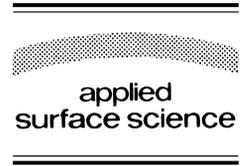




ELSEVIER

Applied Surface Science 154–155 (2000) 593–600



www.elsevier.nl/locate/apsusc

New approach to laser direct writing active and passive mesoscopic circuit elements

D.B. Chrisey^{a,*}, A. Pique^a, J. Fitz-Gerald^a, R.C.Y. Auyeung^a,
R.A. McGill^a, H.D. Wu^a, M. Duignan^b

^a Plasma Processing Section, Code 6372, Naval Research Laboratory, Washington, DC 20375-5345, USA

^b Potomac Photonics, Lanham, MD, USA

Received 1 June 1999; accepted 9 September 1999

Abstract

We have combined some of the major positive advantages of laser-induced forward transfer (LIFT) and matrix-assisted pulsed laser evaporation (MAPLE), to produce a novel excimer laser driven direct writing technique which has demonstrated the deposition in air and at room temperature and with sub-10 μm resolution of active and passive prototype circuit elements on planar and nonplanar substrates. We have termed this technique MAPLE DW (matrix-assisted pulsed laser evaporation direct write) and present its historical evolution from pulsed laser deposition. This paper describes the simplistic approach to carry out MAPLE DW, gives experimental conditions, and physical characterization results for the deposition of NiCr thin film resistors, Au conducting lines, and multilayer depositions of Au conductors and BaTiO₃ dielectrics to produce prototype capacitors. In general, the electrical properties of the materials deposited (conductivity, dielectric constant, and loss tangent) are comparable or superior to those produced by other commonly used industrial processes such as screen printing. The mechanism of the MAPLE DW process, especially the novel aspects making it a powerful approach for direct writing all classes of materials (metals, oxide ceramics, polymers and composites), is also described. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Thin films; Electronic devices; Laser deposition; Direct writing; Matrix-assisted pulsed laser evaporation; Matrix-assisted pulsed laser evaporation direct write

1. Introduction

1.1. Laser processing of materials

Shortly after the discovery and fabrication of lasers researchers representing all disciplines of sci-

ence began aiming them at materials in different forms. The interaction of lasers with materials can result in a wide range of effects that depend on the properties of the laser, the material, and the ambient environment. As a function of beam energy, these effects can start from simple photothermal heating to photolytic chemical reactions and to ablation and plasma formation, just to name a few of the possible effects.

It is interesting to look at the evolution of laser interactions with materials as it applies to materials

* Corresponding author. Tel.: +1-202-767-4788; fax: +1-202-767-5301.

E-mail address: chrisey@ccf.nrl.navy.mil (D.B. Chrisey).

processing in the time since lasers were discovered and became easily available. In the first 20 years after the discovery of the laser ('60–'80), the laser interaction for materials processing could be described as being based on the primary laser–material interaction. That is, most of the research was focussed on studying how the laser interacting with the material could be used for important processing applications such as etching, ablation, annealing and simple photochemistry. Simple stated, the emphasis was on the primary laser–material interaction. For the last 20 years or since about 1980, the laser–material interaction for processing materials has expanded to include secondary effects such as laser ablation for film formation and laser-based developing of photolithographic resists. In these examples, the laser–material interaction is used to do subsequent processing of materials and as such, it is a secondary effect. In the last few years an argument could be made that this secondary effect has been expanded to include laser interactions with novel materials, thus greatly expanding the capability of lasers to do materials processing. Examples of these secondary effects with novel materials would include laser capture microdissection [1–3], matrix assisted pulsed laser deposition (MAPLE), and MAPLE di-

rect write (MAPLE DW). These latter two topics deal with laser processing for coatings and are ones that our group at the Naval Research Laboratory has pioneered and are the subject of this paper. A simple graphic description of the evolution of laser interactions used to process materials is given in Fig. 1.

