Maskless deposition of ZnO films

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Abstract

Maskless Mesoscale Materials Deposition (M^3D^{TM}) is a new direct write technique, which is versatile enough to deposit a large variety of precursors and colloidal suspensions. It is a simple and convenient process for rapid prototyping of structures and components. This maskless deposition method operates in air and at room temperature. In this study, a glycerol based polymeric precursor was used for depositing ZnO thin films on surface modified glass substrates. The parameters for deposition using M^3D^{TM} were thoroughly examined and optimized.

1. Introduction

ZnO is a II-VI wide band gap semiconductor with important technological applications in the areas of transparent conducting electrodes in solar cells, and in flat panel displays as a low voltage phosphor [1 – 3]. ZnO has a large exciton binding energy (60 meV) which provides efficient exciton emissions at high temperatures. These properties of ZnO have applications in ultraviolet light emitting diodes and laser devices [4]. ZnO is also used in synthesis of planar waveguides [5].

Rapid prototyping technologies are gaining importance due to the tremendous pressure for shorter life cycle, higher quality, and reliability. At present, electronic components are manufactured by screen printing and photolithography. In [5], the authors used photolithography and wet chemical etching methods to fabricate Er-doped ZnO planar waveguide structures. These methods are expensive and highly inconvenient. Furthermore, they are subtractive, a situation which can be averted by direct write technologies [6]. Direct write techniques provide suitable alternative methods to traditional lithographic routes by reducing processing coat and time. Direct write technologies are additive by producing prototypes directly on substrates without the use of masks [7]. Different direct write processes, such as laser direct writing [8 - 10], and ink-jet printing [11, 12], can deposit desirable patterns in a single step. Maskless Mesoscale Materials Deposition (M^3D^{TM}), being commercialized by Optomec Inc., is also a method that can be developed into a high volume component manufacturing technique [13, 14].

Maskless Mesoscale Materials Deposition (M^3D^{TM}) is an aerosol-based technology for deposition of various materials with particle sizes less than 0.5 μm. To date, barium titanate, metallic contacts like Au, Ag, Cu and Pt [14, 15], and biological materials [13] on various substrates have been deposited using this process. In this method, patterns of sub-micron sized aerosol droplets of molecular precursors and colloidal suspensions are deposited with ease. The desired patterns are drawn using CAD software, which can be conveniently converted into CAM tool-paths. This enables rapid prototyping of components. In this direct write technology, the

precursors or colloidal dispersions are atomized pneumatically or ultrasonically. The atomized particles are guided and deposited onto substrate surfaces through the use of a carrier gas.

In this paper, patterned ZnO films have been deposited by M^3D^{TM} technology. A specific goal of this work was to deposit continuous ZnO lines using a pneumatic configuration. Parameters affecting the quality of deposition of polymeric precursor aerosols, such as rate of atomization, carrier gas flow rates, and viscosity of precursors, were optimized. An attempt was made to measure the electrical resistivity of the deposited patterns.

2. Experimental Methods

All chemicals were of analytic grade and were used as received, without further purification. 99% pure zinc nitrate, $Zn(NO_3)_2.xH_2O$, 99% glycerol, 70% nitric acid (HNO_3) and ACS grade potassium hydroxide (KOH) pellets were obtained from Alfa Aesar, J. T. Baker, and EMD chemical Inc., respectively. Deionized and filtered water (resistivity = 18.2MΩ) was utilized in preparing the solution. Glass microslides were ultrasonically cleaned in acetone, methanol and deionized water. The cleaned substrates were immersed in a 1N potassium hydroxide (KOH) solution to make the surface hydrophilic and to improve wetting characteristics. Polymeric precursors for depositing ZnO films were prepared using a modified Pechini process [16]. In this process, 0.1 moles $Zn(NO_3)_2$, 0.9 moles glycerol, and 0.1 moles of HNO_3, were added together. To this solution, deionized water was added and the resulting solution was heated at a constant temperature of 70°C, while stirring continuously to synthesize a clear, homogeneous solution. The prepared solutions were utilized in depositing maskless patterns using Maskless Mesoscale Materials Deposition (M^3D^{TM}, Optomec Inc.,) on surface modified glass substrates, followed by curing at 70°C on a hot plate for 1 hour. The films were then annealed at 600°C for 10 min in an ambient furnace for pyrolization of the organic precursors and ZnO formation.

In this work, M^3D^{TM} deposition system has been used to make patterns of ZnO using glycerol based polymeric precursors. Fig. 1 shows the schematic diagram of the M^3D^{TM} deposition system in a pneumatic configuration. It shows an overview of general processes used

to aerosolize polymeric precursors. The polymeric precursor is kept in a glass atomization container. Compressed nitrogen gas is expanded through the atomizer nozzle to produce a high-velocity jet. The velocity of the compressed nitrogen gas, also referred to as the atomizer flow rate, is controlled by a unit called the process control module. Due to the Bernoulli effect, the precursor is drawn into the atomizer nozzle. The high velocity gas stream then atomizes the precursor and the resulting droplets are suspended in a gas flow. After exiting the atomizer nozzle, this gas flow collides with the sidewalls of the atomization container to eliminate large droplets while smaller droplets are carried towards the deposition head. On atomizing the precursors, the aerosol is transported to a virtual impactor by nitrogen carrier gas. In pneumatic atomization, there is a size distribution of atomized droplets. The virtual impactor helps in limiting the size variations and eliminates droplets which are below the minimum value. This excess gas flowing out of the virtual impactor is referred to as the impact exhaust flow. The difference between the atomizer and the impact exhaust flow is actually the material injected into the deposition head. Another line of nitrogen gas forms an annular ring around the aerosol material. This sheath gas focuses the atomized flow and guides it through the deposition head. The aerosol is then deposited on surface modified glass substrates. The prepared samples were later heat treated for pyrolization of organic material and formation of ZnO.

