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Patterning of fine particles by means of supercritical CO_2

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A new method for positioning fine particles on surfaces has been developed. Supercritical CO_2-assisted printing (SCAP) was utilized to spray and deposit the prepared particles on solid substrates. By means of masks, regular arrays of the particles were successfully created in designed patterns. Typical size of the particles employed was in the range of submicrometers to micrometers. Supercritical CO_2 (sc-CO_2) acted as an effective dispersion and transportation medium in this process. Good dispersion state of the particles was achieved by stirring in sc-CO_2. Fabrications of fine patterns of solder particles and other ceramic powders on smooth plates were demonstrated. Under optimum operation conditions, fine structures of 30 μm in width can be formed in a minimal pitch of 60 μm. Ultra high yield of the patterning was obtained since the deposition rate could be as high as 100 μm per second. Main factors affecting the process were discussed. The research results indicate that the SCAP is a potential approach to the organization of fine particles into microstructures. Hopefully, it may find wide industrial applications where lithography is needed, such as solder printing in surface mounting technology for higher density electronics and thick film fabrication for miniature systems. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

Fabrication technology for miniature devices plays an important role in various industrial applications. New technologies make it much easier to obtain microparticles and nanoparticles than before so that manufacture of miniature structures by deposition of fine powders becomes more reasonable with low cost. For example, endless efforts have been paid in microelectronics to develop miniature components to meet the strong desire for portable products that requires more functions to be achieved in smaller sizes. Solder printing on printed circuits boards probably is one of the most important parts in surface mounting technology. Fabrication of thick films in high precision is also of great importance for miniature electronic or mechanical devices. Many fabrication methods have been invented for these purposes, such as screen printing, ink-jet printing, electroplating and gas deposition, etc.

The screen printing method has been widely employed for chip scale packages. Generally, the average bump size of printable solders ought to be about 200–400 μm but engineers keep trying to improve it [1]. Recently, a high precision commercial screen printer has been produced by the Micro-tec in Japan. Its state-of-the-art technology claimed that solder bumps in diameter of 100 μm can be printed in pitch of 150–200 μm and the line and space for printing conductive pastes can be 10–20 μm. The slumping of solder bumps is usually considered as one of the main obstacles to obtain ultrafine pitches less than 150 μm.

The concept of ink-jet printer technology has been used to print solders and other materials without masks. The MicroFab reported that the micro-jet method produced droplets of solders or polymers in diameter of 25–125 μm and the print speed was as high as 600 bumps per second [2–4]. Its advantages, such as high precision, high

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yield, low cost and mask-less make it very attractive. The disadvantages might be that an inert environment heated to about 200–300°C is required and the powders need to be charged or molten.

Electroplating can successfully fill high aspect ratio (print height/aperture diameter or width) patterns with high resolutions in micrometer scale [5]. The minimum solder bump can be as fine as 25–75 μm with 100–200 μm pitches at a deposition rate around 10 μm/min. Unfortunately, the toxic effects of sulfonates used in the electroplating solutions result in environmental risks. This method lacks some flexibility to deal with particles and substrate materials that are not suitable for electroplating.

Other technologies based on gas-dynamic spraying had been studied for a long time. For example, thermal spray and cold spray were developed in which 1–3 MPa compressed gas like air, nitrogen or helium were used to spray 1–50 μm particles to form films on a variety of substrate materials [6–8]. Recently, a "jet molding system" has been reported in which the achieved line widths were 15 μm for Ag pastes and about 100 μm for PZT powders [9]. For these kinds of methods, however, operation at high temperatures are still unavoidable either in the print process or the sintering treatments. Even in the so-called "cold spray" process, preheating the gas to as high as 900 K was needed [6]. Probably these methods should be applied to heat-resistant powders. Sometimes, organic precursors like polyvinyl chloride was used to improve the poor rheological property of fine powders [9]. Thus, emission of organic volatile compounds(VOCs) is still a problem for the above methods due to strict environmental criteria.