1.2. Laser processing of thin films

The continuing evolution of applications of lasers to do materials processing is a natural outcome of different types of lasers becoming more available and reliable and because of researchers becoming more comfortable exploiting the unique capabilities of lasers. Some of the novel features of lasers-based processing of materials for coatings are listed in Table 1. In all cases, these are compared to conventional particle (e-, ion), solution, and chemical vapor deposition techniques for fabricating coatings.

For the processing of high quality coatings, lasers provided unique solutions in many areas. In the early days of the high T_c revolution, pulsed laser deposition (PLD) was the dominant technique to make high quality thin films in situ, in large part, because film deposition could occur in a high background pressure of oxygen [4]. Unlike particle deposition tech-

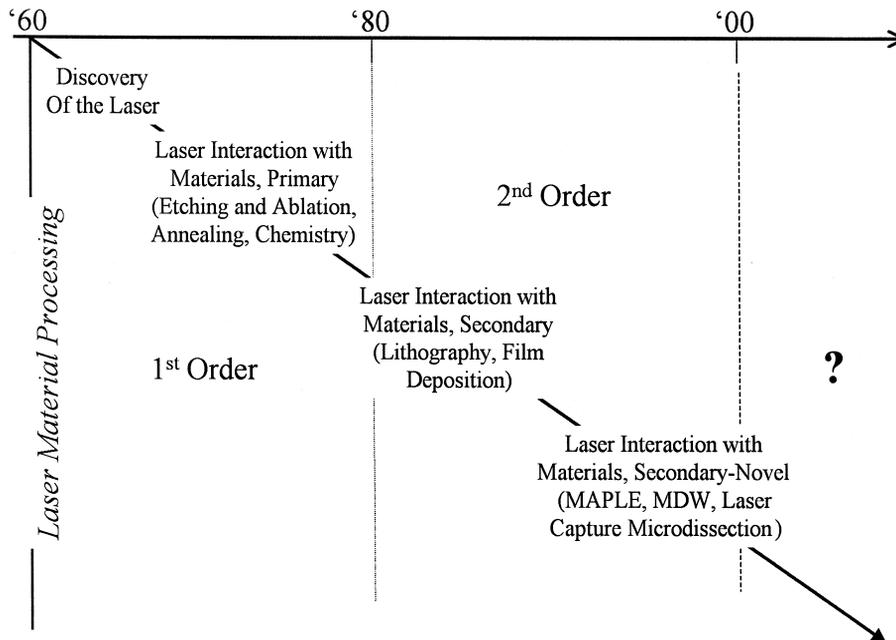


Fig. 1. A graphic description of the evolution of lasers used in processing materials since the discovery of the laser.

Table 1
Novel features of laser-based processing for coatings

Vacuum not required, can process metals, polymers, ceramics, and biological materials
Selective absorption (photolytic as well as pyrolytic)
Wide range of fluences ($< 100 \text{ J/cm}^2$), powers ($< 10^{12} \text{ W/cm}^2$)
Femtosecond pulsed to continuous
Optical path readily amenable to imaging
Safe and clean, no impurities
Feature size (submicron– 10 cm^2)
Directionality (0–1)
Electrons, ions, solutions, organics, high voltages

niques, the transport of the volatilizing laser beam can occur in vacuum or in air. Lasers can also selectively tune to absorption resonances in specific molecules to break bonds and/or to initiate chemical reactions. Also, unique to lasers is their ability to control the fluence and pulse length over extremely large ranges. Because photons have momentum and are highly coherent, lasers can be used to direct motion of species. This feature is exploited with optical tweezers. Unlike most conventional coating techniques, lasers are very safe and do not introduce impurities. Many of these unique features of laser-based processing have been exploited in matrix-assisted pulsed laser evaporation (MAPLE) and MAPLE DW which are the subjects of this paper.

