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Multi-material direct printing
by Pulsed-Nano Particle Deposition System
(P-NPDS)

펄스 방식 나노 입자 적층 시스템을 이용한
다종 재료의 다이렉트 프린팅

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이길용
Abstract

Multi-material direct printing by Pulsed-Nano Particle Deposition System (P-NPDS)

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Recently, modern products or devices are expected to have more multi-functionality, compactness and reliability as integrated system. Works for improving manufacturing technologies are getting more important to satisfy these requirements of the products or devices. Also as product life cycle is getting shorter, the needs for reducing manufacturing costs and time are getting more important. By these reasons, many engineers and researchers are working to develop and evaluate new manufacturing technologies which is cost effective, fast, compact and reliable. Direct printing technology represented by ink-jet is one of the main category of these new manufacturing technologies. It is an additive manufacturing process to deposit controlled patterns and features onto various substrates. Nowadays, many direct printing systems have been developed and applied to fabrication of flexible and transparent substrate based functional devices. Among these, solid particle based dry deposition processes which is represented by nano particle deposition system (NPDS), cold spray (or cold gas dynamic spray) and aerosol deposition method (ADM) have a lot of
potential advantages for the application of direct printing technique. They are dry and room temperature process and they usually do not need thermal treatment while ink-jet or similar processes need additional thermal treatment or substrate heating.

In this dissertation, a new concept based on the solid particle based deposition process is suggested to print directly onto a hard and flexible substrates with multi-materials (metal and ceramic) simultaneously at room temperature. The shock induced particle dispersion and aerosol generation method are developed by fast acting solenoid valves and the amount of particle transported and injecting timing are studied to control the shape and position of the printed features as high resolution. The system design and performance evaluation are presented with various experimental setups and measurement instruments such as high speed camera, scanning electron microscope (SEM) or focused ion beam (FIB).

From these, a novel multi-material direct printing system which is named as ‘Pulsed-nano particle Deposition System, P-NPDS’ is integrated with hardware, software, controller and other components. Using the integrated system, multi-material direct printing examples are presented with functional metal and ceramic materials (Tin, Silver as metal and Barium Titanate as ceramic). Finally, several experiments and results are presented to show capability of functional structure fabrication and applications of electronic components and energy harvesting devices using developed direct printing system

Keywords: direct printing, pulsed-nano particle deposition system (P-NPDS), flexible substrate, multi-material, aerosol generation

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Chapter 1.

Introduction

1.1 Overview

Recently, modern products or devices are expected to have more multifunctionality, compactness and reliability as an integrated system. Works for improving manufacturing technologies are getting more important to satisfy these requirements of the products or devices. Also as product life cycle is getting shorter, the needs for reducing manufacturing costs and time are getting more important. By these reasons, many engineers and researchers are working to develop and evaluate new manufacturing technologies which is cost effective, fast, compact and reliable one [1, 2].

Direct printing technology is one of the main category of these new manufacturing technologies. It is an additive manufacturing process to deposit controlled patterns and features onto various substrates directly without any masks [1-3].

The ability to print patterns with functional materials is of paramount importance in the fabrication of integrated micro-/nano systems such as miniaturized sensors or actuators, as well as photonic, electronic, microfluidic, bio analytical, and biomedical devices [4]. The most important applications of direct printing
technology is its use for the fabrication of functional patterns or structures on a flexible and transparent substrate represented by polymer or plastic substrates. Researchers in the field of flexible displays and organic devices are currently trying to use polymer or plastic substrates in commercial products [5, 6]. Usually these substrates are vulnerable to heat and chemical reaction with solutions, so low temperature and dry manufacturing process is essential. In addition the related environmental issues and the high price of raw materials are great incentives for minimizing waste and the use of toxic materials. Because of these reasons, additive processes are more suitable than subtractive processes [7]. In Figure 1.1, various application fields and technologies for the direct printing are summarized [1-4, 8-26].

![Figure 1.1 Applications of direct printing technologies](image_url)

Nowadays, many kinds of direct printing systems have been developed and applied to fabrication of flexible and transparent substrate based functional devices. Among
those, solid particle based dry deposition processes which are represented by nano particle deposition system (NPDS), cold spray (or cold gas dynamic spray) and aerosol deposition method (ADM) have a lot of potential advantages to these engineering fields. These processes are dry and do not need pre- or post- treatment and also dry solid particles are deposited at room temperature without any thermal damage on the substrate. But still, these processes have not shown the capability of multi-material and direct (mask-less) printing results on a flexible and transparent substrate. Typically, they are used to coat or deposit on a large area of substrate [7, 27-34].

In this dissertation, a new concept based on these solid particle based deposition process is suggested to print directly onto a hard and flexible substrates with multi-materials (metal and ceramic) simultaneously at room temperature.

At the beginning of this dissertation, direct printing technology is briefly reviewed and solid particle aerosol based deposition processes are reviewed more detail with system configuration, mechanism, current state of arts and their limitations focused on the NPDS. By defining the current limitations of NPDS, a new concept to solve these limitations and to realize small-scale (micro scale), high resolution multi-material direct printing is suggested. The system design and performance evaluation with the fundamental experiments are followed. A novel multi-material direct printing system which is named as ‘Pulsed-nano particle Deposition System, P-NPDS’ is integrated with hardware, software, controller and other components. Using this integrated system multi-material direct printing examples are shown with functional metal and ceramic materials (Tin, Silver as metal and Barium Titanate as ceramic). Finally, several experiments and results are presented to show capability of functional structure fabrication and applications of electronic components and energy harvesting devices using developed direct printing system.
1.2 Review of direct printing technology

1.2.1 Definition of direct printing technology

In this dissertation, the existing definitions of direct printing are introduced and several direct printing techniques were categorized and summarized by the definitions. Various definitions of direct printing or direct writing technologies have been suggested and proposed by many papers [1]. Several important definitions of direct printing are listed as follows:

- Any techniques or process capable of depositing, dispensing or processing different types of materials over various surfaces following a preset pattern or layout.
- A range of technologies, possibly in reconfigurable short production runs, of two- or three-dimensional functional structures using processes that are compatible with being carried out directly on to potentially large complex shapes.
- Fabrication methods that employ a computer-controlled translation stage, which move a pattern-generating device, e.g. ink deposition nozzle or laser writing optics, to create materials with controlled architecture and composition.

While such definitions describe some of the essential properties of direct printing processes, they are unable to distinguish direct printing from some of the well-established rapid prototyping processes such as Fused Deposition Modelling, 3D
printing or Object printing. A more precise and accurate definition is therefore required for direct printing: direct printing denotes a group of processes which are used to precisely deposit functional and/or structural materials on to a substrate in digitally defined locations. Direct printing is distinguished from conventional RP in terms of the following characteristics [1]:

- The track width ranges from sub-microns to millimeters.
- The range of materials deposited can include metals, ceramics and polymers, electronically and optically functional materials as well as biological materials including living cells.
- The substrate is an integral part of the final product.

1.2.2 Classification of direct printing technology

As an additive process, direct printing can be classified as three main categories by printing or deposition mechanism. These classifications are depicted as a diagram in Figure 1.2 [1, 22]. Liquid or solution based direct printing represented by the ink-jet and electrohydrodynamic jet (E-jet) is one of the most famous direct printing process and many recent researches were reported by a lot of researchers. These direct printing processes use ink or solution for printing materials. These liquid droplets are dropped by the pressure exerted in nozzle or electric potential difference between nozzle and substrate. Usually these kinds of direct printing methods show high resolution pattern printing. Viscosity of ink, droplet formation and exposal mechanism are important issues to be controlled as process parameters. These liquid based direct printing technology need substrate heating or post heat treatment to
evaporate binders. And the printing materials should be made as a solution to be printed. Also nozzle clogging is another problem to be solved [4-6, 9, 21, 24, 25, 35-39].

![Diagram of Direct Printing Technology]

**Figure 1.** 2 Classification of direct printing technologies

Direct printing process uses high energy beam such as focused ion beam or laser beam is another representative printing process. By using highly focused energy beam, very small features can be printed directly onto various substrates as much higher resolution than ink-jet or E-jet. But these processes need very complex and expensive system [1, 22, 40-43].

An aerosol based direct printing technology is another main research area of direct printing process. Aerosol-jet printing, aerosol deposition method (ADM), cold spray and nano particle deposition system (NPDS) are the most representative direct printing processes which use mixture of gas and liquid or solid particles (aerosol) as a printing material [7, 20, 27, 28, 44]. Generally aerosol-jet printing uses ink for
printing material and it needs post curing process by the thermal oven or laser [1, 22, 43, 45].

Aerosol deposition method, cold spray and nano particle deposition system use dry ceramic and metal particles as starting or printing materials and the deposition occurred by the high speed inertial impaction of particles onto the substrate at room temperature [20, 29, 32, 34, 46]. These manufacturing processes are low temperature additive manufacturing processes suitable for metal and ceramic deposition which have similar system configurations.

Among these, NPDS is most recent and advanced dry solid particle printing process. It can print or deposit metals and ceramics at room temperature without any thermal or other treatment [7, 47]. It is dry and room temperature process and no thermal treatment is required. And solid particles can be directly deposited onto the substrates. Metal and ceramic particles can be deposited onto metal, ceramic and polymer substrates at room temperature by NPDS. So it can be applicable to flexible substrates. By these reasons, we can say that NPDS has enough potentials to be applied to direct printing technology and it has many advantages compared with the liquid ink based direct printing methods. However, until now micro scale multi-material direct printing has not been realized by NPDS because that it has limitations to print precise patterns onto substrates. NPDS is suitable for depositing large scale pattern and it does not consider robust control of aerosol generation, the amount and timing of aerosol transported to nozzle and aerosol jet formation. Also it is very hard to control feature size, position and geometry due to the continuous particle feeding and difficulties of aerosol flow control. In Figure 1.3 the examples showing feature size printed by the liquid ink and dry solid particles are presented. As shown in the Figure, there is large scale gap between the patterns printed by ink-jet or E-jet and NPDS, ADM and cold spray.
Because the main objective of this paper is realization and development of micro scale direct printing based on NPDS, in the following sections, NPDS, ADM and Cold spray are explained in more detail.

Figure 1. The direct printing examples showing feature size printed by the liquid ink (ink-jet, E-jet) and dry solid particles (NPDS, ADM and Cold spray) [4, 27, 28, 39, 48]
1.3 Review of aerosol based printing

The aerosol deposition method, cold spray and nano particle deposition system are dry printing processes and no chemical treatments or post curing processes are needed. So they have special advantages compared with ink-jet, E-jet and aerosol-jet printing. These advantages can be helpful to apply these processes to print features with functional materials directly onto flexible substrates at a precisely controlled position and with a controlled structure shape. However, until now there is no research reported to print metal and ceramic patterns directly onto flexible substrates without any mask and as a high resolution using these solid particle (aerosol) based direct printing process. In generally, they are used for fabrication of surface coating or large scale pattern deposition with functional metal or ceramic materials to increase mechanical properties or to give electronic or chemical functionalities to the various substrate materials.

