Direct Writing of Conventional Thick Film Inks Using MAPLE-DW Process

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Matrix Assisted Pulsed Laser Evaporation – Direct Write (MAPLE-DW) was investigated for use with conventional thick-film (screen printable) inks. A layer of ink, coated onto a glass slide, was transferred to an alumina substrate after being irradiated with 1047-nm, 20-ns laser pulses in a forward transfer configuration. The effect of different parameters on this process was studied and optimized. The process was demonstrated to be capable of depositing 20-µm conducting lines with a high linear speed.

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1. Introduction

Increases in operational frequency and interconnect density are driving the demand for inexpensive mesoscopic fabrication technologies. This regime, defined by feature sizes between 10 and 100 µm, falls in between what can be economically fabricated by thin and thick film technologies. In addition to morphological constraints, many hybrid microcircuits require that the resistive and high-Q reactive elements be integrated into the package because these can not be effectively fabricated on an integrated circuit (IC).

Conventional thick film technology (e.g., screen printing) involves forcing a viscous paste through apertures in the screen and produces film thicknesses greater than 2.5 µm [1]. Patterns are generated by sealing apertures in the mesh except where ink can be passed through. After the ink has been patterned onto the substrate it is dried and fired in a furnace. Firing temperatures (850°C for most inks) restrict the acceptable substrates to ceramics such as alumina. Multiple layer devices can be built using the Low-Temperature Co-fired Ceramic (LTCC) process. This involves screen printing onto a green substrate (alumina mixed with organics and binders). Vias are punched mechanically and these layers are stacked and aligned before being pressed and fired together. This allows the design of high-density devices with buried passive components. This is a mature technology capable of very high throughputs, but it has several limitations. Even with a high mesh number (325-400 openings per linear inch), the finest lines and spacing that can be consistently produced are 3-5 mil (75-100 µm) [1]. Thin lines may also have a serrated pattern because of the mesh. This, along with limitations in the feature size, restricts the use of screen printing for very high frequencies because the majority of the current is carried along the surface of the conductor.

There are several other thick-film techniques that have smaller feature sizes than screen printing. This includes photo-imagable inks such as DuPont's Fodel™ system [1]. A positive mask is used with collimated UV light to drive a photo-polymerization reaction in the ink. Both conductors and dielectrics can be fabricated using this method, by which feature sizes down to 25 µm with 50 µm spacing and 75 µm vias may be obtained [1]. However, the inks must still be fired and there are issues with shrinkage.

Recently there have been new initiatives to develop technologies to satisfy morphological demands at low processing temperatures and on nonplanar substrates [2]. A typical example is metallizing a GPS antenna on a soldier's helmet. An additional motivation is to reduce the development cycle with rapid prototyping electronic devices directly from CAD files without the fabrication of a mask. Neither the patterning nor functionalization steps can heat the substrate above its damage threshold, which can be much lower than the processing temperature for conventional thick-film inks (e.g., 400°C for Kapton and lower for other polymer substrates). Two solutions are to use inks with a lower functionalization temperature or to locally heat the ink so that the exposure of the substrate to damaging temperatures is minimized. Thick-film inks with firing temperatures as low as 500°C have been developed. In addition, air-dry polymer based inks that cure at 150°C can also be used, but the lower functionalization temperatures correspond to higher sheet resistances. Nanoscale particles have very high surface energies that reduce the thermal processing requirements without reducing the conductivity, but they are generally too expensive for mass production.

A laser can also be used to selectively sinter the pattern. The laser energy is absorbed very near the surface of the ink and transferred via conduction down to the substrate. Chrisey et al. [3] propose using a pulsed IR laser to locally anneal the material. There are several failure modes involved with the laser sintering process. The laser power may be high enough to vaporize the ink at the surface. If the pattern thickness is greater than the thermal penetration depth, the ink may not adequately bond to the substrate, limiting the thickness of a given layer. If too much power reaches the substrate, it will become damaged. High thermal gradients may cause stress fractures in the pattern. Most importantly, all organic components must be driven off prior to sintering because their vaporization would produce high pressures that could destroy the pattern.

