasonic nozzles was accomplished for the first time. The narrow bandwidth of the resonance frequency of the multiple-Fourier horn nozzles facilitates production of monodisperse drops. In fact, the drop diameter obtained at 0.5 MHz is as small as the peak diameter produced by the conventional ultrasonic nebulizers that operate at a much higher ultrasonic frequency (1.65 MHz).

In addition, nanoparticles such as Au in colloid solution (at least in dilute concentrations) appear to have no significant effects on atomization using such MHz ultrasonic nozzles. Furthermore, the nanoparticles remain dispersed on silicon substrates. Thus, the MEMS-based MHz silicon ultrasonic nozzles may have the following applications: thin-film spray coating for micro- and nano-electronics processing, nanoparticles synthesis, and alveolar delivery of medicines.

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