Photonic Curing of Low-Cost Aqueous Silver Flake Inks for Printed Conductors with Increased Yield

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Abstract

Printing of highly conductive tracks at low cost is of primary importance for the emerging field of flexible, plastic and large area electronics. Commonly, this is achieved by printing of metallic conductive inks, often based on Ag or Cu nanoparticles dispersed in organic solvents. The solvents must be safely removed and have particular storage and handling requirements, increasing process costs. By using water-based inks containing micron-sized silver flakes both material and process costs can be reduced, making these inks attractive for industrial applications. However, the sintering of flake inks requires higher temperatures than nano-sized inks owing to the particles’ smaller surface area-to-volume ratio, meaning that when cured thermally the conductivity of many flake inks is lower than nano-particle alternatives. This problem can be addressed by the application of visible light photonic curing; however, the substrate must be protected and so process parameters must be defined for each material / substrate combination. Here we report results of a large scale trial of photonic curing of aqueous flake silver inks on PET substrates in an industrial setting.

The resistivity of printed patterns after an optimised photo-curing regime matched those reported for typical nano-particle inks; on the order of 100 $\mu\Omega\cdot$cm depending on substrate and geometry. Scanning electron microscopy (SEM) revealed evidence for structural changes within the printed films consistent with localised melting and necking between adjacent particles, leading to an improved percolation network. Furthermore, in the large-scale industrial trial employing screen printed silver lines, the manufacturing yield of conductive lines was increased from 44% untreated to 80% after photo-curing, and reached 100% when photo-curing was combined with thermal curing. We believe this to be the first reported observation of an increase in the yield of printed electronic structures following photo-curing. We propose a crack-healing mechanism to explain these increases in yield and conductivity. We further report on the effects of the photonic curing on the mechanical bending stability of the printed conductors, and discuss their suitability for wearable applications.
1. Introduction

The rapidly-growing field of flexible plastic electronics promises to enable high volume production of electronic devices via large-scale, roll-to-roll processes. Such devices have much lower production costs than traditional methods of electronics manufacture due to their non-vacuum and low-temperature based processes, and can be made on flexible plastic or paper substrates along with other novel form factors\(^1,2\). Lately, silver inks are becoming more important as the conductive material of choice for printed electronics. Current applications of silver inks include printed solar cells, where silver layers may either be used in a grid structure as transmitting electrodes or in a bulk layer structure as back contacts\(^3,4\). Printed silver structures have also been successfully demonstrated in organic light emitting diodes (OLEDs)\(^4\), Radio Frequency Identification (RFID) antennae\(^5,6\) and electrodes for touch screens\(^7\). In all of these applications, despite how good the bulk conductivity of the pure silver material may be, the conductivity of the printed layers will vary widely, since the silver needs to be applied and patterned via a suitable ink and printing process. Therefore the morphology of the printed patterns, and crucially the percolation networks which form between the nano- or micron-scale particles of the conductive material, will drive the conductivity values achieved. Homogeneity of the printed layer and adhesion to flexible substrates are further key performance parameters\(^8\).

Current commercially-available silver inks for applications on flexible substrates are often based on silver nanoparticles, which require expensive and time consuming synthesis techniques. A lower-cost alternative is copper nanoparticle or flake inks, but these are prone to oxidation\(^9\). In many cases nanoparticle inks use volatile organic solvents, which may require specific solvent handling measures to be implemented in production, storage and transportation, thus further driving up overall system costs\(^10\). A water-based, low-cost ink is therefore desirable, and one approach is to move to micron-sized silver flakes, which are
generally significantly cheaper than silver nanoparticles due to their higher-yielding synthesis methods \(^{11}\). Conductive flake inks are commonly used in applications which can tolerate high temperatures needed to sinter the flakes (usually \(> 800^\circ\text{C}\)), including PV applications \(^{12,13}\) and ceramic tapes \(^{14}\). As a further advantage of flake inks, the high aspect ratio of the flakes could have advantages in terms of the stretchability and flexibility of printed conductive structures. This is becoming a key consideration in ink materials research due to the trend towards wearable electronic devices.

Many functional inks require curing and/or sintering in order to become conductive. Here the term curing is used to mean the removal of residual solvents and crosslinking of binders, while sintering is used to mean the densification of particles driven by surface free energy minimisation, leading to increased inter-particle contact. Owing to the melting point suppression of nanoparticles caused by their very high surface area-to-volume ratios \(^{15}\), full sintering can often be achieved in these systems within a temperature range tolerable to the substrate \(^{16}\). Flake inks however have the same melting point as the bulk material, so full sintering is not usually possible within such a temperature range. Therefore, the conductivity which can be achieved with such inks is often lower than nanoparticle-based inks. In order to improve conductivity with flake inks we have applied broadband intense pulsed light photonic curing to screen printed conductive traces.