Several patterning technologies that satisfy these requirements include ink-jet based printing [4], Selective Laser Sintering (SLS), Laser-Induced Forward Transfer (LIFT), Laser micro-cladding, MicroPen, and Matrix-Assisted Pulsed Laser Evaporation-Direct Write (MAPLE-DW). These technologies are discussed in detail in [2]. MAPLE-DW has several advantages over competing technologies for microelectronics fabrication. First, it is capable of depositing small feature and requires much lower laser fluences than either SLS or LIFT. Unlike the MicroPen, Laser micro-cladding, or ink-jet technologies MAPLE-DW is also scalable because a common technology platform can be used for both rapid prototyping and mass manufacturing by using a mask. The development of digital light processing (DLP) gives the potential for a mask-free parallel process. Like ink-jet printing and the MicroPen, MAPLE-DW is capable of depositing virtually any type of material, including chemicals and biological samples which are important for developing sensors and batteries [2]. In MAPLE-DW, the ribbon, which is a supporting substrate with a layer of material to be coated (ink), is placed in close proximity (25-100 μm) to another substrate where the material needs to be deposited in the forward transfer configuration. A laser is focused through the transparent support onto the ink-support interface. The ink absorbs the laser radiation and is rapidly heated and vaporized. This provides a pressure pulse which pushes the fluid material outward and deposits it onto the substrate. The substrate can be translated relative to the laser to create very precise patterns. The entire process takes place in ambient conditions and does not require heating of the substrate. In addition when the ribbon is removed, the same laser system that is used to write the pattern can also be used for laser trimming of the components (direct erase), or surface modification such as cutting vias. A sintering laser is also easy to integrate with MAPLE for *in situ* sintering.

This paper investigates the implementation of MAPLE-DW using conventional microelectronic inks with an IR laser and X-Y scanner for high-speed writing. Previous investigations have used either Excimer or frequency-tripled Nd:YAG lasers, which both produce UV wavelengths [2,3,5,6]. Using IR wavelengths is more convenient because glass supports can be used. In addition, if an IR laser is to be used to sinter the material after deposition, the same optical system can be used for both the patterning and functionalization processes. We focus on creating conductors with QS300. This is a Ag/Pt conductive ink manufactured by Dupont and specifically developed for the screen printing industry. It is widely available and has been designed for producing fine lines down to 75 μm using screen-printing. QS300 has a specified sheet resistance of 4.5 mΩ/square for a fired film thickness of 10 μm at 850°C. The rheology of screen printing inks is specifically designed to vary with the shear force applied to the ink. In the absence of shear forces, the ink is very viscous. This helps deposited patterns resist distortions once they are on the substrate.

2. Experimental

Figure 1 shows a schematic of our experimental setup. An X-Y scanner moves the laser beam according to a computer-controlled path relative to a fixed substrate. This offers higher write speeds than translation stages would otherwise allow. The ribbon and substrate are both stationary. The Nd:YLF laser produces 20-ns pulses at a given pulse repetition frequency (PRF) and a wavelength of 1047 nm. The PRF of this laser can be varied from continuous wave (CW) to 10 kHz. By expanding the beam, a waist of ~16 μm can be achieved at the focal plane. The size of the mirrors on the X-Y scanner limits the diameter to which the beam may be expanded to ~1 inch. Shot-to-shot spacing is controlled by adjusting PRF and the speed of the X-Y scanner. A CCD camera allows the substrate to be positioned using the x-y stages as well as monitoring the process *in situ*. A CW JDSU fiber laser (λ = 1100 nm) can be used to sinter the patterns deposited by MAPLE-DW. The two lasers are aligned so that they have the same optical path through the system.

