Lasers in Manufacturing Conference 2015

Laser printing and curing/sintering of silver paste lines for solar cell metallization

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Abstract

The main objective of this work is to adapt the Laser Induced Forward Transfer (LIFT), a well-known laser direct writing technique for material transfer, to define metallic contacts (fingers and busbars) onto c-Si cells and to use continuous wave laser sources to curing and sintering the deposited line.
Commercial silver pastes (with viscosity around 30-50 kcPs) are applied over a donor glass substrate using a coater with a controlled thickness in the range of tens of microns. A solid state pulsed laser (532 nm) is focused at the glass/silver interface producing a droplet of silver that it is transferred to an acceptor substrate. Lines are drawn by means of scanning the laser spot. The influence of the process parameters (silver paste thickness, gap between donor and acceptor, and laser parameters - spot size, pulse energy and overlapping of pulses) is studied as a function of the morphology of the deposited lines using confocal and scanning electron microscopy. With an appropriate process parameterization it is possible to transfer a high paste volume per pulse (~ 400 pL) and then large aspect ratio lines (~ 0.5) can be drawn at high speeds (2 m/s).
After the printing process a continuous wave green laser is used to heat the silver paste line to remove the organic layer (curing) or even to produce some melting between the silver grains (sintering) in order to reduce the line resistance. Process parameters such as laser power, spot size, processing velocity, and number of scans are studied. Results show that all-laser based metallization processes are possible.

Keywords: Laser Direct Write; Laser induced forward transfer; Silver paste; Photovoltaic; Metallization;

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1. Introduction

Laser Induced Forward Transfer (LIFT) is a direct-write laser technique, capable to transfer different materials (especially metallic solid materials or material dissolved in an assisting matrix) and in different sizes onto a number of different substrates (Arnold et al. 2007). It is thus possible to use LIFT for printing metallic contacts onto flexible optoelectronics devices in flex/3D electronics industry, patterning solder paste for microelectronics (Mathews et al. 2015) or for the metallization of the front side of solar cells (Morales et al. 2015). For these applications, LIFT has some attractive features such as flexibility in choice of inks, the complexity of the designed patterns, and an easy setup, that has even led to an industrial implementation (Hennig et al. 2012).

LIFT uses laser pulses to push thin disks of a ribbon material from a transparent substrate and deposit them onto an acceptor substrate. The laser beam is focused in the donor substrate/ribbon interface. During the pulse duration, the laser energy is deposited within the laser spot size into the interface, evaporating a little amount of the material and generating the expansion of the remaining material, accelerating the non-evaporated part of the metal film towards the acceptor substrate, as it is shown in Figure 1.

The aim of solar cell researchers and manufacturers is to find technologies leading to an increase in the efficiencies of solar cells and, at the same time, keep low costs. Procedures capable of making better contacts by improving the aspect ratio, decreasing contact losses and keeping low costs, is one of the goals to reach (Aakella et al. 2013). LIFT made with ns pulses is a well-known technology to generate structured metallization onto substrates but have not been applied up to the moment to define in a single step the fingers of front contact in a photovoltaics device, although two steps approaches has been developed in the last years (Roder et al. 2010). The main objective of this work is thus to adapt the LIFT technique to define metallic contacts (fingers and busbars) using a silver paste of high viscosity onto c-Si cells that can fulfill these requirements.

The complete metallization process of a solar cell includes a series of heating steps in furnace, needed for evaporate the paste solvents (curing), melting the metal particles (sintering) and etching the anti-reflective coating and electrically contacting the paste and the substrate (firing) (Luque and Hegedus 2003). These thermal treatments could be also done by laser heating of the deposited material using continuous wave (CW) laser sources. Laser processing has the advantage of being a low-temperature process, in the sense that only the deposited material is heated up, avoiding any furnace steps that could affect negatively the performance of the electronic device. Combining the deposition of the metallic contact using LIFT and the laser sintering of the contact, an all-laser based process for metallization of solar cells can be thus developed.