Broadband photonic curing, consisting of exposing the samples to short pulses of high intensity light, is a technique which has been known for a number of years, and is commonly applied to the sintering of nanoparticle-based inks based on both copper and silver \(^{9,16–22}\). While a range of curing and sintering methods are available, including pure thermal curing, or a range of Ohmic, optical, plasma- or microwave- assisted technologies \(^{16,23–26}\), the advantages of photonic curing include its high speed, wide coverage area and the ability to heat the printed layer to a much higher temperature than the substrate \(^{27}\). Photonic curing is commonly used where there is a need to keep flexible plastic substrates below their glass
transition temperature. However, the maximum temperature which can be tolerated within the printed structure is also limited by the need to avoid potentially damaging decomposition of the binders within the printed layer which would lead to mechanical failure. Therefore, photonic curing settings must be defined for each new material/substrate combination.

Probably due to these factors, combined with their higher temperature curing requirements, relatively little work has been reported on photo-curing of flake inks. Tam et al. applied intense pulsed light sintering to a Cu ink with mixed nanoparticles and flakes, however the main sintering effect was attributed to the nanoparticles. Park et al. applied infrared (IR) curing to flake silver inks, showing a reduction in sheet resistance, but this technique has a lower power density and longer treatment time than visible light photo-curing. Cui et al. reported photonic curing of electrically conductive adhesives containing silver flakes. Although in this work the authors’ aim was to crosslink the polymers to form an adhesive bond, they did report the observation of a sintering effect on the silver flakes; however it required the use of very high power densities and the authors noted that the adhesion within the deposited layer was severely reduced. Therefore if a photonic processing technique can be demonstrated that improves the conductivity of Ag flake inks while retaining good adhesion in the printed layers as well as protecting the PET substrates, this would be advantageous for industrial applications.

Here we demonstrate that, despite their higher melting point compared with nanoparticles, visible light photonic curing can nevertheless be used to cause inter-particle necking of flake silver inks of average flake sizes 1–3 μm, and thereby improve the existing percolation network for charge conduction, without destroying the adhesion in the printed layer or damaging the substrate. In addition to the removal of solvent and some binder, such necking between adjacent flakes greatly increases conductivity by increasing the contact area between adjacent flakes and introducing additional percolation pathways.
Furthermore, we present for the first time results of a large scale trial of such a technique carried out in an industrial setting. This trial revealed an increase in manufacturing yield after the photonic curing. This observation is explained by a crack healing process in the samples as a result of photonic curing, in which the observed inter-particle necking is able to bridge cracks in the samples. Since very fine cracks are a common failure mode in the manufacture of printed lines, this allows many non-conductive structures to be repaired in-line. In a typical screen printed interconnect application, this crack healing led to an increased yield of conductive lines from 44% untreated to 80% using photonic curing alone, and 100% when photonic curing was combined with thermal curing. Increased manufacturing yield is a vital consideration, along with choice of ink formulation and solvent, in order to reduce overall process costs within industrial settings. Note that here we use the term manufacturing yield to refer to the percentage of printed lines which are conductive.

2. Experimental Procedure

Poly(ethylene terephthalate) (PET) substrates were cleaned using an isopropyl alcohol (IPA) wash followed by contact cleaning with an adhesive roller system (Teknek). Samples were screen printed using a 400 mesh stainless steel screen from aqueous Ag inks with 1-3 µm Ag flake size, 60 wt% Ag (DZP Technologies, Cambridge, UK). The samples were separated into four groups; control, photonic treatment only, thermal treatment only and thermal plus photonic treatment. The control group were held with no further treatment. Samples requiring thermal curing were baked under ambient atmospheric conditions in an oven at 120°C for 1.5 hours. Note that the curing temperature of 120°C was set by the maximum tolerable by the PET substrate, which begins to deform above this temperature.

Photonic treatment was carried out using a Xenon flash lamp system (Heraeus Noblelight Ltd., Cambridge, UK). A typical regime consisted of 3 consecutive pulses of 3 ms duration at
a frequency of 100 Hz, using a 400 V lamp input voltage with a 30 mm working distance under ambient atmospheric conditions. These conditions were measured to correspond to an energy input of approximately 1.0 J/cm² to the samples. A Ce-doped glass envelope was used on the lamp to reduce UV exposure, which might be damaging to both polymeric binders in the ink and the substrate.

Samples were characterised electrically using a Keithley 4200 SCS source meter. Sheet resistance was measured using a custom-built four-point probe head with spring-loaded, copper-coated probe tips spaced linearly with a 3 mm tip separation. The resistivity of the fine lines was measured according to the standard ASTM F1896-10 using specially-adapted probe tips to avoid damaging the samples. The cross sectional area of the printed lines was measured at several points along each sample using an optical microscope. Scanning Electron Microscopy (SEM) was carried out using an FEI Quanta ESEM in secondary electron mode at an accelerating voltage of 10 kV. Adhesion testing was carried out by cross-cut tape peel testing.