1.3.1 Cold spray

Cold gas dynamic spray is a free-form fabrication process with a high coating rate, low porosity, low oxidation and low residual stress that uses high-pressure gas to accelerate powder particles without any particle melting before impact. Cold spray, often referred to as cold gas dynamic spray or kinetic spray, was developed in Russia in the early 1980s by Dr. Papyrin [32]. This process accelerates powder particles, generally metals and cermet powder, through a supersonic nozzle using heated gas or helium, the powder particles are sprayed onto a substrate. The kinetic energy of the particles impacting on the substrate is used for bonding.
Cold spray was developed to overcome the thermal deformation and oxidation inherent in thermal spray methods such as plasma spraying, high velocity oxy-fuel, wire-arc and flame spraying. Cold spray has following distinctive advantages:

1. Low-temperature process conditions for metal and cermet coatings with low thermal deformation and oxidation
2. Good coating quality, low porosity, high hardness and high adhesion force
3. High deposition rate compared with other coating fabrication processes
4. Wide range of coating thicknesses
5. Fabrication of various metal, cermet and some polymer coatings
6. Various available substrate materials

![Cold spray system configuration](image)

Figure 1.4 Cold spray system configuration [29, 32, 47, 49]

Various types of cold spray systems exist. Figure 1.4 shows a typical cold spray system configuration consisting of a supersonic nozzle, powder feeder and carrier gas supplier. This requires a high particle velocity generated by the supersonic nozzle. In addition, the process uses high pressure gas and a gas heater to achieve sufficient
kinetic energy. The pressure, gas flow rate and powder feed speed are controlled by a computer according to the deposition conditions such as material type and particle size. Stages, substrate holders, a ventilation system and other equipment are required in the complete setup.

The process parameters, such as particle material, equipment and substrate material are important for making good quality coatings. Cold spray systems range from high pressure, high temperature devices to portable cold spray units. Table 1.1 shows the range of various process parameters in typical cold spray systems.

Table 1.1 Range of process parameters of cold spray [29, 32, 47, 49]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder size</td>
<td>10μm ~ 120μm</td>
</tr>
<tr>
<td>Particle velocity</td>
<td>400m/s~1200m/s</td>
</tr>
<tr>
<td>Inlet air temperature</td>
<td>Room temp. ~ 800°C</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>0.7~4.5MPa</td>
</tr>
<tr>
<td>Accelerating gas</td>
<td>He, Ar, N₂, air</td>
</tr>
<tr>
<td>Spraying distance</td>
<td>10mm ~ 100mm</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>13.1g/min ~ 113g/min</td>
</tr>
<tr>
<td>Powder preheat temperature</td>
<td>Room temperature ~ 500°C</td>
</tr>
</tbody>
</table>
Many sorts of metal and cermet powder have been deposited on substrates using the cold spray process. Aluminum and copper powders have received the most attention, more recently, the results of metal matrix composites have been widely reported. Table 1.2 lists deposited materials and substrates.

Table 1.2 List of powders and substrates for cold spray [29, 30, 32, 47, 49-51]

<table>
<thead>
<tr>
<th>Classification</th>
<th>Powder</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>Al, Cu, Fe</td>
<td>Al, Brass, Cu Steel</td>
</tr>
<tr>
<td>Metals</td>
<td>316L stainless steel</td>
<td>-</td>
</tr>
<tr>
<td>Metals</td>
<td>Titanium</td>
<td>-</td>
</tr>
<tr>
<td>Metals</td>
<td>Ni (Nanocrystaline)</td>
<td>Al</td>
</tr>
<tr>
<td>Cermets</td>
<td>WC-Co</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Composite</td>
<td>Al2319 – TiN</td>
<td>Al alloy</td>
</tr>
<tr>
<td>Composite</td>
<td>Al – SiC</td>
<td>Al alloy</td>
</tr>
<tr>
<td>Composite</td>
<td>Diamond/Al, Sic/Al, AlN/Al, W/Al</td>
<td>Brass</td>
</tr>
<tr>
<td>Ceramic</td>
<td>TiO2 – Zn</td>
<td>Cu</td>
</tr>
<tr>
<td>Ceramic</td>
<td>W – Cu</td>
<td>6061 Al alloy</td>
</tr>
<tr>
<td>Polymer</td>
<td>Polyolefin</td>
<td>Polyethylene, Al</td>
</tr>
</tbody>
</table>
1.3.2 Aerosol deposition method

The aerosol deposition method (ADM) is a new room temperature process for ceramic coating developed by Dr. Akedo in late 1990s [27, 28]. This process involves aerosol generation, particle impact and deposition on the substrate. It uses the aerosol state of submicron particles to accelerate ultrafine particles and mix them in gas flow. Aerosol with particles is accelerated by a gas flow in the nozzle and sprayed onto the substrate. The kinetic energy of the particles is used for bonding during impact. The process occurs without any additional sources of energy or chemical reactions and no additional post-processing of the deposited film is required. ADM has the following distinct advantages:

(1) Room temperature process conditions for ceramic film fabrication
(2) Similar material properties of the films and primary particles
(3) High deposition rate compared with other ceramic fabrication processes (~ 70 μm/min)
(4) Wide range of film thickness (~ 500 μm)
(5) Fabrication of various ceramic films
(6) Various substrate materials available, including metal, ceramics and some polymers
(7) Patterning without additional etching
Figure 1. 5 ADM system configuration [28]

Figure 1.5 shows the configuration of a typical ADM system consisting of two vacuum chambers, a carrier gas supplier and a vacuum system. The two vacuum chambers are the deposition chamber and the aerosol chamber, which are interconnected by a gas pipe. The deposition chamber contains the nozzle for accelerating the carrier gas, a substrate holder with a heating system and mask alignment system, a three-axis stage and a tilting system. The aerosol chamber contains the mixing and vibration system to generate the ultrafine particle aerosol. The vacuum system maintains the vacuum in these two chambers. The pressure difference between the two chambers is the source of kinetic energy in this system. The pressure and flow rate can be controlled by the mass flow controller. The particle filter blocks large particles because they may damage the deposited film.
Since the process parameters depend on the purpose of the experiment and the equipment, many papers have dealt with particular process parameters of interest according to the type of particle and experimental issues. Table 1.3 shows the wide range of various process parameters that cover the whole range of ADM systems at National Institute of Advanced Industrial Science and Technology (AIST) in Japan.

Table 1.3 Range process parameters of aerosol deposition [27, 28, 47]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder size</td>
<td>0.1μm ~ 2μm</td>
</tr>
<tr>
<td>Particle velocity</td>
<td>150m/s~500m/s</td>
</tr>
<tr>
<td>Pressure in deposition chamber</td>
<td>0.002-0.3 kPa</td>
</tr>
<tr>
<td>Pressure in aerosol chamber</td>
<td>10-80 kPa</td>
</tr>
<tr>
<td>Size of nozzle orifice</td>
<td>5mm X 0.3mm</td>
</tr>
<tr>
<td></td>
<td>10mm X 0.4mm</td>
</tr>
<tr>
<td>Accelerating gas</td>
<td>He, N$_2$, O$_2$, air</td>
</tr>
<tr>
<td>Consumption of accelerating gas</td>
<td>1-10 L/min</td>
</tr>
<tr>
<td>Beam incident angle</td>
<td>0° ~ 60°</td>
</tr>
<tr>
<td>Maintained substrate temperature</td>
<td>-30°C ~ 700°C</td>
</tr>
<tr>
<td>Distance between the nozzle and substrate</td>
<td>1-40 mm</td>
</tr>
</tbody>
</table>
ADM has been used to deposit various types of ceramic powder. PZT films have received the most research attention as substrates because of their wide application in electronics.

1.3.3 Nano particle deposition system

Even though many varieties of cold spray and ADM exist, there had been little effort to combine cold spray and ADM. By this reason nano particle deposition system (NPDS) was developed by Dr. Chun in 2006 [47], to fabricate metal and ceramic film by spraying nano/micro sized particles at room temperature under low vacuum conditions to achieve micro scale deposition. To minimize the effect of the strong bow shock and reduce the operating cost, the pressure of the carrier gas was decreased and a vacuum environment was used. Figure 1.6 shows the fabrication envelope of pressure in the deposition chamber and the pressure of the carrier gas. NPDS combines low cost compressed air with low vacuum conditions (> 25 Torr). A supersonic nozzle is used to increase the particle velocity and the powder feeder is an original design [7].

Although cold-spray and ADM can be used to coat at room temperature, both processes support only a limited specific velocity and powder size, so the powder type and the deposition substrates are limited. However, NPDS could cover a broader range using the supersonic/subsonic nozzle and low-vacuum deposition conditions, as depicted in Figure 1.6.
The NPDS could make thin coating layer through dry-spray method under low vacuum and low temperature condition. As shown in Figure 1.7, NPDS consists of controller, deposition chamber with substrate holder and nozzle, powder supplier, air compressor, and vacuum pump, etc.
The pressure condition of deposition chamber was maintained in atmospheric pressure condition to increase the economic feasibility and productivity. Various metal and ceramic particles can be successfully deposited onto the various substrate materials. The deposition combinations of substrates and particles are summarized in Table 1.4.

Figure 1.7 System configuration of NPDS [7]
1.3.4 Comparison of cold spray, ADM and NPDS

Most studies of ADM has been focused on ceramic deposition, while most studies of cold spray have involved metals and metal matrix composite deposition. And NPDS was developed to combine these two processes and extend these to the room temperature metal and ceramic particle deposition. However, their main applications are for the fabrication of surface coating or large scale pattern deposition with functional metal and ceramic materials to increase mechanical properties or to give electronic or chemical functionalities to the various substrate materials. And generally, these processes use a continuous particle and carrier gas feeding to deposit patterns onto substrate.

Figure 1.8 shows the evolution of cold spray, ADM and NPDS. In ADM and NPDS, fine ceramic patterns are reported to be fabricated using mask [27, 28, 31, 32, 49, 52]. But most of direct printing technologies do not need any mask and there is no
research to fabricate multi material (metal and ceramic) patterns on the same substrate in a micro scale resolution. Chun et al. showed Tin and Nickel line patterns onto various substrates [47], but the length scale was still large compared with other micro scale direct printing techniques such as ink-jet or aerosol-jet printing.

Jodoin et al. suggested and developed pulsed gas dynamic spraying in 2007 [30] which uses discontinuous compression waves produced by valves and injecting inert gas into a spray gun contains the powder feedstock material to be sprayed. This process accelerates particles to impact velocities similar to what is used in cold spray. This system has additional particle injection system and control of the particle injection timing and particle injection amount is difficult. And only the similar coating results and feature sizes with cold spray process were reported [30, 50].

Figure 1.8 History of low temperature deposition processes using solid particle
As mentioned earlier, while these ADM, cold spray and NPDS have unique advantages and potentials to be applied to small scale multi-material direct printing technique, there is no study to print metal and ceramic materials onto substrate simultaneously as a precise and high resolution features. So it is very challenging work to develop direct printing process to print metal and ceramic particles onto the various substrates (especially flexible and transparent substrates) in one printing process with high resolution as precise as the scale realized by the other competitive direct printing processes such as ink-jet or aerosol-jet printing.

1.3.5 Development of new direct printing technique

Among cold spray, ADM or other similar deposition processes, NPDS can be utilized as more flexible system to print various materials onto various substrates including flexible and transparent substrates such as polymer and plastic as reviewed here. So in this research, a new direct printing technique is suggested, realized and integrated based on the early NPDS as a reliable one which is capable of printing metal and ceramic functional particles onto various substrates with a precise feature size and shape controls.