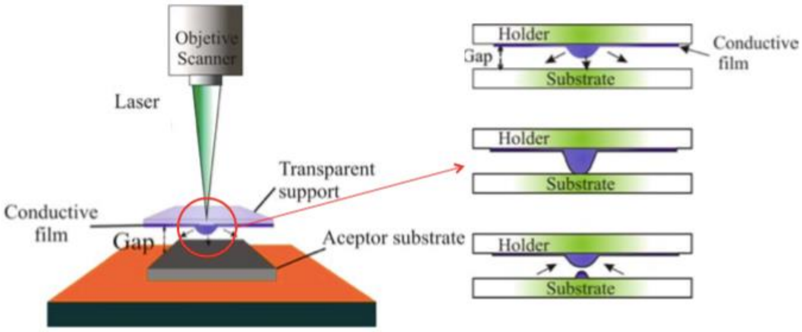

Fig. 1. Principle of LIFT process for metallization of thin-film solar cells.

In order to achieve these objectives the LIFT process parameters (silver paste thickness, gap and laser parameters -spot size, pulse energy and overlapping of pulses) are modified and the morphology of the lines is studied using confocal microscopy and scanning electron microscopy (SEM). When the optimum paste transfer parameters have been determined, cm-long lines were printed. The best lines were also cured and sintered using a CW laser in order to improve the electrical conductivity of the line. Some examples of metallization of larger areas (up to 10 cm x 10 cm) are also presented.

2. Experimental method

2.1. Sample preparation and characterization

The paste used in these experiments is the Solamet PV17F (DuPont), which is a highly conductive silver paste that provides excellent efficiency, reliable soldered adhesion, low lay down, rapid dry, and very fast firing. Although it is designed for screen printing, its excellent electrical and sintering properties makes it a good candidate for LIFT metallization. The main challenge when using this paste for LIFT is its high viscosity (30-50 kcPs), much higher than the typical Newtonian fluids used normally for LIFT like inks. The paste was deposited onto microscope slides (donor substrate) using a commercial coater (Control Coater model 101, RK PrintCoat Instruments Ltd). The ribbon thickness on the donor substrate was selected in the range from 20 to 100 µm. c-Si wafers and solar cells were used as acceptor substrates. The donor substrate was set at a gap distance over the acceptor substrate using Kapton tape, stuck on the microscope slide. The gap is controlled using tape of different thickness or using several layers of tape. The basic LIFT configuration, without any intermediate absorbing layer or assisting liquid matrix (Arnold et al. 2007), was used. As a laser source, a diode-pumped, solid state, ns-pulsed Nd:YVO4 laser (Spectra Physics Explorer) with wavelength of 532 nm was used. The beam is focused onto the interface between glass and silver paste. The spot diameter in the focus is 25 µm. An optical scanner (Scanlab hurrySCAN II) is used to print lines overlapping different laser pulses. More details on the paste properties, the pre-deposition process, and the laser station used for LIFT can be found elsewhere (Morales et al. 2015).

The morphology of the transferred paste is measured using confocal microscopy (Leica DCM3D) and SEM (Hitachi 3000N).

2.2. Sample curing and sintering

Those lines with the best morphology were thermally treated using a diode-pumped, solid state, CW laser (Spectra Physics Millenia), emitting at 532 nm. The laser focused spot, with a diameter of 35 µm, was scanned over the line using the same optical scanner. The microstructure of the irradiated lines was studied using SEM while their electrical response was characterized by means of measuring the electrical resistance of 1 cm lines.

3. Results and discussion

3.1. Metallization using LIFT

As a first approximation, single dots of paste or voxels were transferred using a single laser shot. Figure 2 shows microscope images of voxels transferred using different energies and two ribbon thicknesses (35 and 50 um). From these studies, it was determined a small parametric window in which is possible to print compact voxels. The LIFT process using high viscosity pastes is highly dependent on the paste thickness and on the gap. The laser pulse energy threshold, needed to start the transfer process increases with the paste thickness. When using energies above the transfer threshold and the ribbon thickness is small, explosive transfer occurs and the printed voxels show heights similar to the silver powder size. Only when the ribbon thickness is similar to the gap distance, it is possible to transfer concrete dots with small width and large height. To explain these results a two steps transfer process is proposed (Figure 3). LIFT generates a column of paste that connects both donor and acceptor substrates. When the donor substrate is removed the paste is stretched until the final shape is obtained. This two-step process allows the printing of high volume voxels (~ 100 pL).

