Transfer Printing of Semiconductor Nanowires with Lasing Emission for Controllable Nano-photonic Device Fabrication

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ABSTRACT. Accurate positioning and organization of Indium Phosphide (InP) Nanowires (NW) with lasing emission at room temperature is achieved using a nanoscale Transfer Printing (TP) technique. The NWs retained their lasing emission after their transfer to targeted locations on different receiving substrates (e.g. polymers, silica and metal surfaces). The NWs were also organized into complex spatial patterns, including 1D and 2D arrays, with a controlled number of elements and dimensions. The developed TP technique enables the fabrication of bespoke nano-photonic systems using NW lasers and other NW devices as building blocks.

Semiconductor nanowires (NW) have revolutionized the field of photonics allowing a wide range of novel ultra-small devices with key impact across scientific disciplines, i.e. on-chip communications, solid-state lighting, healthcare, renewable energies, etc. For reviews on the topic (see for instance references 1 and 2) and references therein. In particular, amongst the multiple applications of semiconductor NWs, their use as nanoscale laser sources has been intensively investigated in recent years (see for instance references 1-10). Since the first report of a NW laser, advances have occurred rapidly and devices built from different material systems, e.g. Group III-nitrides, Group II-VI and Group III-V have been reported. These features added to their nanoscale dimensions ensure that NW lasers will play a key role in nano-photonics for ultra-small light sources in photonic integrated circuits, optical interconnects, nanoscale light sensors, etc.1-10

However, due to their ultra-small dimensions, the manipulation, organization and transfer of Semiconductor NWs in general and NW lasers in particular is a fundamental challenge.1,2 This problem limits the development of functional nano-photonics systems with NWs. Different techniques have appeared for the manipulation of NWs, i.e. optical tweezers, fluidic, electric
field and Langmuir-Blodgett assembly processes, the use of microscope probes or large-scale printing approaches. However, to date these have relevant drawbacks, i.e. require complex equipment, need the NWs to be in solution, do not allow transfer between different substrates, reduced positioning accuracy, do not allow manipulation of individual NWs or to print different types of NWs onto a single system. Thus, the precise, simple and efficient manipulation of individual or small groups of NWs remains a challenge. Moreover, the effective manipulation of NW lasers ensuring that they keep their lasing emission is yet to be achieved. In recent years a technique usually referred as Transfer Printing (TP) has emerged. This uses polymer stamps to capture and release semiconductor structures allowing their controlled and precise transfer from a donor to a receiver substrate. Breakthroughs on TP technology have followed promptly (for a review, see reference 21 and therein). These include the printing of LEDs onto flexible and diamond substrates, printing of lasers on silicon etc. These advances have already yielded impact in a wide range of technologies (e.g. visible light communications, flexible optoelectronics for healthcare and sensing, photonic circuits). However, to date TP protocols have been mainly applied to the printing of large semiconductor structures. Initial works have also started to apply TP techniques to manipulate nanoscale devices, e.g. large assemblies of passive NWs (see for instance [19-23]), nano-ribbons. However, these focused on large printing approaches to simultaneously transfer a high density of devices; thus not allowing the manipulation of individual NWs. Furthermore, the effective and accurate transfer printing of NW lasers (at targeted positions onto selected surface) guaranteeing that their lasing emission is maintained is a key objective yet to be achieved.

In this work we report a novel nanoscale TP technique enabling the accurate manipulation, transfer and printing of NWs, individually or forming small bundles of devices at targeted locations onto
heterogeneous substrates (e.g. polymers, silica and metals). Specifically, in the experiments we used Indium Phosphide (InP) NWs showing lasing emission at room temperature. Bespoke polymer µ-stamps were fabricated allowing the capturing and releasing of the InP NWs individually. Moreover, the transfer-printing process did not damage the NWs and lasing emission was achieved from the InP NW lasers after their controllable release onto the targeted substrates at desired locations. Furthermore, lasing emission from the transfer-printed InP NWs was observed at room temperature and onto all the targeted receiver substrates (polymers, silica and metals). This TP technique was also used to integrate NW lasers with different dimensions onto a single device and to fabricate complex spatial patterns with NW lasers, such as 1- and 2-Dimensional arrays (1D & 2D). The developed nanoscale TP technique offers exciting prospects for novel routes to fabricate functional nano-photonic systems using NW lasers and other NW devices as building blocks.