Before explaining more detail about the new direct printing technique, it is necessary to compare the performance of the existing direct printing processes. In Table 1.5, the comparison of various printing performances are listed and summarized for selected direct printing techniques (Inkjet, E-Jet, Aerosol-Jet, NPDS, ADM and Cold Spray).

In Table 1.5, the two main categories of direct printing systems are listed. The first one is liquid based direct printing techniques which uses liquid ink as a starting materials. Usually these processes show micro or sub-nano scale direct printing
feature scale, while, the thickness is not high. And also these printing processes need further heat treatment after printing. Another category is dry solid particle based direct printing processes which is represented by NPDS. Generally these processes need no heat treatment and they use dry solid particles as a starting materials. And they use high speed gas to accelerate and deposit particles onto the substrate. However, as shown in the Table 1.5, their printing capabilities are not good compared with liquid ink based direct printing processes to apply them to direct printing techniques.
Table 1. Comparison of the printing performance of various direct printing technologies [1, 4, 7, 28, 39, 53]

<table>
<thead>
<tr>
<th></th>
<th>Ink-Jet</th>
<th>E-Jet</th>
<th>Aerosol-Jet</th>
<th>NPDS</th>
<th>ADM</th>
<th>Cold Spray</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Printing material</strong></td>
<td>Liquid ink</td>
<td>Liquid ink</td>
<td>Liquid ink</td>
<td>Solid particle (Metal/Ceramic)</td>
<td>Solid particle (Ceramic)</td>
<td>Solid particle (Metal)</td>
</tr>
<tr>
<td><strong>Kinetic energy source</strong></td>
<td>Viscous liquid flow</td>
<td>Viscous liquid flow</td>
<td>Gas (Viscous Drag force of gas)</td>
<td>Gas (Viscous Drag force of gas)</td>
<td>Gas (Viscous Drag force of gas)</td>
<td></td>
</tr>
<tr>
<td><strong>Heat treatment</strong></td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>X (Usually not necessary)</td>
<td>X (Usually not necessary)</td>
<td>X (Usually not necessary)</td>
</tr>
<tr>
<td><strong>Particle (droplet) speed</strong></td>
<td>&lt; 50m/s</td>
<td>&lt; 50m/s</td>
<td>~ 100m/s</td>
<td>300 ~ 1,000m/s</td>
<td>100 ~ 500m/s</td>
<td>400 ~ 1,200m/s</td>
</tr>
<tr>
<td><strong>Particle (droplet) diameter</strong></td>
<td>10 ~ 150 μm</td>
<td>0.5 ~ 100 μm</td>
<td>1 ~ 5μm</td>
<td>0.1 ~ 1μm</td>
<td>0.1 ~ 1μm</td>
<td>10 ~ 120μm</td>
</tr>
<tr>
<td><strong>Feature scale</strong></td>
<td>10~100μm</td>
<td>&lt; 10μm</td>
<td>~ 10μm</td>
<td>500μm ~ 10mm</td>
<td>500μm ~ 10mm</td>
<td>500μm ~ 10mm</td>
</tr>
<tr>
<td><strong>Thickness</strong></td>
<td>&lt; 1μm</td>
<td>&lt; 100nm</td>
<td>&lt; 1μm</td>
<td>1 ~ 500μm</td>
<td>1 ~ 500μm</td>
<td>&lt; 1 mm</td>
</tr>
</tbody>
</table>
In Figure 1.9, the envelope of these direct printing processes is depicted in the various feature width and thickness scale. As shown in Figure 1.9, NPDS is lying in the region of large scale range compared with other liquid based direct printing techniques. So, in this work, the new and novel direct printing process which is named as Pulsed-Nano Particle Deposition System (P-NPDS) is studied to extend the feature scale range of NPDS to micro meter scale region as shown in Figure 1.9 with red solid outlined square.

![Feature scale envelop of selected direct printing processes](image)

Figure 1.9 Feature scale envelop of selected direct printing processes

In generally, NPDS or other similar deposition processes use high speed accelerated gas flow as a transporting agent of the particles to the substrate while liquid droplet based ink-jet, E-jet or aerosol-jet printing use low speed viscous flow. Also the process gas is controlled to be flowed in continuous manner. So in these process conditions, it is very hard to control the amount of particle transported from particle
reservoir, particle feeder or aerosol generator to the substrate keeping high speed acceleration of particles by the carrier gas with achieving high velocity impaction. So the control of the generation of aerosol from solid particles (starting particles) and also their transporting amount and timing controls are very important factors to be controlled for the application of these processes to direct printing. The advantages, current state of art and limitations of NPDS are summarized as below:

Advantages of NPDS (current state of art)

- Dry and Room temperature process
- No thermal treatment
- Direct solid particle deposition
- Metal and ceramic materials onto metal, ceramic and polymer substrate
- Applicable to flexible substrate

Limitations of NPDS

- Large feature scale
- Hard to control feature size, position and geometry due to continuous particle feeding and difficulties of aerosol flow control

From this we can conclude that the NPDS has enough potentials to be applied to direct printing technique. But until now, multi-material direct printing has not been realized due to the existing difficulties of NPDS.

To overcome these limitations or difficulties of NPDS, P-NPDS is designed and integrated by considering several key issues:
1) Aerosol generation and particle dispersing method

2) The control of aerosol transported from particle reservoir to nozzle

3) Particle focusing method during high speed impaction of particles onto the substrate

In generally, NPDS or other similar processes use high cost commercial aerosol generator or particle injection system [54-65]. And they use continuous particle feeding scheme which is the main fact to decrease the pressure difference between particle feeder and deposition or printing chamber. Because the particles are accelerated by the carrier gas whose velocity is dependent on the large pressure difference between the feeding regulator and the vacuum chamber, it is very important to keep large pressure difference during the process.

And to make pattern size smaller, the amount of particles transported from particle feeder and jetted through nozzle to the substrate should be controlled in a precise manner. That is why the drop on demand jetting is more preferable than the continuous jetting in ink-jet or other similar direct printing processes. The conventional printing technique which uses gas as an accelerating agent is not suitable for drop on demand jetting. The excessive carrier gas and particles can be transported from the particle feeder to the chamber or substrate due to the same reason. As a result, it is very difficult to scale down the feature size by the conventional methods.

It is well known that the small particles can be controlled to be focused as a particle beam by the aerodynamic effect and forces exerted by the expansion of gas jet [54-62, 64, 66]. However, NPDS or other similar processes do not consider the particle focusing to print or deposit particles as a controlled shape and geometry. In Figure

26
Aerosol generation

Commercial aerosol generator

- High cost
- Continuous particle feeding
- Excessive carrier gas
- Can not control feeding timing
- Complex system

Powder feeders

Flow meter

Valve

Filters for dust, oil, humidity

Vacuum pump

Air compressor

Substrate

Nozzle

2. Transporting of aerosol to nozzle

Is not considered and controlled:
- Particle transported amount should be as small as possible to print small scale as controlled geometry

1. Aerosol generation

3. High speed inertial impaction of particle onto substrate

Is not controlled to be focused:
- Particle beams should be controlled to be focused to print small scale as controlled geometry

To solve these existing problems and realize much smaller scale direct printing capabilities, P-NPDS is designed and developed by the following concepts and ideas.

Firstly, the instantaneous aerosol generation mechanism from the starting particles is suggested based on the shock wave induced particle dispersion. Particles or particle clouds excited by the high speed shock wave or compression wave can be dispersed very quickly and the motion of particles dispersed terminates following the wave strength and their relaxation time [57, 67-70]. This is quite simple and cost efficient method of starting particle dispersion as a starting agent to be used for direct printing. The shock wave or compression wave can be initiated by a sudden removing of separator initially separate the high pressure region and the low pressure.
region. The strength of wave is determined by the initial pressure difference. This sudden removing of separator can be realized by sudden opening of valve. By switching the opening and closing state of the excitation gas flow valve (driving valve) by using fast acting solenoid valve, the transportation amount of particle or aerosol and its timing can be controlled at high rate to prevent excessive aerosol flow to the substrate.

And also by keeping the pressure ratio between driver section (high pressure region) and the vacuum chamber high enough (several hundreds of order) by initially separating the high pressure and low pressure regions, the particle and carrier gas can be reached to high speed as fast as the deposition can occur. In the previous research, it was reported that the use of pulsed (transient) carrier gas flow to accelerate particles can achieve much faster impact velocity than when we use continuous carrier gas feeding.

Particle focusing by high speed carrier gas by using converging nozzle was reported in the previous researches about the particle beam and aerosol generation [55-66, 71-74]. But the existing researches for NPDS or other similar processes do not considered the particle focusing and its use to direct printing technique. Usually, NPDS or Cold Spray use converging and diverging nozzle to make the carrier gas flow to be a supersonic flow to accelerate the particles at the very high speed onto the substrate. But this supersonic nozzle needs high manufacturing cost and also by using these supersonic nozzle, particles cannot be focused well due to the nature of expansion of gas stream through converging and diverging nozzle. But the converging nozzle can be made with very cheap cost and it can be used to focus particles with aerodynamic focusing [57, 72, 75].

The newly developed direct printing system in this thesis names as P-NPDS is designed to use the shock induced aerosol generation for starting agent by using fast
acting valves. These valves are controlled in the integrated hardware and software system. By switching these valves at high rate the pulsed carrier gas and particle feeding can be realized. So the total pressure difference between before nozzle and the vacuum chamber can be maintained as high level. The particles can be fed small amount to pattern small scale features and the high pressure difference ensure the high speed impaction of particles onto the substrate. Furthermore, particle focusing is considered and realized by P-NPDS and the printed features can be controlled as a small scale level.
Chapter 2.

System design and integration

2.1 System configuration

The objective of development of new direct printing system based on NPDS is to realize the controlled particle excitation and transportation keeping high impact velocity and finally print controlled multi-material pattern on the various substrates especially onto the flexible and transparent substrates. Also the printing should be done at room temperature condition and the minimum target scale of feature size is under 50 \( \mu \text{m} \) which is general in ink-jet printing [74].

In Figure 2.1, the schematic diagram of developed system is shown. And the main design considerations are as follows.

1) Reliable and repeatable printing process
2) Real-time printing process monitoring and control
3) Precise pattern printing on-demand and on-position
4) Direct pattern printing
5) High resolution printing (micro-scale)
6) Multiple particle feeding system

The particle to be printed inside the particle reservoir or supplier is accelerated by the flow of high pressurized carrier gas to the vacuum chamber connected to the rotary pump through printing nozzle. The particles are accelerated through nozzle and just before impaction to the substrate the velocity reaches to its highest value. Usually this impact velocity is several hundreds of meter per second and this high speed impaction of particles onto substrate is the key of explanation of the deposition mechanism of NPDS or other similar processes (ADM and cold spray) [7].