Bend testing was carried out using a home-built testing rig which bends the samples around a radius of 20 mm. Bending occurred at 2.5 Hz, and the samples were returned to the flat state between each bend. Electrodes were attached by conductive adhesive to the sample terminals and a current of between 1 – 100 mA applied by an external power source. The resulting voltage drop along each trace as a function of time was monitored by a PicoLog 1000 data logger (Pico Technologies), and used to calculate the resistance of each trace as a function of the number of bends.

3. Results and Discussion

3.1 Optimisation of Lamp Settings
Lamp settings were first optimised by using 20x20 mm² printed squares (termed “bulk” samples). Two factors were used for the optimisation; the conductivity improvement achieved and the presence of any damage to the sample. In some cases sample damage is immediately obvious (where significant ablation or blow-off occurs), while in other cases it was revealed by subsequent adhesion testing. The lamp parameters varied were; voltage, pulse number, and pulse length, while working distance was fixed at 30 mm and frequency at 100 Hz (with the exception of 10 ms pulses, which were carried out at 50 Hz in order to allow some off-time). The resistance of printed squares was measured before and after exposure, and the resistance improvement ratio (defined as the difference in resistance before and after the treatment, divided by the initial resistance) was used to quantify the effect of the treatment. Summary results are shown in Figure 1.

As discussed by Niittynen et al. 22, when working distance is fixed, lamp voltage is the main factor affecting the optical power input to the samples. This is reflected in the results shown in Figure 1, where we find that by far the largest factor determining the improvement in resistance is the lamp voltage (Fig 1A), with voltages less than 400 V tending to have less positive impact on the resistance. The maximum voltage available in the experiment was 400 V, and this was found to be necessary to cause a reduction in the resistance in the majority of samples. Unexpectedly, at voltages of 300 V, there were a significant number of samples showing negative values for the “resistance improvement” measurement (implying resistance has increased). It is likely that this resistance increase arises due to damage to the samples caused by incomplete curing through the depth of the sample, in which the lamp energy is not sufficient to cause any beneficial curing effect, but is sufficient to cause blow-off or otherwise damage the samples. When the lamp voltage is increased from 300 to 308 V, there is a dramatic change in this behavior, likely indicating the onset of a beneficial sintering effect which compensates for any sample damage seen. This is maintained for subsequent higher lamp voltages up to the maximum of 400 V. Therefore, 300 V appears to be the
threshold voltage beyond which improved conduction can result for these conditions of 3ms, 3 pulses, 100Hz lamp conditions.

Having fixed the voltage at 400 V, the number of consecutive pulses (at 100 Hz) was varied. Figure 1B demonstrates that this parameter has a less dramatic impact on performance than lamp voltage, with 3 pulses here found to be optimum. Finally, with voltage set at 400 V and pulse number set at 3, the pulse length was varied. While pulse length would be expected to determine the overall energy input, this relationship is non-linear due to droop of the capacitors in the power supply over time. However, as pulse length was increased from 3 ms to 10 ms, the number of samples which were noticeably damaged by the photonic treatment increased, which is reflected in the trend towards more negative values of the resistance improvement at longer time scales. Based on these measurements, lamp settings of 400 V and 3 pulses of 3 ms length at 100 Hz were used for the remainder of the study.

Finally, it was found that in some cases it was possible to greatly improve the resistance of the samples by using ‘extreme’ lamp settings (for example very long pulses), but that this had a detrimental impact on the adhesion between the sample and the substrate due to excessive removal of the polymer binder. In order to explore this effect, bulk samples which had been photo-cured using the optimised settings were further characterised by tape-peel adhesion testing according to ASTM D3359-09, using scotch tape. This standard defines six classes depending on the amount of material removed by the tape, from Class 5B (no removal) to Class 0B (major removal). While all samples in the control, thermal, and thermal-photonic samples showed good adhesion, with the tape removing little or no material (<5% material removed, Class 4B), approximately 50% of samples in the photonic-only group showed poor adhesion, with a large amount of material removed by the tape (Class 1B, 35 – 65% material removed). Optical microscopy (Fig 1d) showed that the failure in these samples was not an adhesive or interfacial failure between the printed layer and the substrate, but rather a cohesive failure within the layer. This cohesive failure likely points to the existence of a two-
layer structure which has developed within the silver layer as a result of the photonic treatment being applied directly to uncured samples which have not fully dried, since samples which had been given >24 h drying time between printing and photo-curing did not show this effect. This effect does not affect the conclusions drawn here, but would need to be accounted for in future applications, in which it is highly likely that a step curing regime can be adopted to ensure there is no cohesive failure within the printed layer, while still delivering the desired conductivity improvement.
Figure 1. Optimisation of the lamp settings for the silver flake inks. Lamp voltage (a) was first optimised and a setting of 400 V was used for further trials. Pulse number (b) and length (c) were found to have less of an effect on the resistance of the samples. Optical micrographs (d) of samples after cross-cut tape peel testing, with areas of material removal demarcated with red dashed line.

