Nanoparticle Deposition of Al₂O₃ Powders on Various Substrates

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Al₂O₃ powders of 100 nm diameter were deposited on Al, Cu, and Si substrates using a micro-nozzle in nano-particle deposition system (NPDS). This procedure allowed the production of fine-scale depositional patterns or templates not possible using conventional semiconductor processing techniques. For a given set of depositional conditions, the Al₂O₃ powder layers developed different thicknesses on different substrates. Following deposition, the powders were sintered to provide ceramic layers. In the first instance, the depositional behavior of Al₂O₃ was determined by Stokes number, where a number greater than 1 meant that more powder was deposited. However, the extent of deposition was also influenced by substrate type, where a Si substrate yielded the thickest powder layer. This phenomenon was related to both substrate hardness and melting temperature. Most powder particles fragmented on impact (with pieces deposited on the substrate) when substrate hardness was high. In addition, when the melting temperature of a substrate was low, more powder accumulated as a result of the kinetic energy of a colliding powder particle being transformed into heat. The Al substrate, with its relatively low melting point, developed a thicker powder deposit than those formed on Cu. Therefore, hardness and melting temperature of substrates are the key parameters influencing the depositional behavior of powders.

1. Introduction

Most means of powder deposition impart high energy to the particles involved by means of high acceleration. Cold gas dynamic spray (CGDS)¹-³ and the aerosol deposition method (ADM)⁴-⁶ are typical conventional processes. The depositional rate of both methods is faster than other traditional methods such as chemical vapor deposition or sputtering. In CGDS, the metallic powders exceed supersonic speed prior to being deposited on a substrate. In ADM, ceramic powders are accelerated to subsonic speeds. Both methods also offer the advantages of a low processing temperature and can be used with flexible substrates involving film deposition.

ADM has been widely studied in various types of microstructure fabrication, especially in forming thick Lead Zirconate Titanate (PZT) films used in micro electro mechanical systems (MEMS).⁷-¹⁰ In these cases, a sacrificial layer is employed to provide fine patterns or templates on the substrate.

Nano particle deposition systems (NPDS) are novel methods of powder deposition that offer new benefits for both ceramic and metallic powders, not available with either CGDS or ADM.¹¹ Air provides the carrier gas to transport the particles that are accelerated up to supersonic speeds at the nozzle tip. The much greater velocity of the powder in NPDS is the major difference from ADM. Moreover, powder deposition occurs at room temperature, considerably lower than the conditions commonly used for CGDS. A previous study showed that NPDS can be used successfully to deposit a variety of powders on different substrates.¹¹

In all of the methods discussed above, the collision between the rapidly moving particles and substrate is the most critical part of the depositional process. Different depositional behaviors of metallic powders on different substrates have been observed with CGDS.¹² However, no fundamental study has been undertaken that relates various substrates to depositional behavior. In this study, the substrate dependence of powder deposition was evaluated using NPDS to deposit ceramic powders on different substrate types.

2. Experimental Procedures

Figure 1 shows the fabrication process of a micro-nozzle used for powder deposition as specified in Ref. 13). The nozzle used has cross in shape where the width of the arm...
is defined as “nozzle diameter” (Fig. 2). The originally designed width at the arm in the cross pattern was 200 μm, but due to the isotropic etching step during micro nozzle fabrication (Fig. 1(e)), some undercuts beneath the photoresist were induced so that the total dimension of the nozzle was enlarged to 326 μm. The dimension of the nozzle throat was approximately 150 μm due to the tapered profile of micro-nozzle as shown in Fig. 2. The width of the powder deposition depends greatly on the nozzle throat where the powders get sprayed.