Figure 2. 1 System configuration of new direct printing system

In conventional NPDS, particle deposition or printing on large scale is general as mentioned earlier. To apply this system to direct printing process, the amount of transported particles from the particle reservoir to the substrate and jetted particles through nozzle to the substrate are critical factors to be carefully controlled. Also the fact that printing phenomena in NPDS is occurred by the inertial impaction of
particle onto substrate with high velocity leads us that the acceleration of particles and letting particles reach high speed at impact is another important factors to be considered. In conventional NPDS, continuous carrier gas feeding is used to accelerate particles and ultrasonic vibration of particle feeder can help particle to be dispersed uniformly. The flow rate is around 1-30 liters per min and carrier gas feeding pressure is around 300~700 kPa [7]. This large amount of gas flow rate causes increase of the pressure inside the vacuum chamber. This increased chamber pressure can decrease the impact velocity of particle due to the reduced pressure difference between vacuum chamber and carrier gas inlet and as a result the printing efficiency is degraded. Moreover, this large amount of gas flow may transport excessive particles to the substrate and this is not desirable for small scale feature printing. To overcome these disadvantages and to apply NPDS to direct printing system, it is proposed to use pulsed carrier gas and particle feeding system. The pulsed particle feeding can be helpful not only to keep the pressure inside the vacuum chamber low but also to make the particle velocity high at the impact because the gas and particle velocity can be much higher when we use transient flow compared with continuous flow [47].

To explain more detail about the process, the printing process is divided three important steps as shown in Figure 2.2.
At first, the starting aerosol are generated from the starting particles by interaction of the initially rest particles and the incident shock or compression waves which is generated by the sudden opening of driving valve initially separate the high pressure driver section and low pressure driven section. This aerosol which can be defined as the state of the particles are dispersed in the carrier gas (particle-gas mixture) is transported through nozzle to the substrate by the initial pressure difference. In this situation, small particles are accelerated and transported much faster than the large particles because small particles have low relaxation time compared with large particles. If we close the driving valve before the large particles are not accelerated and transported to nozzle, the large particles can settle down to the initial state due to their large gravity. The purge valve which is connected to the secondary vacuum pump can be helpful to remove the remaining gas in the feeding system and stabilize the large particles accelerated by the initial wave. The more detail concept of process sequence is depicted in Figure 2.3. The most important idea of the suggested method is to keep high pressure difference at the initial state and prevent excessive aerosol transportation to the printing nozzle, and to achieve these requirements the timing
control of opening and closing state of the fast acting valves is introduced and realized in the integrated system.

Figure 2. 3 The detail process sequence of P-NPDS

(1) Initial state, (2) Shock wave or compression wave induced aerosol generation and transportation of the aerosol to the printing nozzle, (3-4) aerosol stabilization and removing excessive aerosol inside the particle feeder by closing the driving valve and opening the purge valve.

The aerosol generated by the sudden opening of driving valve is transported to the printing nozzle and the particles to be printed are focused by the aerodynamic force and focusing mechanism through the converging nozzle. During jetting the particles through the nozzle exit, the highly focused particle beam are generated and impacted onto the substrate occurring the bonding of the particles onto the substrate. And by
controlling the amount of the aerosol transported onto the substrate as a small amount with highly focused particle beam formation at the nozzle exit, very small scale features and structures can be printed directly onto the substrates.

The whole processes are controlled in real-time by the integrated system and the printed features, position and results are monitored by the in-situ microscope image feedback.

### 2.2 System design and integration

The entire system is consist of vacuum chamber, multiple particle feeding system, 3-axis motion control stage, vision system for real-time monitoring of the printed results, rotary pumps, pressure sensors, interface circuits and data acquisition (DAQ) board to measure pressure data and for the valves opening and closing control.

Figure 2.4 shows the schematic of integrated direct printing system. The main components of the system are vacuum chamber, particle feeding system with valves, substrate motion control unit which determines printing position, DAQ and interfaces, vision system and software.
Figure 2. 4 Schematic diagram of integrated direct printing system

Figure 2. 5 Integrated direct printing system
Vacuum chamber and the particle feeding system are designed, manufactured and assembled. The optical microscope (Olympus, Japan) and CCD camera (IDS Imaging Development Systems GmbH, Germany) are integrated to the system. 3-axis motion controller and motorized stage unit (Sigma Koki, Japan), DAQ board (C-Rio with NI9205, NI9264 modules, National Instruments, USA) and homemade interface circuits and relay drives to control on and off signal for the solenoid valves are integrated also. Software of the integrated system is developed using LabView.

All of those for the system operation, control and monitoring are integrated to this software such as the particle feeding system, valve control and monitoring, stage motion control, vision monitoring and feedback, pressure measurements and etc.

In the flowing sections, the fundamental theory, analysis and experiments to verify the suggested ideas and concepts were presented in more detail with process performance evaluations.
Chapter 3.

*System modeling, analysis and experiments*

3.1 Shock induced aerosol generation

As shown in Figure 2.2, the first step of the direct printing by the suggested idea is to generate aerosol from the starting particles. The basic requirements of typical aerosol generation are as follows [75]:

1. A means of continuously metering a particles into generator at a constant rate
2. A means of dispersing the particles to form an aerosol
3. To disperse particles fully, sufficient energy should be supplied to a small volume of starting particles (bulk powder) to separate the particles by overcoming the attractive forces between them
In this work, the continuous particle feeding is not necessary because it is not helpful to print small scale patterns. Usually, it is difficult to control the feature size and scale by the continuous particle feeding method as explained in the previous sections.

The simplest method of aerosol generation is to feed loose particles into an air stream by means of gravity, usually assisted by vibrators [75]. But in this research a new concept of aerosol generation method is suggested based on the shock tube and shock induced particle dispersion and acceleration.

In this system, the starting particles are at rest at the beginning. And by sudden opening of driving valve connected to the compressor the moving shock wave is generated and propagated through the starting particles and to the printing nozzle. This moving shock wave excites the starting particles and disperse them to a dilute phase. Figure 3.1 shows the general shock wave interaction with clouds of particles for various concentrations of disperse phase [67, 69].
Figure 3.1 Shock wave interaction with clouds of particles for various concentrations of disperse phase [67, 69]
3.1.1 Shock tube theory

The general concept of this pulsed particle feeding mechanism is from the shock induced particle dispersion and shock induced high speed accelerating of gas and particles. Large pressure difference between the driving and driven section of particle feeding system is enough to generate shock wave and shock induced particle dispersion. Generally, the chamber pressure of P-NPDS is around 100 Pa and the compressor pressure is 100 kPa to 400 kPa, so the pressure ratio is high enough to generate high strength wave during the process.

A basic theory of shock tube is as follow [67, 70, 76, 77]. A shock tube is generally used to create a shock wave in a controlled environment. A shock tube consists of two sections: a driver and a driven section. In general, a diaphragm is used to separate these high (driver) and low (driven) pressure sections. To generate strong shock waves, the driver gas is usually chosen to have a high speed of sound. A large pressure difference across the diaphragm causes it to rupture at certain time. The expansion of the driver gas produces a shock wave that propagates supersonically into the driven section of the shock tube. This is shown in Figure 3.2.
The shock speed and gas speed of region 1 to 4 can be calculated from the moving shock relationship [77]. The local speed of sound of gas, density, temperature and pressure are determined by the initial pressure difference between the driver and driven section.

Knowledge of the initial pressures and temperatures in the driver section \((p_4, T_4)\) and in the driven \((p_1, T_1)\) prior to the shock wave generation enables us to calculate the pressure in the flow generated by the resulting shock wave in region 2, \(p_2\), using the following relation [78] and an iterative solution process:
\[
\frac{p_4}{p_1} = \frac{p_2}{p_1} \left(1 - \frac{(\gamma_4 - 1)(a_1 / a_4)(p_2 / p_1 - 1)}{\sqrt{2\gamma_1[2\gamma_1 + (\gamma_1 + 1)(p_2 / p_1 - 1)]}} \right)^{-2\gamma_4(\gamma_4 - 1)}
\]

(1)

\(a\) is the speed of sound and \(\gamma\) the specific heat ratio. The induced shock wave velocity, \(u_s\), can be found using [78]:

\[
u_s = a_1 \sqrt{\frac{\gamma + 1}{2\gamma} \left(\frac{p_2}{p_1} - 1\right) + 1}
\]

(2)

While the induced gas velocity behind the shock wave, in region 2, can be found using [78]:

\[
u_2 = \frac{a_1}{\gamma} \sqrt{\frac{2\gamma}{\gamma + 1}} \left(\frac{p_2 + \gamma - 1}{p_2 + \gamma + 1}\right)^{1/2}
\]

(3)
3.1.2 Shock induced particle dispersion

Figure 3.3 shows schematic of this shock induced particle dispersion of the developed system (P-NPDS). The instantaneous rupture of diaphragm is achieved by using fast acting solenoid valve and aerosol can be formed from interaction of shock wave and the starting particles.

Figure 3.3 Shock induced particle dispersion and aerosol generation

To analyze and design the suggested aerosol generation and particle dispersion scheme, we need to study the interaction between the shock wave and initially rest particles. And also the shock induced flow and particle dynamics should be studied theoretically. For these purposes, several important variables and dimensionless numbers are introduced.
The shock strength and shock induced flow regime is dependent only to the initial pressure difference between the high pressure driver section and the low pressure driven section. This is shown in eq. (1) as \( p_4/p_1 \).

And the valve opening and closing timing are also important variables to determine the aerosol and particle dispersing time scale. This is involved to particle excitation and settling time. And it is related to particle relaxation time [75].

Particle relaxation time is defined as eq. (4),

\[
\tau = \frac{\rho_p d_p^2 C_C}{18 \eta}
\]  

(4)

This particle relaxation time scale is related to the time scale of particle excitation and settling to control particle dispersion and transporting to printing nozzle.

For the analysis of flow regime, the flow Reynolds number is introduced as in eq. (5) [79],

\[
\text{Re}_f = \frac{\rho_s u_s D}{\mu}
\]  

(5)

The flow Reynolds number is the dimensionless number which defines the flow characteristic whether the flow regime is in the laminar flow or turbulent flow. Generally speaking the laminar flow is preferable to reduce turbulent effect. And for
the flow in the pipe of diameter D, if the Reynolds number is less than 2300, the flow can be said to be in the laminar flow regime [79].

\[
\text{Re}_f \leq 2300
\]  \hspace{1cm} (6)

The particle Reynolds number is defined as in eq. (7) [75, 79]

\[
\text{Re}_p = \frac{\rho_g (u_g - u_p) d_p}{\mu}
\]  \hspace{1cm} (7)

If the particle Reynolds number is less than 0.1, Stokes’ law can be applied to the particle motion in the flow field [75].

From eq. (1) to (3), the flow properties of the region 1-4 can be calculated from the 1-D model of shock tube theory. The flow properties calculated from these equations are plotted in Figure 3.4 and 3.5 with varying the initial pressure difference. In the all calculations and the experiments in this paper, the driving and driven gas are air.
Figure 3. 4 Flow properties in zone 2 (the static pressure, static temperature and the flow density) calculated from 1-D model
Figure 3.5 Flow properties in zone 2 (flow velocity and speed of sound) calculated from 1-D model: Low values of $p_1$ (high initial pressure difference) is desirable for high starting flow velocity.

From these results, as initial pressure ratio getting larger static pressure and flow density decrease while static temperature and induced flow velocity increase. If we increase the initial pressure difference, the flow velocity and so the particle velocity can be reached higher value at the aerosol outlet.