Glycerol based polymeric precursors were used to directly write ZnO lines and patterns on surface modified glass substrates, as shown in Fig. 2. After annealing the samples at 600°C, the ZnO films were analyzed by optical microscopy (Nikon Digital Optical Microscope), field emission scanning electron microscopy (FESEM, Nova Nanolab 200, FEI Co.) and two probe resistivity measurements across the deposited line (Model 6430 sub-femto sourcemeter, Keithley Instruments). Prior to FESEM, the patterned samples were coated with a 10 nm gold film.

3. Effects of deposition conditions

3.1. Viscosity

Experiments were performed to study the effect of the viscosity of polymeric precursors on the direct writing of patterns on substrates. Figures 3a and 3b show the patterns made using glycerol based polymeric precursors of 5 cP and 1 cP viscous solutions under similar deposition

conditions. SEM micrographs of these samples reveal that continuous lines with uniform thickness are obtained with 5 cP viscous solution whereas a broken line consisting of spherical droplets is formed from the 1 cP viscous solution. The width of the deposited continuous line was measured to be 200 μm. We observe that for the less viscous solution, there is over-spray of the solution.

3.2. Write Speed

Glycerol based polymeric precursor of 1cP viscosity was used to write lines at different speeds with a M^3D^{TM} system. The lines were deposited on surface modified glass substrates at sheath gas flow rate of 60 cc/min, impact exhaust flow rate of 500 cc/min, and atomizer flow rate of 1000 cc/min. The deposited samples were cured at 70°C and annealed at 600°C. The lines were generated at different writing speeds, in the range of 1 mm/s (Fig. 4a) to 20 mm/s (Fig. 4b). It is observed that the write speeds affect the shape of lines drawn at similar deposition conditions. At write speed of 1 mm/s, the lines are of uniform width and as the write speed increases, the width of these lines decreases. Moreover, the lines appear broken and formed of droplets with increase in write speed. The shape of these droplets becomes circular and smaller as the speed increases to 20 mm/s. When the write speed is slow, there is more deposition of aerosol with sufficient time for the atomized particles to deposit and flow together uniformly. As the write speed increases, the amount of atomized material being deposited on a spot decreases. This results in a non-uniform deposition and flow of the aerosol.

3.3. Substrate Condition

Direct write ZnO films using polymeric precursors were deposited on surface modified glass substrates using M^3D^{TM} technology. SEM micrographs shown in figure 5 (a and b) illustrate that the directly written straight lines are of uniform width (200 μm) when deposited on surface modified glass substrates. In comparison, the lines deposited on a heated (at 70°C) surface modified substrate, are not straight and are of non – uniform width. A closer examination of the micrographs (Fig. 5b) reveals that the initial deposition of the aerosol is uniform, which may be due to the aerosol getting heated while nucleating on the substrate. After being in contact with the hot substrate, there may be evaporation of the residual water from the deposited aerosol. This

evaporation causes the material to dry out faster, leading to shrinkage along the width. Hence, it can be concluded that the patterns, with uniform widths, have to be deposited on surface modified substrate without curing at 70°C while writing.

3. 4. Flow Rates

Glycerol based polymeric precursor of 5 cP viscosity was used to write patterns on surface modified glass substrates. Lines were also written by varying the atomizer flow rate while keeping the sheath gas flow rate and the impact exhaust flow rate at 60 cc/min and 500 cc/min respectively. Figure 6 illustrates the change in line width and shape with change in atomizer flow rates when written at a speed of 2 mm/s. There is increase in line width with an increase in atomizer flow rate.

To begin atomization, the atomizer flow rate has to be higher than the impact exhaust flow rate. When an atomizer flow rate of 600 cc/min was chosen, there was no deposition due to inadequate atomization of the polymeric precursor. SEM micrographs of the samples (Fig. 7) illustrate a change in line width and shape with change in atomizer flow rate. The lines drawn at 700 cc/min of atomizer flow rate are not continuous, with varying width but narrow. When the atomizer flow rate is set to 800 cc/min, there is a significant improvement in deposition with some over-spray. At 900 cc/min flow rate of atomizer, the over spray of the aerosol decreases considerably and the average width of the lines is 195 μm. Uniform lines of 237 μm wide are deposited at 1000 cc/min with considerable amount of over spray.

Lines were also drawn by varying the impact exhaust flow rate, while keeping other conditions constant. In this study, 5 cP viscous glycerol based polymeric precursor was used for atomization. The sheath gas flow rate and atomizer flow rates were maintained at 70 cc/min and 900 cc/min respectively. The patterns were directly written at a speed of 2 mm/s. Figure 8 illustrates the change in line width and shape with change in impact exhaust flow rates. SEM micrographs of the samples illustrate changes in the type of line drawn as the impact exhaust flow rate changes. There is an increase in line widths with the increase in impact exhaust flow rate. At higher impact exhaust flow rates, the deposition also improves and the lines obtained after annealing are uniformly drawn with no cracking. The lines drawn at 300 cc/min of impact exhaust flow rate are narrow (80 μm) and discontinuous (Fig. 9a). At 400 cc/min, the lines are

not broken but their width varies (Fig. 9b); average line width was determined to be 120 μm. There is significant improvement in deposition (Fig. 9c) at 500 cc/min flow rate of impact exhaust with uniform line widths averaging 210 μm. This trend continues even when the impact exhaust flow rate is set at 600 cc/min (width = 260 μm) (Fig. 9d).

On being atomized, the aerosol is carried by nitrogen gas to the virtual impactor (Fig. 1). Here, the excess gas is stripped off to reduce the aerosol flow rate and concentrate the material. When the impact exhaust flow was held constant at 500 cc/min and the atomizer flow rate was varied ranging from 700 cc/min to 1000 cc/min, the difference in these flow rates is increased. Hence, more aerosol material is available to deposit, leading to wider lines. Since less carrier gas is being removed, there is an increase in the over spray or spread in the deposition of aerosol. In another study, the impact exhaust flow rate was varied keeping the atomizer flow rate constant at 900 cc/min. In this case, as the difference in impact exhaust and atomizer flow rates was observed to decrease, the lines appear to be uniformly wide due to a reduction in excess carrier gas. Therefore, the material entering the deposition head consists mostly of the atomized particles, which results in wide uniform lines.