Figure 3 shows a schematic of NPDS.11) As powders are difficult to accelerate directly, air was used as the carrier gas. Filtered compressed air was passed through the line to pick up powder at the supply point where a rotary pump ensured a constant feed rate. The powders passed through the tilted nozzle and then were accelerated to supersonic speeds. The high-speed particles were ejected from the tip to collide with the substrate, where they accumulated. The distance between the tip of the nozzle and the substrate is termed the stand-off distance (SoD); this was adjusted by moving the substrate along the z-axis. The fabricated micro-nozzle was attached to the main nozzle to obtain micron-sized patterns, made by moving the substrates along the x- or y-axis. A vacuum pump was used to lower the internal pressure of the chamber to facilitate injection of the powders at supersonic levels. Table 1 shows the process conditions used for powder deposition. The Al₂O₃ powders (Cotronics Corp., New York, USA) were used for injection in this experiment. The average size of powders ranged from 80 nm to 120 nm with its mean diameter of 100 nm. The powders were spherical shape.

Following deposition, the substrates were heated in air at 200°C for 4 h in a box furnace to sinter the Al₂O₃ particles. This temperature is the maximum processing temperature used for most flexible substrates. After the heat treatment, the adhesion between powders and substrates was tested by subjecting the sample to ultrasonicate in acetone for 2 and 7 s, respectively. The subsequent thickness and roughness of each substrate were determined using an alpha-step, while the hardness was measured with a Vickers micro hardness tester to establish bonding quality, and the indentation load was determined using 100 gf for metal substrates and 200 gf for semiconductor substrates. The hardness of each substrate is given in Table 2.
3. Results and Discussion

3.1 Micro-nozzle fabrication

Figure 2 shows an optical image of the micro-nozzle used in NPDS. The width and length of each arm was 326 μm and 499 μm, respectively. The sidewall profile of 78° proved suitable to provide supersonic flow. Previous reports employed an 85° profile.\(^{14}\)

\[\text{Stk} = \frac{(\tau x u_0)}{d_c}, \quad (1)\]

where \(\tau\) is the relaxation time, \(u_0\) is the velocity of undisturbed air, and \(d_c\) is the characteristic dimension of obstacle. The value of \(\tau\) in eq. (1) can be obtained from:

\[\tau = \frac{\rho x d_a^2 x C_c}{(18\eta)} \quad (2)\]

where \(\rho\) is the standard particle density, \(d_a\) is the size of particles carried by air, \(C_c\) is the slip correction factor, and \(\eta\) is the coefficient of dynamic viscosity. According to this model, particles will continue to move in a straight line even if the carrier gas flow changes direction where \(\text{Stk} > 1\). If \(\text{Stk} < 1\), the gas and particles will move coherently. Hence, it appears that \(\text{Stk} > 1\) in the central portion of the deposited layer (the dark area in Fig. 5) but \(\text{Stk} < 1\) in the boundary region where the deposit was thinner than in the center. Equations (1) and (2) make it clear that the Stokes number is determined by \(d_a\) and \(u_0\). Therefore, because small particles have a low Stokes number, they follow the gas flow even when they lie at the center of the flow but change direction before colliding with the substrate. Moreover, after the fluid gas and powder mix passes through the throat of the micro-nozzle, its diameter increases and the fluid begins to slow down, with particle velocity in the boundary zone abruptly decreasing where geometrical conditions create a non-slip boundary. As a consequence, the \(\text{Al}_2\text{O}_3\) powder layer exhibits two distinct regions of differing thickness.

with the deposited \(\text{Al}_2\text{O}_3\) layer in Fig. 4 shows how the nozzle image was transcribed in the patterns of the deposited \(\text{Al}_2\text{O}_3\) powders. However, differences exist in the thickness at the center and boundary of the deposited powder. These differences can be explained by the Stokes number,\(^{15}\) defined as:

Table 1 NPDS deposition process conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Aluminum oxide ((\text{Al}_2\text{O}_3), 100 nm in diameter)</td>
</tr>
<tr>
<td>Shape of micro-nozzle</td>
<td>Cross</td>
</tr>
<tr>
<td>Substrate</td>
<td>Al, Cu, Si</td>
</tr>
<tr>
<td>Injection gas flow rate</td>
<td>30 L/min</td>
</tr>
<tr>
<td>SoD</td>
<td>500 μm</td>
</tr>
<tr>
<td>Deposition time</td>
<td>1 min</td>
</tr>
<tr>
<td>Working pressure</td>
<td>0.0133–0.0266 MPa</td>
</tr>
</tbody>
</table>

Table 2 Hardness measurement of substrates with \(\text{Al}_2\text{O}_3\) powder deposition.

