Journal of Materials Processing Technology 214 (2014) 1935–1945

Contents lists available at ScienceDirect

Journal of Materials Processing Technology

journal homepage: www.elsevier.com/locate/jmatprotec

Laser curing of silver-based conductive inks for *in situ* 3D structural electronics fabrication in stereolithography

Amit J. Lopes[a,*], In Hwan Lee[b], Eric MacDonald[a], Rolando Quintana[c], Ryan Wicker[a]

[a] W.M. Keck Center for 3D Innovation, The University of Texas at El Paso, El Paso, TX, USA
[b] School of Mechanical Engineering, Chungbuk National University, Cheongju, Republic of Korea
[c] Department of Management Science and Statistics, The University of Texas at San Antonio, San Antonio, TX, USA

ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 10 March 2014
Accepted 10 April 2014
Available online 24 April 2014

Keywords:
In situ laser curing
3D structural electronics
Direct print
Multiple materials
Additive manufacturing

ABSTRACT

A hybrid stereolithography (SL)/direct print (DP) system has been developed and previously described that fabricates three-dimensional (3D) structural electronic devices in which component placement, interconnect routing, and system boundaries are not confined to two dimensions as is the case with traditional printed circuit boards (PCBs). The resulting increased level of design and fabrication freedom provides potential for a reduction in both volume and weight as well as the capability of fabricating systems in arbitrary and complex shapes as required to conform to unique application requirements (*e.g.*, human anatomy, airframe structures, and other volumetrically-constrained mechanical systems). The fabrication of these devices without intermediate part removal between SL and DP processes requires *in situ* curing of DP-dispensed silver-based inks to sufficiently cure the inks prior to continuing additional SL fabrication. This paper describes investigations into the laser curing process using the two laser wavelengths, 355 nm and 325 nm, which have been used in commercial SL machines. Various laser curing parameters, including energy (laser power and scan speed), scanning location, and laser wavelength were investigated. The trace resistances and structural changes in the SL substrate and printed trace were compared for each experiment to determine the most preferred laser ink curing method. Furthermore, oven curing of partially laser cured ink traces was investigated as a means for minimizing the number of *in situ* laser passes required to embed ink traces during SL fabrication. The laser curing process was repeated for a wide variety of conductive inks, having different structure, composition, and curing properties to determine if certain inks were more responsive to laser curing and if the ink curing results could be generalized. A statistical study was conducted under the hypothesis that laser curing of inks at 325 nm wavelength would be better, due to lower silver reflectance, as compared to 355 nm wavelength. Results indicated that particulate silver based conductive inks can be successfully cured *in situ* using SL lasers with various laser curing parameters. Curing ink traces at high laser power and slow scan speeds with the laser beam located on the substrate adjacent to the ink channel resulted in the most effective ink curing but resulted in discoloration of the ink and/or charring of the SL substrate. Comparatively, when laser power was reduced sufficiently to eliminate the charring, lower effective ink curing was achieved. Irradiating the laser directly on the ink did not damage the ink or the substrate, while providing low trace resistances, and represents the most viable laser curing alternative to achieve acceptable trace resistance without charring the SL substrate. The results further indicated that partial laser curing of ink using a reduced number of laser passes with subsequent oven cure seem to work effectively and may decrease overall manufacturing time. SL lasers with low power (<100 mW) may not be effective for curing conductive inks that have high viscosities and require high curing temperatures. Finally, a statistical study determined that 325 nm is more effective for direct curing of the ink as compared to the 355 nm laser.

1. Introduction

Electronics require continual advancements in fabrication technology to provide smaller, lighter, more customizable, and faster devices. A substantial reduction in circuit volume and weight can be realized by embedding electronic components within truly three-dimensional (3D) dielectric substrates at various depths and

* Corresponding author at: The University of Texas at El Paso, W.M. Keck Center for 3D Innovation, Industrial, Manufacturing, and Systems Engineering Department, 500 W. University Avenue, E201G, Engineering Building, El Paso, TX 79968, USA. Tel.: +1 915 747 5958; fax: +1 915 747 6013.
E-mail address: ajlopes@utep.edu (A.J. Lopes).

http://dx.doi.org/10.1016/j.jmatprotec.2014.04.009
0924-0136/

orientations. For almost two decades, several researchers have been exploring the capabilities of using traditional additive manufacturing (AM) technology in the context of fabricating and prototyping functional products including conformal 3D structural electronic devices (see Lopes et al., 2012 for additional references). Briefly, Palmer et al. (2006) integrated high resolution stereolithography (SL) and micro wire electrodischarge machining (μEDM) technologies to realize a functional high power mesoscale relay, thus demonstrating the potential for batch assembly of electromechanical systems. De Nava et al. (2008) described a 3D magnetic flux sensor with microcontroller to illustrate how 3D off-axis placement of components and routing of conductive traces can potentially reduce the size of electronics packages. To provide an automated manufacturing environment for developing unique, freeform packages with embedded 3D structural electronics, Lopes et al. (2012) demonstrated a combination of SL and direct print (DP) in a single hybrid manufacturing system (see also Lopes, 2010). The hybrid SL/DP system was utilized to successfully fabricate functional two-dimensional (2D) and 3D 555 timer circuits packaged within SL substrates. A key enabler of 3D structural electronic device fabrication is controlled deposition of conductive ink and sufficient curing (to eliminate resin/ink contamination) of the conductive traces *in situ* during the manufacturing process. For realizing functional interconnects using DP, a wide range of metals that include gold, silver, copper, and nickel can be utilized (Jagt, 1998).

