Laser Induced Forward Transfer of Metals

M.Tech Thesis

By

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Candidate's Declaration

I here by certify that work which is being presented in the thesis entitled **Laser Induced Forward Transfer of Metals** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE, Indian Institute of Technology Indore,** is an authentic record of my own work carried out during the time period July 2015 to May 2017 under the supervision of **Dr. I.A. Palani** and **Dr. Vipul Singh** of Discipline of Mechanical and Electrical Engineering respectively.

The matter contained in this thesis has not been submitted by me for the award of any degree from any other institute.

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(Dr. I.A. Palani) (**Dr. Vipul Singh)**

Punkit Sood has successfully completed his M.Tech Oral Examination held on…………

Signature of the Thesis Supervisors **Signature of Convener, DPGC**
Date: **Date:**

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Date: **Date:**

Acknowledgement

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Dedicated to my Guide –

my mother,

my father,

my grandparents,

my teacher,

and my friends

Abstract

Laser Induced Forward Transfer (LIFT) is a direct-writing technique that allows depositing materials on unconventional substrates. Further it can be used to design complex patterns during transfer thereby reducing the tedious process of post-processing to get the desired shape. In this work Copper thin films have been transferred to flexible substrates through Laser-induced forward transfer (LIFT) micro-patterning.

The ability to deposit patterns, spots, and lines, with sub-μm resolution may have applications in microelectronics as well as in the optoelectronics fabrication industries. In this work we demonstrate, direct micro deposition of high-quality patterns with sub-μm features using LIFT process.

The present approach also exploits all advantages over conventional methods including simplicity in terms of vacuum handling, deposition purity, position selectivity, and high-accuracy sub-μm pattern transfer. The intensity and substrate heating on the transferred material is studied in detail. Nd:YAG laser having wavelength of 532 nm and 355nm (10 Hz) is impinged using single shots onto the target material through a focusing lens having 30 cm focal length.

In this work, we have deposited both the micro patterns as well as 3D structures. The 3D structures are used in gas sensors to find velocity. The tip of the 3D structures is connected to the Atomic Force Microscope and subjected to a flowing gas. Since the pillar is fixed at one end it behaves like a cantilever beam. Now the deflection of the beam gives a measure of the velocity of the flowing gas. The structures are also used to find the leak detection.

LIST OF PUBLICATIONS

Papers in Conference Proceedings

- Punkit Sood, Jayachandran S, Rajagopalan P, Akash K, Vipul Singh, I.A. Palani, "Parametric Investigations on Developing Copper Micropatterns on Flexible film using Solid state Nd:YAG 532nm Laser Induced Forward Transfer", International Conference on Emerging trends on Materials & Manufacturing Engineering(IMME-2017), National Institute of Technology Trichy, Tiruchirappalli, Tamil Nadu, 10^{th}-13^{th} March, 2017.

- Best presentation award in material processing session in IMME-2017.

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Chapter1: Introduction

1.1 Background

LASER, an acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation has the capability to produce a beam of electromagnetic radiation with wavelength ranging from ultraviolet to infrared which is highly coherent, convergent and monochromatic in nature. Lasers are capable of delivering power from a few milliwatts (mW) to hundreds of kilowatts with accurate spot dimensions. Due to these unique properties lasers have found applications in fields like communication and broadcasting, metrology, military, chemical and medical, material processing, micro fabrication and maskless lithography[1][2]. Due to the increasing availability of high power ultrafast short pulse lasers, new technologies on material processing using lasers have been developing rapidly. A few examples include micromachining, patterning, sintering, cleaning, surface modification, 3D structuring and additive manufacturing. Even though the applications of Short-pulse lasers in Micro- and Nano-technological systems is exhaustive, a few of the applications where lasers have attracted attention include pulsed laser deposition[3], micro-pattering for flexible electronics[4], flexible Organic Light Emitting Diodes [4] and drug delivery devices, biosensors[5] etc.

Lasers have acquired significant attention in direct write technique and one of these emerging technologies include Laser Induced Forward Transfer (LIFT), an additive patterning process allowing transfer of materials from a transparent donor substrate to a receiver substrate.

In this process, the material to be transferred is applied on a laser wavelength transparent donor substrate and kept in close proximity to a receiver substrate; a laser beam is then focused on the obverse surface with a certain fluence which helps in transfer of material from donor to the receiver substrate. A schematic of the basic working principle of LIFT is shown in Figure 1.

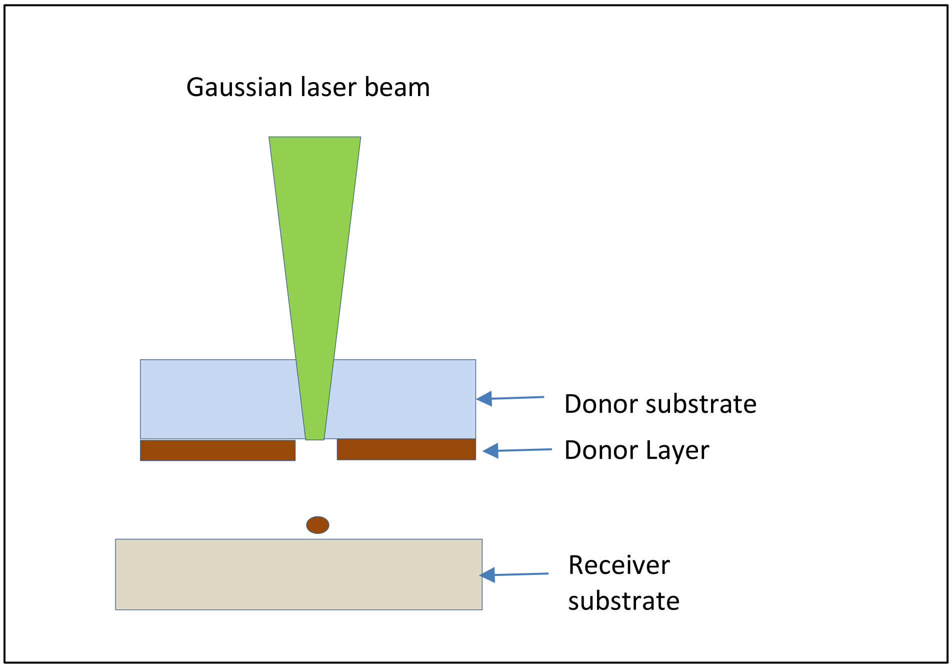


Figure 1 Schematic diagram showing working principle of LIFT

The versatility of LIFT lies in the transfer of a wide range of materials starting from metals, inks, pastes, semiconductors and dielectrics to sensitive materials like proteins which is not possible with the conventional printing technology. The possible applications of LIFT include fabrication of interconnects, backplanes for thin film transistor displays, organic light emitting diodes etc. Since LIFT is an additive process, one possible application could be to use it for repairing devices in microelectronic industry e.g. open circuit due to less deposition of material during manufacture. LIFT has shown enormous improvement over the years and now it is possible to even LIFT active materials like protein and biological solution with proper selection of wavelength and energy [6].

In order to optimize and have a better control of the transfer process during LIFT, laser as well as material parameters such as wavelength, pulse duration, thermal conductivity, and heat capacity needs to be controlled and investigated respectively. Since LIFT utilizes high power laser source, one of the important aspect to understand the physical mechanism of the transfer process include the knowledge of heat transfer and resulting temperature change when the material is irradiated with a laser pulse.

1.2 Basics of laser-material interaction

The ability to precisely control rate and place of energy deposition using lasers makes it a preferable tool in materials processing. With the proper selection of laser parameters, a control on material modification can be achieved. A number of phenomena can take place when a laser beam interacts with a material. The material can be modified and it can undergo property changes depending on the physical mechanisms of the interactions such as, the interaction may lead to trapped electronic state or bond modification resulting in densification and defect formation. A high intensity laser beam can cause heating, melting, boiling and even material ionization leading to void formation and material ablation. Figure 2 shows some of the physical interaction when material is irradiated with a laser beam.

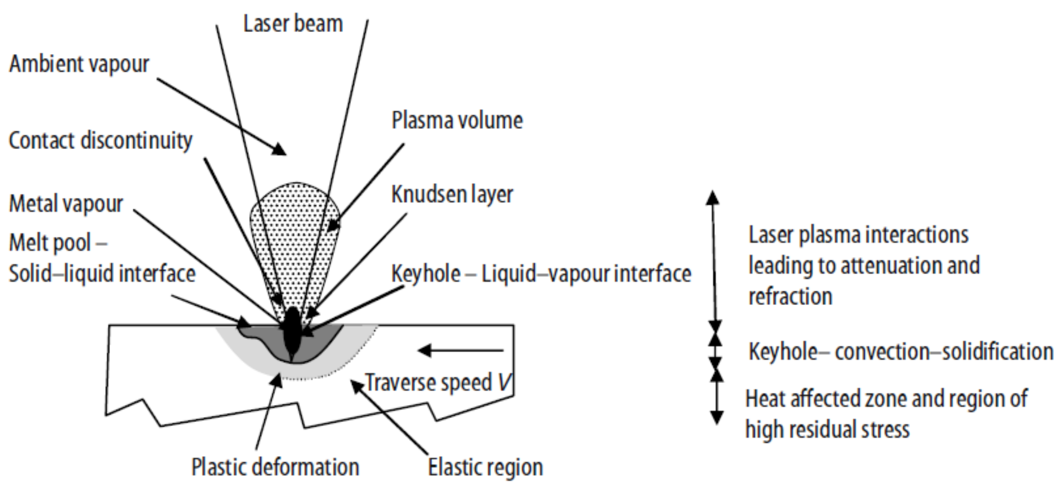


Figure 2 Physical interactions during laser material interaction [7]

1.3 Propagation of Light in material

When laser light is incident on a material surface, a part is reflected back in the medium, parts get transmitted and some gets absorbed. The attenuation of incident laser intensity inside the target material can be explained by Lambert-Beer's law [7], and can be expressed mathematically by Eq.2.1.

$$I(z,t) = (1-R)Io\,\exp(-\propto z) \qquad \text{Eq. 1}$$

where Io(W/m^2) is the incident laser intensity at a given time, t (s), z (m) is thickness of the material, R, reflectivity and $\propto$ (m^{-1}) is absorption coefficient which depends on material, wavelength and laser intensity.

In order to knock off an atom from the surface of a metal, it is necessary to deliver energy exceeding the binding energy of the atom. When an electromagnetic radiation passes over a small charged particle it induces strong vibration. On adequate supply of energy, the vibration becomes so strong that it stretches the molecular bonding and the mechanical strength becomes very weak, this is termed as melting. Addition of more energy leads to strong molecular vibration and hence evaporation starts. Now, the vapor has only bound electrons and on abundant absorption the electrons are set free and the material is in plasma state. Laser interaction with plasma is outside the scope of this thesis so we restrict the discussion to melting.

The reflectivity of a material can take values between 0 and 1 i.e. for a perfectly reflective surface R=1 and R=0 for highly absorptive surface. A metallic material shows very high value of reflectivity and low absorption. Not only wavelength and temperature but the values of reflectivity and absorptivity can also be influenced by physical condition of the material such as surface roughness and chemical composition such as formation of oxide layers. In this work, change in reflectivity with respect to change in temperature is considered at a fixed wavelength.