<table>
<thead>
<tr>
<th>Substrate type</th>
<th>Indentation Load (gf)</th>
<th>Hardness (GPa)</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>100</td>
<td>1.16</td>
<td>—</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>1.31</td>
<td>—</td>
</tr>
<tr>
<td>Si</td>
<td>200</td>
<td>10.55</td>
<td>Wafer (100)</td>
</tr>
</tbody>
</table>

Fig. 3 Schematics of NPDS.\(^{11}\)
3.3 Heat treatment and adhesion test

Figure 4 shows the deposited layers following sintering for 2 and 7 s of ultrasonic treatment, respectively. The vibrations failed to dislodge the deposited Al₂O₃ powders, which remained firmly bonded to the substrate.

Figure 6 shows the thickness of Al₂O₃ layers on each substrate after ultrasonic treatment. The thickness was measured using an alpha step where 1000 points were taken at a sampling rate of 50 Hz. The average thickness was taken from those 1000 points for each set of experiment. As shown in the Figure, the average thickness for each set hardly changed with different ultrasonicallyating time, the layers were strongly bonded to each of the substrates, and the Al₂O₃ powders sintered successfully even at low temperatures.

In previous ADM studies, the mechanism of ceramic powder deposition has been characterized as fragmentation and deposition. The particles are accelerating as they collide with the substrates, causing them to shatter into fragments. The faster the particles move, the more they shatter and the finer are the deposited particles. The extent of fracture also depends on the hardness of the substrate. As shown in Table 2 and Fig. 6, there is a relationship between substrate hardness and depositional thickness. The Si substrate has the greatest hardness among the three used, and accumulated the greatest thickness of deposited
Al$_2$O$_3$ powders. This implies that the greater hardness of the Si substrate caused the Al$_2$O$_3$ particles to fracture extensively, with their fragments depositing across the substrate. The two metallic substrates, Al and Cu, have lower hardnesses and resulted in relatively lower thicknesses of deposited Al$_2$O$_3$ layers compared to Si.

Of the two metallic substrates, Cu had a slightly thinner deposit of Al$_2$O$_3$ powders. Studies conducted by Hutchings have shown that, following impact between powder and substrate, most kinetic energy is released as heat, causing metallic substrates to melt locally. This may have occurred in the present case and, if so, because Al has much lower melting temperature than that of Cu, it would melt more easily and cause more Al$_2$O$_3$ powders to bond. Al which melts or becomes softened faster than Cu, promotes adhesion of powders to the substrate, transferring its heat energy to the powders to be deposited so that thicker coating is induced. Clearly, hardness and melting temperature of substrates are the key parameters in affecting the depositional behavior of powders.

4. Conclusions

The present study demonstrated the following:

1. A micro-nozzle less than 1 mm in diameter fabricated by deep reactive ion etching with a sidewall profile less than 80° can accelerate powder to supersonic speeds and impart the high energy required for powder deposition.

2. Al$_2$O$_3$ powder can be deposited on Cu, Al, and Si substrates, with the depositional thickness being greatest on Si. The speed of the ceramic powder is such that it fragments on impact with the substrate. Deposition was the thickest on Si, the hardest of the substrates, where the level of fragmentation was the highest.

3. During particle collision with the substrate, considerable energy is converted into heat, producing localized melting or softening of metallic substrates and allowing more Al$_2$O$_3$ powders to adhere to the surface due to efficient heat transfer. As the melting temperature of Al is lower than that of Cu, more Al$_2$O$_3$ powders adhere to the surface of the Al substrate than that of Cu, explaining the greater powder depositional thickness found on Al in the present study.

Future work should examine the depositional behavior of other powder types on other substrates.

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