Although most conductive inks are thermally cured in temperature-controlled ovens, several researchers have utilized lasers of different wavelengths as an alternative method for selective curing of a variety of conductive media. The laser curing process is:

(1) much faster than traditional oven curing for curing short conductive traces,
(2) capable of localized curing while protecting nearby heat sensitive electronic components and substrates (Fearon et al., 2007), and
(3) an enabler of the fabrication of 3D structural electronic devices by providing sufficient curing of the conductive traces *in situ* during the manufacturing process and thus allowing for fabrication of subsequent AM layers without ink/resin contamination (Lopes et al., 2012).

The third aspect allows for the continual fabrication of 3D structural electronics (*i.e.*, embedded electrical components and conductive traces within mechanical structures) using AM equipment such as SL without requiring removal of the partially-built structures. There has been quite substantial research into using lasers to cure dispensed conductive media. Bieri et al. (2003) utilized an argon-ion laser at 488 nm wavelength to cure a conductive ink comprised of 30% gold nanoparticle in a toluene solution with a goal of manufacturing microstructures from metal nanoparticles. The optical absorption depth of the gold nanoparticle toluene solution increased to over 100 μm for wavelengths in the near-IR region. The solvent evaporates as a result of the laser irradiation, which is absorbed in the gold nanoparticles and results in thermal diffusion toward the evaporation interfaces (Chung et al., 2004). Palmer et al. (2005) fabricated a functional power supply voltage converter circuit capable of electromagnetic interference filtering using an 800 nm femtosecond laser to cure silver based ink as part of the process. A frequency doubled neodymium doped yttrium aluminum garnet nanosecond laser having pulse width between 3 and 5 ns was utilized by Ko et al. (2006) to sinter an alkanethiol self-assembled monolayer protected gold nanoparticle film on polyimide substrate. Fearon et al. (2007) cured flake based conductive ink consisting of particulate silver, a resin binder, and solvents added for lowering viscosity by using an 8.1 W, 10.6 μm wavelength, CO_2 laser. The ink was cured by laser energy absorption by the silver particles and resin binder and the resulting heat buildup evaporated the solvent and cured the resin binder leading to a continuous network of interconnected silver particulates. The effect of a range of wavelengths (488–1064 nm) was examined by Maekawa et al. (2009), using a variety of laser sources, on laser sintering characteristics of Ag nanoparticles as well as adhesion of the cured ink to a polyimide substrate. In a direct comparison between a laser diode (LD) (980 nm, 50 W) and argon ion (Ar+) laser (488 nm, 1.3 W), it was found that resistivity decreased with increasing laser power. Additionally, the lowest resistivity in LD curing was around 5 μΩ cm (resistivity of bulk silver is 1.59 μΩ cm) at laser power higher than 3 W, while the resistivity in the Ar+ laser was 8 μΩ cm at about 0.4 W, at which the substrate burned out. Kim et al. (2009) utilized a 532 nm wavelength DPSS solid state laser to cure a silver based ink and concluded that the laser curing process is shorter than furnace curing to achieve comparable resistivity. Repeated irradiations with a 532 nm Nd:YAG laser were utilized by Fu et al. (2012) to successfully cure particulate silver inks. In their research, Shang et al. (2013) established relationships between laser traverse speed and resistivity using a laser assisted direct write (LADW) method to study the effects of laser curing quality of a silver based ink using a CO_2 laser with different beam intensity profiles.

As demonstrated above, several researchers have effectively utilized lasers for curing a variety of conductive inks. In general, for silver based inks, the curing effectiveness increases with increased laser power, limited only by the performance of the selected materials (inks, substrate, *etc.*) under the irradiation conditions. The wavelength of the laser influenced the energy absorption behavior of the silver ink and affected the ink curing process. Finally, when scanning a laser beam, the speed of the laser traverse, in addition to the factors mentioned above, can also affect the resistivity of the final cured ink trace.

Capitalizing on access to the existing SL laser for potential ink curing, this research demonstrates the use of the standard 355 nm and 325 nm SL lasers for *in situ* conductive ink curing to build 3D structural electronic devices. Adding a specialized laser and scanning mirror system to the existing SL/DP setup for ink curing would be costly, and thus, this research was intended to determine if the existing SL lasers could effectively be used to cure the DP-dispensed silver-based conductive traces with the goals of:

(1) determining the most viable laser curing method for *in situ* curing that enables continued fabrication with the resin-based SL process,
(2) improving (or decreasing) interconnect resistance,
(3) reducing manufacturing time during the 3D structural electronic device fabrication process, and
(4) determining the preferred laser curing wavelength among the two commercially available SL lasers.

In SL fabrication, each resin has a recommended critical exposure (E_c) and depth of penetration (D_p) so that the laser scan speed is determined based on the laser power and the resin-specific D_p and E_c parameters (Jacobs, 1992). To control the scan speed during the ink curing experiments, the E_c and D_p parameters were varied. The effects of several parameters on trace curing were explored, including laser energy (based on laser power and scan speed), scanning location relative to the ink to be cured, and laser wavelength. Additionally, the effects of a post-fabrication thermal cure on trace resistance were explored to determine the minimum number of laser scanning passes (and thus, minimum time required) for ink curing in the context of a final, full oven cure after SL/DP fabrication. Laser curing experiments were performed using a variety of inks to determine if a specific type of ink was more responsive to curing by laser as well as to determine if the results could be generalized.