Sheath gas is used in M^3D^{TM} to provide an annular flow of nitrogen gas around the aerosol jet. The change in written line characteristics with sheath gas flow rate was also studied. The impact exhaust flow rate and the atomizer flow rate were held constant at 500 cc/min and 900 cc/min, respectively. There is no difference in line width or shape with change in sheath gas flow rate for lines written using 5 cP solution at 2 mm/s. The lines are 195 μm wide and are uniform.

4. Electrical Resistivity

As the first step towards the determination of material properties of ZnO lines deposited by M^3D^{TM} and annealed at 550°C, electrical resistivity was calculated from measured resistances of a series of parallel lines of approximately 25 mm length and geometrical data determined by optical microscopy. The average resistivity of the ZnO lines was measured to be $9x10^3$ Ω-m at room temperature. In [17], silver lines were deposited using MAPLE direct-write technique and the electrical resistivity was measured. The authors report resistivity 1000 times higher than the

bulk Ag value. The measured resistance also scaled with respect to cross-section and length as expected. Despite the poor conductivity of the ZnO lines, these initial results demonstrate that patterned ZnO films can be fabricated using M^3D^{TM} technology. By varying the annealing temperatures [18], improvements in conductivity of ZnO patterns produced by M^3D^{TM} process may be achieved.

5. Conclusions

Maskless Mesoscale Materials Deposition (M^3D^{TM}) is a new versatile direct write technique to deposit molecular precursors and colloidal suspensions. A glycerol-based polymeric precursor was used for depositing ZnO thin films on the surface of modified glass substrates. The parameters for deposition were examined and optimized and various types of patterns have been deposited successfully. It is concluded that, to directly write continuous lines of uniform width, solutions of 5 cP or higher have to be used while using pneumatic atomization. The lines need to be written at a speed 2 mm/s on a surface modified glass substrate. The atomization of polymeric precursors has to be adequate to achieve deposition. The atomizer and impact exhaust flow rates have to be chosen appropriately so as to avoid excess stripping of the carrier gas and also to avoid over spray of the aerosol. It is deduced that for glycerol based polymeric precursors, lines 200 μm wide can be written continuously at a speed of 2 mm/s for a solution of 5 cP using atomizer, impact exhaust and sheath gas flow rates of 900 cc/min, 500 cc/min, and 60 cc/min, respectively. The electrical resistivity of these lines was estimated to be $9x10^3$ Ω-m at room temperature. Further studies need to be undertaken to accurately measure the resistivity values of ZnO lines.

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Figure Captions

Figure 1: Schematic diagram of Maskless Mesoscale Materials Deposition system, M^3D^{TM}, in pneumatic configuration.

Figure 2: A complex square pattern of ZnO deposited on surface modified glass substrate using Maskless Mesoscale Materials Deposition (M^3D^{TM}) technology.

Figure 3: SEM micrographs of directly written line in a M^3D^{TM} system using polymeric precursors of different viscosity; (a) 5 cP and (b) 1 cP. These images are being shown to illustrate the fact that highly viscous precursors deposit continuous lines compared to less viscous ones.

Figure 4: SEM micrographs of microlines written directly using M^3D^{TM} system with 1 cP viscous glycerol based polymeric precursor at different writing speeds; (a) 1 mm/s and (b) 20 mm/s. These images illustrate that continuous lines are more likely at lower write speeds.

Figure 5: SEM micrographs of directly written line in a M^3D^{TM} system using polymeric precursors of 5cP viscosity on surface modified substrates; (a) without curing and (b) with curing at 70°C while depositing.

Figure 6: Change in line width of directly written lines with atomizer flow rate.

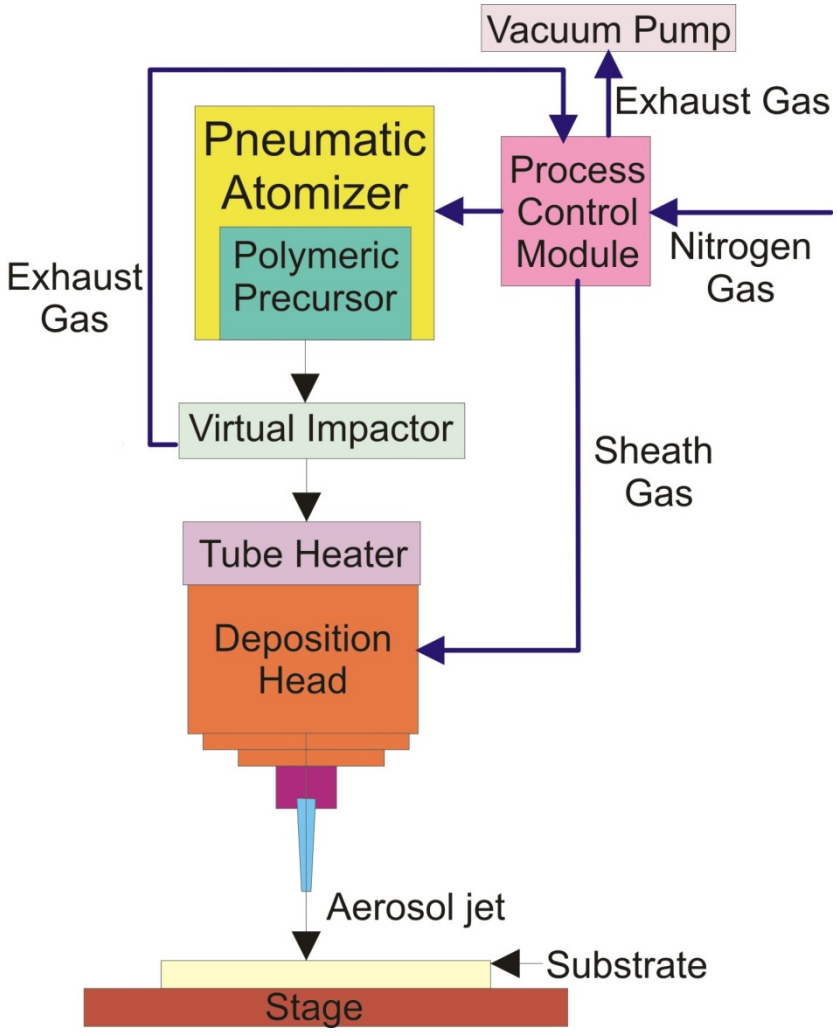
Figure 7: SEM micrographs of directly written line in a M^3D^{TM} system at different atomizer flow rates; (a) 700 cc/min, (b) 800 cc/min, (c) 900 cc/min, and (d) 1000 cc/min. These were made using polymeric precursors of 5cP viscosity on surface modified substrates at a write speed of 2

mm/s. The sheath gas flow rate and the impact exhaust flow rates were maintained at 60 cc/min and 500 cc/min, respectively.

