[Technical Paper]

Silicon Microparticle Ejection Using Mist-jet Technology

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Abstract

The development of a novel mist-jet technology for ejecting a water mist containing silicon microparticles is described and demonstrated. A desired pattern can be drawn successfully on a large substrate using a silicon head specially designed for highly purified mist. The demonstration was performed using water containing silicon microparticles. The ejected mist droplet diameter was observed to be approximately $2.8\ \mu\text{m}$ stimulated by an ultrasonic driving frequency of 5 MHz. The substrate was mobilized by a motorized stage at an optimum speed of 60 mm/s and a working temperature of 100°C for dehydration. The letters “BEANS” were drawn in silicon on a $200\ \text{mm} \times 200\ \text{mm}$ glass substrate without any required surface treatment. A silicon-coated substrate was prepared by mist-jet ejection on a $10\ \text{mm} \times 10\ \text{mm}$ area for thickness uniformity measurement using stylus surface profiler. The silicon pattern achieved uniformity to a standard deviation of 20 nm at a thickness of 380 nm.

Keywords: Mist-jet Technology, Ultrasonic Wave, Silicon Microparticle, Silicon Nozzle, Piezoelectric Element

1. Introduction

The costs of most large-area energy harvesting devices and display devices have been decreasing along with the enlargement of substrates. Recently, substrate sizes have increased further. Today, substrates of meter size are being used. The cost advantage of large substrates is predicted to saturate in the near future because very large vacuum systems such as chemical vapor deposition (CVD) and large equipment needed for safety disposal will become very expensive.

We believe that a solution to this issue is the development of innovative large-area substrate processing using non-vacuum deposition. We began the development of such innovative non-vacuum deposition techniques for high-quality silicon film with our Bio Electromechanical Autonomous Nano Systems (BEANS) project in 2008. Our development target is to form silicon film using a technique that combines the ejection of silicon microparticles with non-vacuum deposition by plasma enhanced chemical transport under atmospheric pressure.[1–4] Figure 1 shows a schematic of this non-vacuum deposition process. To achieve our target, we are currently developing atmospheric-pressure plasma deposition, mist ejected uniform coating, local ambient gas control, and the integration of these techniques.

Fig. 1 Schematic of non-vacuum deposition process.

In mist ejected coating technology, microparticles dispersed in a liquid are ejected onto a substrate. When atmospheric-pressure plasma deposition can be combined with submicron silicon microparticles, high-speed silicon deposition can be achieved. On the other hand, the challenge is to eject silicon microparticles without impurities because contamination degrades the performance of the functional film.

We have previously reported on our development of a method for ejecting contamination-free silicon microparticles using mist-jet technology as an alternative to ink-jet technology.[6] To reduce impurities, the mist-jet head is made of silicon. Previously we used the silicon nozzle made by machining.

In this paper we prepare the silicon nozzle made by wet etching. The improvement with this nozzle is reported. Moreover the letters are drawn in silicon on a large glass substrate without any required surface treatment. We also evaluate the uniformity of the coating thickness by mist-jet ejection.

2. Mist-Jet Technology

As conventional ink-jet technology ejects single droplets that are large in diameter, it is difficult to coat a uniform film on a large substrate. In contrast, mist-jet technology continuously ejects a cluster of fine droplets.[5] Therefore, mist-jet technology is ideal for achieving a uniform functional film.

Figure 2 shows a cross-sectional illustration of the mist-jet head. The head structure comprises a piezoelectric element, a reflector with a parabolic wall, and a nozzle. The liquid is supplied to the space enclosed by the reflector and the piezoelectric element. The mechanism of mist-jet technology uses high-density ultrasonic energy to atomize the water and eject the mist from the nozzle.

When a high-frequency voltage is applied to the piezoelectric element, an ultrasonic wave is transmitted to the liquid. The ultrasonic energy is reflected from the parabolic wall and is concentrated at the focal point. The nozzle diameter is designed to be smaller than the wavelength of the ultrasonic waves, and the ultrasonic wave oscillates along the whole surface of the nozzle. At this time the nozzle

edge is a fixed end, therefore the ultrasonic energy generates traveling surface waves and fine droplets that form the mist are separated from the peak points as shown in Fig. 3.

3. Fabrication of the Silicon Head

The ejected silicon microparticles must be free from impurities since contamination degrades the performance of the functional film. We compared a stainless steel head with the silicon head.