The discovery of high temperature superconductivity a little more than 10 years ago catalyzed the rediscovery or refinement of PLD as a technique to grow high quality epitaxial thin films of YBCO. Since that time, PLD has been successfully used to grow high quality epitaxial thin films of a multitude of other ceramic materials including ferroelectrics, ferrites, colossal magnetoresistance materials, transparent conductors, and biomaterials to name a few [4]. The advantages of PLD over other chemical and physical vapor deposition techniques for ceramic thin films includes the simple experimental design, the ability to transfer the pellet stoichiometry to the growing film, and the ability to do depositions in a high background pressure of reactive gases such as oxygen. The ability to transfer the pellet stoichiometry with fidelity is based on the interaction of the high-energy short-pulsed laser with the ceramic target and the resulting highly forward-directed nature of the laser-produced plasma plume.

Unfortunately for PLD, the advantages for ceramics, and inorganic materials in general, would not likely exist for the more fragile and thermally labile organic materials. Indeed, when a laser interacts with an organic target under the usual conditions for PLD, the material, which is grown in thin film form, is radically and usually irreversibly different from the starting material. For example, in polymers the chemical bonds connecting loosely tethered, but very important for various applications, functional groups are often broken. The backbone organic chain is also often broken leaving the film to be made up of smaller polymeric pieces and with different functional groups terminating the ends. Changing the surface chemistry of polymeric thin films is analogous to changing the stoichiometry and thus the phase and electronic properties of inorganic thin films. While the laser energy absorption and material ablation properties of organic materials should be loosely the same as for inorganic materials, i.e., in each case presenting the growing film with vapor flux whose stoichiometry is similar to the starting material, it is the combination of the substrate processing temperature and the nature in which the interatomic chemical bonds are formed which makes conventional PLD unsuitable for organic materials. It is likely that there would be similar advantages to using a laser to physically deposit organic thin films if a suitable resolution to the aforementioned problems could be resolved. Furthermore, there is a need for high quality organic thin films in the areas of organic electronic devices, circuit passivation, and in gas sensing. In these areas, there is a strong performance requirement that the organic thin films have structural and chemical integrity, as well as, being smooth, thin, dense, and of accurately and precisely predictable thickness.

1.3. MAPLE

We have successfully extended conventional PLD to include organic materials through a process we have termed MAPLE [5,6]. In this process which is shown schematically in Fig. 2, the excimer laser is set to a lower fluence ($\sim 0.2 \text{ J/cm}^2$) from conventional PLD and impacts a dilute matrix target which is typically frozen to low temperatures ($\sim 77 \text{ K}$). The dilute matrix is made up of the organic molecules to be deposited in thin film form and a frozen

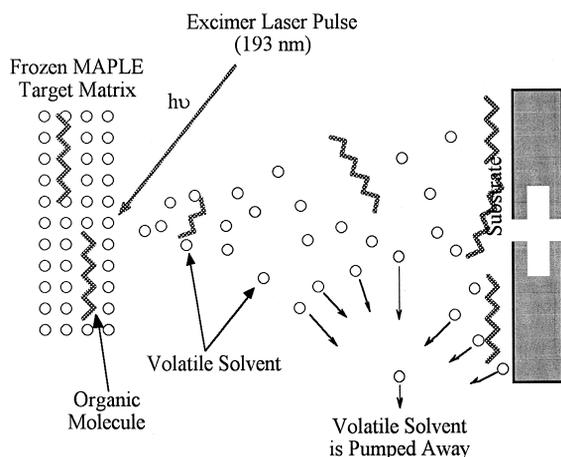


Fig. 2. Schematic diagram of the basic MAPLE processes. Note that the evaporated solvent is rapidly pumped away or it can be trapped for re-use.

solvent. Ideally, the laser is then preferentially tuned to interact with the solvent matrix, but independent of that, the laser warms a local region of the target. This is similar to the laser–solid interaction in PLD only at a level that is orders of magnitude lower. The laser-produced temperature rise is large compared to the melting point of the solvent, but small compared to the decomposition temperature of the organic solute. The matrix can then be characterized as a colloidal suspension of mixed volatility and the laser–matrix interaction a secondary and novel interaction from Fig. 1. When the MAPLE process is optimized, the collective collisions of the evaporating solvent with the organic molecule act to gently desorb the organic molecule intact, i.e., with only minimal decomposition as determined by FTIR and mass spectrometry [7]. The evaporating solvent has a near zero sticking coefficient with the substrate and is rapidly pumped away or it can be trapped for re-use.