Figure 8: Change in line width of directly written lines with increase in impact exhaust gas flow rates at constant sheath gas flow rate and atomizer flow rates at 70 cc/min and 900 cc/min respectively.

Figure 9: SEM micrographs of directly written lines in a M^3D^{TM} system at different impact exhaust gas flow rates; (a) 300 cc/min, (b) 400 cc/min, (c) 500 cc/min, and (d) 600cc/min using 5cP solution on surface modified substrates at a write speed of 2 mm/s. The sheath gas flow rate and atomizer flow rates were maintained at 70 cc/min and 900 cc/min respectively.

Figure 10: SEM micrographs of ZnO lines directly written with impact exhaust and atomizer flow rates of 500 cc/min and 900 cc/min, respectively and varying sheath gas flow rate; (a) 50 cc/min and (b) 70 cc/min.



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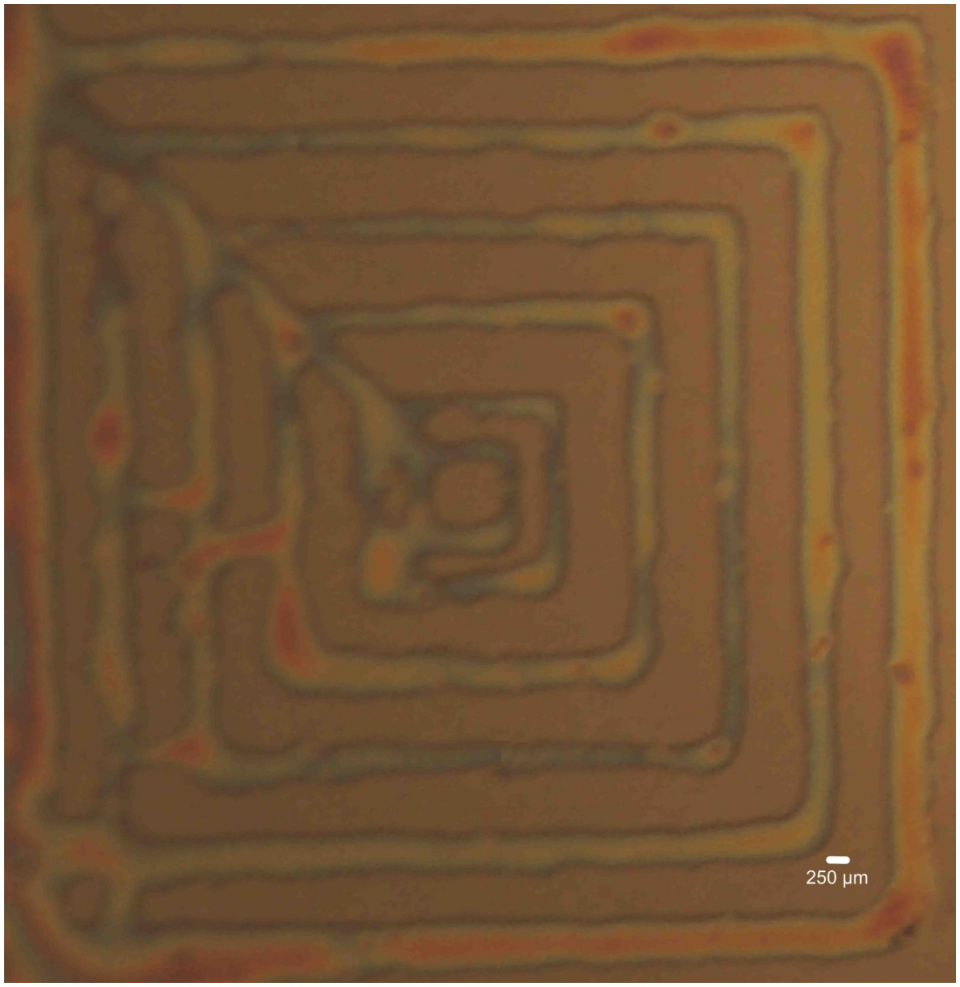

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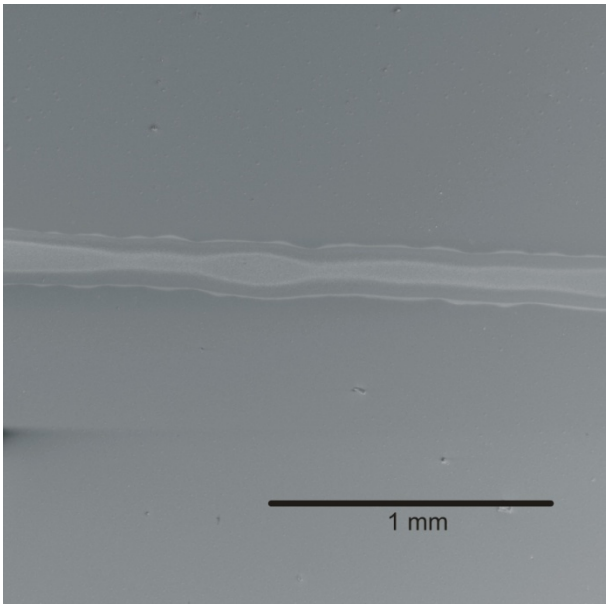