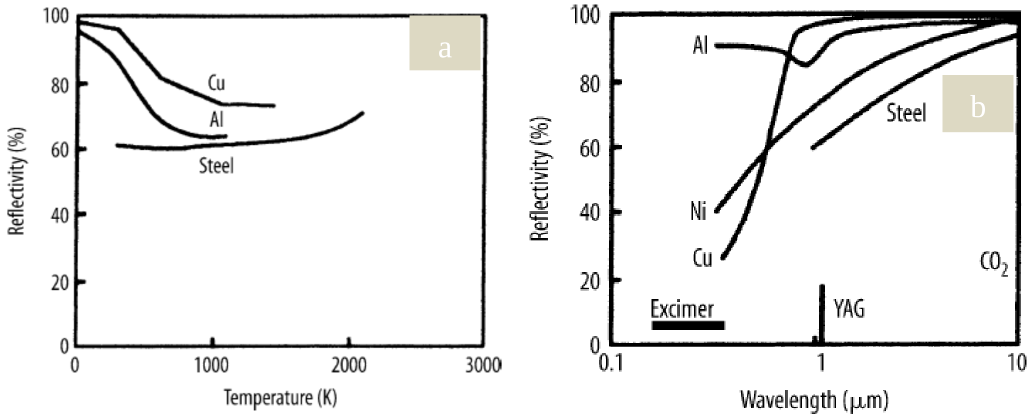


Figure 3 (a) Reflectivity as a function of Temperature for λ=1.06 μm radiation (b) Reflectivity as a function of wavelength [7]

The reflectivity of a material can be influenced by both temperature and wavelength. For comparison, the temperature and wavelength dependence of the reflectivity is represented in Figure 3. Figure 3 (b) shows variation of metal reflectivity with respect to rise in temperature at a fixed wavelength; it can be observed that, the value of reflectivity decreases with increase in target temperature. This change in reflectivity with temperature can be accounted to the increase in phonon population at higher temperature which results in more electron-phonon collisions resulting in energy exchange owing to higher absorptivity and low reflectivity. Figure 3 (b) gives the relation between change in reflectivity with respect to wavelength at fixed temperature, it is evident from the graph that, for shorter wavelength, the energetic photons interact with larger number of bound electrons in metal resulting in absorption and hence the decrease in reflectivity of the material [8].

1.4 History

The discovery of the ruby laser in the year 1960 [9] led to a number of potential applications, which have developed to the extent that lasers is present almost everywhere. Due to the availability of lasers with pulse duration ranging from microsecond to femtosecond regime at higher repetition rates, lasers have shown promising application in material processing such as welding and cutting, material removal such as pulsed laser ablation, material deposition such as pulse laser deposition and laser direct write such as laser induced forward transfer [10].Laser transfer techniques are widely used in microelectronics industry as an alternative to lithography processes to deposit precise patterns of materials without degrading the desirable properties of the bulk material [10]. In this process a laser source is used to stimulate transfer of material from a donor substrate kept either in contact or in close proximity to a receiver substrate. A laser pulse is incident on the transparent donor substrate and is absorbed by the coated material. Above a certain threshold energy the material is ejected and moved to the receiver substrate [11].

The earliest work of laser-induced transfer dates back to 1970 when Levene et.al transferred a black ink from a polyethylene backed typewriter ribbon and colored dyes applied to a Mylar substrate across an air gap of 100-200 μm using Nd:YAG laser source with a wavelength (λ) of 1.06 μm [12]. This work highlighted the simple and high speed writing capability of laser writing technique and also suggested a simple model based on melting and vaporization to explain the transfer process as a function of laser energy. Alas it remained unnoticed for over 15 years since the group did not use a different material.

Bohandy et. al first demonstrated deposition of copper metal using laser transfer inside a vacuum chamber [13]. The group used an excimer laser pulse with =193 nm and pulse width (τ) =15 ns to transfer 0.41 μm copper (Cu) layer deposited on a fused silica plate. The Cu was transferred on a silicon substrate kept in close proximity of the source substrate, where a scotch tape test was conducted to test the adhesion of the transferred material. A measurement on resistivity showed values ranging between 3 and 50 times the values of bulk copper. This group gave the term Laser Induced Forward Transfer. The step by step transfer process is shown in Figure 4.

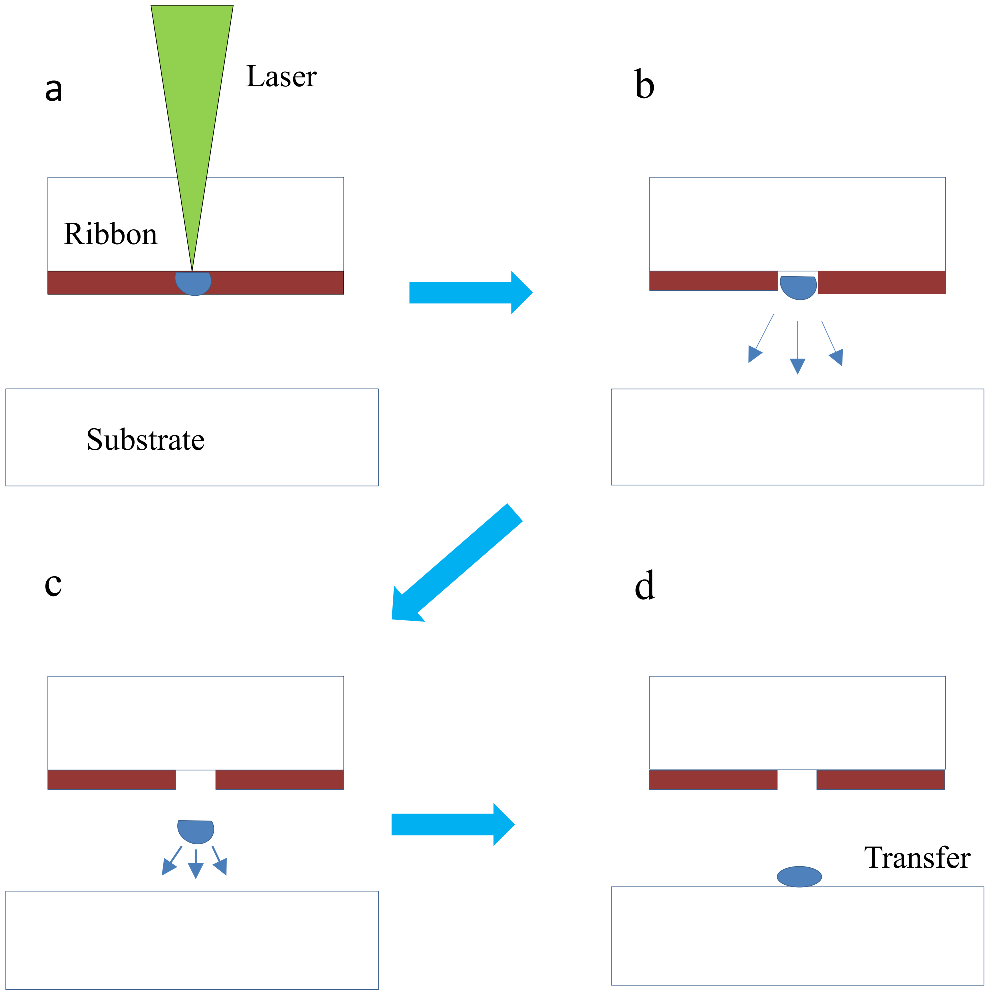


Figure 4 Step by Step transfer process during Laser Induced Forward Transfer

According to this model the transfer takes place in four steps

a) absorption of laser radiation leads to heating of thin film at the interface

b) the confined superheated vapor pushes away the melted film

c) both melted and vaporized film is ejected towards the receiver substrate

d) the ejected material gets deposited on the receiver substrate.

LIFT started gaining popularity and it was applied to transfer large number of materials including semiconductor (Ge/Si) thin film structures, Oxides(Al_2O_3), conducting polymer such as PEDOT (Poly 3, 4-ethylenedioxythiophene)[10] and biomolecules [14].

In order to develop a thicker film repetitive transfer can be performed over the same area, similarly a stack of different materials can be grown by just using a new donor material. By controlling parameters like donor film thickness and laser fluence LIFT can produce uniform pattern with very high resolution. In the next section, basics of major laser direct writing mechanism and their material transfer characteristics are discussed.

1.5 Gaps

LIFT is used in various fields because of its unique properties they possess. Literature review shows some gaps over which work is done here. Listed below are some of the common challenges faced by most of the researchers.

- Electrical connections near the moving stages make the setup clumsy:
    - Electrical wiring for supplying electricity to the XY translational stage uses a lot of space near the apparatus and makes the whole setup cumbersome.
- Focused spot laser is used:
    - In most of papers, laser is used as actuation medium but the laser used is a spot laser which is effective over the area it is falling i.e. rest of the sample remains ineffective of the heat.
- Laser follows Gaussian curve:
    - In a Gaussian beam, 86.5% of the energy gets concentrated at the center and rest 13.5% lost at the edges leads to inhomogeneous intensity distribution.
- Lack of mechanical properties:
    - No analysis for the mechanical properties, like tensile, compressive and fatigue strength is done on the pillars produced.

1.6 Motivation

The conventional techniques for forming patterns having different horizontal and vertical lengths including those using a photoresist material mask as in LIGA. Other techniques include inkjet printing need to be dissolved or dispersed in a rheological system and also they can be only used for transferring low viscosity pastes. LIFT can be used as a system similar to Pulsed to laser deposition. Tedious process of preparing photoresist and inks has always been a problem. The setup is cost effective. The resolution of the patterns obtained from the conventional processes is a limitation. The flexibility of the conventional methods restricts us to transfer different materials like organic materials, oxides like In_2O_3 and superconductors YBaCuO and BiSrCaCuO. The conventional processes do not allow the chamber to be vacuumed which deters the deposition. Hence there was a need for

1.7 Research Objectives

The main objective of this thesis work is to develop 2-D conducting micropatterns and 3-D structures investigate the heat distribution and resulting temperature change in a metallic copper film during LIFT process. The idea is to study the dependence of laser parameters (laser fluence, wavelength) and donor-acceptor distance, temperature. To this purpose, a two-dimensional finite element model (FEM) in COMSOL Multiphysics is developed to study the peak surface temperature and temperature across the thickness of the donor (copper) layer. The qualitative analysis of the obtained result should provide essential information about the laser material interaction and temperature rise in case of a nanosecond and a picosecond laser pulse system. Once the model is made, simulations are done by changing laser pulse duration, wavelength, and donor layer thickness and laser fluence. The heat loss in the donor substrate is also observed in one modeling result and it was noted that there is some amount of heat loss in the donor substrate. The simulated results are compared with the experimental results of LIFT of copper.

Chapter 2: Literature Review

- **(Bohandy(1986)).** Bohandy et al. [13] demonstrated the feasibility of the LIFT process by depositing copper onto a silicon substrate. Bohandy's initial report introduced the first hypothesis of the material removal/ejection process. Bohandy was the first to investigate the transfer of small metal features from thin metal donor films coated on fused silica carriers by the LIFT process. In contrast to the previous studies of graphical print applications where argon-ion and Nd:YAG lasers with emission lines in the visible and IR range, respectively, were used, metal films were irradiated with single pulses of a UV excimer laser (ArF, 193 nm emission wavelength, 15 ns pulse length), and 50 and 15 μm wide lines of copper and silver were transferred in a high-vacuum chamber from fused silica carriers precoated with metal donor films ∼400 nm in thickness onto silicon receiver substrates. With a donor–receptor distance in the range of some micrometers, deposition of metal patterns was observed above a threshold pulse energy of around 60 mJ. With increasing pulse energies, the width of the transferred line got broader, and with energies around 140 mJ more metal ''splatter'' and surrounding molten debris deposits have been observed away from the edges of the line.

- **(Tolbert, "Dynamic release layer LIFT" (1993)).** The Dynamic Release Layer LIFT (DRL-LIFT) is an alternative to the original LIFT process and was proposed by Tolbert et al. [15] The process aims at the transfer of more delicate materials, which must not be exposed to the incident laser pulse energy. Therefore, an additional sacrificial layer, referred as dynamic release layer (DRL) is added in between the carrier and the donor layer, see Figure 5. The ejection process is triggered, as the incident laser pulse is fully absorbed in the DRL, which leads to the full vaporization of that layer. Therefore, the donor remains unaffected and the pressure build-up leads to the transfer of the donor layer to the receiver. DRLLIFT is a highly flexible transfer process, which restrictions are mainly determined by the adaption properties of the involved materials. So far, various materials [16][17] including polymers as well as liquids [18] and living cells [19][14] have been successful transferred. A drawback DRL-LIFT is given by the residual components of the DRL, that may contaminate the deposits on the receiver.