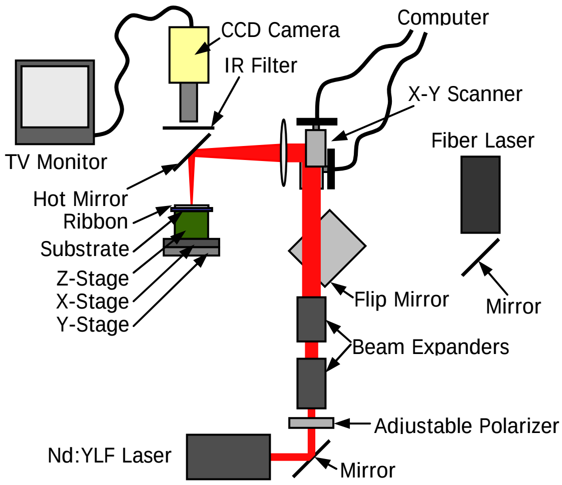

Fig 1. Schematic of setup for MAPLE-DW

The MAPLE-DW process has been previously investigated with time-resolved microscopy by Young et al [5]. They identified three different operational regimes for the MAPLE-DW process: sub-threshold, jetting, and plume, in order of increasing laser fluence. The ink they investigated consisted of $BaTiO_3$ nanopowder in a α-terpineol matrix with a small amount of surfactants.

A photography experiment was also conducted in the present work using the configuration in Fig. 1. The QS300 was mixed with 11% (by mass) α-terpineol. Three regions are also identified, named bubble protrusion regime, jetting and plume, and are correlated with the results of quality of MAPLE-DW process. Examples of these three regimes from our experiment are shown in Fig. 2.

All three responses begin with the protrusion of a bubble from the surface of the ink. The bubble protrusion regime is characterized by an expanding bubble that never fully detaches from the ink surface The bubble eventually collapses back into the ink surface because its kinetic energy is insufficient to overcome surface tension. A jet is formed when the energy is large enough to overcome surface tension and at least some of the ink is detached from the surface. Surface tension then causes this ink to collapse in the radial direction. The plume regime is similar to the jet except that the ink leaves the surface with a high enough velocity that it breaks into small droplets and continues to expand radially as well as normally to the surface.

Fig. 2. Micrographs of different response regimes (a) sub-threshold – 0.79 J/cm^2 (b) jetting 1.02 J/cm^2 and (c) plume – 1.27 J/cm^2.

Working in the jetting regime is appealing because the ink collapses to a smaller diameter than the laser spot. However, considerable instability was observed in the jets and the ink splatters when it comes in contact with the substrate due to the high velocity of the jet. Both of these effects ultimately limit the feature size. Zhang et al [6] used the plume regime with a dried ribbon in direct contact with the substrate. Because the ribbon is dried, it is more suitable for storage and more applicable for printing on conformal substrates. Since the ribbon is in contact with the substrate, radial spreading is minimized when a laser with a small spot size is used with a thin ink layer. However, there can be problems with producing dense unbroken patterns because the deposited ink has a smaller diameter, and therefore is not continuous. Zhang et al used wet ribbons for depositing dielectrics to avoid pinholing [6].

The remaining experiments in this paper use QS300 without the addition of any thinner and operate in the sub-threshold regime. Ink was applied to the glass substrate using a glass rod and steel shims because the unadulterated QS300 is too viscous for the use of a wire or spin coater. The thickness of the ink layer can be controlled by using different sets of shims. Time histories of the MAPLE-DW event were captured using high-speed microscopy for 0.5-, 1.0-, and 2.0-mil ink layer thicknesses, with beam waists of 15 and 30 µm. These experiments showed that as laser fluence is increased, the size of the bubble increases until it ruptures into a plume. For the range of film thicknesses, beam radii, and spot sizes there is no fluence that produces a jet. The maximum bubble displacement for each experiment is graphed in Figure 3. The range of laser fluences was selected to span the range of sub-threshold regime. A correlation was developed that captures the general trends of the experiment.

$$z_{\max} = 1.35 \times 10^{-6} \cdot F^{1.31} \cdot \frac{r_0^2}{d^{0.5}} \qquad (1)$$

where z_{max} is the maximum displacement of the bubble in µm, F is the laser fluence in J/m^2, r_0 is the beam radius at the ink-support interface in µm, and d is the ink thickness in µm. An analytical correlation between the maximum displacement and the processing parameters is currently being developed.