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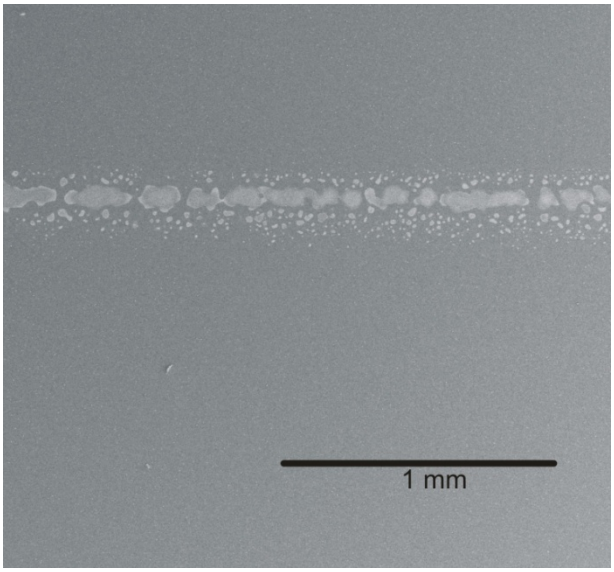
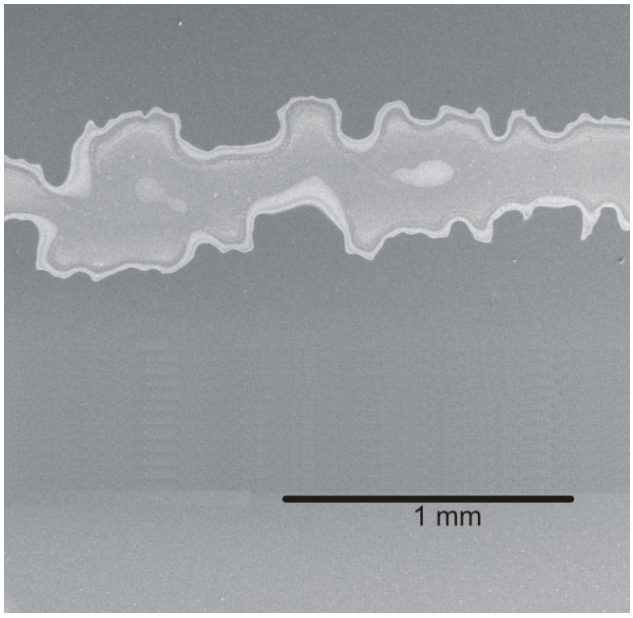


(b)

Figure 3: SEM micrographs of directly written line in a M^3D^{TM} system using polymeric precursors of different viscosity; (a) 5 cP and (b) 1 cP. These images are being shown to illustrate the fact that highly viscous precursors deposit continuous lines compared to less viscous ones.



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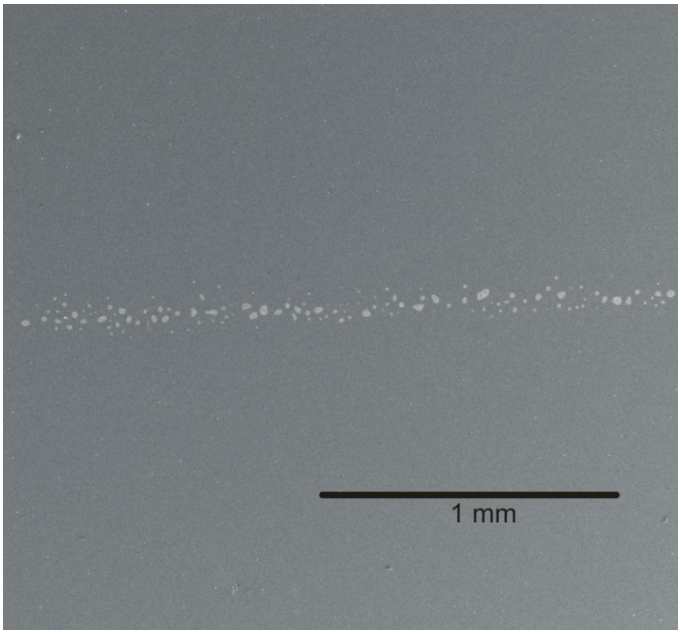
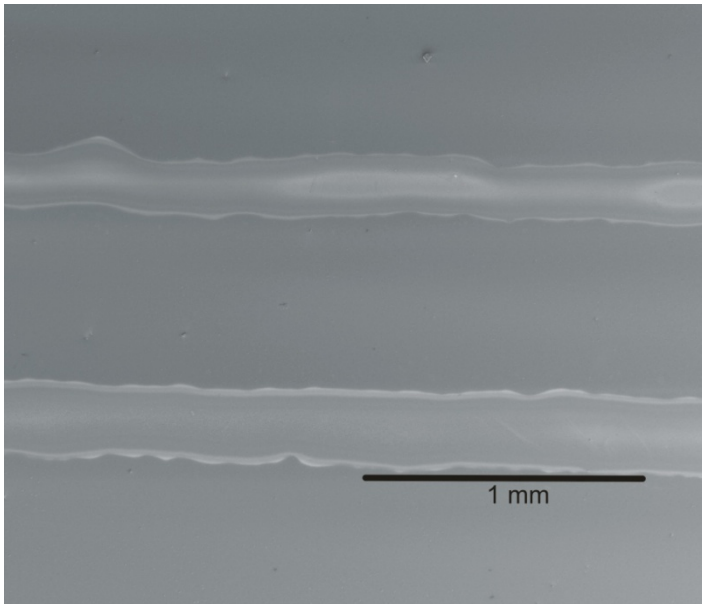


(b)

Figure 4: SEM micrographs of microlines written directly using M^3D^{TM} system with 1 cP viscous glycerol based polymeric precursor at different writing speeds; (a) 1 mm/s and (b) 20 mm/s. These images illustrate that continuous lines are more likely at lower write speeds.