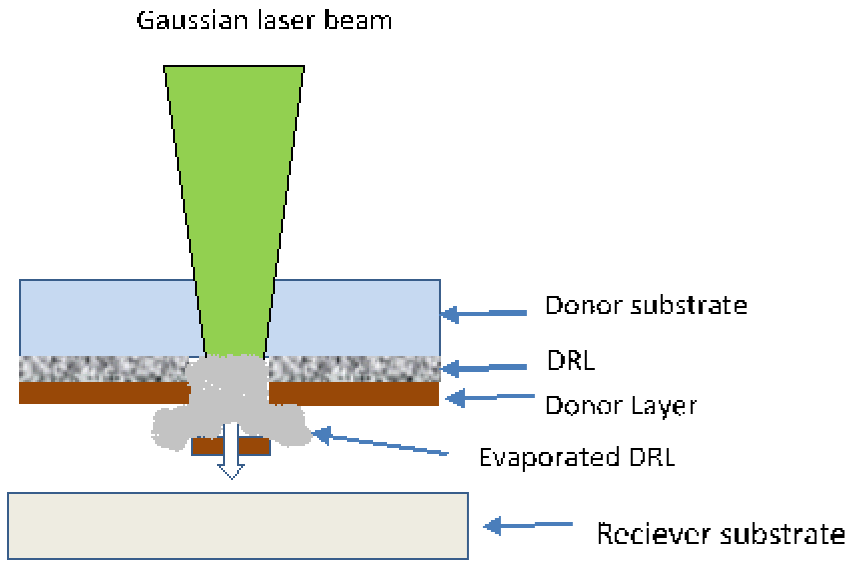


Figure 5 Schematic of DRL-LIFT

- **(Piqu´e, "Matrix-assisted pulsed laser evaporation- Direct-wright" (1999)).** The Matrix-Assisted Pulsed Laser Evaporation - Direct Write (MAPLE-DW) technique, as proposed by Piqu´e et al., combines the established Matrix- Assisted Pulsed Laser Evaporation and the LIFT process, see Figure 6. It provides higher flexibility regarding the choice the of the donor material than the original LIFT process, as it limits the effect of the incident laser pulse on the donor material and therefore prevents the transferred donor from damage. This is achieved by embedding the donor material into a matrix, which is made of a different material than the donor material. The melting point of the matrix material is selected to be significantly lower than the melting point of the donor material. Similar to the DRL-LIFT process, the heat that is generated by the absorbed laser beam, only evaporates the additional matrix material, which subsequently releases the donor material and provides the thrust to transfer the remaining particles towards the receiving substrate. Due to the flexibility of MAPLE-DW a variety of materials, including metals [20] and cells [21] were successfully deposited.

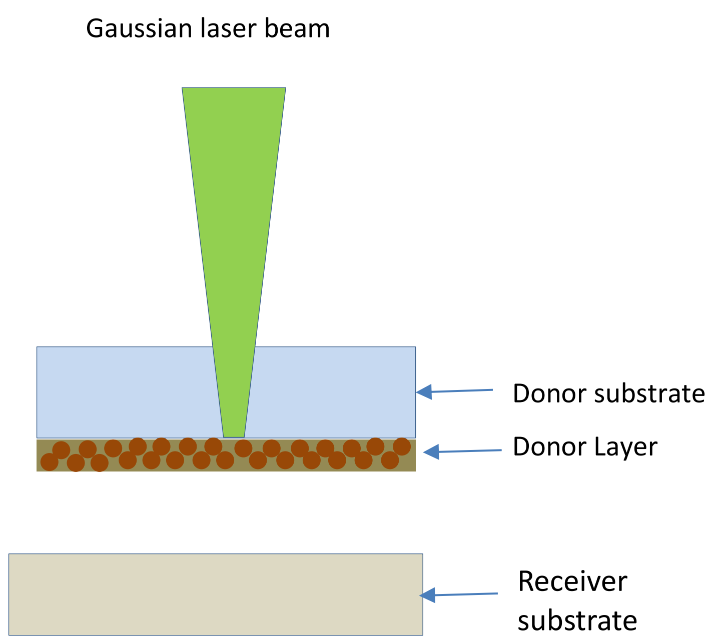


Figure 6 Schematic of MAPLE-DW

- **(Toet, “Hydrogen assisted LIFT (HA-LIFT)”, (2007)).** HA-LIFT was demonstrated by Toet et al. A hydrogenated amorphous Si (α-Si:H) was deposited on a transparent substrate and then it was irradiated with an excimer laser pulse. Upon irradiation with a nanosecond pulse the deposited α-Si:H film melts at the film interface resulting in release of hydrogen which gets confined by the not melted portion of the film and coalesce into a thin film pressure layer. The layer expands and accelerates the film off the substrate. The hydrogen layer is replenished via continuous release of hydrogen at the melt front and progresses towards the free surface of the film resulting in rapid propulsion of the liquid layer towards a receptor substrate. Other materials can also be transferred using HA-LIFT by using similar hydrogen containing metastable alloys or α-Si:H can be used as a sacrificial layer in DRL-LIFT. In Figure 7, step by step schematic representation of the HA-LIFT of α-Si:H is shown.

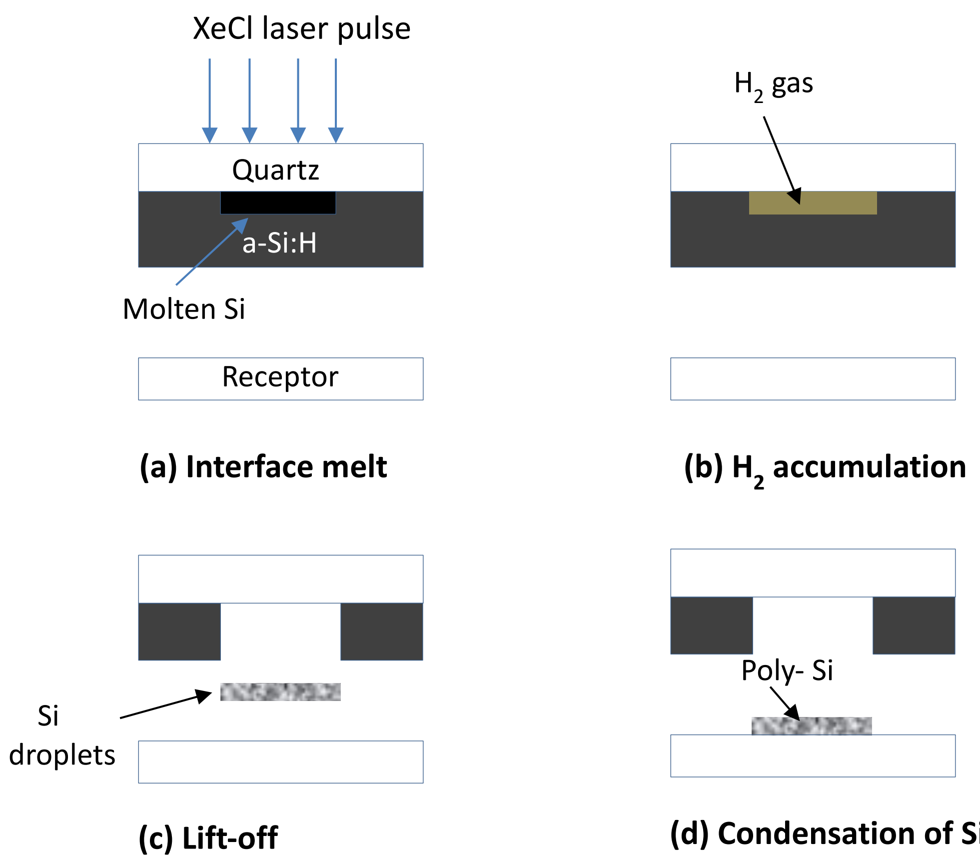


Figure 7 Schematic illustration of HA-LIFT:(a) Exposure of α-Si:H film through a transparent quartz support leads to melting; (b) hydrogen diffuses out of the silicon to the interface; (c) accumulated H2 exerts pressure leading to acceleration of film from targe

- **(Fukumura, "Laser molecular implantation" (1999)).** The Laser Molecular Implantation (LMI) has been demonstrated by Fukumura et al. [22] in 1994. This transfer mechanism aims at the transfer of single dopant molecules instead of complete donor layers. The molecules are implanted in a thin polymer film (source) which is kept in close contact to the receiving layer. The material of the receiving layer is similar to the undoped source. The absorption of the incident laser beam depends on the doping concentration of the polymer, and increases with higher doping concentration. Contrary to the LIFT process, the source is not heated directly, but the absorbed energy is used to activate the dopant molecules. However, due to the interaction of activated dopant molecules and the surrounding polymer, the polymer is heated and expands afterwards. Subsequently, the activated molecules are released from the source and transferred to the undoped, receiving substrate. This technique has been demonstrated in forward- and backward-transfer geometries and was applied to transfer various materials [22][23].

- **(Graciela B. Blanchet, "Laser-induced thermal imaging(LITI)" (2003)).** LITI is a thermally addressed laser forward transfer process mainly used for patterning of conducting polymers. It works on the same principle as DRL-LIFT except that the sacrificial/extra layer used is not ablated. In LITI, usually a metallic layer called light to heat conversion layer (LTHC) is coated on a transparent substrate and then the material to be transferred is coated on top of it. A laser beam is focused through the transparent substrate where light is absorbed by the LTHC layer and converted into heat; this heat decomposes surrounding organics into gaseous products. The expansion thus propels the top layer of the donor film onto receiver substrate [24]. A schematic of LITI process for Organic Light Emitting Device (OLED) layer patterning is shown in Figure 8.

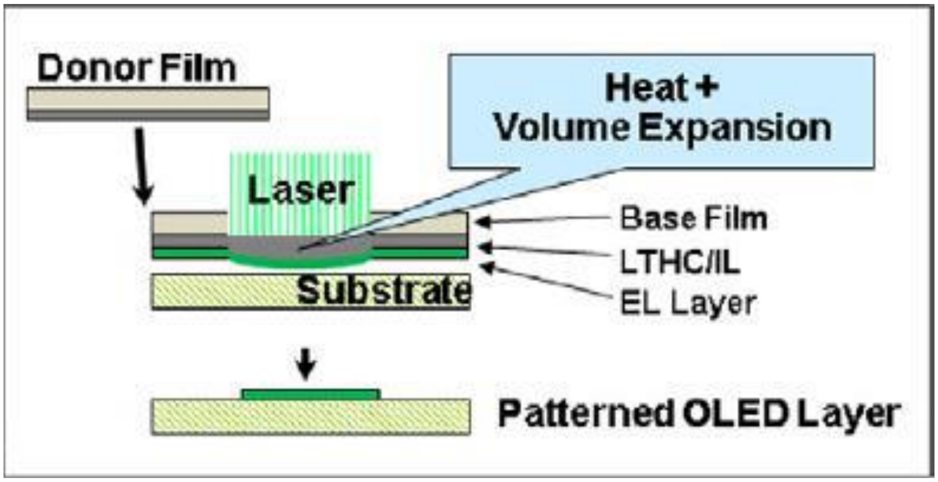


Figure 8 Schematic of LITI process to pattern OLED [24]

K´antor, "Long pulsed LIFT" (1994)). Long-Pulsed LIFT (LP-LIFT) represents yet another complementary LIFT process, see Figure 9. The experimental setup is similar to the common LIFT configuration, but instead of sub-nanosecond laser pulses, laser pulses in the order of microseconds or longer are used. For the LP-LIFT the donor layer and the receiver are in close contact. By heating the donor layer, the expanding donor material tightly contacts the receiver. Due to the long pulse durations used, the donor material is kept at high temperature for a relatively long time. The donor material anneals to the receiver and is bonded locally when the layers are separated. K´antor et al. demonstrated the transfer of a 5 μm tungsten segment in solid phase, which showed no evidence of melting. It was found that in addition to a fluence related threshold, there exists an additional threshold that is related to the pulse duration of the laser pulses applied. Pulse durations shorter than 500 μs did not lead to a transfer of material, which indicates the differences to the common LIFT process, where shorter pulse durations tend to provide better results. As it is based

on annealing, this process in principle allows for the transfer of various materials in solid phase. However, the potential materials are restricted due to the thermal load caused by this process.