InP NWs with a bandgap corresponding to wavelength in the range of ~840-890 nm and diameters (Ø) of 920, 660 and 435 nm were used in this work. A Scanning Electron Microscope (SEM) image of as-grown InP NWs is shown in Figure 1a. Prior to carrying out the TP experiments, the NWs were detached from their growth substrate and placed onto a silicon (Si) substrate by mechanical means. As a result, the NWs were lying down and randomly scattered across the Si substrate either alone or grouping in bundles of a few elements (as shown in the SEM image of Figure 1b). Schematic diagrams of the InP NWs as-lying down on the Si surface are shown in Figure 1c. A µ-photoluminescence (µ-PL) setup was built to characterize the lasing emission from the NWs at room temperature. Full details on the setup can be found in the Supplementary Information. Figure 1d plots a dark micrograph depicting an InP NW Ø 920 nm lying down on Si and which shows lasing emission from its end-facets under optical pumping with sufficient
intensity. The lasing characteristics of individual NW lasers on silicon, including optical spectra and lasing threshold curves were measured using the µ-PL setup. Full details of these results can be found in the Supplementary Information. As stated previously, in this work we have used InP NWs with diameters (Ø) of 920, 660 and 435 nm. These specific diameter values were chosen for two reasons. First, since the threshold gain for lasing in the InP NWs reduces with increasing nanowire diameter\textsuperscript{10} values ensuring the achievement of lasing emission at room temperature from the stand-alone InP NWs were selected. In addition, since our transfer printing technique allows visual detection with white light of the InP NWs at all moments we selected NWs with diameters over the diffraction limit of our system to better investigate the transfer printing protocols. Nevertheless, our technique could in principle also be used to manipulate NWs with smaller dimensions (diameters of 100 nm or lower).

RESULTS/DISCUSSION

The developed nanoscale TP technique utilizes a modified dip-pen lithography system allowing nano-metric positioning control of a bespoke polymer µ-stamp.\textsuperscript{25,26} The latter was fabricated in polydimethylsiloxane (PDMS) and was used to controllably capture the InP NW lasers from the donor substrate (Si) and released them at targeted locations onto a selected receiver substrate. The nanoscale TP technique works as follows: the µ-stamp is first aligned with a NW (or NW bundle, defined as a small group of NWs formed by 2-5 elements) and pressed against it. The µ-stamp deforms conforming to the NW shape allowing its capture. The µ-stamp is then lifted away from the surface, taking with it the attached NW, while returning to its original shape. The reverse process is used to release the NWs. The µ-stamp is aligned at the desired location on the receiver
substrate. The µ-stamp is approached against the surface of the receiver substrate. Finally, the µ-stamp is lifted away leaving behind the printed NWs. Full details on the working mechanism of the nanoscale TP technology of this work and on the µ-stamp fabrication process can be found in the Supplementary Information.