3.2 Photonic Curing of Bulk Samples

Using the optimised settings, a batch of 18 bulk samples were treated in one of four different ways; untreated (control), thermal cure only, photonic only or thermal plus photonic curing. The sheet resistance of samples in the four groups was then measured. The results of the electrical characterisation are outlined in Figure 2A. Note that since we measure sheet resistance and resistivity throughout this work, the desirable outcome is a reduction in these values (showing the conductivity of the sample increased). The uncured samples showed a relatively high sheet resistance with a high standard deviation, of around 1.5 ± 0.6 Ω/□, at a
thickness of 25.4 μm (1 mil). This is as would be expected from an ink which has simply been deposited and dried at room temperature with no further treatment. Both thermal and photonic curing regimes led to a large reduction in sheet resistance and standard deviation. Average sheet resistance after thermal treatment was $0.24 \pm 0.06 \, \Omega/\square$, photonic treatment led to an average sheet resistance of $0.1 \pm 0.02 \, \Omega/\square$, and thermal plus photonic treatment to an average sheet resistance of $0.2 \pm 0.01 \, \Omega/\square$. The difference between the photonic only and thermal plus photonic batches is likely to be due to the increased reflectivity of the ink after thermal curing. The sheet resistance of the most conductive individual sample achieved with photonic curing was $0.05 \, \Omega/\square$, which compares favourably with reports for nano-particle inks, which range from $0.05 - 0.35 \, \Omega/\square$ at 25 μm thickness, depending on substrate and curing used \textsuperscript{31}. The yield of this type of sample was 100% in all cases.

3.3 Photonic Curing of Fine Lines

Using the optimised regime arrived at above, we then proceeded to cure screen printed fine line samples, consisting of a batch of 93 lines with a mean width of 90 μm, mean thickness 13 μm and length (defined by the placement of measurement pads) of 30 mm. The electrical characterisation of fine line samples is shown by the bar chart in Figure 2B, where the height of the bars shows the mean resistivity, and the error bars show standard error. Uncured samples showed a mean resistivity of $7590 \pm 3080 \, \mu\Omega.cm$; thermal curing improved this to $1100 \pm 230 \, \mu\Omega.cm$; photonic curing alone showed a significant further improvement in resistivity to $153 \pm 25 \, \mu\Omega.cm$; and the best results were achieved when combining thermal and photonic curing, which led to a resistivity of $100 \pm 12 \, \mu\Omega.cm$, while the most conductive individual sample had a resistivity of $60 \pm 6 \, \mu\Omega.cm$. Therefore, compared with uncured samples, thermally cured samples showed on average a 6.9x lower resistivity, while samples which were photonically cured showed resistivities on average 50x lower and thermal plus photonically cured samples showed on average 75x lower resistivities, which represents a 10x resistivity improvement, along with reduction in standard deviation, over thermal curing.
alone. More detailed comparisons between uncured and photonically cured and between thermally cured only and thermal followed by photonic curing are shown in Figures 2C and 2D, respectively.

The thermal curing regime used in this work consisted of 1.5 hours at 120°C. This maximum temperature is limited by the PET substrate, which begins to deform at around 130°C. A measurement of the resistance of printed tracks as a function of time (Supporting Information, Figure 1) showed that after 1.5 h there is no further improvement in resistance. Therefore, the samples in the thermal group represent the optimal conductivity achievable by thermal means, with this particular substrate. As a comparison, the same ink was printed on glass slide and cured at 220°C (above this temperature browning of the binder was observed on some samples). These samples had a mean resistivity of $100 \pm 25 \, \mu\Omega\cdot\text{cm}$; comparable to photo-cured samples. However owing to the different substrate (rigid vs. flexible) these values are not directly comparable.