By using eq. (5) and (7), flow Reynolds number and particle Reynolds numbers can be calculated. As shown in Figure 3.6, after diaphragm rupture, the flows are induced and particles are dispersed by the shock wave and induced flow. Normally, particles have small diameter can be accelerated faster than the particles has larger diameter due to the ratio of the inertial and viscous force. Small particles have large
slip effect than larger particles. From this, small particles’ motion is viscous force dominant and large particles’ motion is inertia dominant.

Figure 3.6 Shock induced flow and particle dispersion

In Figure 3.7, the flow Reynolds number is plotted with varying the initial pressure difference. By increasing the initial pressure ratio (decreasing the initial low pressure $p_1$, or increasing initial high pressure $p_4$), the flow Reynolds number decreases. To satisfy the laminar flow condition, the lower initial pressure of low pressure driven section or the higher initial pressure of high pressure driver section is necessary. As
shown in Figure 3.7, if the initial pressure ratio higher than around 200, the flow Reynolds number is smaller than 2300. So in this condition, the flow regime is lying in the laminar flow condition.

![Flow Reynolds number for various Initial pressure ratio $p_4/p_1$](image)

**Figure 3.7** Flow Reynolds number with varying initial vacuum pressure

For laminar flow condition ($Re_f < 2300$)
Large initial pressure ratio (Lower $P_1$ or higher $P_4$)
In Figure 3.8, the particle Reynolds number is plotted with varying particle diameter. We can say that if the particle Reynolds number is smaller than 0.1, the particle’s motion is determined by the Stokes’ drag law [75]. From Figure 3.8, the particle which has diameter smaller than 300 nm has particle Reynolds number smaller than 0.1. So the motion of particles having the diameter in this size can be calculated by the Stokes’ drag law. This means that the particles are lying in the viscous force dominant region and Cunningham correction factor and mean free path of surrounding flow is important. The Cunningham correction factor and mean free path of surrounding flow are defined as follows [51, 67-70, 76-78, 80-93],
\[
C_C = 1 + Kn \left[ 1.142 + 0.558 \exp \left( \frac{-0.999}{Kn} \right) \right]
\]  \hspace{1cm} (8)

\[
K_n = 2 \frac{\lambda}{d_p}
\]  \hspace{1cm} \lambda: \text{Mean free path of gas}  \hspace{1cm} (9)

Figure 3. 9 Cunningham correction factor with varying particle diameter
Low values of \(p_1\): large slip correction (Especially for small particle)
By calculating flow conditions and Cunningham correction factor, we can calculate the particle relaxation time which was defined as in eq. (4) for various particle diameter and density. In Figure 3.10, this calculation example was shown and plotted with various particle diameter. For the particles having diameter of 100 nm has relaxation time as order of 1 msec. And for the particles having diameter of 1 μm has relaxation time as order of 10 msec. This means that the particles can be excited and...
accelerated in different time scale. So from this value, we can decide the time scale of valve switching (open – exciting and closing – settling).

To verify the shock induced particle excitation and particle size separation, the high speed camera was setup with suggested particle dispersion and aerosol generating system. This is shown in Figure 3.11. The high speed camera has maximum frame rate of 250,000 fps and UV light source was installed as the light source. The initial particles are loaded in the home made transparent small acryl chamber

Figure 3. 11 Experimental setup for shock induced particle dispersing (high speed camera was used)
Figure 3. Image captured by high speed camera showing the shock induced particle dispersion and the acceleration (time scale) of particles.

Valve

Valve switching time scale

\[ \tau = \frac{\rho_p d_p^2 C_C}{18 \eta} \]

Relaxation time scale:
1 msec for 100nm particle
8.5 msec for 1 \( \mu \)m particle
at 100 Pa initial pressure

Starting particle

Dispersed particle

Small particles transportation ends

Larger particles are excited
In this experiment, Barium Titanate (BaTiO\textsubscript{3}) particle (Sigma-Aldrich, 3 µm) is used as a starting particles. BaTiO\textsubscript{3} is loaded in the acrylic chamber as shown in Figure 3.12, and after sudden opening of the driving valve the particles are dispersed by the shock wave. The scanning electron microscope image (SEM) of the starting BaTiO\textsubscript{3} particles are shown in Figure 3.13.

![Scanning electron microscope (SEM) image of BaTiO3 particles](image)

Figure 3. 13 Scanning electron microscope (SEM) image of BaTiO3 particles

The particle sizes are distributed from around 100 nm to 3 µm from the SEM images. The small particles are agglomerated. To disperse these small particles fully, sufficient energy should be supplied to the starting particles to separate the particles by overcoming the attractive forces between them. Due to the nature of high energy of shock wave, it can be a promising way to supply the sufficient energy to the starting particles.

As shown in Figure 3.12, in the early stage after valve opening, small particles are dispersed in the gas flow and they are accelerated to the aerosol outlet which is located very top side of the acryl chamber. And as explained and expected previous sections, the larger particles are accelerated slower than small particles due to their
large particle relaxation time. The main purpose of this research is to make pattern size smaller than the conventional NPDS, so the particles which have small diameter are preferable to be used for printing patterns. Consequently it is required to prevent large particles or the agglomeration of small particles being transported to the printing nozzle. Considering these, the pulsed shock wave induced particle dispersion can be efficient way to generate the starting aerosol of P-NPDS.

During the particle dispersion and aerosol generation process by the suggested method, the initial pressure difference is important process parameter that determine the particle dispersion efficiency and the initial aerosol and particle velocity.
Figure 3. 14 Experimental results and image captured by high speed camera showing aerosol outlet particle velocity
In Figure 3.14, the experimental results were shown as the image captured by the high speed camera showing aerosol outlet particle velocity with varying the initial pressure difference ratio. The high driving pressure $p_4$ is set to be as 100 $kPa$, 200 $kPa$ and 400 $kPa$ and the low driven pressure $p_1$ is set to be as 100 $Pa$ for these experiments. The images are captured at $t = 0$ ms, 0.5 ms and 0.1 ms with the high speed camera. In Figure 3.15, the particle velocity which was approximately calculated from the image was plotted with the flow velocity calculated from the 1-D shock tube relations. The theoretical flow velocity reaches as high as 1,000 m/s from the 1-D shock tube model, while the particle velocity is much lower than the flow velocity calculated. But as we increase the initial pressure difference ratio, the particle velocity at the aerosol outlet can be increased faster (100 m/s ~ 200 m/s). And after this aerosol exits the aerosol outlet it can be further accelerated by the nozzle expansion of the jet. The initial pressure difference is an important process parameter to be carefully controlled for these purposes, but as increasing the initial pressure difference of the high and low pressure regions the more particles are dispersed and transported to the printing nozzle. From the high speed camera images as shown in Figure 3.14, the large initial pressure difference can cause the more dispersed particle concentrations near the aerosol outlet. And this can lead over spray of particles during printing process. So the opening and closing timing of the driving and purge valve is another important process parameter to be carefully controlled to prevent the excessive aerosol formation and transportation. In the large initial pressure difference condition, we can reduce the particle transportation amount by keeping shorter driving valve opening time. From this the particle can be accelerated much faster and transported for short time duration without over spray. These will be explained more detail in the following section with further experiments.
Figure 3. The particle velocity which was approximately calculated from the high speed camera image and the flow velocity calculated from the 1-D shock tube relations

3.2 Particle transportation control

To realize reliable and repeatable high resolution direct printing on-demand and on-position, we designed the particle feeding method with a pulsed gas flow. For this we use solenoid valves and control opening and closing timing of the valves for pulsed carrier gas feeding instead of using mass flow controller (MFC) generally used in NPDS or other similar systems (ADM, cold spray). There are two solenoid valves for one particle feeder system. One is for flowing carrier gas from the compressor (driving valve) and the other is for purging (purge valve) which is connected to the secondary vacuum pump. Solenoid valve has very fast response time [94] (a few milliseconds) and much cheaper than MFC unit. Furthermore, it is
ideal not only to achieve pulsed excitation of gas and particle but also for on-demand and on-position printing by simple opening and closing control of valve. And also the additional purge valve system helps to keep the pressure inside the particle feeding system low and prevent unwanted or excessive particle feeding. In Figure 3.16, the example of timing diagram of opening and closing sequence of each valve and the figure depicts carrier gas and purge flow directions are shown.

![Figure 3.16](image)

Figure 3.16 (a) The example of timing diagram of valves opening and closing sequence and (b) the schematic figure depicts carrier gas and purge gas flow directions

As shown in Figure 3.16, when the driving valve is opened (at $t = t_1$), purge valve is closed and make the shock wave propagates through the particles and disperse the particles inside the particle reservoir. The flowing carrier gas generates aerosol and
it is transported to the substrate inside the vacuum chamber through aerodynamic particle filters and printing nozzle. This aerodynamic particle filter is designed based on the particle focusing and particle filtering mechanism of aerodynamic lens. After some time duration \( (D) \), driving valve is closed and purge valve is opened (at \( t = t_2 \)) to purge the remained gas inside the particle feeding system and keep the pressure inside the particle feeding system low until the next opening of flow control valve (at \( t = t_3 \)). The time duration \( D \) determines the feeding timing of particle dispersed by the shock wave from the particle feeder to nozzle. To print small scale patterns onto the substrate, this time duration should be set as short value. But if we choose too short time duration \( D \), excitation and transportation of particles might be finished before they reached to the substrate. So this time duration should be determined by considering the particle relaxation time scale. From the fundamental experiments and theoretical studies which were conducted in the previous sections, the relaxation time scale of the particles whose diameter are lying in the range of 100 \( \text{nm} \) to 10 \( \mu\text{m} \) is in the range of 1 \( \text{milliseconds} \) to several tens of \( \text{milliseconds} \). So by considering the response time of solenoid valves, it is reasonable to choose the value \( D \) as the order \( \text{milliseconds} \).

To verify that the amount of particle transported from the particle feeder to the printing nozzle can be controlled by the valve opening and closing timing control, similar experiments are conducted by using high speed camera. BaTiO\(_3\) particles are used as a starting particles and the home made transparent cubic acryl chamber is installed between the aerosol outlet of the particle feeder and the entrance of the printing nozzle. The initial pressure difference between the high pressure driver section and the low pressure driven section is set as \( p_4 = 200 \text{ kPa} \) and \( p_1 = 100 \text{ Pa} \). The substrate is Si. The high speed camera images are captured from the transparent
acryl chamber with varying the opening time duration of driving valve $D$. In Figure 3.17, the results are shown with the in-situ monitored printed pattern inside the vacuum chamber. In the same initial pressure difference condition, the amount of particles (i.e. aerosol) transported from the particle feeder to the nozzle can be controlled by the valve opening timing. And it is directly influence the scale of the printed pattern.