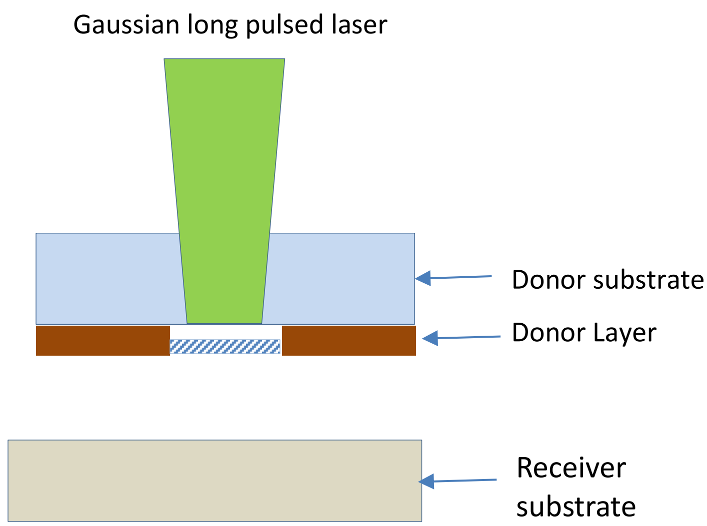


Figure 9 Schematic of LP-LIFT

Chapter3: Experimental Setup

Test setup is developed to perform experiments based on the medium used. It comprises of a laser source, focusing lens, triangular prism, micropatterning apparatus and a substrate heater. The setup is used in two different configurations to generate 2D conducting patterns and 3D structures respectively. Copper material is used as the donor material. Copper thin films are deposited using thermal evaporation (PVD technique). Following are the specifications of Copper material.

Table 1 Specifications of Copper material

Thermal conductivity(W/m-K)	400
Density(kg/m^3)	8700
Specific heat capacity(J/kg-K)	385
Young’s modulus(GPa)	110
Poisson’s ratio	0.33

3.1 Thermal Evaporation

It is a common method of thin-film deposition. A schematic diagram is shown in Figure 10. The source material is evaporated in a vacuum. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. Evaporation is used in microfabrication, and to make macro-scale products such as metallized plastic film. Evaporation involves two basic processes: a hot source material evaporates and condenses on the substrate. It resembles the familiar process by which liquid water appears on the lid of a boiling pot. However, the gaseous environment and heat source are different. Evaporation takes place in a vacuum, i.e. vapors other than the source material are almost entirely removed before the process begins. In high vacuum (with a long mean free path), evaporated particles can travel directly to the deposition target without colliding with the background gas [25]

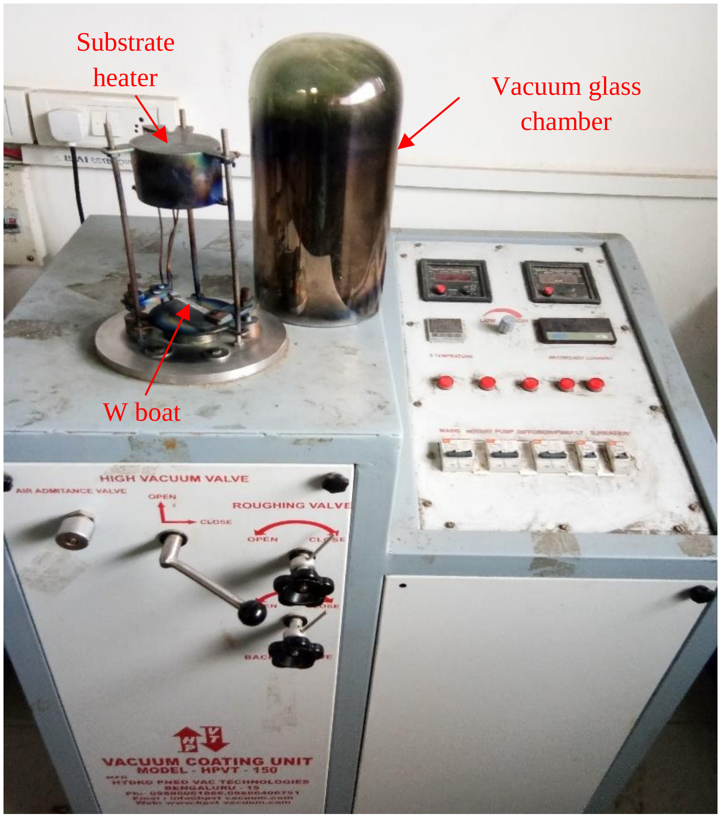


Figure 10 Thin film deposition on glass substrate using Thermal evaporation

3.2 LIFT set up

The block diagram of the entire setup is shown in Figure 11. The setup consists of a Laser source, power meter, triangular prism, converging lens, micropatterning apparatus and a substrate heater. The solid state Nd:YAG laser source is capable of providing power upto 4W. The laser beam is operated in 2 modes- long pulsed and Q-switched. The long-pulsed mode is used only for the alignment purpose and the Q-switched mode is used for the final experimentation. In long pulsed mode the laser is only of 1064nm. In Q-switched mode the 1064nm laser beam is split into two beams to give 532nm. Or it is made to split in 3 beams to give 355nm. In this work both the wavelengths have been used. For developing 2-D patterns 532 nm wavelength is used whereas for generating 3-D structures 355nm wavelength is used. Solid state Nd:YAG 532nm was used for ablating the copper thin films on donor samples. Preprocessing of the glass substrate were carried out through Hydrophilic cleaning and ultrasonic cleaning. The schematic diagram for LIFT is shown in Fig 1. The laser beam was made to divert by 90° with the help of a triangular prism. Then the beam was made to focus on the donor thin film using a focusing lens of focal length 30cm. The holder is specifically designed for holding the glass substrate which contains substrate heater. The substrate along with the holder is placed in the X-Y micro positioner which can be controlled micro position controller. The power intensity is changed from 15mW to 45mW and ablation is done at different intensities and also with different substrate heating temperatures.

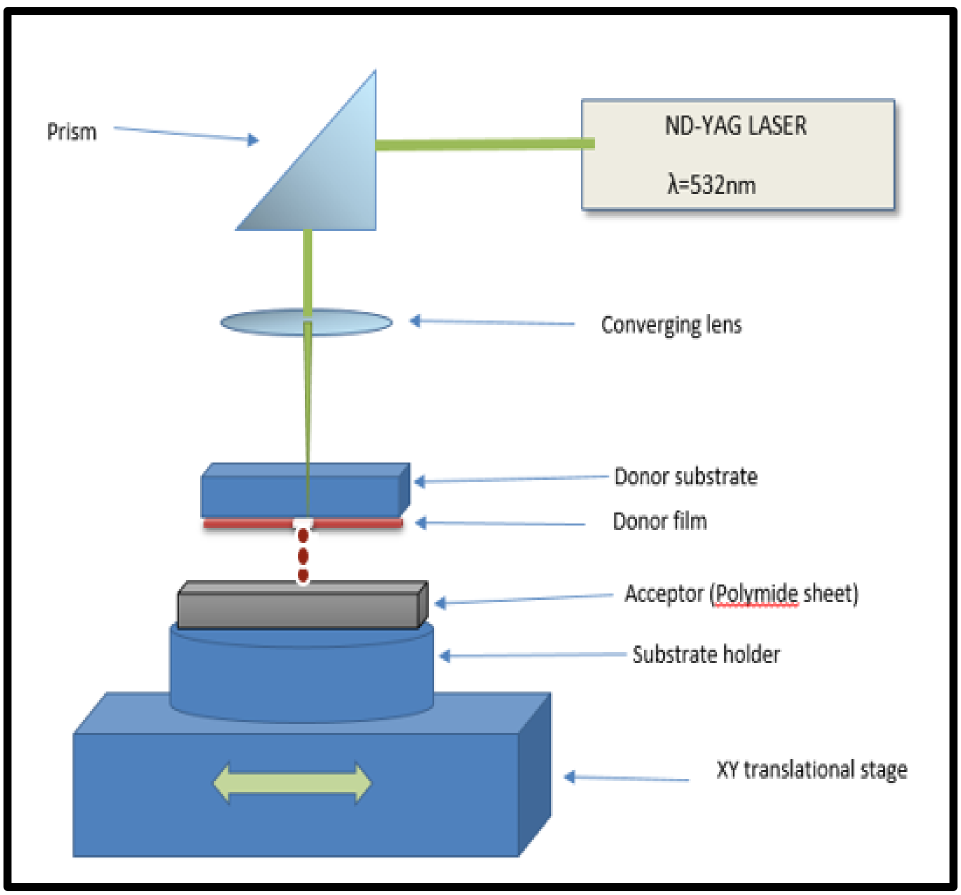


Figure 11 Experimental set up of LIFT

3.3 Micropatterning apparatus

The present invention relates to an apparatus for forming micro patterns of a semiconductor material, metals or more precisely micro patterns for opto-electronic devices. Laser-induced forward transfer (LIFT) is a direct-writing technique that allows printing micron order circuits for Opto-Electronic Devices. See **Figure 12 Various components of LIFT** The material to be patterned is first deposited on a glass substrate (donor) which is transferred using a nanosecond laser to a flexible substrate (acceptor) such as PET, PMMA. The acceptor and the donor substrate are kept inside a vacuum sealed chamber. The distance between the acceptor and donor can be varied precisely with the proposed apparatus. An incoming laser pulse with strike the donor substrate on the back side, thereby transferring the material from the front side to the acceptor substrate placed at close proximity. Further the transfer can be done at varying substrate temperatures. The product helps in obtaining homogenous and high-resolution micro patterns.

Figure 12 Various components of LIFT

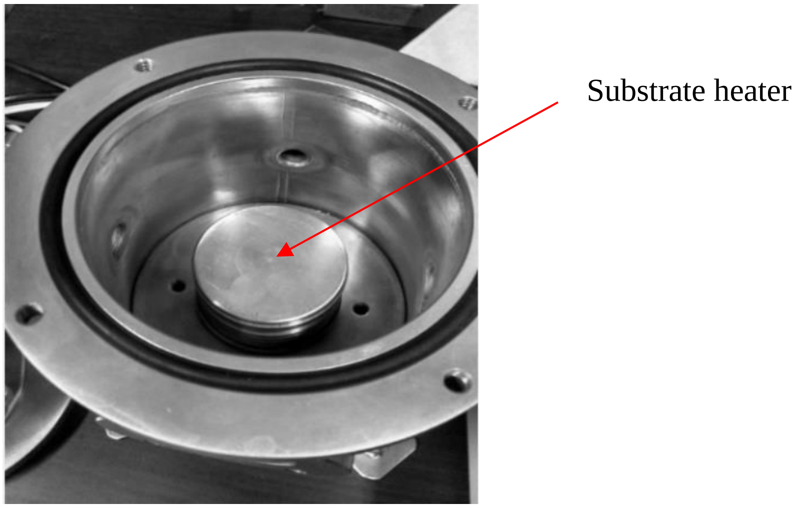


Figure 13 Substrate heater

The substrate heater as shown in Figure 13 is capable of heating the glass substrate upto 800^{o}C. The conventional techniques for forming patterns having different horizontal and vertical lengths including those using a photoresist material mask as in LIGA. Other techniques include inkjet printing need to be dissolved or dispersed in a rheological system and also, they can be only used for transferring low viscosity pastes. The proposed device can be used as a system similar to Pulsed to laser deposition. Tedious process of preparing photoresist and inks can be avoided. The setup is cost effective. The resolution of the patterns obtained is high. The flexibility of the setup allows us to transfer different materials like organic materials, oxides like In_2O_3 and superconductors YBaCuO and BiSrCaCuO [26]. Although the LIFT process doesn't require the vacuum conditions, yet the LIFT chamber can be vacuumed up to 10^{-3} mbar. The setup contains a substrate heater which can heat the acceptor substrate to increase the adhesion on the acceptor substrate. The setup doesn't limit to any specific laser wavelength. Various wavelengths like 1064nm, 532etc can be used. Various dimensions are shown in **Figure 14**.