2. Results

2.1. Laser-Induced Forward Transfer (LIFT) and MAPLE DW

With the new found success of PLD, there has also been a parallel increase in the attention given to other laser-based thin film processing methods, in

general. One such method is LIFT [8–14]. LIFT is a simple technique that employs laser radiation to transfer a thin film (target) from an optically transparent support onto a substrate placed next to it. Patterning is achieved by moving the laser beam (or substrate) or by pattern projection. The former is a method of direct writing patterns. There are several experimental requirements for LIFT to produce useful patterns including: the laser fluence should just exceed the threshold fluence for removing the thin film from the transparent support, the target thin film should not be too thick, i.e., less than a few 1000 Å, the target film should be in close contact to the substrate, and the absorption of the target film should be high. Operating outside this regime results in problems with morphology, spatial resolution, and adherence of the transferred patterns. Repetitive transfer of material can control the film thickness deposited on the substrate. Laser induced modification of the transferred material can occur through the transparent substrate after deposition. Overall, LIFT is a simple and powerful technique that can be used on mostly metallic target films. Because the laser energy absorbed in the coated substrate atomizes the layer, LIFT is inherently a pyrolytic technique and cannot be used to deposit complex crystalline, multi-component materials whose crystallization temperature is well above room temperature. Other disadvantages of the LIFT technique include uniformity, morphology, and adhesion of the film, poor linewidth, ablation of the support and impurities in the film, and material implantation into the substrate.

There is a strong need in industry for new design and Just In Time Manufacturing (JITM) methods, materials, and tools to direct write for rapid prototyping passive circuit elements on various substrates, especially in the mesoscopic regime, i.e., electronic devices that straddle the size range between conventional microelectronics (sub-micron range) and traditional surface mount components (10-mm range). The need is based on the desire: to rapidly fabricate prototype circuits without iterations in photolithographic mask design, in part, in an effort to optimize the performance on circuits too difficult to accurately model, to reduce the size of PCBs and other structures (~30–50% or more) by conformally incorporating passive circuit elements into the structure, and to fabricate parts of electronic circuits by methods

which occupy a smaller footprint, which are CAD/CAM compatible, and which can be operated by unskilled personnel or totally controlled from the designers computer to the working prototype. Mesoscopic direct write approaches are not intended to compete with current photolithographic circuit design and fabrication. Instead, these technologies will enable new capabilities satisfying next generation applications in the mesoscopic regime.

In MAPLE DW [5], see Fig. 3, we have combined and enhanced some of the major positive advantages of LIFT and MAPLE, to produce a novel excimer laser driven direct writing technique which has demonstrated the deposition in air, at atmospheric pressure, and at room temperature and with sub-10 μm resolution of active and passive prototype circuit elements on planar and non-planar substrates [15,16]. Compared to LIFT, MAPLE is an energetically soft and pseudo-dry laser based vacuum deposition technique used to desorb and form coatings of polymers and fragile organics in a highly controllable fashion. The MAPLE target is composed of a dilute matrix of soluble material to be deposited and a solvent phase, in which it is contained, and is usually pre-cooled to low temperatures (~ 77 K). It is based on the relative volatility of the matrix and the solute, as well as the relative coupling of the laser energy to the solvent over the solute. When the target is irradiated

with fluences, which are low, compared to the decomposition temperature of the solute, but high with respect to the solvent, the solvent is rapidly evaporated. The combined and collective effects of the desorbing solvent gently desorb the solute species intact. The vapor pressure of the solvent causes it to adhere weakly and be rapidly pumped away where it can be trapped for re-use.