![Images](Image)

Figure 3. 17 The images captured by the high speed camera with varying the driving valve opening time and in-situ monitored printed pattern

In Figure 3.18, the magnified image is shown. By choosing shorter valve opening time, the aerosol can be transported to the nozzle as a highly focused shape and the amount can be reduced dramatically.
3.3 Measuring of particle impact velocity and particle focusing

Usually, in NPDS or other similar processes, the particle impact velocity is very important factor which can determine the deposition and following material bonding possibility and quality [32, 47, 49]. Many researches have been reported to measure the velocity of particle at the impact onto the substrates for cold spray [30, 49]. But ADM or NPDS use vacuum condition, so it is hard to measure or visualize inside the chamber and the particle imaging at the impact.
In this section, it is tried to visualize the particle injection and velocity by using high speed camera from window view port of the vacuum chamber and the particle cloud velocity is roughly measured as approximately 200 m/s right after nozzle. Because nano particles are accelerated by free expansion from the nozzle exit to the substrate it is expected that the actual impact velocity is much faster than the measured value [53]. So the bonding and deposition is expected still to be hold and actual printing results which will be shown in the following chapters support these. Figure 3.19 shows the images taken inside the vacuum chamber during Barium Titanate particle printing by the high speed camera. In this case the valve opening time duration is 20 ms and driver gas pressure is 100 kPa and vacuum pressure is kept as 100 Pa. The frame rate of the high speed camera is 50,000 fps and the time duration between two images is 19 μsec. The printing nozzle has 500 μm exit diameter.
3.3.1 Mechanism of particle focusing

Researches on the particle focusing and particle beam formation by the aerodynamic force have been reported by many researchers in aerosol science and other related engineering fields [53, 55, 71, 72, 95, 96]. To explain the particle focusing mechanism, it is helpful to define the concentration factor $\eta$ defined as in eq. (11) [55, 58-60, 71]. Concentration factor is used for describing near axis particle...
motion. It is defined the ratio of the radial distance of particle before nozzle exit and after nozzle exit which is depicted in Figure 3.20.

If the third term of eq. (11) is negative or smaller than the second term of eq. (11), the concentration factor is less than unity. In this case, particle’s radial distance is decreased after passing through the nozzle and particle can be jetted as a focused particle beam.

\[
\eta = \frac{r(x)}{r(-x)} = 1 - \frac{3}{4} S \int_{-\infty}^{\infty} \frac{1}{T^2 \rho^3 u_x} \left( \frac{d}{dx} (\rho u_x) \right)^2 dx + \frac{1}{2} S \int_{-\infty}^{\infty} \frac{1}{T^2 \rho^3} \frac{d^2}{dx^2} (\rho u_x) dx, \quad S \to 0
\]

(11)

Figure 3. 20 Mechanism of particle focusing and particle beam formation [59]

Israel et al. [72] reported the high speed particle beam of small particles by several experiments. And they explained the focusing mechanism of the small particles under nozzle expansion. This is depicted in Figure 3.21.
In this thesis, experimental works are conducted to show the focused particle beam formation and its use for the small scale direct pattern printing by P-NPDS. By using P-NPDS, BaTiO$_3$ particles are printed and the CCD camera installed inside the chamber captures the in-situ particle jetting and printing onto the substrate. In this experiment, the nozzle of which the exit diameter $d$ is 500 $\mu$m is used. The converging angle of the nozzle $\alpha$ is 15°. The detail process parameters are summarized in Table 3.1.
Table 3.1 Process parameters of the experiment for visualizing and in-situ monitoring of the particle focusing

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pressure of driver section</td>
<td>100 kPa</td>
</tr>
<tr>
<td>Initial pressure of driven section</td>
<td>100 Pa</td>
</tr>
<tr>
<td>Initial pressure ratio ($p_4/p_1$)</td>
<td>1,000</td>
</tr>
<tr>
<td>Time duration of driving valve opening</td>
<td>20 ms</td>
</tr>
<tr>
<td>Nozzle exit diameter</td>
<td>500 µm</td>
</tr>
<tr>
<td>Converging angle of nozzle</td>
<td>15°</td>
</tr>
<tr>
<td>Stand off distance, SoD (The distance between nozzle and substrate)</td>
<td>700 µm</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si</td>
</tr>
</tbody>
</table>

In Figure 3.22, the in-situ monitoring of particle beam formation and particle focusing is shown. This image was captured with the CCD camera inside the printing chamber. The particles are jetted by P-NPDS as a highly focused particle beam and the printed pattern can be deposited as a small scale. In this experiment the diameter of printed BaTiO$_3$ pattern is measured under 100 µm.
Another similar experiment was conducted to show the particle focusing during printing process by P-NPDS. The high speed camera was used to visualize the particle beam formation near the printing nozzle. In Figure 3.23, the image captured from the high speed camera is shown. In this experiment, we can see the particle beam formation more clearly and the focal point of the particle beam is also shown.
It is noticeable that we can generate the particle jet as a tightly focused beam by using P-NPDS which is much smaller than the diameter of the nozzle exit. If we define the ratio of the diameter of particle beam with respect to the nozzle exit diameter as focusing ratio, $FR$, then from this experiment, $FR$ is measured as approximately 0.1.

$$FR = \frac{d_{\text{particle beam}}}{d_{\text{nozzle}}}$$  \hspace{1cm} (12)

---

Figure 3. 23 High speed in-situ camera captured image inside the vacuum chamber
Chapter 4.

Performance evaluation of P-NPDS

4.1 Overview

In this chapter, process parameters of P-NPDS are studied with experiments focusing on the shape and size of the printed patterns. Point patterns of metal and ceramic particles are directly printed onto the Si substrate and the cross section of these patterns are observed. Focused ion beam (FIB) is used for cross sectioning of the patterns. Silver (Ag) patterns are printed as metal particle and Barium Titanate (BaTiO$_3$) patterns are printed as ceramic particle. Ag is widely used as a conductive material or pattern in the various applications and BaTiO$_3$ is representative dielectric material for capacitors. Recently BaTiO$_3$ is studied for the energy harvesting device using its piezoelectric properties [97, 98].
The cross sectional profile which is machined by FIB with the pattern diameter and height of the pattern is analyzed with varying important process parameters of P-NPDS such as the initial pressure difference $p_4/p_1$, time duration of driving valve opening $\gamma$ (printing time) and the number of repeated printing on the same position $n$.

### 4.2 Process parameter study of P-NPDS

In Table 4.1, important process parameters of P-NPDS are listed. The physical properties of particle such as particle density or particle diameter influence the particle Reynolds number, particle relaxation time and etc. Details of these properties have been explained in Chapter 2 with system modeling, theoretical analysis and experiments. In this section, the initial pressure difference $\psi$, printing time $\gamma$ and the number of repeated printing $n$ are studied with detail pattern shape, size and profiles. For the experiments, Ag particle (Sigma-Aldrich, $100 \text{ nm}$) and BaTiO$_3$ (Sigma-Aldrich, $< 3 \text{ \mu m}$) particle are used as purchased. These two particles are independently loaded in different particle feeder and the direct printing was conducted by using P-NPDS.

In Figure 4.1, the examples of profile cutting of Ag point pattern printed onto the Si substrate are shown. The profile cutting is conducted by FIB milling and the images are taken with FIB after milling. Similarly, the examples of profile cutting of BaTiO$_3$ point pattern printed onto the Si substrate are shown in Figure 4.2.
Table 4.1 Important process parameters of P-NPDS

<table>
<thead>
<tr>
<th>Definition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>Particle density</td>
<td>$\rho_p$</td>
</tr>
<tr>
<td>(particle)</td>
<td>(kg/m$^3$)</td>
</tr>
<tr>
<td>properties</td>
<td>$d_p$</td>
</tr>
<tr>
<td></td>
<td>diameter (mm)</td>
</tr>
<tr>
<td><strong>Process</strong></td>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>parameters</td>
<td>Initial pressure difference : driver pressure ($p_4$) vacuum pressure ($p_1$)</td>
</tr>
<tr>
<td>$\psi$</td>
<td>$p_4/p_1$</td>
</tr>
<tr>
<td></td>
<td>Time duration between driving valve opening and closing (sec)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Printing time</td>
</tr>
<tr>
<td></td>
<td>Number of driving valve opening (&amp; closing) at the same position</td>
</tr>
<tr>
<td>$n$</td>
<td>repeated</td>
</tr>
</tbody>
</table>

74
Figure 4. 1 Examples of FIB Cross sectioning of point pattern of Silver (Ag) with various process parameters

Figure 4. 2 Examples of FIB Cross sectioning of point pattern of Barium Titanate (BaTiO3) with various process parameters
From Figure 4.1 and 4.2, pattern diameter, height and profiles can be obtained. Ag pattern can be printed with much higher height than BaTiO$_3$. And in both cases the pattern diameter can have $30 \, \mu m$ to $100 \, \mu m$ by the process condition. With these information the cross sectional profile of each pattern is plotted in the following figures. In Figure 4.3, Ag pattern profile is plotted with varying the initial pressure difference and printing time. For this case, the number of repeated printing is set to be 1. Pattern size is getting larger as we increase the initial pressure difference. And also similar trends are observed as we increase printing timing. To reduce the number of process parameter, we can define the product of the initial pressure difference and the printing time as $\Lambda$.

$$\Lambda = \gamma \psi = \gamma \frac{p_1}{p_4}$$

(13)

$\Lambda$ is important process parameter which determines the printed pattern size and height. If we increase $\Lambda$, pattern diameter and height is increased. In Figure 4.3 the influence of $\Lambda$ to the pattern profile is plotted.

Another process parameter $n$ which is defined the number of repeated printing on the same position is important for the pattern height. In the same process condition, pattern height increases dramatically by increasing the number of repeated printing compared with by increasing $\Lambda$. By repeating multiple printing on the same position it can be possible to print extremely high aspect ratio structure.
Figure 4. 3 Silver printed pattern profile for \( \Lambda = \gamma p_1/p_4 \) (for \( n=1 \))

Figure 4. 4 Silver printed pattern profile for \( n = 1, 2, 4, 8, 16, 32 \)
BaTiO₃ patterns show similar trends as shown in Ag pattern, but the height of pattern is lower than Ag. The cross sectional profiles are shown in Figure 4.5 and 4.6 for BaTiO₃ patterns.

Figure 4.5 Barium Titanate printed pattern profile for

\[ \Lambda (= \gamma p_1/p_4) \text{ (for } n=1) \]
Figure 4. 6 Barium Titanate printed pattern profile for $n = 1, 2, 4, 8, 16, 32$
Chapter 5.

Multi-material direct printing results

5.1 Overview

In this chapter, the selected direct printing examples by the developed P-NPDS were presented. The target feature scale, shape and material configurations are shown in Figure 5.1. As shown in Figure 5.1, the single and multi material point patterns which have the resolution under 50 μm are shown in the following sections. And line pattern, 2-D planar patterns and 2.5-D high aspect ratio tip structure printing results are presented by followed.