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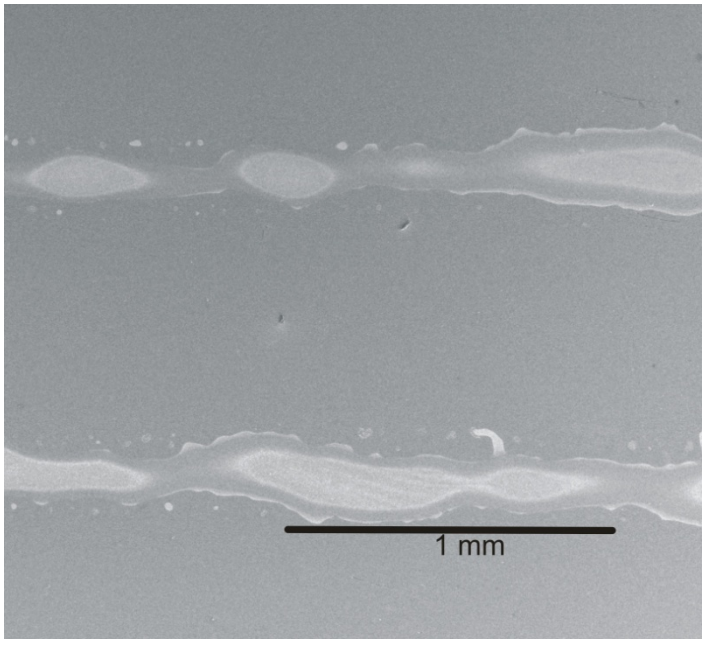

(b)

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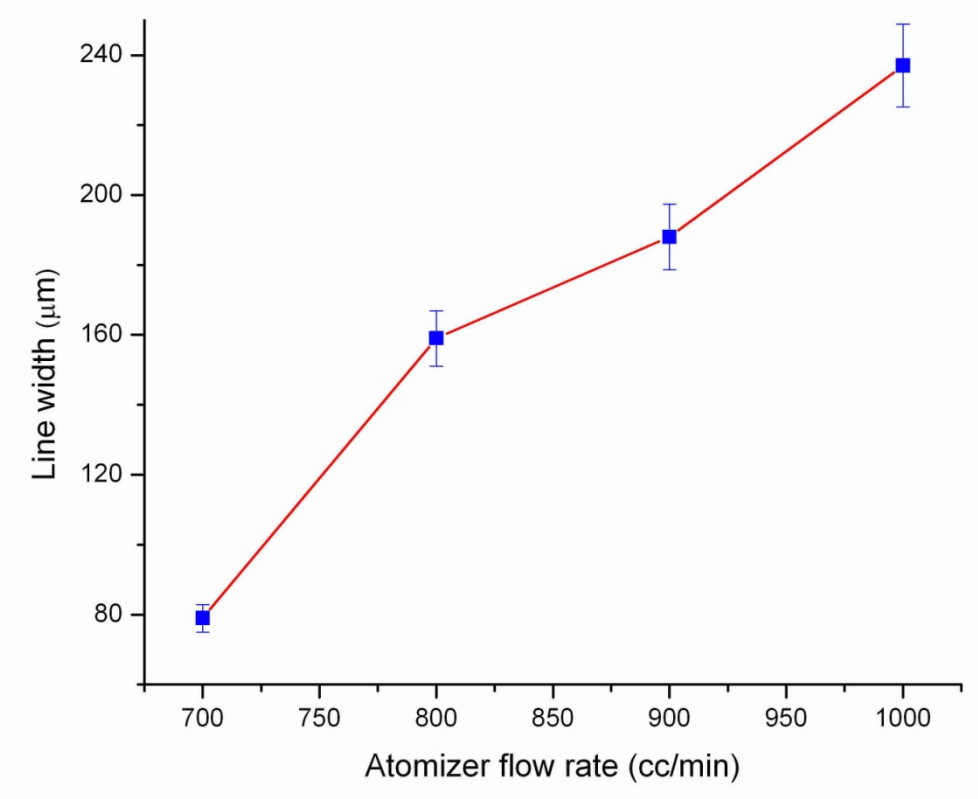
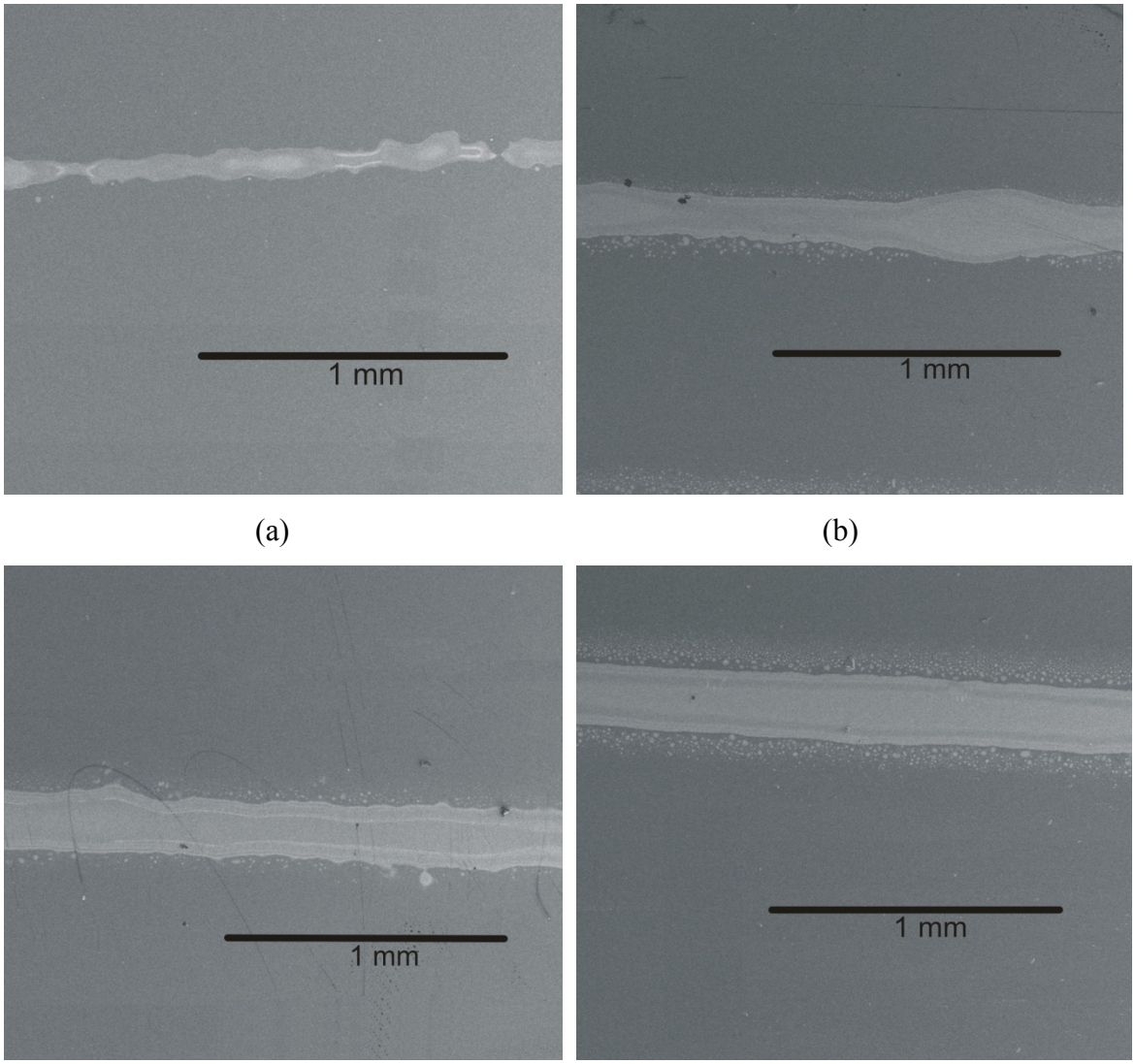