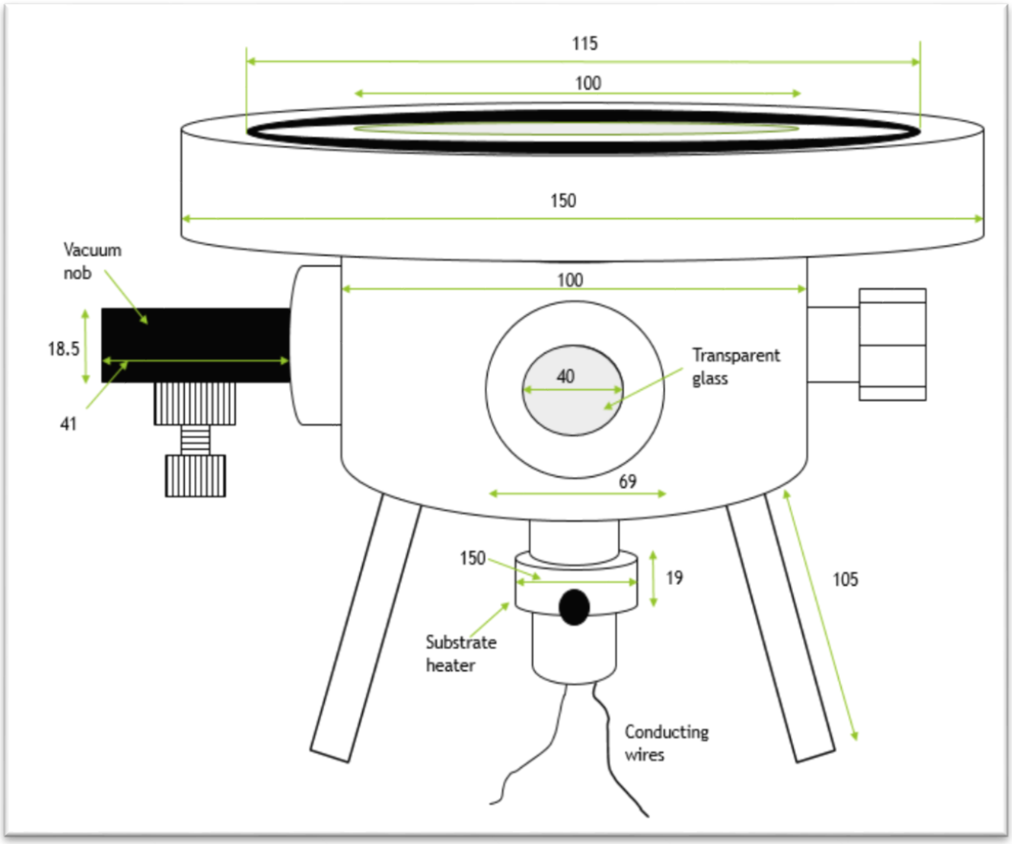


Figure 14 Dimensions of Micro patterning apparatus

3.4 XY Translational stage

The donor substrate is moved in the horizontal plane using a motorized translation stage. The donor and the receiver are placed in a 10 x 10 x 1 mm^3 sample holder (see Figure 15) which is mounted onto a motorized 3axis translation stage. The translation is controlled and synchronized with the release of single laser pulses ensuring proper donor refreshment during processing. This stage offers micrometer accuracy positioning of the receiver, when used with the provided micrometer thumbscrew drives. However, for more accurate positioning, closed-loop piezo actuators are implemented in this stage, that allow for high accuracy positioning within a travel range of 20 μm.

Figure 15 XY Translational stage

Each stage is capable of providing translation movement along one axis only but the XY translational stage is capable of moving along both X as well as Y axes when connected with in parallel connection with each other.

3.5 Sample preparation

3.5.1 Preparation of donor samples

Glass samples of size 1cm x 1cm were cut by using a diamond cutter and cleaned by using ultrasonic cleaning with acetone, isopropyl alcohol(IPA) and distilled water each for 10min. Hydrophilic treatment was done on the glass substrate to enhance the adhesion of the donor thin film with glass substrate. The solution used for this purpose was of water, ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2) in a ratio of 5:1:1 respectively. The cleaned samples are stored in water, and before adding a new film, they are wiped with a lint-free paper. Copper was deposited on the glass samples using the technique of thermal evaporation (Physical Vapor Deposition). Thickness of the copper thin film was estimated to be 350nm.

3.5.2 Preparation of acceptor samples

Flexible polyimide sheets and kapton tape were used as the acceptor substrates. The size used for the acceptor was 2cmx2cm. Polyimide sheets were used while developing 2D conducting patterns. Polyimide sheets were cleaned using acetone and Isopropyl alcohol. Kapton tapes provide better adhesion can also withstand high temperatures. So Kapton tapes allow us to heat the substrate upto high temperatures. Kapton tapes were used for developing 3D structures. Acceptor sheets were also cleaned using the same methodology as that that of the donor samples. No such cleaning operation was performed on kapton tape because it lessens the adhesion of Kapton tape which is the primary purpose of using Kapton tape as the acceptor substrate since the glass substrates were not capable enough to provide adhesion between the incoming copper particles from the donor thin film.

Chapter 4: Results and Discussion

4.1 Glass substrate as acceptor

Fused silica is glass consisting of silica in amorphous (non-crystalline) form. It differs from traditional glasses in containing no other ingredients, which are typically added to glass to lower the melt temperature. Fused silica, therefore, has high working and melting temperatures. The optical and thermal properties of fused quartz are superior to those of other types of glass due to its purity. For these reasons, it finds use in situations such as semiconductor fabrication and laboratory equipment. It has better ultraviolet transmission than most other glasses, so is used to make lenses and other optics for the ultraviolet spectrum. Its low coefficient of thermal expansion also makes it a useful material for precision mirror substrates.

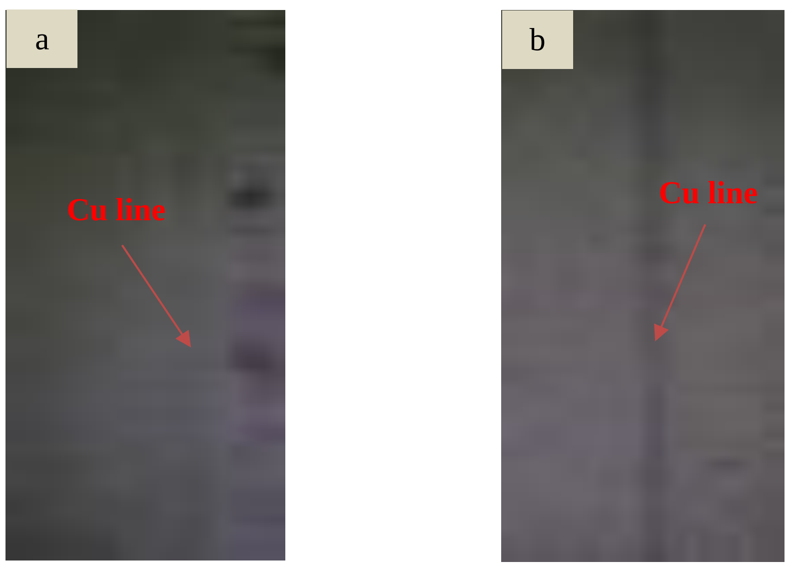


Figure 16 Glass substrate as acceptor substrate, (a) P=0.85W, f=30cm, velocity=2mm/s, (b) P=1.5W, f=30cm, velocity=2mm/s.

In the early experiments glass substrate was used as acceptor. The glass substrate was first cleaned in acetone, Isopropyl alcohol and distilled water by using ultrasonic cleaning. The adhesion of glass substrates was enhanced by hydrophilic treatment. The solution used for this purpose was of water, ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2) in a ratio of 5:1:1 respectively. The cleaned samples are stored in water, and before adding a new film, they are wiped with a lint-free paper.

The transferred line can be seen in the above image. The darkened line seen is the Copper material. X-Ray Diffractogram (XRD) is taken to prove the presence of Copper material.

Figure 17 shows the XRD image of the glass substrate on which copper material is transferred using laser induced forward transfer technique. Here the laser used was solid state Nd:YAG 532nm. The XRD shows a relatively intense peak at 43.8^{o} which confirms the presence of copper. Since the intensity of the peak is less it means the amount of copper transferred is less.

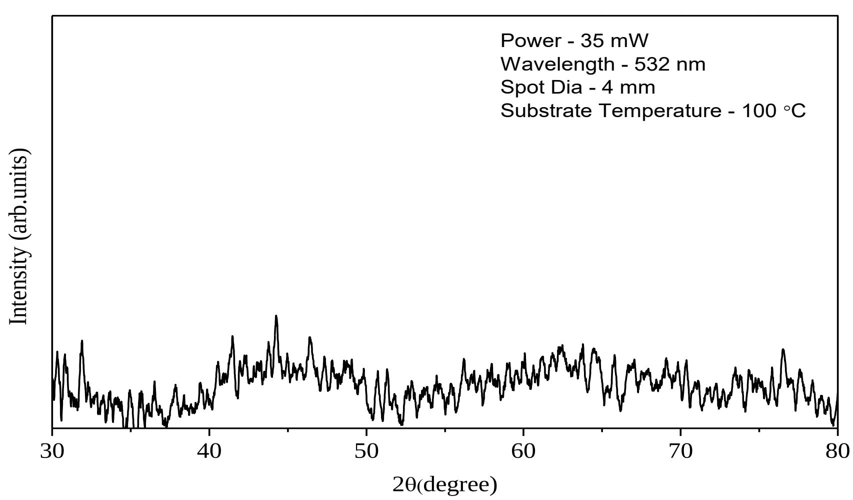


Figure 17 XRD of silica glass substrate deposited with copper

4.2 Polyimide sheets as acceptor

Polyimide is a polymer of imide polymer (Figure 18). As can be seen in Figure 20 the peak intensity is less which signifies that the transfer of copper material is less. Hence to overcome the adhesion problem the silica glass substrates were replaced by flexible polyimide sheets which prove better as far as adhesive properties are concerned. The experiments with flexible polyimide sheets came out with better results when analyzed in XRD.