In this study, the RESS[10] technology is modified as a new method to obtain miniature patterns by combining the gas-dynamic spray concept with modern supercritical fluids technology. By the SCAP method, the problems in operation temperatures, particle transportation and environmental concerns that often occur in other print methods can be solved by the favorable properties of sc-CO_2. For example, particles can be well dispersed and easily transported by sc-CO_2 at room temperatures. During the rapid depressurization of the SCAP process, CO_2 evaporates and the active substances can be deposited on a variety of substrate materials. Release of VOCs can be greatly restrained because employment of organic solvent is no longer indispensable. The SCAP is amazing not only because it is a chemically green process, but also it is able to manufacture fine patterns with extremely high yield and suitable for various combinations of particles and substrates.

2. Experimental methods

2.1. Printing equipments by SCAP

The equipments used in the present study are shown in Fig. 1. Prepared particles of interests, such as solder particles or ceramics powders, were loaded into the high pressure vessel of sc-CO_2. This feature is quite different from the common RESS process in which target substance must be dissolved in the sc-CO_2 [10]. According to the surface properties of the powders, a trace amount of surface activators may be added. Nozzles can be simply made from stainless steel capillary tubes. In order to sustain the supercritical condition in a 500 cc reservoir, usually the inner diameter of the nozzle should be as small as about 100 μm. The whole print process can be done at room temperatures but heating the nozzle is necessary when continuous spraying is conducted for a long time. Laser-cut metal masks with aspect ratios of 0.3–1.0 were used in this study.

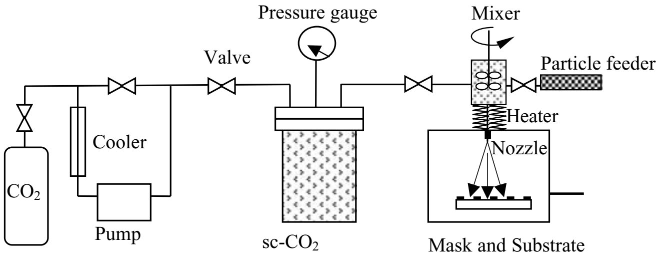

Figure 1 Patterning equipments by SCAP.

2.2. Properties of sc-CO_2

In the present case, sc-CO_2 is employed as a dispersion and transportation medium. The operation condition is modest compared to other supercritical fluids because its critical temperature and pressure are 304.2 K and 7.37 MPa, respectively. It is known that the surface tension of sc-CO_2 is extremely low so that sc-CO_2 can easily permeate into open spaces between fine powders and wet surfaces of particles. This idea had been successfully applied to replication of nanoscale structures [11]. In the present study, a good dispersion state of fine particles in sc-CO_2 can also be expected. On the other hand, the mass transport property of sc-CO_2 is better than that of liquid. The viscosity of sc-CO_2 increases sharply near the critical point as shown in Fig. 2 [12]. According to the Stokes law, the drag force on a particle is proportional to the particle size, viscosity and velocity of the transport medium. Thus, high viscosities of sc-CO_2 make the drag force large enough to disperse the particles in vessels during stirring and to transport them through tubes when spraying. That is one of the advantages in comparison to the cold spray where the gas is not working in supercritical state.

3. Results and discussions

Apparently, many factors have to be considered in the present study, such as operating temperature and pressure of sc-CO_2, powder size and its distribution, nozzle, stencil,

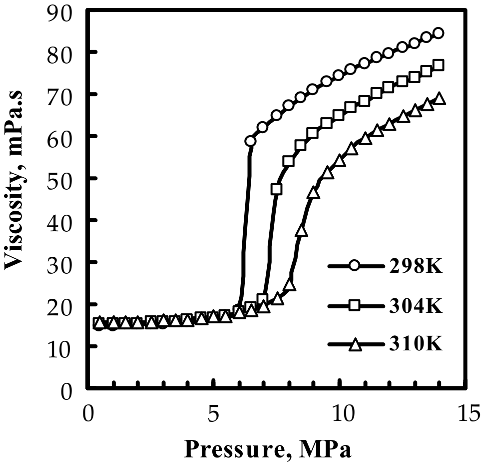

Figure 2 Viscosity of CO_2 as functions of pressure and temperature.

spray geometry, composition of the paste, property of the additives, etc. The experimental results were analyzed by dividing the whole process into three main phases, i.e., the dispersion of particles in the sc-CO_2, spraying through the nozzle and the pattern formation on the substrate.