When comparing the results of this thermal curing with photonic curing, from the present results it appears that while both significantly reduce the resistance compared to uncured samples, the lowest achievable resistance by thermal curing is significantly higher than that achievable by photonic curing. This is likely due to the localised higher temperatures which can be achieved in the printed pattern by photonic curing.
A further difference observed here between thermal curing and photonic curing is the change in yield (percentage of lines which showed end-to-end conductivity). As shown in Figure 2B, there was no significant change in the yield after thermal curing; in both cases approximately 45% of samples were conductive end-to-end. The small difference in yield shown in Figure 2B (44% uncured vs. 47% thermally cured) is within the error of the measurement. When comparing the thermal group before and after thermal curing, the yield was 47% in both...
cases. As such, thermal curing had no effect on yield. In contrast, both sets of samples which were photonically cured showed dramatic yield improvements – from 56% to 80% (photonic only) and from 53% to 100% (thermal plus photonic). The difference between the 80% yield seen after photonic curing and the 100% seen after thermal plus photonic may be due to the former process taking completely uncured samples as a starting point, meaning that significantly higher levels of unremoved water are present, leading to increased risk of sample blow-off and ablation. From these drastic yield improvements, and considering that these are the same samples measured before and after treatment, we can conclude that some lines which were non-conductive before photonic curing (resistance > 20 MΩ) became highly conductive after the treatment. This observation of an increase in yield, taken together with the large additional increase in conductivity seen with photonic-based treatments compared with purely thermal curing, implies physical changes may be occurring in the samples over and above the removal of solvent and crosslinking of binder expected with thermal curing. In order to investigate this hypothesis, we first calculated the expected temperature rise in the samples as a function of depth and time.

3.4 Calculation and Measurement of the Expected Temperature Rise

The expected temperature rise in the printed layers as a function of thickness and time can be calculated using an analytical solution to the heat transfer partial differential equation as a function of depth $z$ and time $t$. For uniform light input this was solved by Carslaw and Jaeger 32, and a simplified form of the solution given by Cengel 33 is;

$$
\Delta T(z, t) = \frac{2[I(1 - R)]}{k} \sqrt{\alpha t} \times ierfc \left[ \frac{z}{2\sqrt{\alpha t}} \right]
$$

where $\alpha$ is the thermal diffusivity of the printed layer, $I$ is the light intensity, $R$ is the surface reflectivity, $k$ is the thermal conductivity of the printed layer and $ierfc$ is the integral of the complementary error function.
In order to solve Equation 1, several material parameters of the printed but uncured layers must be calculated. We estimate the thermal conductivity $k$ of based on the Maxwell equation $^{34}$, an approximate aspect ratio of the flakes of 1/3, and using the known volume fractions of silver flakes and binder, which yields a value of around 0.07 W/m.K. Similarly, the density of the printed layers was calculated from the ratios of the ink constituents based on a rule of mixtures approach, and found to be 8200 kg/m$^3$. The specific heat capacity was calculated according to Kopp’s law from the individual heat capacities and found to be 880 J/kg.K. These values yield a value of the thermal diffusivity $\alpha = 9.6 \times 10^{-9}$ m$^2$/s.

It should be noted that the low estimated value for the thermal conductivity $k$ of the printed but un-cured layers is in agreement with the low electrical conductivity of such layers measured in the present work. This would be expected from consideration of Wiedemann–Franz law, which states that the ratio of thermal to electrical conductivity in metals at constant temperature is a constant $^{35,36}$. Since the electrical conductivity was measured as being low in uncured samples, and the only electrically conductive species present is silver metal, it would be expected that the thermal conductivity would also be low; this effectively represents a situation where a large fraction of the silver flakes are not part of an end-to-end percolation network.

In this model, the printed layer is approximated as being semi-infinite, and heat conduction within the layer is assumed to dominate over convection to the outside air. The validity of the semi-infinite approximation can be checked by calculating the critical length $L_c$ in which heat is expected to diffuse in time $t$, using $L_c = (4at)^{1/2}$, which for a pulse length of 3 ms gives a distance of 10.7 μm$^{37}$, or approximately half the film thickness in this model, which justifies the use of the approximation. Therefore, we can have confidence in the results of this model as long as the samples’ thickness is >10.7 μm, since finite sample thickness or substrate effects do not affect heat diffusion (within 3 ms) above this limit. This was the case in our experiment. Further, the sample width will only affect the temperature rise if the sample is
large enough that part of it falls outside of the uniform area of the beam. This was not the case in our experiment, where the energy profile of the beam is highly uniform over the frontal area of the samples. This represents an advantage of broadband photonic curing over laser-based methods, since large areas are treated simultaneously. Finally, the dominance of heat conduction within the samples over convection or radiation from the surface is a valid assumption if the temperature remains below approximately 1000°C\textsuperscript{38}, which is a valid consideration for our experiment.

The optical power density input \( I \) was calculated by integration of the output spectrum of the lamp (supplied by the manufacturer) over the wavelength range of interest. This output spectrum was measured for a 3 ms pulse at 400 V. In order to estimate a value for the reflectivity \( R \) of the ink surface, UV-Vis spectrometry was employed. These results are shown in Figure 3A. The reflectivity of the silver ink is relatively flat in the wavelength range of interest, with a slight reduction at short wavelengths. This reflects the fact that the reflectivity of silver inks is dominated by scattering from the silver particles, rather than approximating the value of pure silver\textsuperscript{39}.\textsuperscript{39}
Solving Equation [1] for $t$ and varying $z$ for a printed but uncured silver flake/binder layer gives a temperature profile which is shown in Figure 3B. The same calculation for cured layers (Supplementary Figure S2) showed similar behaviour, but with both maximum surface temperature and back surface temperature rise slightly higher. While the precise value for the temperature rise at the front surface may differ between samples due to the complex thermal nature of the printed layers, and the fact that the assumptions outlined above may not always

