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A time-resolved shadowgraphic study of laser transfer of silver nanoparticle ink

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ABSTRACT

The dynamics of liquid phase laser induced forward transfer (LIFT) of silver nanoparticle (NP) ink (particle size 30–50 nm) was investigated by time-resolved shadowgraphic imaging. LIFT was carried out by a KrF excimer laser (248 nm, 35 ns) using two donor substrate configurations: (a) a wet silver NP ink layer spread on a quartz substrate and (b) a wet silver NP ink layer spread on a quartz substrate covered by a 40 nm thick titanium layer. This comparative study revealed a completely different ejection mechanism for the two different donor configurations. The use of the titanium dynamic release layer (DRL) resulted in a highly directional and low velocity ejection of the material for a wide range of laser fluences. On the other hand, LIFT of silver NP ink without using the titanium DRL provoked supersonic velocity ejection and shock wave generation for laser fluences even slightly above the ejection threshold. The velocity of the ejected material (13–240 m/s) in the case of titanium DRL assisted LIFT was significantly lower than the one observed without using DRL (106–830 m/s). The use of the titanium DRL layer expanded, significantly, the processing window for directional and low velocity ejection of the silver NP ink.

1. Introduction

The excellent properties of the commercial silver nanoparticle (NP) inks such as high electrical conductivity, stability and low sintering temperature make these materials ideal for applications like organic photovoltaic, plastic electronics and thin film transistors. The fabrication of those microelectronic devices requires high precision printing of silver NP ink based miniaturized interconnects.

Ink-jet printing of metallic NP inks provides a direct and maskless patterning method, which has been widely used for the fabrication of conductive interconnects [1,2]. Despite its broad appeal, the ink-jet printing technology presents several limitations regarding to the spatial resolution of the deposited patterns (25 μm for printing continuous lines [3]) and the rheological properties of the complex NP ink solutions. In particular, the viscosity and the solid content (NPs concentration) of the metallic NP ink suspensions should be carefully selected to avoid clogging of the nozzles [1].

Recently, laser induced forward transfer (LIFT) [4–6] of silver NP inks is receiving growing interest as it offers an alternative non-lithographic technique for printing uniform and well-defined conductive patterns [7–13]. Liquid phase printing of low viscosity silver NP inks has been performed for patterning conductive lines and dots using both conventional [8–13] and dynamic release layer (DRL) assisted LIFT [7]. Three-dimensional printing of complex patterns has also been demonstrated by employing LIFT of high viscosity silver NP pastes [10,12].

A critical issue for the LIFT of liquid solutions is the definition of the optimum laser processing parameters (i.e. pulse duration, wavelength, laser fluence, and beam size) and donor substrate characteristics (i.e. use of suitable DRL, liquid film rheological properties and thickness) to print uniform and reproducible droplets. To this direction, time-resolved imaging of the LIFT process provides an advanced method to investigate the dynamics of the material ejection and optimize printing capabilities. Most of the studies dealing with liquid phase LIFT dynamics have been performed by using model biological solutions and several metallic and polymeric DRL layers [14–18]. It is a common observation for these studies that under the optimum laser fluence the material ejection takes place through the formation of a long and stable jet. Recently, the jetting behavior has been simulated using hydrodynamic modeling [19,20].

Despite the extended work on the LIFT dynamics of glycerol-based model solutions, there are only few studies dealing with LIFT dynamics of composite solutions [13,21,22]. Our study was focused to the investigation of LIFT dynamics of a commercially available complex Ag NP ink solution, which is widely used for digital printing of interconnects. The dynamics of both conventional and titanium layer assisted liquid phase LIFT of silver NP ink were investigated by using time-resolved shadowgraphic imaging. This comparative study was carried out in order to investigate the effect of a titanium layer on the ejection mechanism. We have found a

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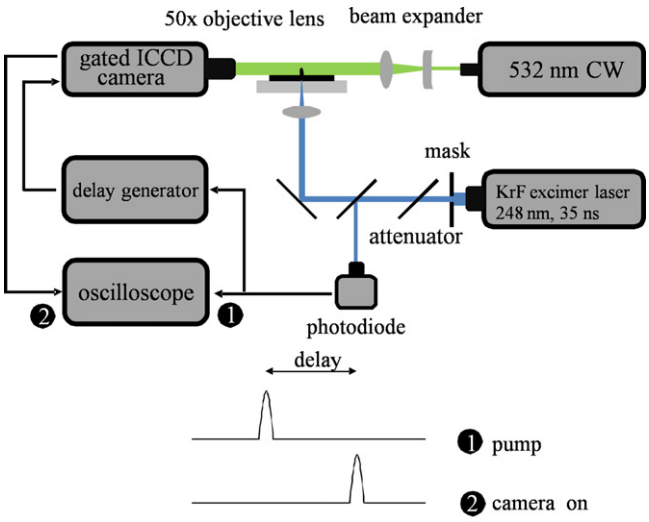

Fig. 1. A sketch of the shadowgraphic time-resolved imaging setup. A pump KrF eximer laser (248 nm, 35 ns) initiates the ejection of silver NP ink. The images are captured with a gated ICCD camera, which is synchronized to the pump laser through a photodiode and a pulse delay generator. Both photodiode and ICCD signals were sent to an oscilloscope for accurate measuring of the delay time.

completely different ejection mechanism for the two different LIFT configurations. In the case of the titanium layer assisted LIFT of the silver NP ink the material was ejected with a directional way and significantly low velocities. On the contrary, LIFT of silver NP ink without using DRL resulted in directional ejection of the material only for a narrow laser fluence range. A slight increase of the laser fluence over the ejection threshold provoked supersonic material ejection and shock wave formation.