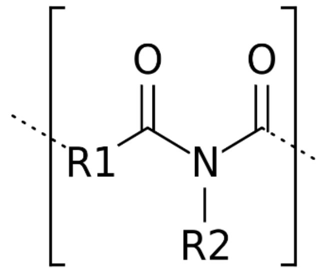
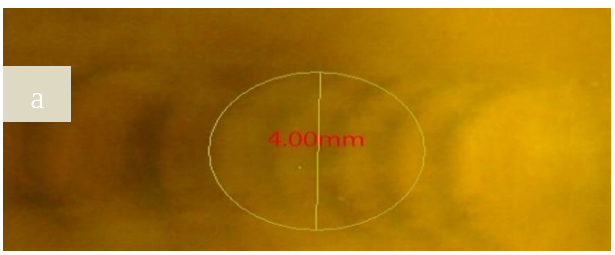


Figure 18 Imide polymer



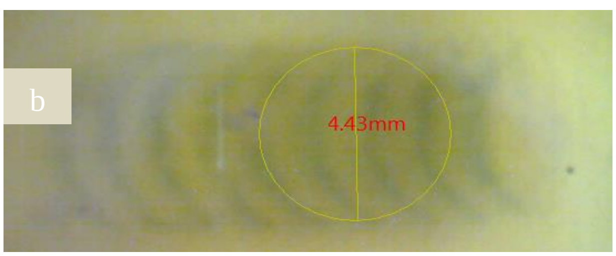


Figure 19 Fig. shows the polyimide sheets deposited with copper rings, (a) P=45mW, λ=532nm, spot dia=4.5mm, Substrate temperature=100ºC, (b) P=35mW, λ=532nm, spot dia=4mm, Substrate temperature=100ºC

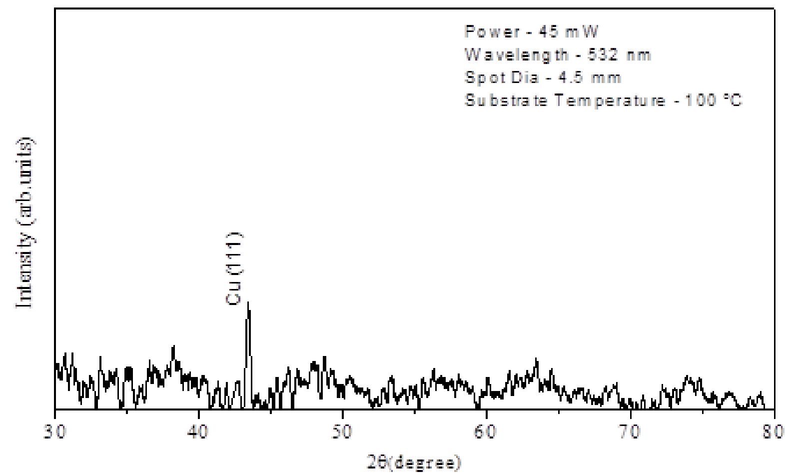


Figure 20 XRD of flexible polyimide sheet deposited with copper

The relatively intense peak at 43.8° in Figure 20 shows that the transfer is more significant in case of flexible polyimide sheet. The relatively intense peak at 43.8° confirms the presence of Cu(1,1,1).

4.3 Effect of donor-acceptor distance

The effect of donor-acceptor(stand-off) distance was studied. On increasing the distance between donor and acceptor the transferred Cu rings were found to get widened in diameter. (Figure 22)

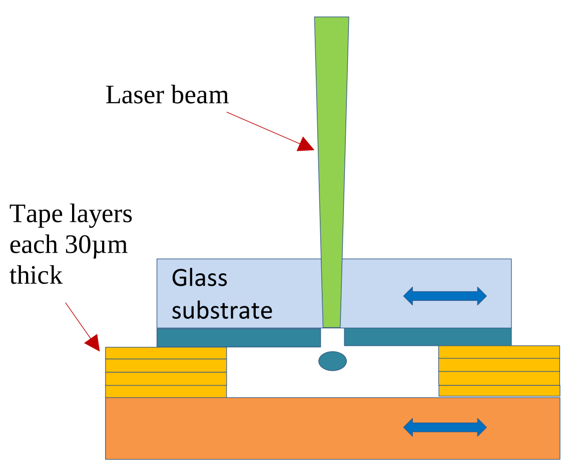


Figure 21 Block diagram used for 2D conducting patterns

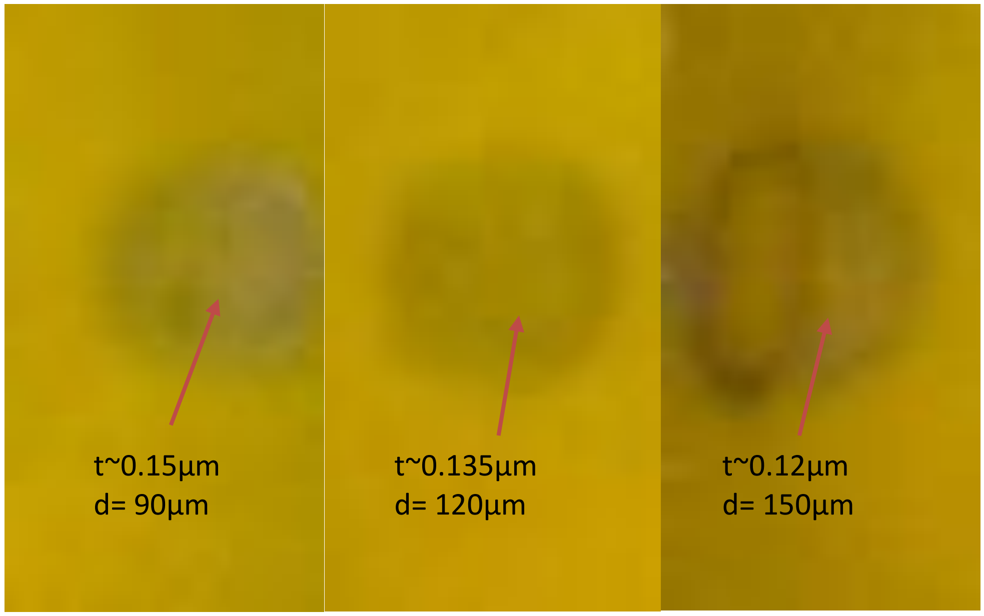


Figure 22 Effect of donor-acceptor distance

As the donor acceptor distance increase the thickness of the copper spot decreases which is accepted. The donor-acceptor distance is changed by changing the number of kapton tapes used as shown in Figure 21 . Each layer of kapton tape is 30µm.

The thickness of the copper spot is found by two methods, (1) mass difference method, (2) equating the volume of ejected material and the transferred copper spot.

(1) $$m_f - m_i = \rho.A.t$$

$\therefore$ $$t = \frac{m_f - m_i}{\rho.A}$$

m_f = mass of glass substrate after copper transfer

m_i = mass of glass substrate before copper transfer

ρ = density of copper material

A = Area of copper ring

t = thichness of deposited feature

(2)$A_f \times t_f = A \times t$

$\therefore \quad \pi\, {d_f}^2 \times t_f = \pi \times d^2 \times t$

$$\therefore \qquad t = \frac{{d_f}^2 \times t_f}{d^2}$$

d_f= Diameter of donor thin film ejected

t_f=thickenss of copper thin film

d= diameter of copper spot

t=thickness of copper spot

Calculation of spot thickness by both methods:

Table 2 Effect of stand-off distance

Stand off distance(μm)	***Method 1 (μm)***	***Method 2 (μm)***	***Average (μm)***
90	***0.1462***	***0.1547***	***0.15***
120	***0.1310***	***0.1392***	***0.135***
150	***0.1439***	***0.1572***	***0.12***

4.4 Effect of substrate temperature

The acceptor substrate was heated at different temperatures and different effects were studied. It was observed that better results were obtained at room tempertaure or slightly elevated temperatures. At higher tempertaures the copper spots were hardly visible as can be seen in Figure 23. At more than 250^oC only white spots were visible. Substrate heating of about 100-200^oC provides very good adhesion. When heated above 300^oC the crystallization of copper metal on the acceptor happens as a result of which the accuracy of the copper spot deposited gets reduced drastically and only the white flumes are seen on the acceptor sample. The image showing the ablation of Copper thin film from the don

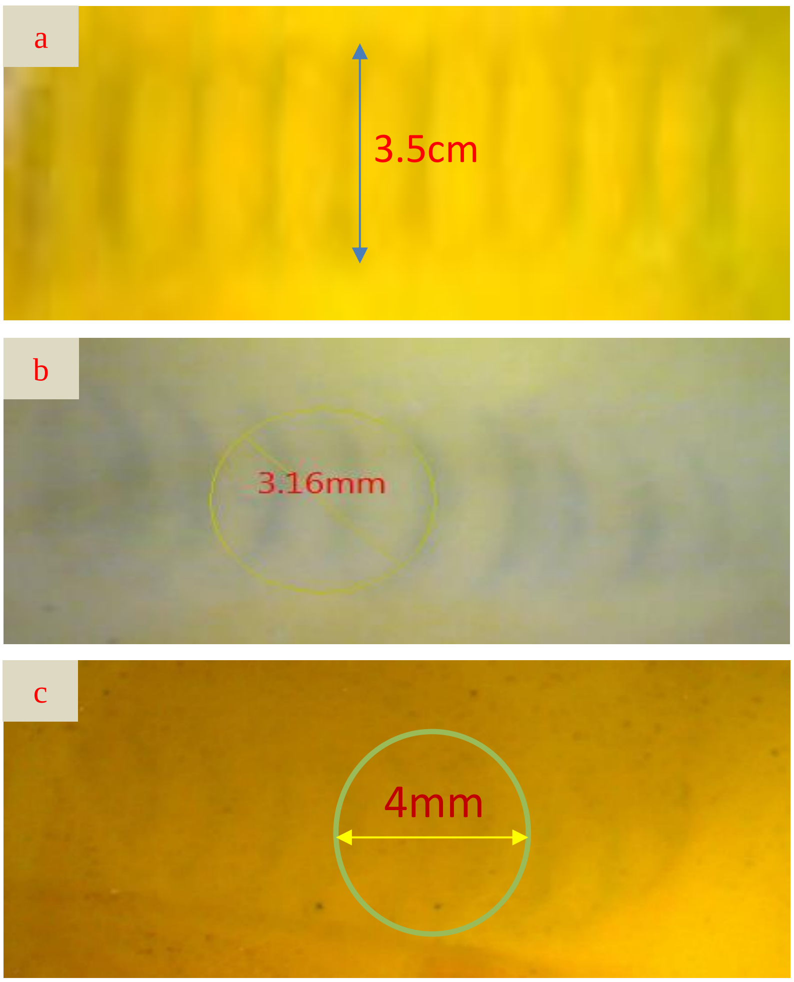


Figure 23 Effect of substrate temperatures, (a)T=200^{o}C, (a)T=250^{o}C, (a)T=300^{o}C

4.5 Effect of fluence

The experiment was performed at different fluence values and the difference was observed. This was done in continuous laser mode not in pulsed mode. The following results were obtained as shown in Figure 24

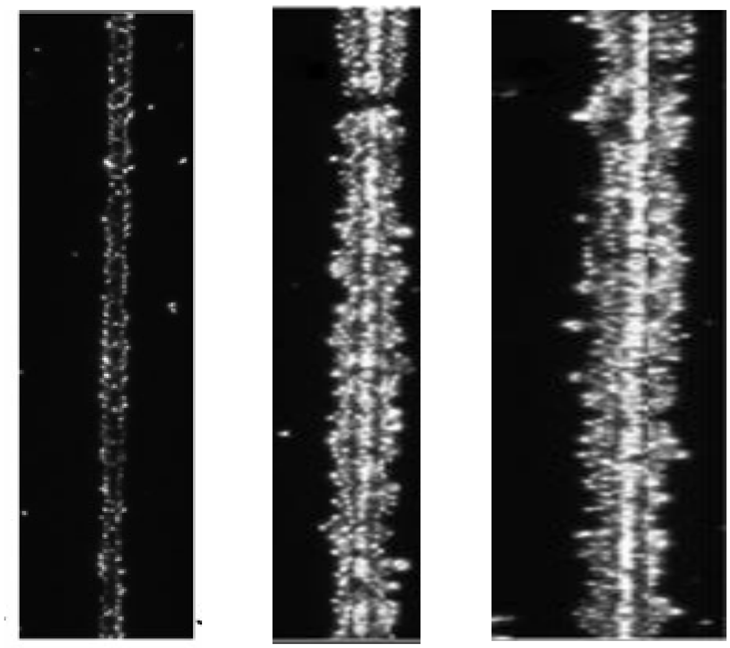


Figure 24 Optical micrographs of laser-machined regions of copper thin films on keptone donor substrates for various values of laser fluences. (a) 63mJ/cm^2, (b) 80 mJ/cm^2, (c) 91.72mJ/cm^2

4.6 Kapton tape as acceptor

Experiments were also performed with kapton tape as acceptor substrate. This was done to further improve the adhesive properties of the acceptor substrate towards the incoming ejected copper particles. The copper spots were found to be 0.24μm thick. The thickness of the copper spots was calculated using the same methods described above.