Figure 3. Optical transmittance and reflectance (a) of silver ink samples by UV-Vis spectrometry. Temperature evolution as a function of depth (b) after photo curing for three 3 ms pulses at 100 Hz. Results of a Finite Element model (c) showing the temperature on the front surface of an Ag line for the third 3ms pulse in a group of 3 pulses. Radiometric temperature measurement (d) of the sample area.
hold, this model shows that achieving high temperatures on the surface is possible while keeping the rear surface below the substrate melting point – a key consideration in many photonic processes\textsuperscript{40}.

Further insights into the temperature evolution were gained by development of a simple finite element model using the SimScale software. The same inputs and material parameters arrived at above were used as inputs to the model. The results of the temperature on the top surface of a representative silver line pattern on the third of three pulses, of 3 ms duration at 100 Hz, are shown for a number of timesteps in Fig 3C. As shown here, the maximum temperature calculated by the software matches well with that calculated analytically in Fig 3B, and the temperature field is uniform across the surface (the slight irregularities shown are artefacts of the mesh).

These calculations were compared with reality by use of radiometric temperature measurement via a thermal camera, as shown in Fig 3D. Note that the camera was not synchronised with the lamp pulse controller, and as such the long frame time of this camera (approx. 8 ms) may have led to an underestimation of the maximum sample surface temperature, since the rise and fall in temperature is very rapid, on the order of milliseconds, as shown in Fig 3B. Nevertheless, the measured temperature of approximately 275$^\circ$C is in reasonable agreement with the calculated temperature by both analytical and finite element methods, which were 332$^\circ$C and 333$^\circ$C, respectively.

These results are in line with previously published experimental data on the temperature rise in similar systems, which was measured at around 200$^\circ$C for three flashes, albeit in a setup that measured back surface temperature\textsuperscript{24}. Previously reported lumped capacitance calculations by Kang et al. estimated a temperature rise of silver nanoparticles (which have very different optical properties compared with flakes) of around 500$^\circ$C\textsuperscript{16}, which is broadly
consistent with our calculations outlined above considering in that study the optical energy input was almost double that employed here.

While the temperature rise in our system would not reach the melting point of bulk silver (962°C), the onset of sintering in many systems is commonly observed to be several hundred degrees below the melting point. Furthermore, localised pre-melting of flakes on the surface might be initiated by localised higher temperatures, possibly owing to plasmonic effects on the metal surfaces. Finally, due to the flattened geometry of silver flakes specifically (as compared with spheres), their edges have a high degree of curvature. Owing to the higher surface free energy of highly curved surfaces, their melting point is reduced compared to bulk\textsuperscript{41}. Therefore pre-melting is expected to initiate at the edges of flakes at temperatures significantly lower than the bulk melting temperature.

Based on these calculations and measurements, we can state that it is certainly plausible that physical changes could occur to the silver flakes. This is consistent with the hypothesis that the photonic curing can lead to partial melting and fusing of adjacent silver particles.

3.5 Characterisation of Photo-cured Samples by SEM

Based on the previously discussed observation of increased yield, along with the observed improvement in conductivity after photonic curing, as well as the calculated temperature rises, we hypothesised that the photonic curing has a physical effect on the samples over and above the removal of solvent which is expected with purely thermal curing. In order to test this hypothesis, the samples were examined by SEM before and after photo-curing, and with or without thermal curing. Typical images obtained are shown in Figure 4.
Figure 4. Typical SEM images of (a) uncured, (b) photonic, (c) thermal only and (d) thermal and photonically cured samples. The scale bars are 5 μm.

From the SEM characterisation it is clear that in no cases do the samples sinter fully, although the photonic-treated samples did show the onset of fusion between the silver flakes, as previously discussed. Given the expected pre-melting behaviour discussed above, these observations support the hypothesis that fine cracks within the samples are being ‘healed’ by the photonic treatment, leading to the increased yield observed in the electrical characterisation.
In order to investigate this effect further, samples were stencil printed, in a manner which increased the chances of their containing fine cracks interrupting the percolation network. Note that these samples had widths ranging from 50 – 200 μm – due to this large dimensional variation resistivity data from these samples was not included in the averages shown in Figure 2. The samples were thermally cured and their resistance measured. The samples were then photo-cured, and their resistance was measured again. Those samples which were not conductive after thermal curing alone (resistance > 20 MΩ), but became conductive after photo-curing were examined by SEM. Typical SEM micrographs are shown in Figure 5.