It is seen from Fig. 3 and Eq. (1) that the maximum displacement of the bubble increases with laser fluence. A larger beam radius pushes the bubble out farther for the same fluence. It also requires more laser fluence to displace a thicker ink layer a given distance than a thinner layer. Considering the micrograph of the sub-threshold response in Fig. 1(a), a bubble with a larger base radius will have lower curvature for a given displacement than a bubble with a smaller radius. The stress in the bubble walls due to surface tension will be proportional to this curvature. Above a certain threshold for the material and thickness the bubble wall will fail and MAPLE-DW moves into the plume regime.

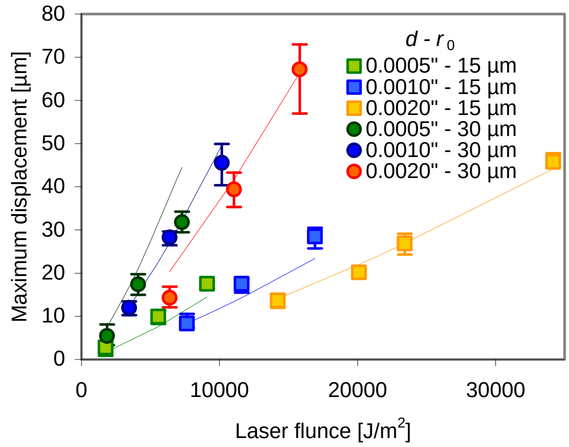

Fig. 3. Maximum displacement as a function of laser fluence. The lines show the correlation in Eq. 1.

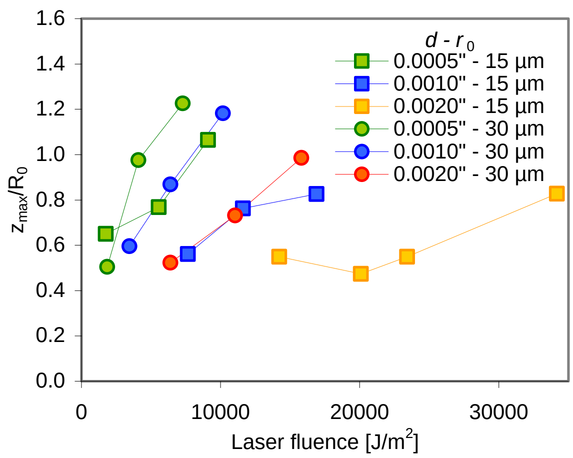

Fig. 4. Ratio of maximum displacement to base radius as a function of laser fluence.

Because of the thixotropy of the ink, there will be effective plastic deformation of the bubble and it will not return to the surface for all but the lowest laser fluences. Because the ribbon is not moving for the setup used in this paper, this can be a great impediment to writing thin lines. The best experimental results are obtained when the ribbon is positioned as close to the substrate as possible and the majority of the displaced ink is deposited. The interaction between the ink and the substrate is also important, and how well the ink wets the substrate can play a critical role in the morphology of the final pattern. Alumina slides coated with a dielectric (Dupont QM44) were used in this work. These substrates have some surface roughness and appear to draw the ink downward and hold it to form fine patterns.

It is convenient to define a quality factor for the sub-threshold event to help quantify the shot to shot interference on the ribbon. The ratio of maximum displacement to the base radius is plotted in Fig. 4 for the same experimental cases as in Fig. 3. The most deposition should occur for bubbles that have a maximum displacement while maintaining a minimum base radius. Fig. 4 shows that this is true for the larger beam radii and lower ink thicknesses.

Figure 5 shows micrographs of the deposited patterns with respect to laser fluence. The lines in the figure were written at 7 cm/s. The separation between the ink and the substrate is ~ 12.5 µm. Figure 6 shows a portion of a 20 µm wide, 5 mm long wire printed with 1.26 J/cm^2. This line was fired in a furnace at 850°C. The conductivity was measured to be 1.6 × 10^7 1/Ω·m, or ~75% of the specified value for QS300. This small reduction is most likely due to inconsistencies in the line dimensions and porosity in the fired material.