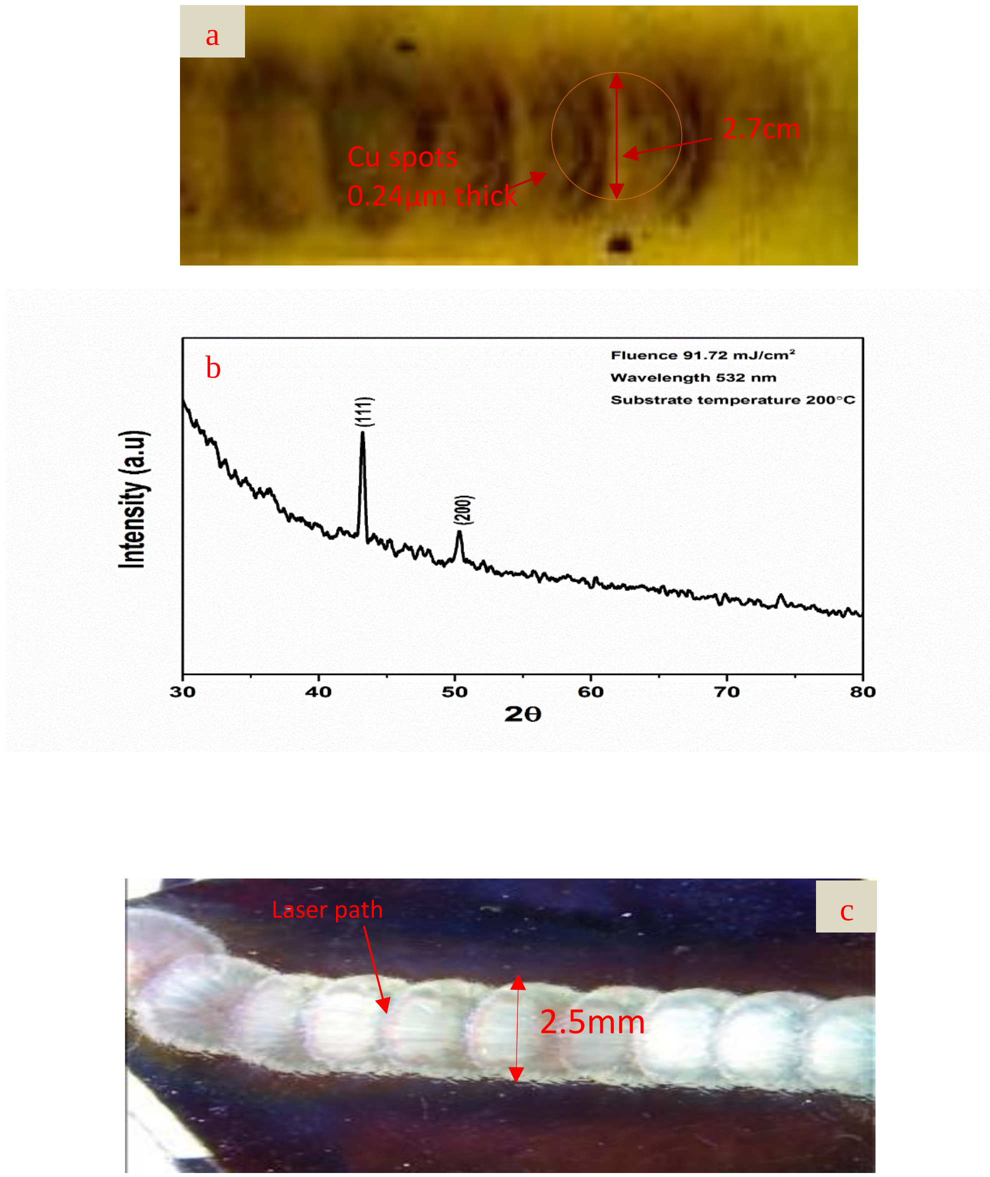


Figure 25 Kapton tape as acceptor, (a) copper rings 0.24µm thick, (b) XRD image of copper transferred on kapton tape, (c) optical image of the donor showing the path of the lase

The XRD of the kapton tape deposited with copper spots was taken and copper was found to be present in two phases (1,1,1) and (2,0,0) signified by the peaks as shown in fig. For further characterization Scanning Electron Microscopic images were taken followed by EDAX analysis.

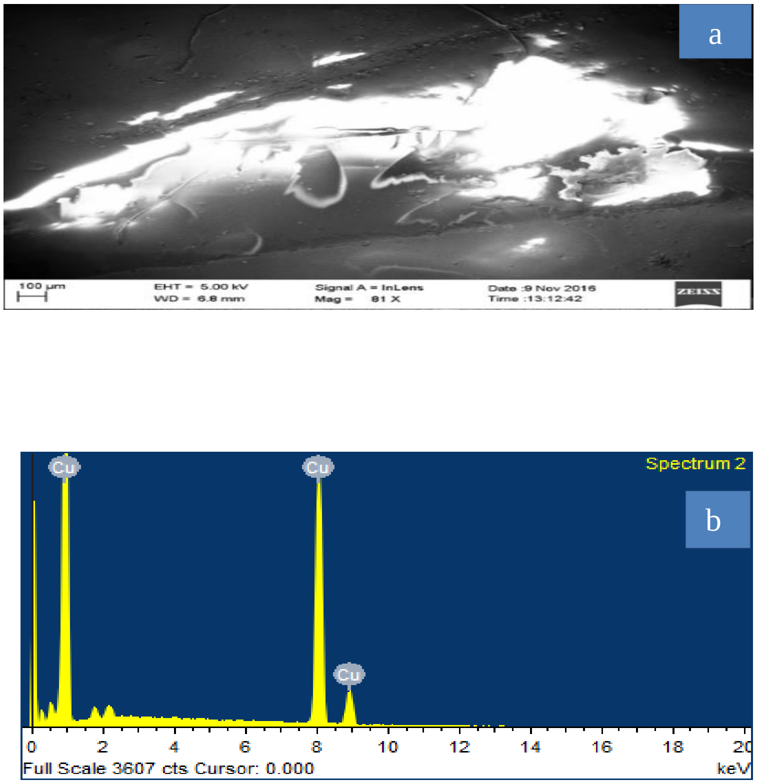


Figure 26 SEM image of acceptor substrate after depositions, (b) EDAX analysis

4.7 3D structuring

3D pillars were made using solid state Nd:YAG 355nm laser induced forward transfer technique. Various values of fluence were used and the results were observed. Not all fluence values were found to support the formation of 3D structures. In developing 2D conducting patterns the acceptor and the donor substrates were moved parallely with equal rates. However for the formation of 3D structures the acceptor was kept stationary

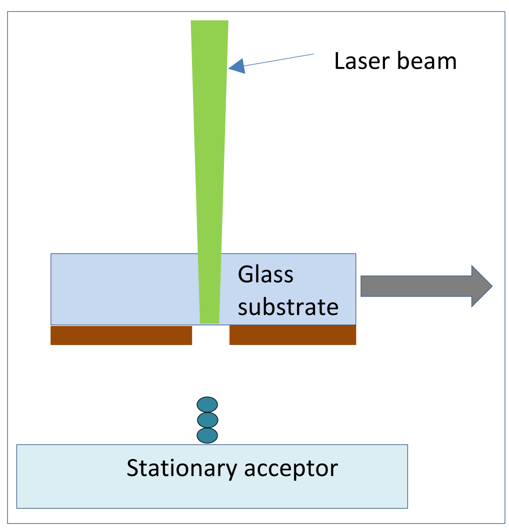


Figure 27 Block diagram for the setup in 3D structures

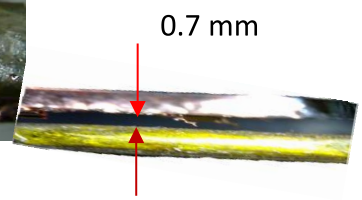


Figure 28 . Holding Jig

Figure 29 Digital microscopic image of donor sample

4.7.1 3D structures with copper

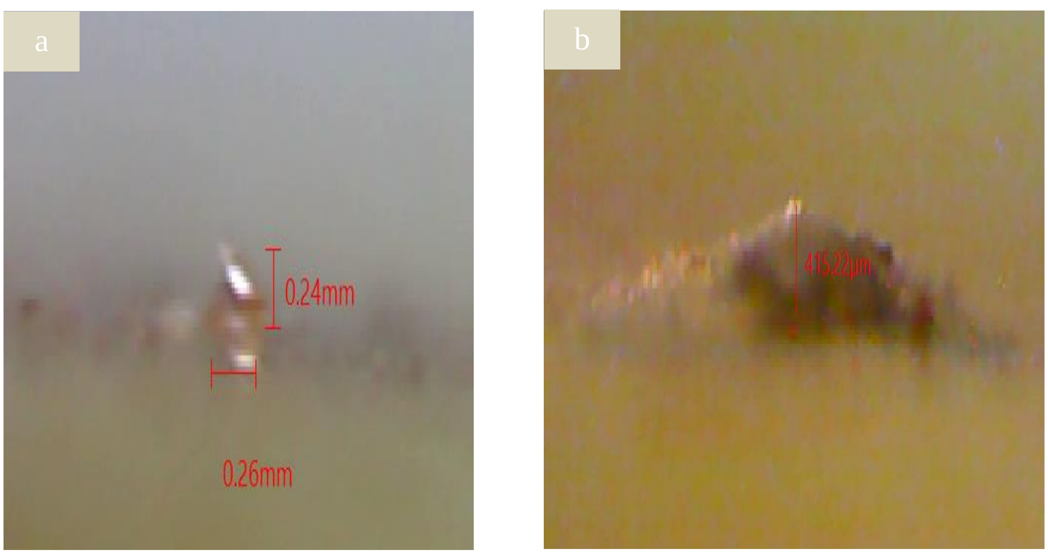


Figure 30. 3D structures of copper at 760mJ/cm^2, (a) 156 shots, (b) 298 shots

4.7.2 3D structures with copper-nickel alloy

3D structures were made with copper as the donor material but were not found to grow significantly. Hence the pillars were again made of copper alloyed with nickel (5%. 10%, 15%) as shown in Figure 31. Results were found to improve significantly after alloying with nickel. The number of laser shots required for a certain pillar height was observed to decrease with the increase in the amount of Ni alloying.

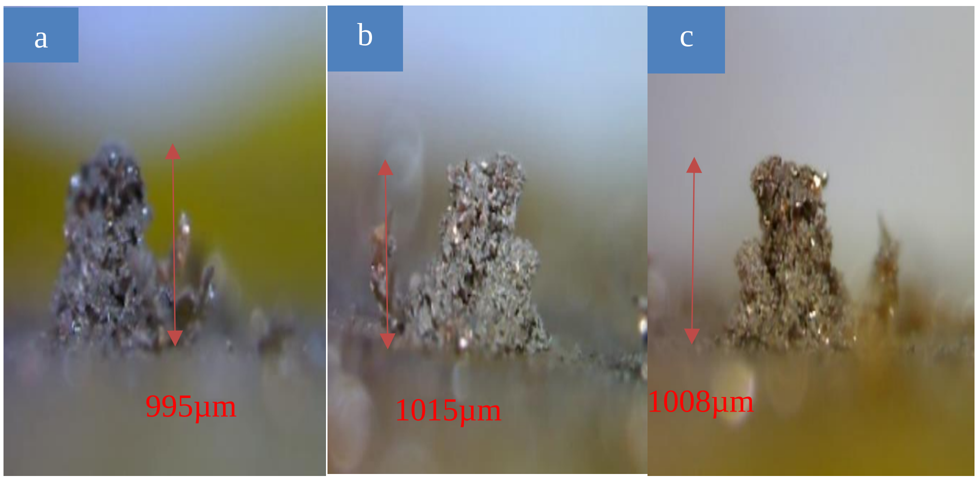


Figure 31 Pillars of cupronickel alloy at 760mJ/cm^2, (a) 378 shots, 5% Ni (b) 325 shots 10% Ni, (c) 276shots, 15% Ni.

4.7.3 Effect of number of laser shots

Some experiments were performed to observe the influence of the number of laser shots on the growth of the pillars. So, the pillars were developed at the most optimized value of fluence i.e. 760mJ/cm^2. Below this value the laser was not able to ablate the copper material. And above this value the energy was so high that the pillars were getting distorted due to the high laser energy. As can be seen in fig the thickness of the pillar was found to increase with the number of laser shots.