All such samples showed the expected fine cracks which spanned the width of the conductive line, as shown in Figure 5A and enlarged in Figure 5B. Figures 5C and 5D show areas within the sample in which the crack is spanned only by a few flakes (Fig. 5C), or not spanned within the examined area of the crack by only around 500 nm (Fig. 5D). In such areas it would be possible for a small expansion in mean particle size to bridge such cracks. Since this sample was not conductive after thermal curing alone (resistance > 20 MΩ), but became conductive after photonic curing, this provides strong evidence that the increased yield observed in the large scale trial can be attributed to this mechanism. Furthermore, such ‘switching’ behaviour (in which non-conductive structures become conductive) has been previously reported in the case of nanoparticle inks in response to photonic curing, but no explanation was given. Based on these observations, we conclude that crack healing may have been the mechanism responsible for the increase in yield observed.
3.6 Crack Healing and Effects of Percolation on Sample Resistivity

In order to further quantify the effects of particle pre-melting seen with photonic treatment, a large library of SEM images were analysed using ImageJ software, to find the particle size distribution as a function of curing regime. For this analysis, the samples were grouped into two sets; those which had not been photo-cured (uncured and thermal only), and those which had (photonic and thermal + photonic). The results of this analysis are shown in Figure 6A. The mean particle size measured by this method was larger in the photonic treated samples.

Figure 5. SEM images of F130 flake ink sample after thermal and photo curing, showing crack formation and bridging. Boxes in (a) and (b) show the position of the enlargements (c) and (d).
than in the untreated samples, increasing from $1.8 \pm 0.06 \, \mu m$ to $2.10 \pm 0.05 \, \mu m$, respectively. A two-tailed Student’s T-test gave a very low $p$ value of $< 0.0003$, implying a high degree of confidence that this measured result is not a statistical fluctuation. This observation is consistent with the hypothesis that the photonic curing causes localised pre-melting at the flakes’ edges. Furthermore, the size distribution of flakes in the two cases, as shown in the histogram in Figure 6, is skewed towards larger flakes for photonic treated samples and towards smaller flakes for untreated samples. This would be consistent with a mechanism causing smaller particle to fuse into larger particles, which would then be counted as one large particle with approximately double the length by the software. This increase in mean particle size, combined with the SEM analysis in Figure 5, provides strong evidence to support the crack-healing hypothesis to explain the increase in yield seen with fine line samples.

**Figure 6.** Histogram (a) of mean particle lengths found by automated image analysis using the software ImageJ, either photonic cured or untreated. TLM resistivity data (b) showing that percolation effects are important for narrow tracks containing 3 μm flakes below approximately 200 μm track width, as observed from the power-law fit to the data.
In addition to this crack-healing behaviour and having established that photonic curing leads to an increase in mean particle size, we can explain the difference in resistance improvement observed between the fine line and bulk samples, by recourse to percolation theory. As the dimensions of the samples are reduced with respect to the size of the conductive particles within them, the likelihood of an individual particle being connected to a structure which spans the entire length of the sample, and therefore contributes to conduction, is reduced \(^{42}\). This can be demonstrated by measuring the resistivity as a function of track width for particles of different sizes using Transfer Line Measurement (TLM) geometry. Such a measurement is shown in Figure 6B, which shows the resistivity of screen printed silver lines of 50 mm length and varying widths, printed from flake silver inks with a 3 μm flake size. The emergence of a power law dependence at the narrowest track widths is visible in below track widths of approximately 200 μm. This is precisely what would be expected if percolative effects were becoming important in contributing to the overall track resistivity (i.e., the sample stops behaving as a homogeneous medium) \(^{42,43}\).

Since the line widths in the fine line photo-curing experiment were 90 μm, it is likely that the fine lines are in this regime, while the bulk samples are not. Therefore, the fine lines’ conductivity is more sensitive to small physical changes, such as healing of cracks, compared to the larger bulk samples. Therefore photo-curing can have a dramatic effect on both conductivity and yield of fine lines while having only modest effects on the physical shape and size of the particles, whereas for larger samples the advantage of photonic curing was more minor compared with conventional thermal curing. This is an important observation, since it allows the conductivity and yield of industrially-interesting fine line samples to be greatly improved, by means of photonic curing, even in situations where the maximum permissible temperature is severely limited by the need to protect both the binder and the substrate.
3.7 Effects of Particle Size on Photonic Curing

The results above imply that there may be a correlation between particle size in the ink and performance after photo-curing. In order to investigate this effect, aqueous silver inks containing small or large spherical particles (of 0.8 μm or 1.9 μm average diameter, respectively) were printed and photo-cured using the previously optimised settings, and also measured using the TLM geometry. The results are shown in Figure 7.

