Thick film laser induced forward transfer for deposition of thermally and mechanically sensitive materials

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Laser forward transfer processes incorporating thin absorbing films can be used to deposit robust organic and inorganic materials but the deposition of more delicate materials has remained elusive due to contamination and stress induced during the transfer process. Here, we present the approach to high resolution patterning of sensitive materials by incorporating a thick film polymer absorbing layer that is able to dissipate shock energy through mechanical deformation. Multiple mechanisms for transfer as a function of incident laser energy are observed and we show viable and contamination-free deposition of living mammalian embryonic stem cells. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2799877]

Laser induced forward transfer and other laser direct write printing methods have been used extensively to deposit and pattern a wide variety of materials for applications with sizes ranging from the nano- to the macroscale.[1,2] Such techniques rely on the absorption of laser energy in the material of interest causing local vaporization and expulsion of material from a donor substrate to a receiver substrate on which the patterns are formed.[3,4] Solid state, simple rheological, multiphase, multicomponent, and other complex materials can be printed in this manner.[5–8] For systems that do not absorb at the desired wavelength or those that are susceptible to laser induced damage, alternative techniques have been developed that rely on laser absorption in a sacrificial component, thereby enabling a slightly modified transfer process.[9] There are two main configurations for such transfer; matrix assisted for which the sacrificial absorbing media are mixed uniformly in the material of interest[10,11] and multilayered thin films in which a thin (nanometer scale) absorbing layer is placed above the material of interest.[9] In both cases, the laser energy is absorbed by the sacrificial material causing its vaporization and thereby providing the necessary conditions for transfer of material.

In the context of organic and biological materials, the use of a thin laser absorbing film has emerged as the preferred transfer method to generate patterns since it can partially remove the direct interaction and absorb much of the incident laser energy.[12] Various examples use an absorptive metal or metal oxide layer, such as Ag, Ti, or TiO_2, to deposit the heat sensitive biological material.[13–15] However, potential contamination and degradation from hot volatilized species, thermal/optical damage from the incident laser, and/or mechanical damage from the laser induced shock propagation through the transferring material require alterna-

tive approaches for laser transfer of acutely sensitive materials, such as those used in organic electronics or embryonic stem cells for tissue engineering applications. Recently, researchers have shown that the use of a photodecomposing volatile polymer can induce transfer and minimize contamination by the absorbing material;[16,17] however, transferred materials are still subject to thermal and mechanical stress. In this paper, we report on an improved forward transfer method employing a thick film absorbing layer, where the film thickness is significantly larger than the laser absorption depth. This approach has the advantage of being able to insulate the transferring materials from thermal and mechanical shocks and is shown to enable viable mammalian embryonic stem cell transfer, one of the most mechanically and thermally sensitive systems available of interest.

The general laser forward transfer process is shown schematically in Fig. 1. Donor substrates are produced by spin coating commercially available polyimide (HD Microsystems PI2525) onto glass slides at 500 rpm for 10 s to allow the polyimide to flow, followed by a high speed spin (5000 rpm) for 40 s to attain a uniform layer thickness of
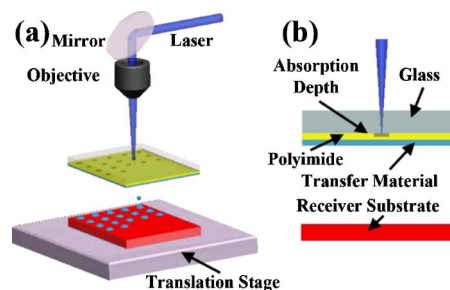

FIG. 1. (Color online) (a) Laser induced forward transfer schematic. (b) Close-up of donor/receiver substrate showing thick polyimide film covered with transfer material. Small shaded region indicates the volume in which the incident laser is absorbed.

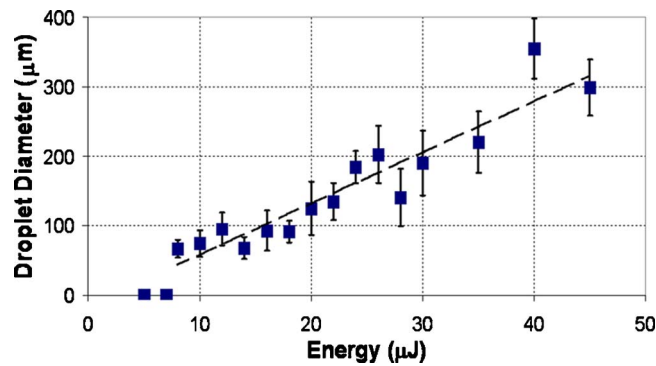[a)]Author to whom correspondence should be addressed. Electronic mail: cbarnold@princeton.edu

FIG. 2. (Color online) Transfer droplet size as a function of laser energy. The dashed line is the guide for the linearity of the data.