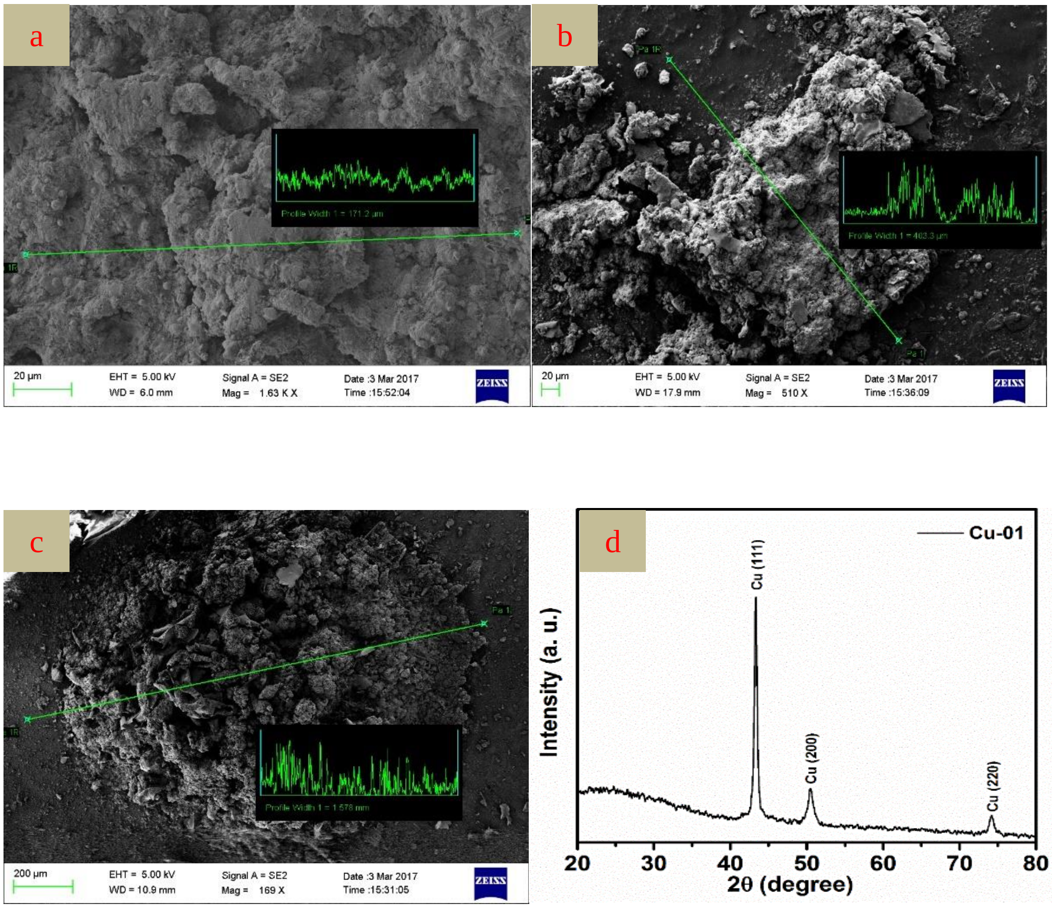


Figure 32. Effect of number of laser shots, (a) 171.2 µm thick, 56 shots, (b) 403.3µm thick, 120shots, (c) 1578µm thick, 276 shots, (d) XRD image

4.8 Modelling by COMSOL Multiphysics

Computer simulations are very strong tools for providing the essential information about physical mechanisms happening in a material irradiated with ultrashort, high intensity laser pulses. It not only gives a reasonable explanation about the processes but also saves time and resources. COMSOL Multiphysics is a strong tool for modeling and simulation. It is a software package based on the Finite Element Analysis (FEA). This package has over 26 different modules to provide software solutions of Multiphysics problems. These modules can be coupled and applied to solve numerous problems based on engineering and physics.

4.8.1 Effect of donor film thickness on temperature

The centre surface temperature is found to increase with the increase in the thickness of donor thin film as shown in Figure 33

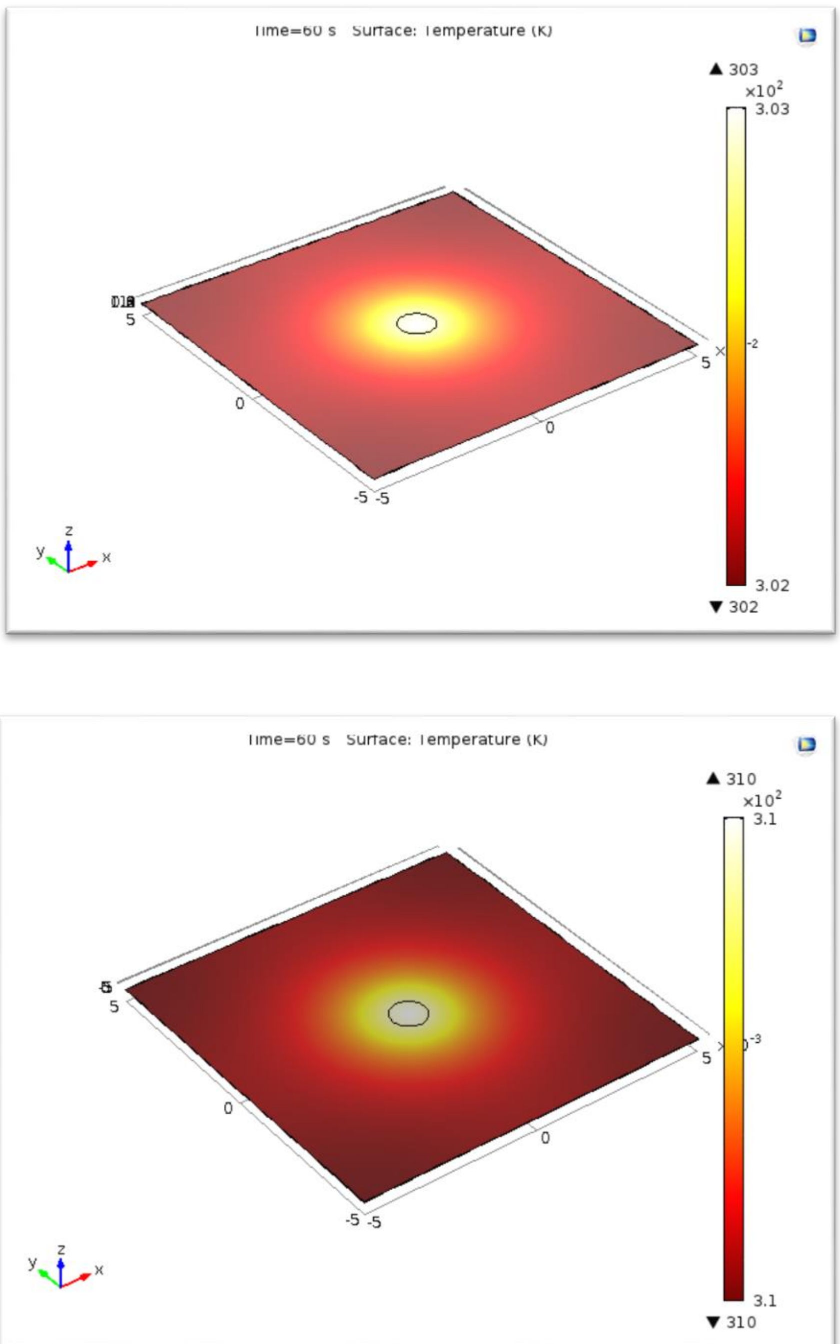


Figure 33 Temperature profile of copper thin film, (a)400nm thick, (b)750nm thick

4.8.2 Effect of fluence on maximum surface temperature

The maximum fluence used in this work is 760mJ/cm^2. The maximum temperature in the thin film as can be seen is 302.6K which is far below the melting point of copper. Hence there is no melting involved. The copper material is ejected by the impact action of laser. The centre surface temperature is found to increase with the increase in the thickness of donor thin film as shown in Figure 33

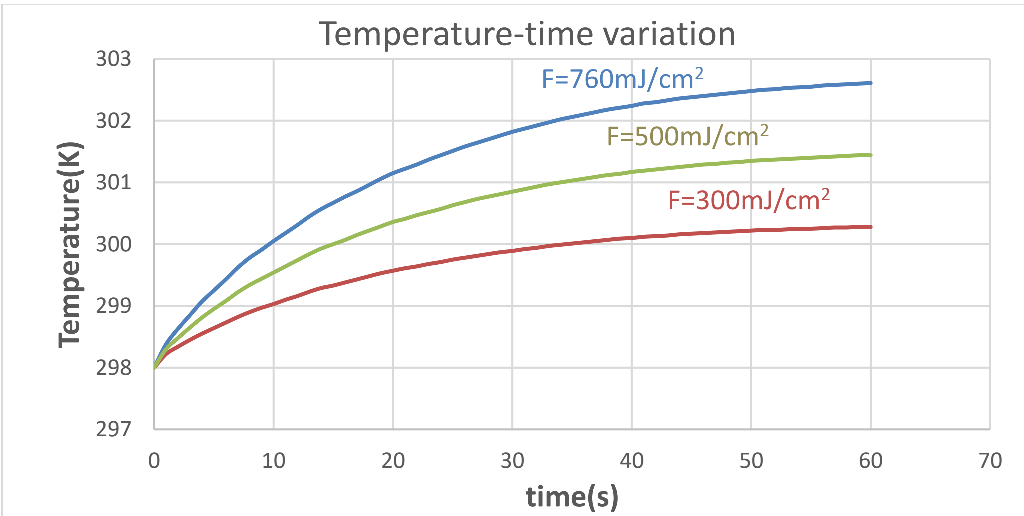


Figure 34 surface temperature variation with fluence after 60s of laser heating

The maximum fluence used in this work is 760mJ/cm^2. The maximum temperature in the thin film as can be seen is 302.6K which is far below the melting point of copper. Hence there is no melting involved. The copper material is ejected by the impact action of laser. The centre surface temperature is found to increase with the increase in the thickness of donor thin film as shown in Figure 33

Chapter 5: Conclusion and Future Recommendations

The main aim of this thesis was to investigate during a LIFT process, the generation of 2D conducting patterns and 3D structures and to optimize the working parameters. In this work, the experimental investigation on micro patterning of copper using solid state Nd:YAG 532nm Laser Induced Forward Transfer on flexible polyimide film and kapton tape has been done.

In conclusion, we proposed applications of LIFT, (a) 2D conducting patterns, (b) 3D structuring. It has been found that both of them can be successfully obtained from the LIFT technique. For 2D conducting patterns, Laser at 532nm is used and optimum power of about 45mW is analyzed with varying the spot diameter from 0.5mm to 2mm. The optimum fluence for the formation of 2D patterns is 91.72mJ/cm^2. The substrate temperature was varied and found to yield optimum results at room temperature or slightly elevated temperature. Characterization of the images using digital microscopy, XRD and Scanning Electron Microscope techniques has been done all of which confirm the presence of the copper material being transferred from the donor thin film.

For 3D structuring, Laser at 355nm is used. The optimum fluence obtained was 760mJ/cm^2. The donor thin film is varied from pure copper material to copper-nickel alloys with 5%, 10% and 15% addition. For a pillar height of 1115µm the number of shots required is found to decrease with the increase in the amount of Ni addition.

Future recommendations

The research can be extended to achieve full 3D printing. The aspect ratio of the pillars produced were impressive but they still remain as just the simplest form of 3D printing. Complete 3D requires joining of incoming particles also in the horizontal plane, which is not addressed in this work, but is necessary to achieve full 3D printing.

The shape of the pillars produced is poorly controlled. The shape is mainly governed by the velocity of the incoming particles which is not controlled in this work. The velocity can be controlled for the optimization of the microstructure and the mechanical properties of the 3D pillars. The LIFT of metals has always faced the problem of the droplets deposited next to the base of pillar which can be improved.

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