Figure 6: Change in line width of directly written lines with atomizer flow rate.



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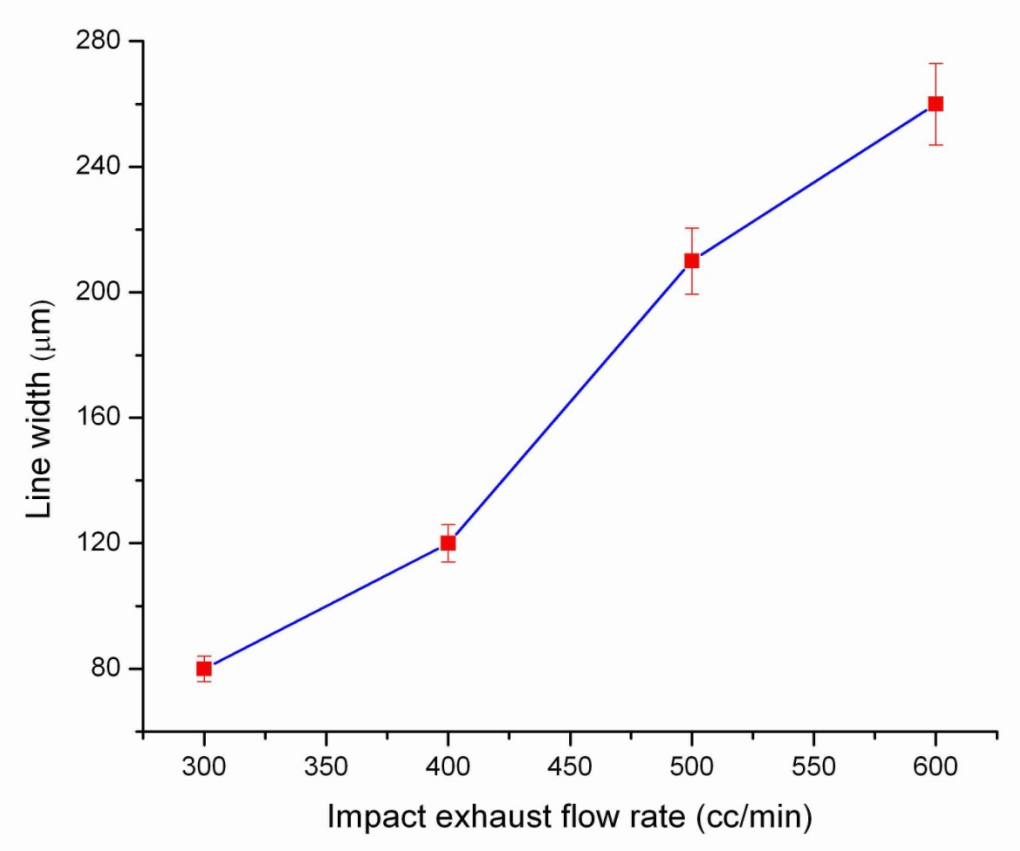