MAPLE DW is a process in which material is transferred from a support or “ribbon” to a substrate by the irradiation of laser light (see Fig. 3B). Our work to date has included excimer laser wavelengths of 248 and 308 nm, but other fundamental wavelengths from UV–VIS into the IR could be used with beneficial effects. The “ribbon” is composed of a support, which is laser transparent and may or may not be reusable, solvent matrix material, and the soluble material to be deposited. The support typically does not participate in the transfer of material although it could be made part of the matrix. The matrix material can take many forms as can the material to be deposited. The matrix material can be deposited as a homogeneous mixture with the soluble material to be deposited. It also can be deposited as a layered structure with the laser-absorbing layer on the support first followed by a layer of the material to be deposited, but other distributions are possible. The matrix material bonds the material to be deposited to the support. It also preferentially absorbs the laser radiation and desorbs the material to be deposited from the support and forms an adherent coating on the substrate. Ideally, the matrix material should evaporate or be decomposed into a volatile non-adherent material, carried away by a purge gas and leaving no residue. The target material can consist of homogeneous solutions of soluble and matrix nanophase powders to micron size particulates or single crystallites. The substrate onto which the MAPLE DW coating is applied can be almost anything varying from kapton, silicon, metal foils, to circuit boards.

The material to be deposited can take many forms such as powders, powders with coatings on the surface, polymers, nanophase materials, etc. Since the electronic, mechanical, and thermal properties of powders often differ with respect to bulk or single crystals, there is a great deal of complexity in designing the material to be deposited for good transfer

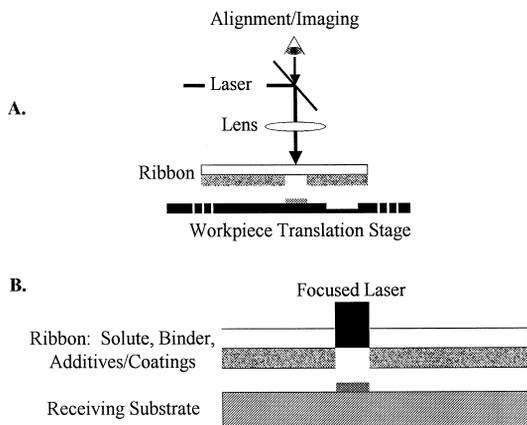


Fig. 3. (A) Schematic diagram of the MAPLE DW approach to laser direct writing thin films. Note the ability of the MAPLE DW system to do laser micromachining, e.g., drilling vias, etching trenches or pre- and post-treating the substrate or deposited film material. (B) A close-up schematic showing the important region of the material transfer and film formation.

ability, for good adherence to the substrate and to other powder, for near 100% packing, and for near bulk-like properties if required. Examples of this include large grain size for near bulk dielectric constant in ferroelectrics and large crystalline platelets of ferrites to minimize the demagnetizing forces. The desired MAPLE DW process has produced deposited material with near bulk like properties.

An important attribute of MAPLE DW that separates it from most other direct write techniques is that it is both additive and subtractive. Thus, a single laser can be used to pre-treat the substrate surface, anneal deposited material, trim circuit elements to meet specifications or even to mill channels or fabricate vias (see Fig. 3A). Furthermore, unlike alternative direct write approaches, MAPLE DW is a pyrolytic technique with respect to the matrix material, but not with respect to the soluble material and powders which are transferred intact, i.e., post-deposition analysis indicates there is no evidence of decomposition. This is the key feature of the technique, which separates it from alternative approaches.

The application of MAPLE DW to the conformal growth of materials takes place using the equipment schematically illustrated in Fig. 3. As shown, an excimer laser impacts a laser transparent ribbon that was pre-coated with a thin film of the material to be deposited and its matrix. To illustrate some of the effects of the laser interaction with the ribbon, we show in Fig. 4 the deposition of Au films from LIFT. As seen in Fig. 4, the optimized growth requires that the fluence be only slightly above the threshold to remove the Au. When the fluence is too high, part of the laser pulse, beyond what is necessary to remove the Au film from the ribbon, goes on to ablate the Au material deposited by previous laser pulses. This results in a non-uniform Au coating. Also shown in Fig. 4 is the coupled effect of moving the work piece with respect to the LIFT deposition.