The printing materials are selected with functional metal and ceramic materials. For metal pattern printing, Tin (Sn) and Silver (Ag) particle are chosen. Sn has low melting temperature so it is widely used for the solder material and conductive material. Ag is used for conductive line patterning or electrodes. Many commercial ink-jet printer uses Ag ink to pattern conductive line onto the substrate. But it is
needed to make or purchase Ag ink to print and also the heat treatment is necessary. P-NPDS does not need to consider pre- or post-processes for the printing material. It uses dry solid particle as purchased and without heat treatment, high conductivity can be achieved. For ceramic pattern printing, BaTiO$_3$ is chosen. The printing materials and substrates are summarized as follows:

- **Printing materials**
  - **Metal**
    - Tin (Sn) (Sigma-Aldrich, 4 mm) : solder, conductive lines
    - Silver (Ag) (Sigma-Aldrich, 100 nm) : conductive line, electrodes
  - **Ceramic**
    - Barium Titanate (BaTiO$_3$) (Sigma-Aldrich, 3 $\mu$m) : capacitor, piezoelectric transducer, piezoelectric energy harvesting device
- **Substrates**
  - Silicon (Si)
  - Polyethylene terephthalate (PET) : Flexible and transparent
5.2 Multi-material point patterns

5.2.1 Direct pattern printing of metal 1 (Tin)

In Figure 5.2, Sn point pattern printing results are shown with SEM image. The Si substrate is used for the substrate and the point pattern has the minimum diameter of 50 μm. The letter pattern of ‘3DPRINTING’ is also printed onto the Si substrate and in Figure 5.3, the optical microscope image and SEM image of printed pattern were shown.
Figure 5. 2 SIM image of micro scale Tin point pattern printing

Figure 5. 3 Optical microscope image of micro scale ‘3DPRINTING’ pattern printing and SIM image of micro scale ‘3DPRINTING’ pattern printing
5.2.2 Direct pattern printing of metal 2 (Ag) on flexible PET substrate

Silver nano particle (Sigma-Aldrich, USA) was loaded inside the particle feeding system as purchased without any further treatment and printed onto flexible PET substrate. Figure 5.4 shows the SEM image of Silver nano particle used to direct printing. The printing time and the number of repeated printing at the same position $n$ is chosen to be 20 ms and 2 for each to make the pattern size to be 30 $\mu m$ by following the experiments described in the previous chapter. The ‘SNU’ letter pattern printed on PET substrate was shown in Figure 5.5 and 5.6 with optical image and detail SEM pictures. The space between each point pattern is 100 $\mu m$.

![Figure 5.4 SEM image of Silver (Ag) nano particle](image-url)
Figure 5. 5 The optical image of the ‘SNU’ letter pattern printed on the flexible PET substrate by using Silver particle

Figure 5. 6 The ‘SNU’ letter pattern printed on the flexible PET substrate by using Silver particle (a) and the detail SEM pictures (b)
5.2.3 Direct pattern printing of ceramic (BaTiO$_3$) on Si substrate

BatiO$_3$ particle (Sigma-Aldrich, USA) was loaded inside the particle feeding system as purchased without any further treatment and printed onto Si substrate. Figure 5.7 shows the SEM image of BatiO$_3$ particle used to direct printing. The printing time and the number of repeated printing at the same position $n$ is chosen to be 10 ms and 2 for each to make the pattern size to be 30$\mu$m by following the experiments described in the previous chapter. The Korean national flower Mugungwha pattern is printed on Si substrate and the results was shown in Figure 5.8. The space between each point pattern is 30$\mu$m.

There is no existing research to print solid metal and ceramic particles directly onto the substrate as a high resolution (< 30 $\mu$m). In this research it was firstly tried to print solid metal and ceramic particles as a micro scale resolution by the newly developed direct printing system (P-NPDS).

![Figure 5. 7 SEM image of Silver (Ag) nano particle](image_url)
5.2.4 Direct printing of ceramic (BaTiO$_3$) onto PET substrate

BaTiO$_3$ pattern is printed onto flexible and transparent PET substrate. BaTiO$_3$ particle (Sigma-Aldrich, USA) was used to print as purchased without any further treatment. The printing time and the number of repeated printing at the same position $n$ is chosen to be 20 $ms$ and 2 for each to make the pattern size to be 30 $\mu m$. The official emblem of Seoul National University was printed to have 30 $\mu m$ spacing between each point pattern and the printing result is shown in Figure 5.9. This result is especially noticeable as the fact that the printing of ceramic particle is done in dry, at room temperature, without mask and any pre- or post-process onto flexible plastic substrate with high resolution.
5.2.5 Multi-material direct printing on flexible and transparent PET substrate

In the previous sections, single material was used for high resolution direct printing. In this section, to show multi-material direct printing capability on the flexible and transparent substrate, the letter ‘SNU’ which is consist of 500 metal point patterns and 500 ceramic point patterns is printed on the flexible PET substrate. Silver is used for metal printing and BaTiO$_3$ is used for ceramic material printing. As shown in Figure 5.10, the outer boundary of the letter ‘SNU’ was printed with Silver and the
inner region of this letter was printed with BaTiO$_3$. The printed result is shown in figure 5.10 with SEM pictures too. The pattern was printed with spacing between each point as 100 $\mu m$ and the whole printing process was done in dry environment, at room temperature, without mask and without any pre- or post-process same as the previous results.

There is no existing research to print solid metal and ceramic particles directly onto the substrate as a high resolution simultaneously. In this research it was firstly tried to print the patterns consist of multi material (solid metal and ceramic particles) as a micro scale resolution by the newly developed direct printing system (P-NPDS).

Figure 5. 10 Multi-material direct printing of the ‘SNU’ letter pattern. The outer boundary of the letter ‘SNU’ was printed with Silver and the inner region of this letter was printed with Barium Titanate and the printed result with SEM pictures was shown also
5.3 Multi-material direct line printing on flexible and transparent PET substrate

As shown in Figure 5.1, the second direct printing example of P-NPDS is line patterns. Line patterns can be used for the conductive line, electric circuit printing and etc. Metal (Sn and Ag) and ceramic (BaTiO₃) line patterns are printed onto the Si substrate.

In Figure 5.11, the SIM images of Sn line pattern of the Si substrate was shown. The line width is around 30 μm and by FIB profile cutting of the cross section, the thickness of these line patterns are measured as 500 nm to 2 μm.

Figure 5.11 SIM image of micro scale line pattern printing of Tin (Sn) on Si substrate
The circular patterns of Sn was also shown in Figure 5.12. The diameter of circle is 200 $\mu$m and the width of pattern is 50 $\mu$m.

![Figure 5.12 SIM image of micro scale circle pattern printing of Tin (Sn) on Si substrate](image)

Ceramic particle (BaTiO$_3$) is printed as a line pattern onto Si substrate. In Figure 5.13 the SEM image of BaTiO$_3$ line pattern was shown. The line width is 30 $\mu$m to 40 $\mu$m and spacing between lines are 70 $\mu$m. The line pattern printed with multi material (Ag and BaTiO$_3$) is also printed onto Si substrate and the SEM result was shown in Figure 5.13.
5.3.1 Electrical resistance measurement

In this section Ag conductive line pattern is printed onto the flexible PET substrate and its electrical resistance was measured by bending. The two external conductive pad is printed using Silver paste and 4 mm length Ag conductive line connecting these two electrode pads is directly printed on PET substrate by P-NPDS. The width of the line pattern is controlled to have 50\,\mu m.

In Figure 5.14 the fabricated samples are shown. The electrical resistance was measured with multi meter with varying bending angle of the sample. The results were plotted in Figure 5.15. The calculated electric resistivity of silver line without bending was 4.24\,\mu \Omega\text{-cm}. it is 3 times greater than the bulk resistivity of Ag (1.59\,\mu \Omega\text{-cm}) [8, 23].
Figure 5. 14 Silver conductive line patterning onto PET substrate

Figure 5. 15 Bending and electrical resistance measurement of directly printed Silver conductive line onto flexible PET substrate
In Figure 5.16 another direct printing example was presented showing the digitized electrode pattern fabrication capabilities of P-NPDS. This result can be used for fabrication of the flexible electronic device and other related applications by P-NPDS.

Figure 5.16 The digitized Ag electrode pattern printed onto PET substrate
5.4 Multi-material direct printing of 2-D planar patterns

2 dimensional planar patterns can also be directly printed by the developed system. To print large area planar patterns by using P-NPDS, process parameters should be controlled well. In Figure 5.17 in-situ monitoring of the direct 2-D planar pattern printing of BaTiO$_3$ is shown. The uniform particle jet is formed during the entire printing process and the pattern can be printed as uniform pattern.

In Figure 5.18 the optical image of the 2-D planar pattern and the surface profile result are shown. The uniform thickness of the printed pattern was shown from the surface profile measurement. The average thickness of the pattern is measured as 2.129 $\mu$m.
Figure 5. 18 The optical microscope image of 2-D planar pattern of BaTiO3 and the surface profile measurement result of the pattern

Mean thickness: 2.129µm
P-NPDS can be used to fabricate more complex and functional structures with metal and ceramic particles. In Figure 5.19, direct printing of multi material 2-D printing results were shown. In the following, section the printing example showing the ability to fabricate high aspect 2.5 dimensional structure by P-NPDS will be shown.

Figure 5. 19 Direct pattern printing of multi-material complex 2-D patterns
5.5 High aspect ratio tip fabrication (2.5-D structure printing)

As shown in chapter 4 with the experiments, by repeating multiple jetting on the same position high aspect ratio structures can be fabricated using P-NPDS. In Figure 5.20, high aspect ratio silver tips printed onto Si substrate are shown. The tip of the structures can be grown as sharp shape by the repeated printing.

Figure 5.20 High aspect ratio tip fabrication metal (Ag)
Ceramic (BaTiO$_3$) tip fabrication results were also shown in Figure 5.21. Furthermore, extremely sharp, long and high aspect ratio tip can be directly printed by using P-NPDS. This results were shown in Figure 5.22. The aspect ratio (height/width) of these sharp tip is greater than 20. This result can be used for tip electrode fabrication by direct printing method.
5.6 Fabrication of energy harvesting device using P-NPDS

Recently, piezoelectric energy harvesting devices are actively studied by many researchers [26, 98]. Recent research trend of energy harvester is to use lead free piezoelectric material. Because BaTiO$_3$ is one of the most famous lead free piezoelectric material which can replace the conventional PZT ceramics. In this research the prototype of energy harvester was successfully fabricated with BaTiO$_3$ as the piezoelectric energy harvesting layer and Ag as the electrodes by using P-NPDS. The electrodes and piezo ceramic patterns are directly printed onto the flexible PET substrate and the voltage generated by the external force exerted to the energy harvester is measured. In Figure 5.23, the fabricated prototype of energy
harvester was shown and in Figure 5.24, the generated voltage was plotted with the test setup. As the future works, the research on the fabrication and evaluation of the more robust energy harvesting device will be conducted by P-NPDS.

Figure 5. 23 The prototype energy harvester fabricated by P-NPDS

Figure 5. 24 Test setup and generated voltage measurement of the energy harvester
Chapter 6.

Conclusions

Novel multi-material direct printing system was developed by utilizing nano particle deposition system which is applicable to metal and ceramic particle printing onto hard substrate and flexible plastic substrate. This direct printing can be done in dry, at room temperature, without mask and any further pre- or post-treatment. The system is designed to transport and accelerate particles to the substrate inside vacuum chamber through nozzle by pulsed carrier gas feeding to fabricate printed features. Driving valve for shock induced aerosol generation and purge valve are controlled at very fast switching rate to realize pulsed particle (aerosol) transportation and this helps to make feature size smaller than conventional NPDS or other similar processes. System design, integration and performance evaluation were done and by using the integrated system high resolution metal (Silver) and ceramic (Barium Titanate) multi-material patterns were directly printed onto Si and flexible/transparent PET substrate with various shapes. The minimum printed feature size can be achieved under 30 μm by P-NPDS.