3.1. Dispersion of fine particles in sc-CO_2

A good suspension state of particles in the medium is vitally important in particle transportation processes. Take the fluidizing technology as an example, when the size of particles is smaller than about 20 μm, it is very difficult to make the particles move steadily. No matter what kinds of particles were used in the present study, however, both submicro particles of 0.3–0.5 μm and microparticles as large as 30–35 μm could be dispersed well in sc-CO_2 by stirring. For example, nanosized fibers of carbon black have a strong tendency to aggregate into very large clusters, but they can be untied to a considerable extent by stirring in sc-CO_2. In Fig. 3, a result is shown in which the coagulated carbon black clusters of 50–100 μm were returned to fibers in size of about 1 μm after stirring in sc-CO_2 for 1 hour. Temperature and pressure are the main factors to control the physical state of the fluid. The supercritical or near supercritical state of CO_2 can be easily achieved at room temperatures when pressure is 8–30 MPa. Due to the extremely low surface tension, sc-CO_2 can penetrate into small cracks and promotes the wetting of the particles. With the help of mechanical stirring, good dispersion of particles in supercritical fluid can be obtained that helps to result in a uniform spraying through the nozzle. Furthermore, the nozzle clogging seldom happens compared to the common aerosol spraying process in which the pressure of carrier gas is not high enough to reach supercritical states. Therefore, reliable and efficient print is possible by the SCAP method.

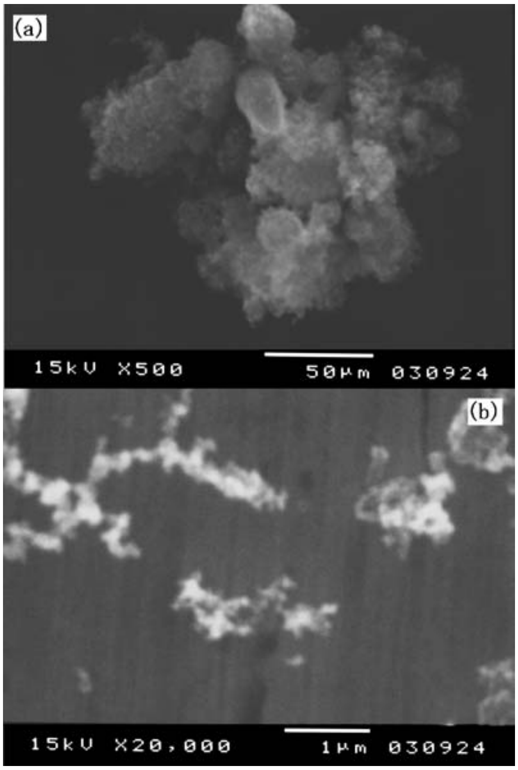

Figure 3 Carbon black fibers before (a) and after (b) the stirring in sc-CO_2.

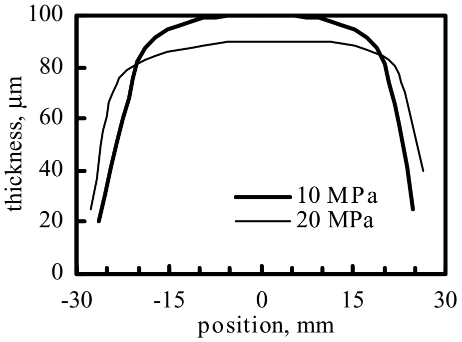

Figure 4 Thickness profile of the film printed by solder particles.