To make conformal electronic devices, except conducting lines, which were deposited by LIFT, we start with a ceramic substrate (Rodgers ceramic R0 4003) which has been pre-coated over the entire surface with a 5000-Å-thick Au film by e-beam evaporation. The laser is then used to etch away the contact pads for the resistor and the bottom electrode for the capacitor.

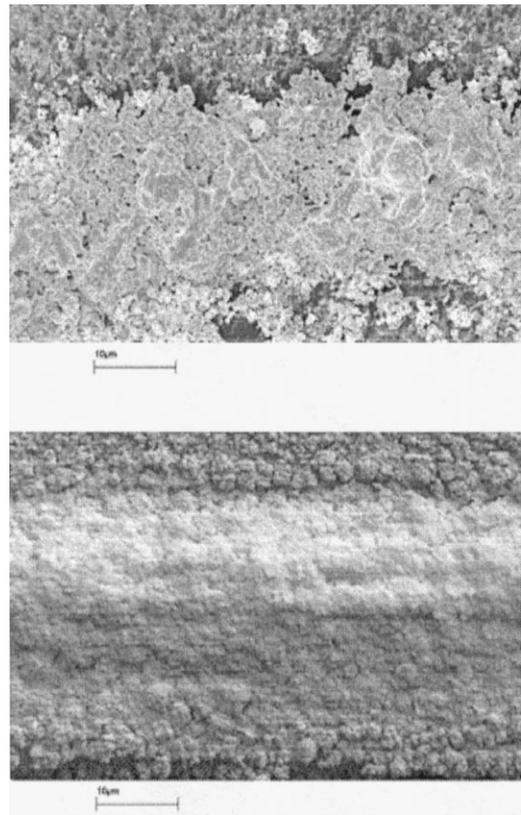


Fig. 4. The effect of varying the fluence and the pulse-to-pulse overlap in the LIFT deposition of Au. The fluence in the upper micrograph was too high and causes subsequent desorption from already deposited layers. In addition, the pulse-to-pulse overlap (i.e., material deposition) did not provide good uniformity. In the lower micrograph, both of these parameters have been optimized.

The Au conducting lines were deposited using LIFT with a 1600-Å-thick Au ribbon with a 100-Å chromium adhesion layer. The ribbon to substrate distance was maintained at 25-μm gap. To reach the desired thickness of 10 μm, 100 laser pulses using a 25-μm-diameter beam spot were required. The pulse-to-pulse overlap was 12.5 μm. After the deposition, the excimer laser was used to etch away the debris that remained to either side of the entire conducting line pattern (see Fig. 5A). The resulting Au linewidth starting from a 25-μm beam spot was 40 μm. The surface roughness of the line reflects largely the surface roughness of the underlying substrate. There is some roughness due to the process

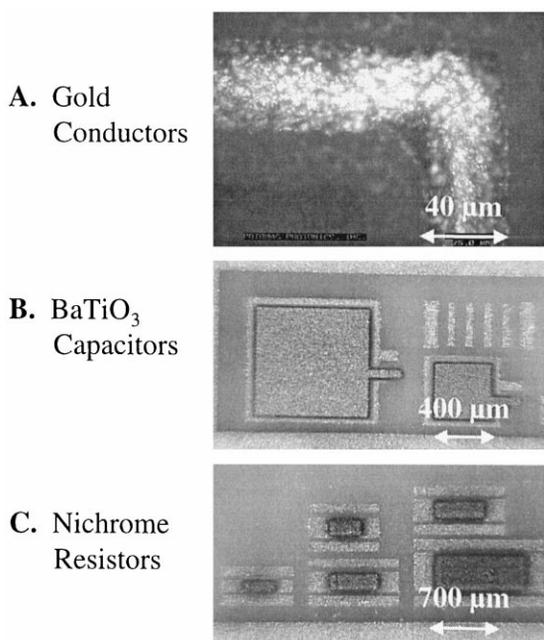


Fig. 5. Examples of mesoscopic circuit elements deposited using the MAPLE DW apparatus shown in Fig. 3: (A) A 40- μm -wide Au line, (B) two BaTiO_3 capacitors, and (C) five coplanar nichrome resistors.

that could be resolved with intermediate laser surface annealing (glazing) and a finer pulse-to-pulse step size. On average, the measured resistivity was more than 10 times bulk Au.