2. Materials and methods

Two different donor substrates were used in order to investigate the effect of the titanium absorbing layer on the dynamics of the silver NP ink ejection. The first type of donor substrates was 1 mm thick quartz plates (25 mm in diameter) purchased from UQG Optics. The second type donor substrates was prepared by using the same type of quartz plates coated with a 40 nm titanium laser absorbing layer. The titanium layer was deposited by electron beam evaporation (typical thickness variation was 2 nm). A thin liquid film of silver NP ink (U5603, SunChemicals, 20 wt.% silver content, solvent: mixture of ethylene glycol, glycerol and ethanol, viscocity: 12 mPa s, NP size: 30–50 nm) was applied to both types of donor substrates by using spin coating (2900 rpm, 30 s). Spin coating ensured reproducibility and high uniformity of the film thickness (~5.5 μm) across the donor target surface. No additional treatment was applied at the donors, which were used for a maximum period of 30 min after their preparation to avoid silver ink film drying. Measurement of the donor mass over the time revealed that solvents' mass loss rate was about 4.5 μg/min. This caused an insignificant reduction (about 4.5%) of the mass of the spin coated silver NP ink layer within the 30 min period. Therefore, we have considered the silver NP ink film as wet and uniform within the time period that each donor was used.

The donor substrates were placed in a "face up" liquid phase LIFT configuration without receiving substrate (Fig. 1). Then, the silver NP ink ejection was initiated by using single pulses of a KrF excimer laser source (248 nm, 35 ns, 1–100 Hz, 0.5 J) and a mask projection optical system. The projected laser beam spot on the donor substrate was rectangular with an edge width of 220 μm. The dynamics of the LIFT process was studied using the experimental configuration which is depicted in Fig. 1. An expanded laser beam of a cw Nd:YAG laser was used to illuminate homogeneously the ejected material. Images were captured by a gated intensified charge-coupled device ICCD (ICCD camera, Princeton Instruments) equipped with a 50X long working distance objective lens. The integration time for each image frame was 20 ns (gate time). The camera synchronization was initiated by the pump KrF excimer laser by using a photodiode and a pulse delay generator. Both photodiode and ICCD signals were sent to an oscilloscope for accurate measuring of the delay time, which was ranged from 145 ns to few microseconds (Fig. 1). Three to five images were taken for each delay time in order to ensure reproducibility. Finally, the images were analyzed using the ImageJ [23] software to extract the front distance of the ejected material as a function of the time.

3. Results and discussion

3.1. Dynamics of titanium layer assisted LIFT of silver NP ink

In the first part of this work we investigated the ejection of the silver NP ink using titanium layer assisted LIFT. Time-resolved shadowgraphic images of the ejected silver NP ink under various laser fluences are depicted in Fig. 2. Pictures were obtained at different time delays (0.145–18.5 μs) with respect to the pump laser pulse.

For a laser fluence range from 100 mJ/cm^2 (ejection threshold) up to 130 mJ/cm^2, which is below the titanium layer ablation threshold (experimentally defined around 200 mJ/cm^2), a directional ejection of the silver NP ink was initiated due to the absorption of the laser energy by the titanium layer. In accordance with the absorption coefficient ($a \sim 6.13 \times 10^5$ cm^{-1}) of the Ti layer at 248 nm [24], the incident laser radiation will not exceed a penetration depth of about 16 nm ($1/a$). As a result of the localized temperature rise at the titanium DRL, a vapor pocket was formed at the titanium–liquid film interface due to the vaporization of the silver NP ink solvents. Since the laser pulse duration was much shorter than the materials dynamic response we consider the expansion of the vapour pocket as the main impulse force for the materials ejection. The observed dynamics can be related to the jet formation in liquids due to the expansion of a bubble near a free surface [25], which has been reported in several experimental [14,15] and simulation modeling works [19] dealing with DRL assisted LIFT of liquid model solutions. However, the jetting behavior observed in our experiments is less directional and presents several discontinuities. This is attributed to the nature of the silver NP ink material that consists of two separated phases; the solid silver NP component embedded in the organic solvents matrix as the liquid phase. The slight right bend of the flyer that is observed for low laser fluence in Fig. 2 (also appeared in Fig. 4) is probably due to laser bean intensity variation within the laser spot. Despite the relative uniform beam profile achieved by the mask projection system, the large laser spot size (220 μm) compared to the Ag NP solution film thickness (5.5 μm) enhanced the effect of the laser intensity variation on the flyer ejection.

For higher energy fluences, above the 130 mJ/cm^2, a different dynamic behavior is observed. The shape of the initial flyer at the silver NP ink layer–air interface clearly reproduced the size and the shape of the laser spot indicating a transfer behavior that is common for solid phase LIFT dynamics [26,27]. The expansion of the initial protrusions of the silver NP ink material was completed in a microseconds time scale. It is also noticed that no shock wave is observed even for a laser fluence of 330 mJ/cm^2 that resulted in plasma formation. The absence of shock wave is in agreement with the calculations for the ejection velocity of the silver NP ink material (240 m/s) that was well below the supersonic velocity threshold (343 m/s).