Two different types of µ-stamps were designed in this work. These were fabricated on PDMS with a PDMS/potting agent composition of 10:1. The two µ-stamp designs had equal dimension (30 x 10 µm rectangular mesas with 50 µm height) but different tip shape. The first design of µ-stamps, depicted in Figure 2a had a flat-tip, whilst the second generation, shown in Figure 2b was characterized by an elongated pyramidal (or “tent-like” shape) tip. Both µ-stamps were used to successfully transfer InP NW lasers from Si and print them on different surfaces. The flat-tip µ-stamp allows a larger contact surface between the µ-stamp and the NWs. This feature facilitates the NW pick-up stage (as the µ-stamp’s adherence overcomes that existing between the NW and the substrate) but makes more complicated the NW release stage on the receiver substrate. This flat-tip stamp was therefore more suitable for the transfer-printing of NWs onto high adhesive substrates such as PDMS. In addition, a second generation of µ-stamps was designed to transfer-print NWs onto less adherent surfaces. This second design of µ-stamps had an elongated pyramidal tip offering a reduced contact surface between µ-stamp and NW. Nevertheless, the latter is still large enough to permit the NWs being picked up from the donor substrate whilst simultaneously enabling an easier NW release onto heterogeneous receiver surfaces (with reduced adherence than that of PDMS). We must note that no structural changes were observed in either of the two designs of µ-stamps following the Transfer Printing experiments. This allowed the continuous reuse of the µ-stamps to successively transfer print different InP NWs onto multiple receiver substrates without any remarkable change in the µ-stamp performance during this work (over 50 repetitions of the
Furthermore, the developed nanoscale Transfer Printing technique does not rely on accurate pressure control on the NWs. Important parameters that need to be taken into consideration for the successful manipulation of NWs with this approach include first the adherence of the stamp. Therefore ‘sticky’ PDMS polymer stamps were used in the experiments. Secondly, the stamp’s shape, thus two different types of stamps (flat and ‘tent-like’ tip) were used here to investigate this point. The conformation of the stamp’s tip shape around the NWs was also an important factor to successfully ‘pick-up’ NWs from the donor substrate. This feature could be visually determined thanks to the optical system of our setup which allows us to see the NWs at all moments during all the stages of the transfer-printing process. In this work we have used PDMS μ-stamp with a monomer/potting agent composition of 10:1. This ensured that the μ-stamps were ‘sticky’ enough whilst allowing significant shape deformation around the NWs to ensure their lift-off from the donor substrate. Finally, another fact to consider is whether we attempt to pick-up single or bundles of NWs. For the latter case, a higher yield was observed for the technique of this work, given the larger surface contact between micro-stamp and NWs in the donor substrate. Finally, our experiments also revealed that the deposition of the previously captured NWs on the different targeted substrates (PDMS, silica and gold) was an easier task with yields approaching 90-100%. Given the different factors that should be taken into consideration it might not be straightforward to provide an exact figure for the yield of the reported technique. Although a comprehensive analysis of the success ratio of the reported technique requires further experimental analyses beyond the scope of this work, our first experiments reveal a success rate in NW pick-up in excess of 20% with the technique as-is without further improvements. We believe that this figure can still be significantly improved controlling multiple factors such as the stamp shape, composition, choice of donor substrate, \textit{etc.}
Figure 2a shows micrographs of the flat-tip µ-stamp, illustrating its alignment with a NW bundle (left plot), capturing the NW bundle (middle plot) and after printing the NW bundle onto PDMS. Analogously, Figure 2b plots micrographs of the elongated pyramidal tip µ-stamp before capturing the NW at its left (left plot), pressing and deforming its shape to capture the NW (middle plot) and located next to two printed NWs onto silica (right plot). Following the fabrication of the first design of flat-tip µ-stamps, TP experiments were performed using PDMS as the receiver substrate. Two reasons explain the choice of PDMS as the first targeted receiver substrate: (1) precisely printing of NWs onto flexible and transparent substrates (such as PDMS) is relevant as it offers exciting prospects for flexible nanophotonic devices; (2) PDMS benefits from a high adherence enabling an easier route for NW release at the printing stage. Figure 3a shows a micrograph illustrating that three types of InP NWs with different diameters (namely Ø 920, 660 and 435 nm) were successfully printed at desired locations onto a PDMS substrate forming a 2D array with controlled number of elements and dimensions. The spacing between different bundles ranges between 20 and 30 µm. Figure 3b,c show respectively two collages merging together bright and dark fields micrographs of the individual elements forming the 2D array. Figure 3b shows with higher resolution the structure of each NW bundle in the array which range from 2 to ~10 grouped NWs. Figure 3c shows dark field micrographs for all the NW bundles in the array when optically-pumped with sufficient energy exceeding their lasing oscillation threshold. All the InP NW laser bundles in the array retained their lasing response and showed light emission through their end-facets. A representative lasing threshold curve and emission spectra for one of the elements in the 2-D array are plotted in Figure 3d,e respectively. Details of the spectral and threshold curve measurements for the printed NW laser bundles can be found in the Supplementary Information. Additionally, in order to better illustrate the versatility of the proposed nanoscale TP technique, we have generated
a pattern with the letters ‘IOP’ onto a PDMS flexible substrate using InP NWs (Ø 435 nm in diameter). The acronym ‘IOP’ corresponding to the initials of the University of Strathclyde’s Institute of Photonics. Figure 4a shows a CCD image of the generated ‘IOP’ pattern using small bundles as well as individual InP NWs. Figure 4b plots a collage of dark field micrographs for the individual elements in the generated ‘IOP’ pattern. These were captured independently and merged into a single plot to show that lasing emission is obtained from all the elements of the pattern after the transfer printing process.