3.2. Spraying process

The sc-CO_2 must spread the particles homogeneously during the spraying process in order to form uniform films. The morphology of the deposited film was observed by SEM. No obvious surface fluctuation is found. A thickness profile of film made of solder particles was shown in Fig. 4. It can be seen that the thickness at the edge of the spraying circle in diameter of 30 mm is about 10% lower than that at the center. Higher pressure tends to cause a little wider distribution. It suggests that thousands of bumps could be finished at one print.

Though the particles can be well dispersed in sc-CO_2, it is found that the major part of the powders is sprayed in clusters instead of monomer particles. To measure the

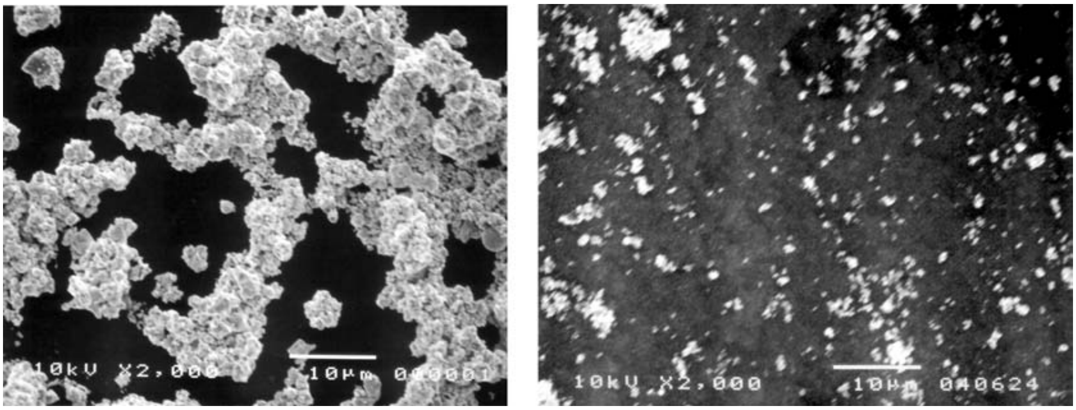

Figure 5 Morphology of the deposited silver particles without (left) and with (right) addition of surfactant.

sizes of the particle clusters, an incomplete deposition by silver powders of 1–3 μm in size was conducted by cutting off the spray jet in a short time. The sizes of the clusters formed on the plate vary from about 1 μm to 20 μm. This indicates that the formation mechanism of the clusters might be different. The scattering in cluster size might be due to three factors. First, the binder in the paste prevents the particles from separation into monomers, especially when the stirring time is short. A typical example is shown in Fig. 5(left). Secondly, the pressure drops down gradually when the sc-CO_2 passes through the valve and the nozzle, so that re-aggregation of the particles becomes reasonable before they reach the exit of the capillary tube. The agglomerated particles deposited directly on the plate and caused large clusters. Addition of a small amount of surface modifier was found very effective to reduce re-aggregations of the particles as shown in Fig. 5(right). Thirdly, if the spraying time is long enough, the Joule-Thompson freezing effect may result in a rapid temperature drop that can cause formation of dry ice. When pure CO_2 was sprayed by SCAP, dry ice powders 60–120 μm in size were observed at 1–20 mm distance from the nozzle by the MALVERN laser diffraction system. So, the dry ice might temporarily freeze some of the solid particles together. This influence can be reduced by placing the plate 20–30 mm away from the nozzle because all the dry ice disappeared by sublimation and released the particles again. As a result, the best print resolution by the SCAP method is probably a few times larger than the original particle size. Small particles with addition of proper surface modifier will be helpful to obtain fine pattern in high precision.