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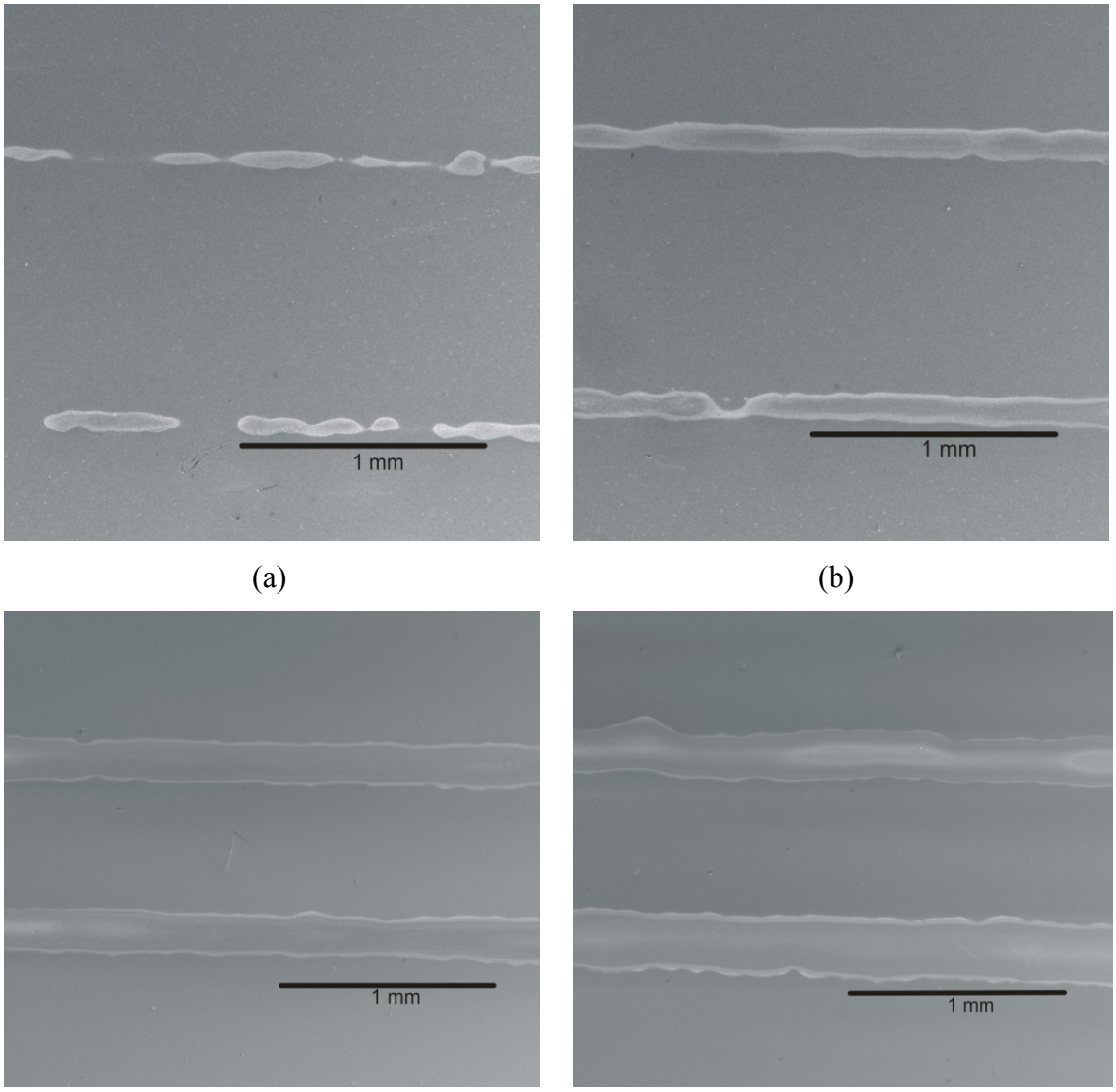
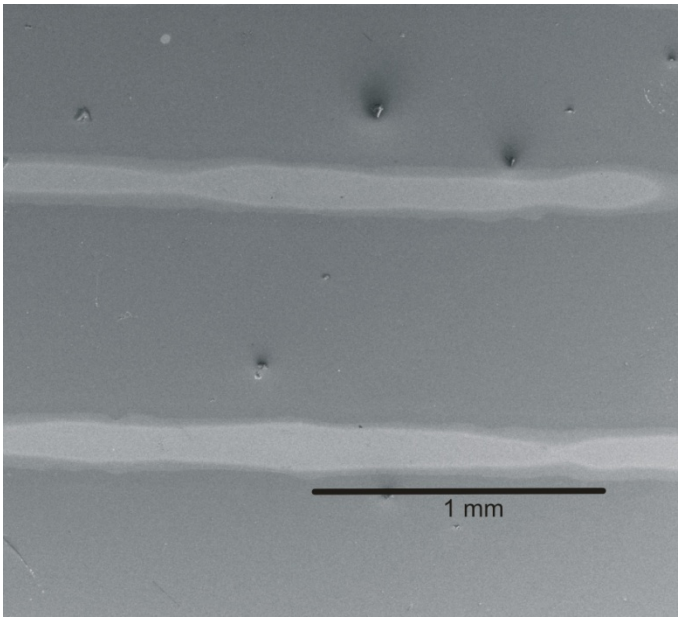


(a) (b)

(c) (d)

Figure 9: SEM micrographs of directly written lines in a M^3D^{TM} system at different impact exhaust gas flow rates; (a) 300 cc/min, (b) 400 cc/min, (c) 500 cc/min, and (d) 600cc/min using 5cP solution on surface modified substrates at a write speed of 2 mm/s. The sheath gas flow rate and atomizer flow rates were maintained at 70 cc/min and 900 cc/min respectively.



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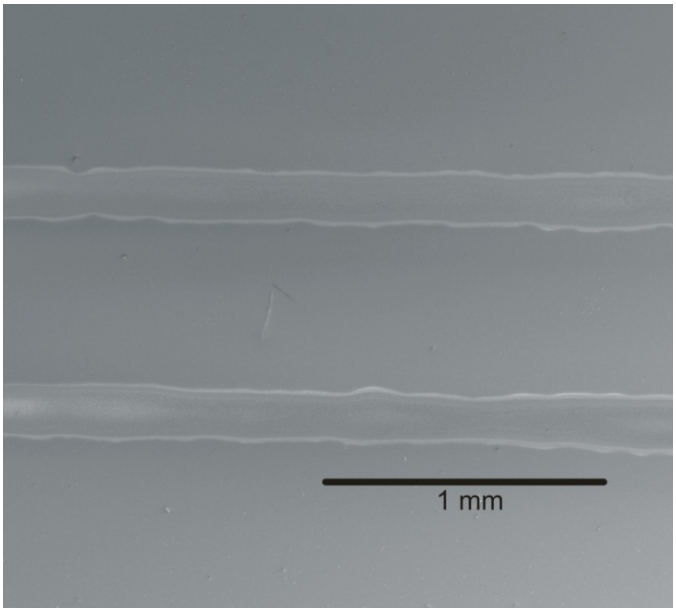

(b)

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