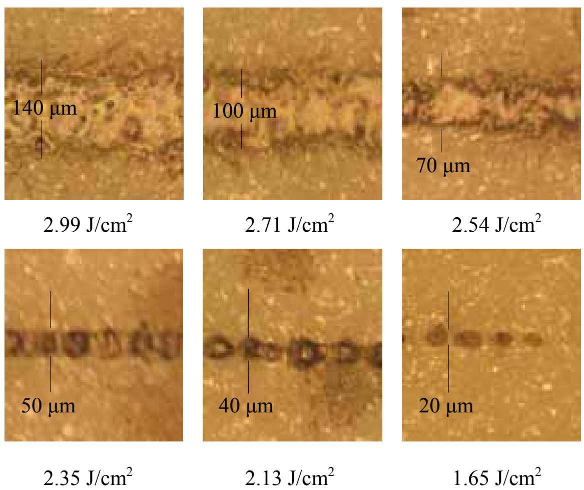

Fig. 5. Deposition on alumina substrate for various fluences.

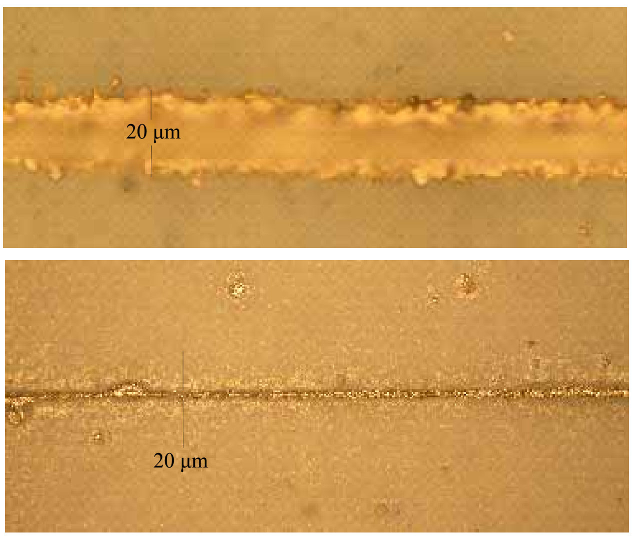

Fig. 6. Micrographs of a 20-µm line

The MAPLE-DW process is very sensitive to the thickness of the ink layer and the separation between the substrate and the ink layer. Using shims to coat the ribbons and separate the substrates makes it difficult to control these parameters precisely across the entire surface of the substrate. The narrowest line obtained in this work is about 10 µm wide. Smaller lines with smother edges can be obtained by ablating the edges of the lines.

When the lines are deposited onto the substrate the material still has the same properties as the ink on the ribbon. Because there is a substantial amount of organic material in the deposited pattern, it is difficult to sinter the pattern *in situ*. The fiber laser was also employed to sinter the ink, which was uniformly coated on the substrate and then dried in a convection oven at 150°C. QS300 has been successfully sintered on soda-lime glass (T_g ~550°C) to produce a conductance that is nearly identical to what is specified for the ink.

MAPLE-DW provides a maskless way to rapid prototype thick film mesoscopic features. The speed of the X-Y scanner may be sufficient for low production runs. If higher throughputs are required, a negative mask can be deposited on the ribbon and the entire pattern deposited with one laser pulse.

3. Conclusions

This paper has demonstrated that conventional screen printable inks can be used with MAPLE-DW using an infrared pulsed laser. The best lines are obtained in the sub-threshold regime when bubbles collapse back to the glass substrate. In addition, an X-Y scanner can also be used to rapidly write the patterns at very high write speeds. Features as small as 10 µm can be written. With higher precision coating and substrate ribbon separation, the quality and consistency of the patterns could be greatly improved.

Acknowledgments and Appendixes

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