Once the optimum parameters are determined, lines are deposited by means of scanning the focused beam. Since the objective of the present work is to applied LIFT technology for the metallization of solar cells, the aspect ratio, calculated as the height divide by the width of the lines, was selected as figure-of-merit. Large aspect ratios implies large electrical conductivity while keeping small the shadow effect (Aakella et al. 2013). Figure 4 shows confocal and SEM images and profiles of a LIFT line printed with the best parameters at large speeds of 2 m/s, fully compatible with industrial requirements. With an appropriate process parameterization (laser pulse energies around 15 µJ) and large speeds (2 m/s), it is possible to transfer lines with high aspect ratios: 0.36 - 0.61 (width: 90-150 µm, height: 55 µm) and without discontinuities. This approach is able to transfer large volume voxels, larger than 400 pL.

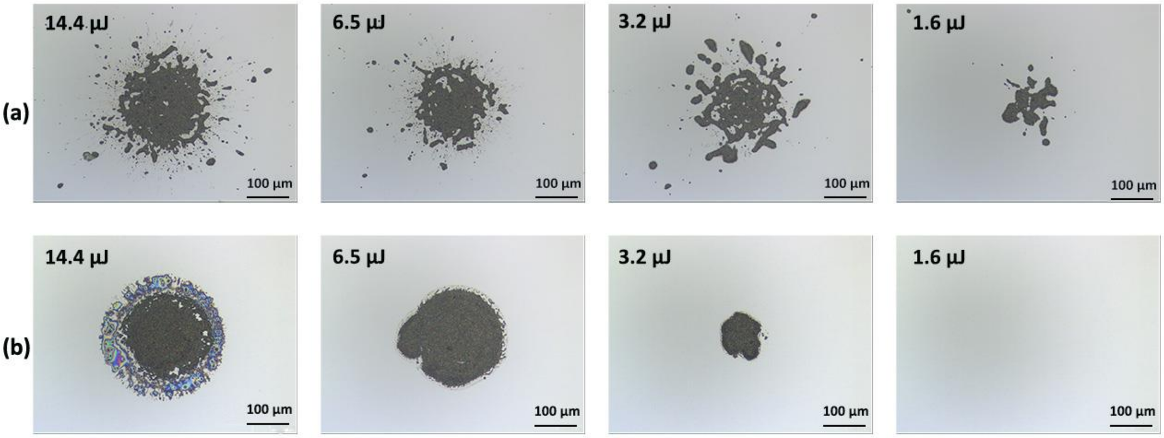

Figure 2. Microscopy images of LIFT dots transferred using single shots of ns laser and pulse energies varies from 25.6 µJ to 1.6 µJ with two different paste thickness: (up) 30 µm and (down) 50 µm

Figure 3. Scheme of the LIFT process for high viscosity pastes. Left: Column generation. Right: Glass removal and final shape definition.

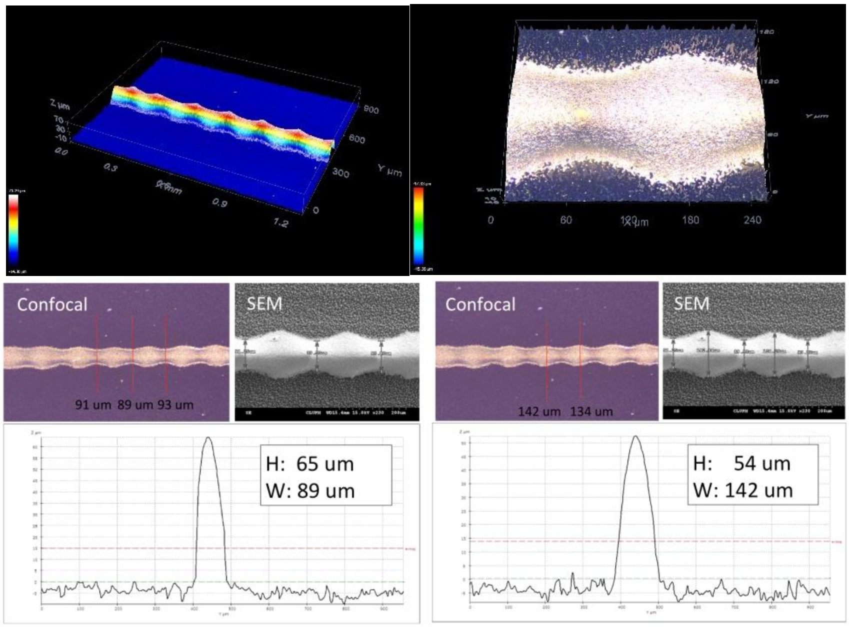

Figure 4. Different LIFT lines confocal and SEM profiles obtained with these process parameters: Paste thickness: 80 µm; Gap: 50 µm; Pulse energy: 14.5 µJ; Speed: 2.0 m/s.