After the initial reports on PDMS, we targeted glass (silica) as the receiver substrate to provide proof-of-concept demonstration of the transfer printing of InP NWs to a less adherent (compared to PDMS) but also transparent substrate. For these experiments, given the reduced adhesion of silica compared to PDMS, we used the second generation of µ-stamps with the elongated pyramidal (or ‘tent-like’ shape) tip. Using this second µ-stamp InP NWs of different dimensions were successfully printed onto silica and integrated onto complex spatial patterns with controllable dimensions. Specifically, we have formed multiple patterns on silica using InP NWs with a diameter of 435 nm. Figure 5a plots a micrograph showing the generation of three different patterns using individual (or pairs of) InP NWs. The three patterns were separated by ~60 µm. At the left side of Figure 5a a loop (or rhomboid shape) pattern was built using four individual elements separated by ~15 µm. In the middle part of Figure 5a a small 1D array of just three elements separated by ~5 µm was built with alternating parallel and perpendicularly disposed elements. Finally, the right side of Figure 5a shows the printing of two elements, namely a single (right) and a pair of (left) NWs separated by only ~5 µm placed parallel to each other. Additionally, Figure 5b plots a collage merging of independently captured dark field micrographs for all the individual elements in the three patterns previously described and showing that lasing emission was achieved
from all the NWs when optically-pumped above their lasing oscillation threshold. Figure 5c plots
the lasing threshold curve for one of the transfer printed NW lasers shown in Figure 5a. Specifically, figure 5c plots results for the NW laser printed at the right hand side in the two parallel lines pattern. A clear transition to lasing oscillation is observed in figure 5c as the optical excitation fluence is above 30 mJ/cm$^2$. Figure 5d shows a narrow lasing peak in the optical spectrum for this specific NW when optically pumped well above its lasing threshold. Finally, threshold curves and optical spectra for all the transfer-printed NWs in Figure 5 are included in the Supplementary Information of this article. We must also note here that the developed transfer printing technique in its present form allows already to controllably print NWs as close as 5$\mu$m (center-to-center distance) from each other (see fig. 5). Also, repeatable printing of NWs with micrometer accuracy was obtained in this work at all moments. Typical deviations of the printed NWs from the targeted positions in the different selected substrates never exceeded a few microns in both the vertical and horizontal axis. Nonetheless, we believe that with future refinements, our technique will allow precise and repeatable printing of NWs with sub-micrometer accuracy and with sub-micrometer separations between adjacent elements.