FIG. 3. (Color online) (a) Light microscopy images of laser transferred droplets taken at 5, 7, 11, and 31 μJ (from left to right). (b) Associated microscopy images of polyimide film. (c) SEM images of polyimide film taken at an angle of 70°.

approximately 4 μm, as measured by stylus profilometry. The slides are subsequently baked at 120 °C for 30 min to partially cure the polyimide, followed by a high temperature bake at 350 °C for 30 min to complete the imidization process and drive off any remaining solvents. The laser absorption length of these films is measured to be 0.75 μm, which compares favorably to the literature value of ~ 0.63 μm (Ref. 18) for bulk polyimide, and is significantly less than the overall film thickness.

The cured polyimide donor substrates are coated with a uniform thickness (~10 μm) of 1:1 glycerol:cell media [Dulbecco's modification of eagle's medium (DMEM) +35% embryonic stem (ES) certified fetal bovine serum (FBS)] using a No. 6 Gardner wirecoater. For cell transfer studies, embryonic stem cells (AINV-15 line, ATCC) are grown in specialized stem cell media (high glucose DMEM without phenol red, 10% ES certified FBS, nonessential amino acids, $5 \times 10^{-5} M$ β-mercaptoethanol, leukemia inhibitory factor, penicillin/streptomycin, and fungin). Cells are grown to confluence in a 150 mn $\times$ 20 mm culture dish coated with 0.1% gelatin, trypsinized, and washed twice with phosphate buffered saline prior to suspension in the glycerol:cell media solution and spreading on the thick polyimide layer, as shown in Fig. 1.

Once the donor substrates are prepared, they are inverted and placed above the receiver substrate using 100 μm spacers. For droplet size characterization, the receiver substrate is glass microscope slide, while for cell transfer and growth studies, receiver substrate is Petri dish coated with a thick layer of Matrigel® (BD Biosciences) (~500 μm). The receiver substrate is subsequently placed on a vacuum chuck situated on a high resolution X-Y-Z translation stage with computer-controlled accuracy. A frequency tripled Nd:YVO$_4$ laser (λ=355 nm, τ=15 ns) is focused to 30 μm diameter spot at the glass/polyimide interface initiating the transfer process. Images of the transferred material and the polyimide absorptive layer are captured using a light microscope equipped with a digital imaging camera and image processing software. The droplet radius is calculated in the software by taking the average distance from the centroid to the perimeter of the droplet in 2° increments. For noncompact splashes, the average radius is determined by visually finding the best-fit circle that approximates the droplet. Higher resolution images of the thick polymer film are acquired using scanning electron microscopy with an in-lens detector.

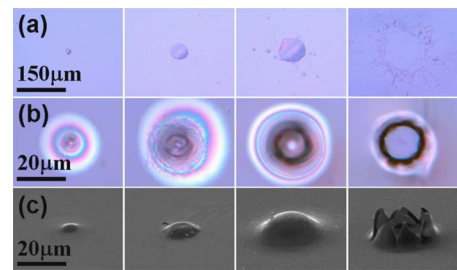Figure 2 shows the average droplet diameter measured from the optical microscopy images as a function of laser energy for a fixed thickness of polyimide. The error bars are determined by taking the standard deviation in droplet diameter of approximately 50 droplets at the given laser energy from multiple experimental runs. As the laser energy increases, there is a steady increase in the droplet diameter throughout the range of energies. It is interesting to note that this increase in size appears linear, which is in contrast to prior literature using a Ti absorbing layer,[19] and is indicative of a fundamentally different transfer mechanism. Furthermore, the transferred spot size increases with a corresponding increase in focus spot dimensions, as previously observed.