To present the novel direct printing capabilities of P-NPDS, detail comparison of material, pattern shape, size and resolutions are summarized in the Table 6.1 to 6.6.
Table 6.1 Comparison of direct printing results (P-NPDS vs. Inkjet)
Single-material point or dot pattern [4, 9]

<table>
<thead>
<tr>
<th></th>
<th>P-NPDS</th>
<th>Ink-jet or other similar printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Metal (conductive) and Ceramic (Functional) particle</td>
<td>Semiconductor material conductive ink</td>
</tr>
<tr>
<td>Pattern resolution</td>
<td>~30μm</td>
<td>10μm ~ 100μm (Inkjet) 1~10μm (E-Jet)</td>
</tr>
<tr>
<td>Printing results</td>
<td>Metal (conductive, Ag)</td>
<td>Inkjet (CdSe-ZnS)</td>
</tr>
<tr>
<td></td>
<td>Ceramic (piezoelectric, BaTiO₃)</td>
<td>E-Jet (PEDOT/PSS)</td>
</tr>
</tbody>
</table>
Table 6. 2 Comparison of direct printing results (P-NPDS vs. Inkjet)

Multi-material point or dot pattern [4, 39]

<table>
<thead>
<tr>
<th>Material</th>
<th>P-NPDS</th>
<th>Ink-jet or other similar printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal (conductive) and Ceramic (Functional) particle</td>
<td>~30µm</td>
<td>10µm ~ 100µm (Inkjet)</td>
</tr>
<tr>
<td>Pattern resolution</td>
<td></td>
<td>1~10µm (E-Jet)</td>
</tr>
<tr>
<td>Metal (conductive, Ag) and Ceramic (Functional, BaTiO₃) particle</td>
<td></td>
<td>Inkjet (CdSe-ZnS) / E-Jet (fluorescent ink)</td>
</tr>
</tbody>
</table>

Table 6. 3Comparison of direct printing results (P-NPDS vs. Inkjet)

Line pattern [8, 39]

<table>
<thead>
<tr>
<th>Material</th>
<th>P-NPDS</th>
<th>Ink-jet or other similar printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal (conductive, Sn)</td>
<td>30µm~100µm</td>
<td>10µm ~ 100µm (Aerosol jet, Inkjet)</td>
</tr>
<tr>
<td>Pattern resolution</td>
<td></td>
<td>1~10µm (E-Jet)</td>
</tr>
<tr>
<td>Metal (conductive, Ag)/ceramic (BaTiO₃)</td>
<td></td>
<td>Aerosol-jet (conductive ink : Ag)</td>
</tr>
</tbody>
</table>

Printing results

Metal (conductive, Ag) / ceramic (BaTiO₃)
### Table 6. Comparison of direct printing results (P-NPDS vs. Inkjet)

**Comparison of electrical property [8]**

<table>
<thead>
<tr>
<th>Material</th>
<th>P-NPDS</th>
<th>Ink-jet or other similar printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Ag nano particle</td>
<td>Conductive Ag ink</td>
</tr>
<tr>
<td>Line width</td>
<td>40 μm</td>
<td>30~50 μm</td>
</tr>
<tr>
<td>Printing results</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metal (conductive, Ag)</td>
<td>Aerosol-jet (conductive ink : Ag)</td>
</tr>
<tr>
<td>Electrical resistivity, $\rho$</td>
<td>4.24μΩ-cm*</td>
<td>3.61μΩ-cm*</td>
</tr>
<tr>
<td>Remarks</td>
<td>Low electrical resistivity without heat treatment Application to flexible electronics</td>
<td>Thermal sintering is required</td>
</tr>
</tbody>
</table>

*Electrical resistivity of bulk Silver : 1.59μΩ-cm*
Table 6. 5 Comparison of direct printing results (P-NPDS vs. Inkjet)

Comparison of planar ceramic film [21]

<table>
<thead>
<tr>
<th>Material</th>
<th>P-NPDS</th>
<th>Ink-jet or other similar printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic (BaTiO$_3$) particle</td>
<td>SEM image after thermal sintering</td>
<td>SEM image without thermal sintering</td>
</tr>
<tr>
<td>Ceramic (BaTiO$_3$) ink</td>
<td>SEM image after thermal sintering</td>
<td>SEM image without thermal sintering</td>
</tr>
</tbody>
</table>

Table 6. 6 Comparison of direct printing results (P-NPDS vs. Inkjet)

High aspect ratio tip fabrication [99]

<table>
<thead>
<tr>
<th>Material</th>
<th>P-NPDS</th>
<th>Ink-jet or other similar printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag nano particle</td>
<td>Extremely high aspect ratio (height/width) &gt; 20</td>
<td>Aspect ratio (height/width) ~ 1</td>
</tr>
<tr>
<td>Ag ink</td>
<td>Printing results</td>
<td>Printing results</td>
</tr>
</tbody>
</table>
Appendix

To verify the printing system’s performance focused on the flow acceleration and impact velocity, CFD analysis was conducted using ANSYS Fluent software. After generating computational grid domain with mesh the set of equations were solved by Fluent solver. The mass conservation equation along with the linear momentum equations and the energy equation in the unsteady axisymmetric form (no swirl) are solved. These equations relate the values of axial and radial components of velocity to pressure, treating temperature as a variable. Due to compressibility effects, the gas mass density is a variable in these equations and is related to pressure and temperature through the ideal-gas law (constant heat capacities are assumed).

\[
\frac{\partial \rho}{\partial t} = -\rho \mathbf{\nabla} \cdot \mathbf{U} \tag{A-1}
\]

\[
\frac{\partial (\rho \mathbf{U})}{\partial t} + \nabla \cdot (\rho \mathbf{U} \otimes \mathbf{U}) = -\nabla p + \nabla \cdot \mathbf{\tau} + S_m \tag{A-2}
\]

\[
\frac{\partial (\rho h_{tot})}{\partial t} - \frac{\partial p}{\partial t} + \nabla \cdot (\rho U h_{tot}) = \nabla \cdot (\lambda \nabla T) + \nabla \cdot (\mathbf{U} \cdot \mathbf{\tau}) + U \cdot S_m + S_E \tag{A-3}
\]
Where $\rho$ is density, $t$ is time, $U$ is velocity vector, $p$ is pressure, $\tau$ is stress tensor, $S_M$ is the momentum source, $h_{tot}$ is the total entalphy, $\lambda$ is thermal conductivity, and $S_E$ is the energy source.

Turbulence effects are accounted for through the Spalart–Allmaras one-equation model that is used to estimate a value for kinematic eddy (turbulent) viscosity. It was proposed for aerospace applications involving wall-bounded flows and has been shown to yield good results for boundary layers subjected to adverse pressure gradients [31].

A quadrilateral block mesh is used throughout the entire domain. The grid system initially contains 20,000 cells, increasing through the simulation to approximately 100,000. This is mainly due to grid adaption that is used in order to better capture the moving shock-wave. This grid size and level of refinement is verified through a grid sensitivity analysis and shown to be the optimum size for accurate results and minimal computation time.

The actual measured time dependent profile of the back pressure inside the vacuum chamber was used as the pressure outlet boundary condition as a user defined function.

$$P_v = 100 + 1000(1 - e^{-23t}) \text{ Pa}$$ (A-4)

And the initial conditions of driver section is set to be process condition (100 kPa) by using the cell patch after solution initialization. And pressure inside the driver section is patched to little higher than the back pressure to keep flow reversing from the outlet boundary.

At first, the particle feeder was simulated and the maximum flow velocity caused by the coalescing of the compression wave which is initially generated by the sudden opening of valve is more than 1,000 m/sec. In figure A.1 this result is shown.
And for the simulation of whole printing system from the particle feeder (driver section) to the substrate, entire computational domain was modeled and simulated with similar process. And this result was shown in Figure A.2.
Figure A. 2 CFD analysis results of particle feeder and nozzle
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초 록

오늘날 많은 제품들의 생산 공정에 있어 고집적화가 이루어지고 있고, 제품의 다기능성과 신뢰성이 강조되고 있다. 또한 제품의 수명이 짧아지고 저비용, 고효율의 생산공정 개발에 대한 필요성이 커짐에 따라 기존에 없던 새로운 방식의 제품 개발과 생산공정에 관한 연구가 활발하게 이루어지고 있다. 기능성 제품의 기판에 대한 직접 인쇄공정은 이러한 새로운 생산공정 중의 한 예로서 최근 활발히 연구되고 있는 분야 중 하나이다. 직접 인쇄공정은 기판 상에 원하는 위치에 원하는 형태로 여러 가지 재료를 적층하는 공정이며, 산업용 잉크젯프린팅 기술이 대표적이라고 할 수 있다. 하지만 이러한 잉크젯공정은 액상의 잉크를 사용하는 공정으로 인쇄공정 후 열처리 등의 후처리를 필요로 하며 기본적으로 습식공정이라는 단점이 있다. 한편, 나노입자적층시스템(Nano particle deposition system), 에어로졸적층(Aerosol deposition method), 저온분사적층(Cold spray) 등은 저온 건식이라는 장점을 갖는 적층방법으로서 고체의 금속 혹은 세라믹입자를 직접 기판에 적층하여 좋은 결과를 보고되고 있다. 하지만 이들공정은 주로 대면적 코팅 혹은 박막 제작에 주로 이용되고 있으며, 충분히 직접 인쇄공정에 응용이 가능한 장점을 가지고 있으나 이에 대한 연구는 아직 충분히 이루어지지 않았다.

본 논문에서는 상온에서 금속과 세라믹입자를 순간적으로 가속하여 기판상의 원하는 위치에 원하는 형상으로 직접 인쇄할 수 있는 새로운
개념의 공정인 펄스방식 나노입자적층시스템 (Pulsed-Nano Particle Deposition System)을 개발하였다. 기존의 나노입자적층시스템의 입자 공급 방식을 개선하기 위하여 빠른 응답 속도의 개폐 벨브를 이용하여 충격파를 이용한 입자 분산 방식을 개발하고 입자 분산과 노즐 및 기판으로의 이송 타이밍 제어에 관해 연구하였다. 하드웨어와 소프트웨어 등이 통합된 전체 시스템을 설계, 제작하였으며, 시스템의 성능을 고속 카메라, 전자 현미경, 점속 이온빔 가공 및 기타 측정 방법을 이용하여 분석하였다. 또한 노즐을 통해 기판에 분사되는 입자의 집속에 관한 연구를 통하여 마이크로 스케일의 (≤30 μm) 금속(Ag, Sn)과 세라믹(BaTiO3)을 이용한 단일/다종 재료 패턴을 실리콘과 유연한 플라스틱 기판에 직접 인쇄하여 다양한 구조의 제작이 가능함을 보였다. 응용 분야로서 최근 활발히 연구되고 있는 에너지 하베스팅 장치를 개발된 시스템으로 제작하여 성능을 보이고 유연 기판, 인쇄 전자, 마이크로 제조 공정 등에 응용 가능성을 보였다.

주요어 : 직접 인쇄, 펄스 방식 나노 입자 적층 시스템, 유연 기판, 다종 재료, 에어로졸
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