Similarly, we have carried transfer printed experiments using metallic layers as the receiving substrate. The objective was to demonstrate the versatility and independence on the receiver surface of the reported platform to transfer-print NWs. Specifically, in this work we have focused on the printing of InP NWs onto gold. For these TP experiments we also used the $\mu$-stamps with elongated pyramidal tips. A 1D array of transfer-printed InP NWs (diameter 660 nm) was fabricated by TP means across the length of the gold track used as the receiver substrate, as shown in Figure 6a. The individual elements were printed with a controlled and equidistant separation of $\sim$50 $\mu$m. Figure 6b plots collages of bright (top) and dark (bottom) micrographs showing in detail
the NW bundles and the lasing emission from the individual elements forming the array printed onto the gold surface. Lasing thresholds and optical spectra were recorded systematically for the NWs forming the 1D array. Full details on the characterization measurements are given in the Supplementary Information. For illustration, Figure 6c plots the measured lasing threshold curve for one of the InP NW bundles forming the 1D array. The latter is marked by green dotted boxes in Figure 6a,b. Figure 6c shows that a clear lasing onset is observed after a threshold in optical excitation is exceeded. Also, Figure 6d shows that narrow lasing peaks appear in the optical spectrum of the InP NW laser bundle when optically pumped above threshold.

CONCLUSIONS

In summary, in this work we report a nanoscale TP technique allowing the precise and controlled manipulation, printing and organization of InP NWs of different dimensions (Ø 920, 660 and 435 nm). Using this technique InP NWs, individually or forming small bundles were successfully transferred from Si substrates and printed onto heterogeneous surfaces, including PDMS, silica and gold. Bespoke designs of polymer µ-stamps were fabricated and used in combination with a modified dip-pen lithography system to perform transfer-printing protocols with very high positioning accuracy. Furthermore, the quality of the NWs was not compromised during the transfer-printing processes. Proof of this is the fact that lasing emission was achieved from the InP NWs after their controlled printing onto the different targeted receiver substrates. Moreover, InP NWs were successfully integrated into complex spatial patterns, including the fabrication of 1D and 2D arrays onto PDMS, silica and gold. These patterns were built with controlled dimensions, number of elements and spacing between them. This technique was also used to integrate NWs of
different diameters onto a single device. Additionally, while in this work we have solely used InP NWs, the reported technique could be applied to manipulate NWs built from different material systems. This reported nanoscale TP technique therefore offers great prospects for novel routes to fabricate tailored nanophotonic devices and systems using NWs as building blocks, and thereby opening new paths for applications of NW-based devices across multiple fields, e.g. on-chip communications, sensing and biophotonics, among others.

METHODS

*Nanowire Growth.*

The InP NWs of this work were grown by selective area metalorganic vapour phase epitaxy. First, a 30 nm-thick SiO$_2$ layer was deposited on InP substrates. Hexagonal arrays of circles with diameters of 680, 420, 195 nm and spacings of 2, 1.5, 1 µm were patterned on the SiO$_2$ layer using electron beam lithography and removed by wet chemical etching prior to growth of the nanowires. Due to lateral undercut caused by wet etching, the final diameters of the SiO$_2$ openings were slightly larger. As a result, the NWs have the diameters of 920, 660 and 435 nm.

*µ-stamp Fabrication*

The µ-stamps are fabricated in polydimethylsiloxane (PDMS) at a 10:1 mixture with the potting agent. A mold is fabricated using a silicon <100> substrate selectively etched with a potassium hydroxide solution (26.6 g of KOH platelets as received from supplier diluted in 40 mL of deionised water) which etches following specific crystallographic planes and thus forms the pyramid. A 50 µm-thick SU-8 layer is patterned by photolithography and forms the body of the µ-
stamp. The degased liquid PDMS is poured in the fabricated mold and hardened at room temperature for 24h before it is released and cut to size to fabricate individual µ-stamps.

**Nanowire Characterization**

A µ-photoluminescence (µ-PL) setup was built to characterize the lasing emission from the InP NWs at room temperature. The designed µ-PL setup allowed to measure lasing spectra and lasing threshold curves as well as capturing CCD micrographs of the NWs under optical pumping. The NWs were optically-pumped with a frequency-doubled Nd:YAG laser with emission wavelength at 532 nm. The pumping laser delivered 1.6 ns long optical pulses at 10 kHz repetition rate. The pumping laser energy was controlled using a λ/2 waveplate, a polariser, a neutral density filter and an attenuator wheel. A 60x microscope objective with a Numerical Aperture (NA) of 0.85 was used to focus the pumping light onto the InP NWs. Subsequently, the PL of the InP NW was collected through the same 60x objective realising a confocal configuration and analysed with a fibre-coupled spectrometer.