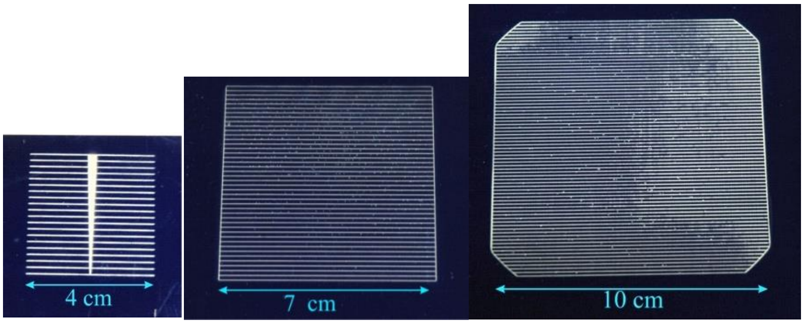

Figure 5. Different front grids printed with LIFT onto a c-Si cell.

Therefore, LIFT metallization can be used to print the front grid of a cell without the need of any screen. This allows printing different grid designs just changing the program of the optical scanner and giving to the process great flexibility. Figure 5 shows the possibilities of this technique: three different grid designs for different size cells done with the same LIFT parameters.

3.2. Laser curing and sintering

The objective of the heat treatment is to obtain the lowest possible resistance of the printed features at the lowest possible temperature. A low curing temperature of a metallic ink or paste is important in flexible electronic and photovoltaic applications where low temperature are needed to avoid damaging to the substrate, this effect can be increased with the laser local heating that will prevent heating areas of the substrate where no ink or paste is present. For particle-based inks or pastes, the curing temperature is defined as the temperature where particles lose their organic shell and start showing conductance by direct physical contact, whereas sintering takes place at a higher temperature and particles start showing a neck formation between them. Conductivity will thus arise when metallic contact between the particles is present, and a continuous percolating network is formed throughout the printed feature.

The optical system used for laser heating was the same than in LIFT, although the scanning speeds were now much slower (in the order of tens of mm/s). The effect of the laser power and the scanning speed on the electrical properties of the cured line was studied. Confocal microscopy shows that the geometry of the lines (i.e. aspect ratio) was not affected by the laser treatment, while the microstructure of the silver paste was strongly modified, as it is shown in Figure 6.