The reflectors shown in Fig. 4 are machined from silicon and stainless steel. There are ring machining marks on the surface of the silicon reflector. Because these marks are much smaller than the wavelength in the liquid, which is $300\text{ }\mu\text{m}$ at 5 MHz, they do not affect the ejection of the mist.[6]

The silicon nozzle shown in Fig. 5 is similarly made by machining. Figure 5(b) shows an enlarged view of the silicon nozzle edge. The nozzle edge is larger than the wavelength of the traveling surface wave, which is $2.6\text{ }\mu\text{m}$ at 5 MHz. The nozzle edge is made a fixed end. The nozzle edge should be sharper, so the silicon nozzle was made by anisotropic wet etching. A Si substrate is etched by Tetra Methyl Ammonium Hydroxide (TMAH) using a SiO_2 mask. Figure 6 shows the result of the anisotropic wet etching. These SEM images in Fig. 5(a) and Fig. 6(a) show different shape. However, there was no specific ejection pattern at the nozzle and the mist was ejected on the whole

Fig. 2 Illustration of the mist-jet head cross-section.

Fig. 3 Mist-jet ejection mechanism.

Fig. 4 Stainless steel and silicon reflector with parabolic wall.

Fig. 5 Silicon nozzle made by machining.

Fig. 6 Silicon nozzle made by anisotropic wet etching.

Fig. 7 Distribution of mist droplet diameters.

area regardless of the nozzle shapes from high speed camera observations. So, we think the difference of geometrical shape does not affect the mist-jet ejection. Figure 6(b) shows an enlarged view of the silicon nozzle edge. These SEM images in Fig. 5(b) and 6(b) were taken at the same angle of view. While edge of the nozzle made by machining is indistinct, the edge of the nozzle made by anisotropic wet etching is clearly sharper than the wavelength of the traveling surface wave.

In addition, the mist ejections of these two nozzles were examined using deionized water. Figure 7 shows the distribution of the mist droplet diameters directly measured using a laser-scattering particle size distribution measuring device. The droplet diameters were measured using the same piezoelectric element and silicon reflector by just re-

placing the two nozzles.

The driving frequency of the piezoelectric element was 5 MHz. First, using the silicon nozzle made by wet etching, the Sauter mean diameter (SMD) of the ejected mist droplets was $2.8 \mu\text{m}$ when the drive voltage was 110 Vpp. Next, using the silicon nozzle made by machining, the SMD was $2.6 \mu\text{m}$ when the drive voltage was 150 Vpp. When the driving voltage was 110 Vpp, the head did not eject the mist.

The SMD value of the droplet diameter is comparable to the wavelength of the traveling surface wave. The distribution of the machined nozzle was wider than that of the wet-etched nozzle. Moreover, when using the machined nozzle, there were many mist droplet diameters of $10 \mu\text{m}$ or more. Because the machined nozzle edge is indistinct, the mist was ejected when the driving voltage was increased and the amplitude of the traveling surface wave was increased. Therefore, because the anisotropic wet-etched nozzle edge is sharp, the driving voltage for mist ejection could be decreased and the driving efficiency improved.

In the following experiments, the silicon nozzle made by wet etching was used.

4. Ejection of Silicon Microparticles

We examined our mist-jet technology performance using water containing silicon microparticles (average diameter of $2 \mu\text{m}$). Because the ultrasonic energy is used, the mist can be ejected without receiving the influence of gravity. An upward ejection was experimented though it differed from the form of Fig. 2. The upward ejection prevents the large particles and the impurities from falling to the substrate.

Impurities in the ejected silicon microparticles were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) since the material of the reflector and the nozzle might contaminate the silicon microparticles. For this analysis we used a silicon head composed of a silicon reflector and wet etching silicon nozzle, and a stainless steel head composed of a stainless steel reflector and stainless steel nozzle. As a reference, water drops containing Si microparticles from a plastic dropper were also analyzed. The

Table 1 Impurities in the ejected silicon microparticles.

Impurities, $\mu\text{g/g}$	Fe	Cr	Ni
Silicon head	1.3	0.032	0.30
Stainless steel head	83	1.1	2.8
Drops (reference)	1.6	0.021	0.11

amounts of impurities in the Si microparticles applied by mist ejection and by water drops were measured. Table 1 shows the result of the impurities in the mist-ejected silicon microparticles. The amounts of detected Fe were 1.3 ppm, 83 ppm, and 1.6 ppm, for the silicon head, stainless steel head and reference water drops, respectively. The impurities of mist ejection using the silicon head and water drops are almost same. Therefore if impurities from the raw materials and the environment can be removed, contamination of the silicon microparticles can be prevented.