To elucidate the mechanism, we look at the shape of the transferred droplets and the absorbing film after deposition. At the lowest laser energies, the droplets remain compact with little spreading. As the laser energy is increased, the droplet size increases until it reaches a regime in which a large droplet is deposited within a background of smaller, recondensed droplets. At the greatest laser energies, the transfer becomes unstable resulting in a deposition characterized by splashes and spraying of smaller droplets [Fig. 3(a)].

Figure 3(b) shows optical microscopy images of the thick polyimide film corresponding to the transferred droplets. At low energies, the polyimide film is permanently modified but appears to remain intact. Scanning electron microscopy (SEM) images of Fig. 3(c) further confirm this interpretation by showing the polyimide film to be plastically deformed into a dome shape. As the laser energy is increased, the diameter of the modified region grows, leading to a larger transferred volume and a correspondingly larger droplet diameter. Once the incident energy reaches a high enough level, the polyimide films experience the onset of rupture, eventually leading to extensive cracking and delamination at the highest energies. Such an effect leads to widespread heating of the transferring material and a more violent transfer resulting in the observed splashes. These observations are in contrast to other polymer absorbing layer experiments in which transfers are characterized by the thin polymer layer being completely vaporized after laser irradiation.[17,20]

In this case, the laser is absorbed by the polymer within the absorption depth, causing vaporization below the surface of the thick film. The polymer expands due to the generated pressure, but eventually exceeds the yield stress, leading to the observed plastic deformation. As the vapor expands, it cools and recondenses on the bottom of the remaining polyimide film, thereby remaining isolated from the transferred material. As the laser energy is increased, the amount of
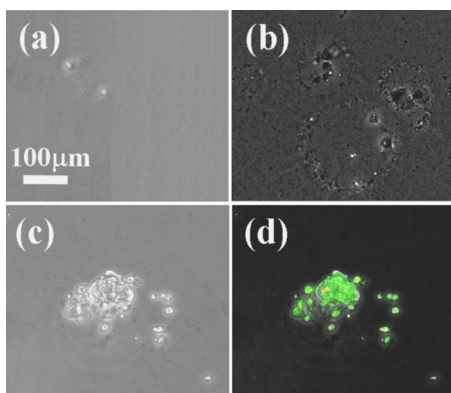
FIG. 4. (Color online) (a) Bright field micrograph of laser transferred mouse embryonic stem (mES) cells one day after deposition in low laser energy regime. (b) Bright field micrograph of damaged mES cells after deposition from high energy regime. Fractured cell membranes and contamination from polyimide layer are present. (c) Bright field micrograph of mES cells after eight days of growth from conditions of (a). (d) Green fluorescent image of (c) indicating viable cells.

vaporized material increases and causes the remaining polyimide film to be thinner and susceptible to rupture. Once the film ruptures, hot vapor from the ablation process is able to escape into the transferring material causing rapid heating and a more energetic deposition process that leads to the observed splashes. These proposed mechanisms are characteristically different than those in metal films for which a melting transition can produce protrusions on the surface and lead to droplet ejection.[21,22]

The ability of thick film laser induced forward transfer to deposit sensitive material is demonstrated by transferring viable mouse embryonic stem cells. Figure 4 shows representative optical micrographs of transferred stem cells in the low energy transfer regime as a function of time after deposition. The first day after deposition [Fig. 4(a)] shows well defined cells in the Matrigel substrate without an indication of damaged cells. As the laser energy is increased, the appearance of damaged cells [Fig. 4(b)] reduces the overall efficiency of the process due to the explosive transfer kinetics and corresponding cell rupture. After eight days of incubation [Fig. 4(c)], the region of cells exhibits clear signs of growth as indicated by the larger mass of cells and expression of green fluorescent protein [Fig. 4(d)]. Furthermore, the fact that the cells appear both in and out of focus is indicative of three-dimensional growth into the Matrigel substrate. As the laser energy is increased, the penetration depth into the Matrigel appears to increase, indicating a greater momentum of the depositing cells with laser energy.

In summary, this work presents an approach to laser forward transfer based on a thick film polyimide absorbing layer. This technique is unique in its ability to deposit delicate materials that are sensitive to mechanical and thermal shocks. By using a film thicker than the laser absorption length, two regimes of polymer response to laser irradiation are identified corresponding to plastic deformation and rupture of the film. We use this approach to demonstrate viable transfer of mammalian embryonic stem cells with applications in tissue engineering and disease treatment.

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