As shown in Figure 7A, for small particles, there is only a weak correlation between track width and resistivity. In this case, the printed ink is behaving like a homogeneous material. In the case of larger particles, however, there is a clear power law dependence of the measured resistivity on the track width – i.e. percolation is important below a track width of approximately 800 μm. This behaviour was mirrored in the effects of photo-curing on these two inks. As shown in Figures 7B and 7D, the small spheres (in which percolation was not an important consideration) showed no advantage of photonic curing over thermal curing within error, similar to the ‘bulk’ flake ink samples. Larger spheres, however, showed an order of magnitude reduction in resistivity after photonic curing, as seen for the ‘fine line’ flake ink samples. As such, percolative effects are an important consideration for explaining the response of many inks to photonic curing.

Finally, the yield of all samples in this trial was 100% after thermal curing. This is likely owing to the different viscosities of the inks; however, it means we cannot comment on whether crack healing was a factor in contributing to the resistivity reduction in these samples.
Figure 7: Resistivity of ink tracks of different widths comparing small (a) and large (c) spherical silver inks. The fits compared are linear and power law fits of the data. Resistivity change of different particle size inks after photo curing; small spheres (b), showing no advantage of photo curing, and large spheres (d) showing an order of magnitude advantage. The yield after thermal curing was 100% in all cases.

3.8 Effects of Photonic Curing on Flexibility of Ag Flake Inks

As previously outlined, one key advantage of flake inks which makes them interesting subjects for industrial applications, apart from their lower cost compared with nano-sized alternatives, is their enhanced flexibility and stretchability performance. An experiment was therefore carried out to quantify any effects which photo-curing may have on these properties.
Figure 8A shows the results of a bending test in which samples were bent around a 20 mm radius for up to 9000 cycles. The results, showing the average of three samples resistance/original resistance (R/R₀) are shown in Fig 8A. As shown in the figure, uncured samples showed a dramatic increase in resistance, up to 3.5x the original resistance. This behaviour can be attributed to incomplete cross linking of the binder in the ink when only dried at room temperature, meaning that the adhesion in the sample is poor compared to a thermally cured sample, in which the binder is more fully cross-linked. The remaining samples (thermally cured, photonic only and thermal plus photonic) showed very similar behaviour to each other; the resistance initially rose but approached a stable value of approximately 1.2-1.3x the initial resistance. This demonstrates that the photonic curing has no negative effects on the flexibility of the inks, which will be of importance for future adoption of this technology. Furthermore, since the performance of the photonic-only samples in this test was similar to that of the thermally cured samples, this implies that photonic curing is able to cross-link the binder, but in a much shorter time compared with thermal curing (9 ms vs 90 minutes).

Finally, as an example of a real world application of these properties, in Figure 8B we demonstrate the use of silver flake ink in a prototype sensor application. In this application, the printed pattern is able to distinguish clearly between different inputs. Furthermore, the ink is highly robust not only to bending (as shown in Figure 8A), but also stretching to 10% strain – as shown for thermally cured samples in Supplementary Figure S3. This demonstrates the potential future applications of this technology in enabling a novel form factor electronics.
4. Conclusions

Photonic curing was applied to aqueous conductive inks consisting of micron-sized silver flakes. This technique is observed to increase the conductivity over and above that which is possible by purely thermal curing. Evidence is presented that the photonic curing is able to partially pre-melt silver flakes in the ink, leading to necking between adjacent particles and healing of cracks, forming percolation pathways where none previously existed, and improving resistivity of screen printed fine lines from an average of 1100 ± 230 μΩ.cm with purely thermal curing to an average of 100 ± 12 μΩ.cm with the addition of photonic curing, while the most conductive patterns had a resistivity of 60 ± 6 μΩ.cm after photonic curing. This last value corresponds to a conductivity of \((1.7 ± 0.2) \times 10^7\) S/m.

In addition to improvements in conductivity, the yield of conductive fine lines rose from 52% with thermal curing to 80% with only photonic curing, and 100% with the optimised
photonic-plus-thermal curing regime. This yield improvement is striking, and to the best of our knowledge is the first reported observation of such a yield improvement of printed conductive patterns made from water based flake silver inks by the application of visible light photo-curing. Based on the experimental and modelling work, we ascribe this effect to a crack-healing mechanism, driven by the surface melting effects described.

As photo-curing is a high-throughput, wide area technique, we envisage that our results will be of interest to the wider printed electronics industry, in enabling a reduced-cost production methodology for a wide range of printed electronic components. Furthermore, although this study concentrated on flake silver inks on PET substrates, this technique is applicable to a wide range of functional materials and substrates.

Supporting Information.

Conductivity as a function of thermal cure time and sample diagrams can be found in the electronic supporting information.

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Author Contributions

HC designed the experiments, collected and analyzed the data and wrote the manuscript. ZS formulated the conductive inks, and assisted with data collection. MB operated the photo-curing lamp. MS and RS contributed to data analysis and editing of the manuscript. RS, MS and ZS supervised the project. All authors have given approval to the final version of the manuscript.

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