As illustrated in Fig. 8, the ejection system with the mist-jet head was used to draw the letters "BEANS" in silicon on a 200 mm × 200 mm glass substrate without the requirement of surface treatment. The letters were 20 mm wide × 40 mm high. The driving frequency of the mist-jet head was 5 MHz. The substrate was mobilized by a motorized stage at an optimum speed of 60 mm/s and a working temperature of 100°C for dehydration.

A silicon-coated substrate was prepared by mist-jet ejection on a 10 mm × 10 mm area for measuring the uniformity of the coating thickness. Figure 9 shows the surface of

Fig. 8 Letters drawn using the mist-jet head.

Fig. 9 SEM image of the coated silicon microparticle surface.

the coated silicon pattern. Many microparticles at a level of several hundred nm can be seen. The microparticles seem to have gotten smaller by grinding in the head. The coating time was adjusted to 8, 12, 22, 31 minutes, and the thickness was measured. Figure 10 shows the thickness of the coated silicon pattern measured using a stylus surface profiler when the coating time was 22 minutes. There is a position with some sudden change in thickness caused by a large microparticle. The mean value of the scanning result of 8 mm in the center part, where there was no influence from the surrounding area, was assumed to be the film thickness. Seven arbitrary places on the coated pattern were measured. Figure 11 shows that the resulting thickness was 380 nm, 550 nm, 1.3 μm, 1.8 μm, and the standard deviation was 20 nm, 30 nm, 42 nm, 58 nm, respectively. These results confirmed that the silicon microparticles were uniformly coated. Figure 12 shows the relationship between the coating time and thickness. These

Fig. 10 Thickness of silicon pattern.

Fig. 11 Uniformity of silicon pattern.

Fig. 12 Relationship between coating time and thickness.

results confirm that the coating time and thickness are in a proportional relationship though the coating was slow at first.

5. Conclusion

This paper reports on the development of a novel mist-jet technology for ejecting a water mist containing silicon microparticles.

The fabrication method for the silicon nozzle was changed from machining to wet etching to produce a sharp nozzle edge. This sharp edge enabled the driving voltage for mist ejection to be decreased and the driving efficiency to be improved.

The impurities in the mist ejection using the silicon head were about 1 ppm. Therefore if impurities from raw materials and the environment can be removed, contamination of the silicon microparticles can be prevented.

Using a silicon head specially designed for a highly purified mist, a desired pattern can be drawn successfully on a large substrate without any requirement for surface treatment. The uniformity of the silicon pattern was achieved to a standard deviation of 20 nm at a thickness of 380 nm. These results confirmed that the silicon microparticles were uniformly coated.

In the near future we will form a silicon film directly on a substrate using a technique that combines the ejection of

silicon microparticles with non-vacuum deposition by plasma enhanced chemical transport under atmospheric pressure.

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References

- [1] S. Vepřek and V. Mareček, "The Preparation of Thin Layers of Ge and Si by Chemical Hydrogen Plasma Transport," *Solid-State Electronics*, Vol. **11**, pp. 683–684, 1968.
- [2] H. Ohmi, K. Kishimoto, H. Kakiuchi, and K. Yasutake, "Impacts of Noble Gas Dilution on Si Film Structure prepared by atmospheric-pressure plasma enhanced chemical transport," *J. Physics D: Appl. Phys.* Vol. **41**, 195208, 2008.
- [3] Y. Yokoyama, T. Murakami, S. Izuo, Y. Yoshida, and T. Itoh, "SILANE-FREE ATMOSPHERIC -PLASMA SILICON DEPOSITION FOR MEMS DEVICES," the 24th IEEE International Conference on Micro Electro Mechanical Systems (MEMS 2011), pp. 320–323, 2011.
- [4] T. Murakami, Y. Yoshida, Y. Yokoyama, and T. Itoh, "Structural Properties of Si Films Deposited by Plasma Enhanced Chemical Transport," *IEEJ Transactions on Sensors and Micromachines*, Vol. **130** No. 6, pp. 219–220, 2010 (in Japanese).
- [5] H. Fukumoto, J. Aizawa, H. Nakagawa, H. Narumiya, and Y. Ozaki, "Printing with Ink Mist Ejected by Ultrasonic Waves," *The Journal of IMAGING SCIENCE and TECHNOLOGY*, Vol. **44**, No. 5, pp. 398–405, 2000.
- [6] Y. Yokoyama, T. Murakami, Y. Yoshida, and T. Itoh, "Mist Ejection of Silicon Microparticle using a Silicon Nozzle," *IEEJ Transactions on Sensors and Micromachines*, Vol. **131** No. 6, pp. 230–234, 2011 (in Japanese).