3.3. Pattern transfer with masks

It was found that particle size, aperture size and shape, surface smoothness of the substrate as well as the properties of additives have large impact on the quality of pattern transfer. A close contact between the mask and the substrate is always required for high quality printing. Usually, smooth substrates with calendered surfaces are good enough for printing. According to the experiments, the suitable aspect ratio of masks is considered as smaller than one for this method. Print results using small solder particles of 0.3–5 μm in diameter were shown in Figs 6–9, in which laser-cut metal masks of 30 μm thickness were employed. It can be seen that the solder particles stacked very closely and their distribution was quite homogenous. The minimum print resolution could be as fine as 30–50 μm for solder particles, although there were minor incompletes at the corners and edges that were damaged when the mask was removed. By means of SEM observation, the slope angle of the bumps was roughly estimated as about 80–85°. It should also be noted that fine print can be achieved either with or without addition of organic solvents. In Fig. 9, circular bumps of 50 μm in diameter with a pitch of 100 μm were formed under completely solvent free conditions, i.e., using only solder particles together with sc-CO_2. However, addition of about 1–5 wt% ethanol was found helpful to obtain lower void fraction of the bumps as shown in Figs 7–8. Probably, the ethanol left on the surface acted as lubricant so that the particles' self-organization could be processed to cause a higher density package.

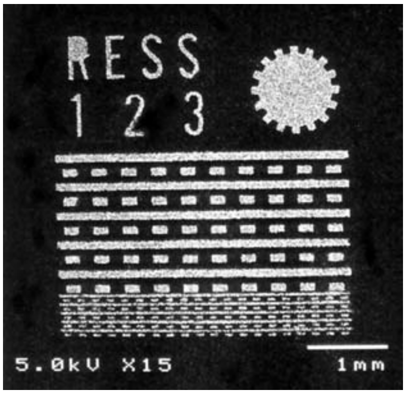

Figure 6 Pattern of solder particles.

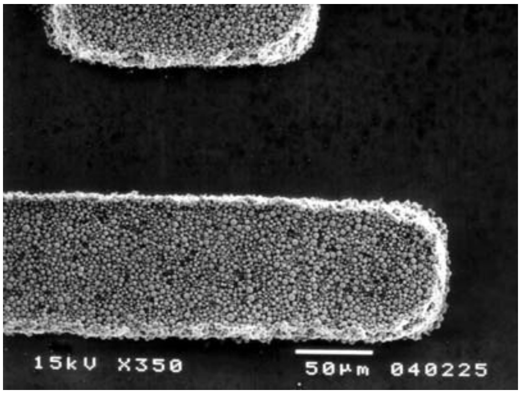

Figure 7 Oblong pattern 100 μm in width.

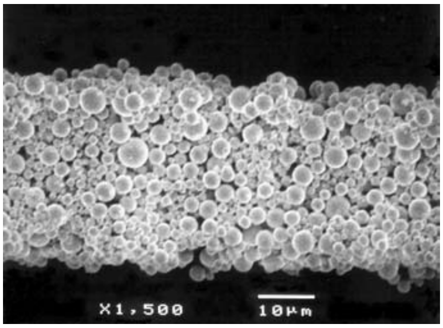

Figure 8 30 μm wide line pattern.

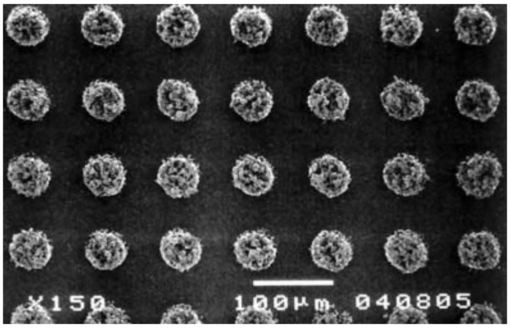

Figure 9 50 μm solder bumps.