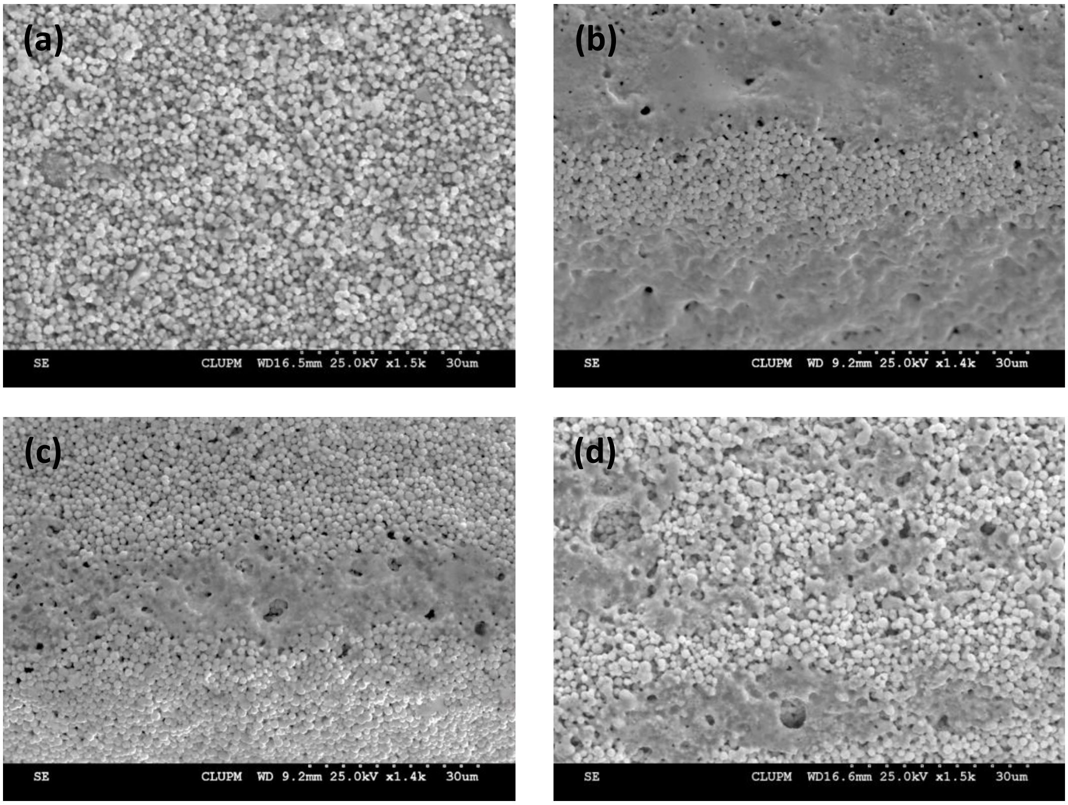

Figure 6. SEM images of lines cured by laser irradiation using different process parameters: (a) as-deposited line; (b) 4.7 W and 40 mm/s; (c) 2.7W and 40 mm/s, and (d) 2.7 W and 70 mm/s.

Figure 6a shows an as-deposited SEM image of a line transferred using LIFT. The silver particles can be clearly seen. When scanning the line with the CW laser using a large power or a slow speed the silver grains melt and sintered, as it is shown in figures 6b and 6c. However the adherence of the line to the substrate is also affected, resulting on the peel off of the lines during or after the laser treatment. Therefore is necessary to treat the line with a lower energy dose. Figure 6d shows a line irradiated with 2.7 W and 70 mm/s. This line does not peel off and the silver particles are not completely melted but percolation channels were created between particles, which should imply a larger electrical conductivity. The electrical response of these lines has been characterized by measuring the electrical resistance of 1 cm lines. The as-deposited line had an electrical resistivity of 1200 µΩ·cm, while the resistivity decreases down to 26 µΩ·cm after laser treatment using the optimum parameters (2.7 W and 70 mm/s).

4. Conclusions

In the present work, two different laser direct writing techniques have been studied for the all-laser based metallization of a solar cell, from the deposition of the silver paste using LIFT to the local sintering and curing of lines drawn using a CW laser.

The parameterization of the LIFT process has shown that laser power, paste thickness, and gap distance are key factors to transfer high viscosity pastes: the minimum pulse energy required to transfer the paste increases with the thickness of the paste In addition, gaps with lengths similar or smaller that the ribbon thickness are required. Moreover, a two steps transfer process has been proposed: LIFT generates a column of paste connecting donor and acceptor substrates and the voxel is transferred when the donor substrate is removed.

LIFT has been successfully used for printing lines by scanning the laser spot. Using the best results from our parametric window the parameterization it is possible to print lines with large aspect ratios (~ 0.36-0.60). The volume transferred per pulse is also quite large (~ 400 pL). LIFT of commercial screen-printing pastes with optical scanners allows fast processing and flexible design to print large areas becoming a promising technique for the metallization of photovoltaic devices.

CW laser curing and sintering of lines printed used LIFT has been also achieved using different laser powers and scanning speeds, but there is a small parametric window in which the lines do not peel off due to the heating process. The bulk resistivity of those lines that remain on the substrate after the laser heating is reduced in two orders of magnitude, while neither the geometry of the line nor the substrate are affected. Curing process can be achieved at speeds large enough to be used in future industrial applications.

Acknowledgements

This work was supported by EUROPEAN COMISSION APPOLO FP7-2013-NMP-ICT-FOF. 609355 and Spanish MINECO projects: SIMLASPV-MET (ENE2014-58454-R) and HELLO (ENE2013-48629-C4-3-R).

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