**ASSOCIATED CONTENT**

**Supporting Information.** Section 1: Nanoscale TP of InP NWs. (1.1.) Description of the technique. (1.2.) µ-Stamp fabrication. (1.3.) TP of InP NWs onto multiple substrates. Section 2: Optical characterization of InP NW lasers before and after transfer printing. (2.1.) µ-PL setup. (2.2.) Characterization of individual InP NW lasers lying down on a silicon substrate. (2.3.) Characterization of InP NW lasers printed onto PDMS. (2.4.) Characterization of InP NW lasers
Characterization of InP NW lasers printed onto gold. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The team at the University of Strathclyde carried out the Transfer Printing and NW laser characterization experiments. The team at the Australian National University fabricated the InP NWs used in this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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**Figure 1.** SEM images of (a) as-grown InP NWs Ø 660 nm grown vertically on an InP substrate viewed at an angle of 45° and (b) InP NWs Ø 920 nm after they have been randomly dispersed on the Si substrate. (c) Diagram showing the dimensions of an InP NW. d) Dark field micrograph of an InP NW on Si showing lasing emission from its end facets under optical pumping exceeding the NW’s lasing threshold.
Figure 2. (a) Flat tip µ-stamp aligned with an InP NW bundle Ø 660 nm lying down on Si (left), with the NW bundle capture (middle) and after printing the NW bundle on PDMS. (b) Elongated pyramidal-tip µ-stamp next to an InP NW Ø 435 nm lying down on Si (left), pressing the NW to capture it (middle) and next to two printed NWs on Silica (right).
Figure 3. (a) CCD image of the built 2D array of InP NWs on PDMS by means of TP technique. Scale bar is 20 µm. (b & c) Collages merging independently captured bright (b) and dark (c) field micrographs of the individual elements forming the 2D array. (d) Lasing threshold curve and (e) emission spectrum of a representative NW bundle printed in the 2D array on PDMS. Specifically, plots (d) and (e) show results measured for the NW bundle marked as ‘d1’ in fig. 3(c).
Figure 4. (a) CCD image of the pattern ‘IOP’, initials of the University of Strathclyde’s Institute of Photonics formed with InP NWs (diameter Ø 435 nm) onto a PDMS substrate. (b) Collage merging independently captured dark field micrographs of the individual elements on the ‘IOP’ pattern. Scale bars correspond to 20 µm. The dashed lines connecting the NWs are plotted as a guide to the eye.
Figure 5. (a) Bright field micrographs of a 1x3 1D array of fabricated patterns with printed InP NW lasers (Ø 435 nm) onto a silica receiver substrate by means of TP. Scale bar is 15 µm. Three patterns are formed: a loop or rhomboid (left), a three element pattern alternating parallel and orthogonally printed NWs (middle) and two parallel lines with NWs (right). (b) Collage merging captured dark field micrographs of the printed NWs forming the patterns in (a) under optical excitation above the lasing oscillation threshold. (c) Lasing threshold curve and (d) emission spectrum for a representative printed InP NW laser onto silica. In particular, plots (c) and (d) show measured results for the NW marked with the green dot-dash square box in figure 5b.
Figure 6. (a) Micrograph showing a 1D array of InP NW lasers transfer-printed onto the gold track. Scale bar is 50 µm. (b) Collages merging bright (top) and dark (bottom) field micrographs of the individual elements in the 1D array of (a). The dark field images were taken under optical excitation above the lasing threshold of the NW bundles. (c) Lasing threshold curve and (d) measured spectrum for the NW bundle marked with the green dot-dash squares in (a) and (b).