TABLE 1 Comparison of selected printing methods

Method	Features
Screen print	Advantages: demonstrated reliability, minimal line/space 10–20 μm for conductive pastes Disadvantages: solder bump minimal dia. 100 μm, minimal pitch 150–200 μm, drying process needed, VOCs release
Electroplating	Advantages: solder bump minimal dia. 25–75 μm, minimal pitch 100–200 μm, deposition rate 10 μm/min, Disadvantages: alloys redistribution, lack of long time stability, unsuitable for non-metallic powders
Ink-jet; Micro-jet	Advantages: solder bump minimal dia. 25–125 μm, minimal line/space 10–20 μm for conductive pastes, high yields, mask-less, high aspect ratio Disadvantages: preparation and post-treatment of precursors, molten solder used to form the droplets, VOCs release.
Cold spray; Jet-molding	Advantages: minimal line width. 15 μm for Ag, high print rate 1–2 μm/min, high aspect ratio, without mask or with non-contact masks Disadvantages: preheat at high temperatures, difficult to deposit non-ductile powders, VOCs release, transport difficulty, nozzle clogging.
SCAP	Advantages: Ultra-high print rate up to 100 μm/sec, little limitations on particles and substrates, bump size 30–100 μm, operation at room temperatures, minor VOCs release, no nozzle clogging Disadvantages: particles recovery, CO_2 recycle, mask cleaning, substrate smoothness

3.4. Particle bonding mechanism

Although good separation of the powders is essential during the suspension and spray processes, a strong bonding of the particles is required to prevent the formed pattern from slumping. It is of interest to know how the particles are bonded together without being blown away in the high flux of CO_2. According to the DLVO theory, both adhesion and detachment forces play important roles in determining the equilibrium state of the particles, in which the forces may include Van der Waals, capillary, Coulomb and the external forces from the carrier gas. When a particle impacts the substrate or other particles by violent bombardment, bonding happens if the kinetic energy is high enough to overcome the obstacle in the potential energy curve. After the kinetic energy is lost by energy exchanges, the potential well prevents the particles from separation. This is almost the same with the case in the cold spray. As concluded by Grujicic at al., large kinetic energy of the particles is the major factor controlling the strength of interfacial bonding in case of cold spray [13]. As the sc-CO_2 provides much higher particle/substrate contact pressures, stronger bonding becomes much easier for most of the particles. Thus, even non-ductile ceramics powders were able to be deposited on metal and ceramic plates by the SCAP although this was difficult for the cold spray [7]. Further, the risk of pattern slumping that sometimes occurs in the screen print becomes extremely low by the SCAP because of the compressive residual stresses in the deposited structures.

3.5. Comparisons and potential applications

Similar experiments were also carried out by using nano or submicro powders of Cu, Ag, TiO_2, ZnO, Fe_2O_3, MnO_2 and carbon black. The shape of the particles was either spherical or irregular. The patterns were able to be completed on smooth substrates of glass, plastic, Cu, paper as well as transparent film etc. From the demonstrations in the present study, line width of 100 μm could be always achieved for most of the cases. In order to produce line width around 30 μm, however, the deposition thickness has to be lower than that of the mask due to the sticking problem caused by the masks. Proper surface modifiers may be helpful to reduce the sticking problem in some cases. The SCAP method shows competitive features compared to other print technologies as listed in Table I. Apart from its ultra-high deposition rate with good resolution, it also possesses excellent flexibility. There are no other limitations on particles as long as the powders are not dissoluble in sc-CO_2. Thus, this method is suitable for fabrications of miniature devices where high yield and high resolution are required, such as conductors, resistors, thermistors, photovoltaic cell, permanent magnetic device and gas sensors etc. as the screen print method does [14–19].

4. Conclusions

A new particle patterning method called the Supercritical CO_2-assisted printing was developed. It was found that submicro particles and microparticles could be well dispersed in sc-CO_2 and uniform spraying could be conducted. Printing of solder particles, metal powders and ceramics on solid substrates were successfully demonstrated at room temperatures. The results indicated that high printing rate of about 100 μm/sec and high print resolution up to about 30–50 μm could be achieved. Its excellent flexibility makes it attractive for fabrications of various miniature devices.

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