In Fig. 5B, we show the MAPLE DW of two BaTiO_3 capacitors with Au electrodes. The bottom electrode was deposited by e-beam evaporation as described earlier and the top electrode was deposited by LIFT. At 1 MHz, the capacitance was a few pF and the dissipation, after annealing at 200°C, was 0.02. The thickness of the BaTiO_3 was $\sim 15 \mu\text{m}$. At this thickness, the yield of non-shortng capacitors was very high. The ratio of capacitance did not always scale well with geometry presumably due to variations in the deposition process, e.g., non-uniformities in the MAPLE DW ribbons used. The thickness of the capacitor across the entire 0.8-mm length is very uniform. The variations in thickness were due predominately to the surface roughness that originate from the underlying substrate as can be seen from the profilometer trace at the edge of the capacitor.

In Fig. 5C, we show the LIFT of five nickel chromium coplanar resistors. The resistance of these structures was significantly larger than expected from bulk and likely due to a highly defective microstructure. The resistance of these resistors varies as expected with the thickness of the deposited nickel chromium. The values of resistance ranged from 10s of Ω to $\text{k}\Omega$. In addition, the resistance scaled approximately as expected from the geometry (length and width).

3. Conclusion

There are many advantages to MAPLE DW compared to other existing direct write technologies for 3D structure fabrication. These advantages include the ability to do adherent depositions at room temperature and in air and the ability to rapidly change between different materials. The latter is accomplished because MAPLE DW is a dry technique meaning there is no interval of time required for transferring one layer on top of another. The ultimate spatial resolution of the MAPLE DW approach can be as small as ~ 1 or $\sim 3 \mu\text{m}$. The technique is 100% computer controlled, can process multilayers of different materials, is scaleable to multiple sources and gives you accurate thickness control. The MAPLE DW equipment is based on a laser micromachining system so in addition to material deposition, substrate pre-cleaning prior to deposition, in situ annealing and laser trimming can be performed. Also, because the technique is optically based, we can do in situ characterization by techniques such as FTIR, ellipsometry, etc. MAPLE DW is lastly an environmentally friendly direct write technique.

We have demonstrated that by combining some of the major positive advantages of LIFT and MAPLE, that we could produce a novel excimer laser driven direct writing technique termed MAPLE DW. We have also shown that MAPLE DW can fabricate novel nickel–chromium thin film resistors, interconnecting gold conducting lines, and high ϵ multilayer ferroelectric capacitors. In addition, an overview of other important aspects contained in the MAPLE DW approach, e.g., the ability to do in situ laser micromachining, surface pre-treatment and annealing was described.

Acknowledgements

The Office of Naval Research and the DARPA MICE Program supported this work.

References

- [1] M. Emmert-Buck, R.F. Bonner, P.D. Smith, R.F. Chuaqui, Z. Zhuang, S.R. Goldstein, R.A. Weiss, L.A. Liotta, *Science* 274 (1996) 998–1001.
- [2] R.F. Bonner, M. Emmert-Buck, K. Cole, T. Pohida, R. Chuaqui, S. Goldstein, L.A. Liotta, *Science* 275 (1997) 1481–1483.
- [3] D.A. Relman, *Science* 284 (1999) 1308–1310.
- [4] D.B. Chrisey, G.K. Hubler (Eds.), *Pulsed Laser Deposition of Thin Films*, Wiley, New York, NY, 1994.
- [5] Method of producing a coating by matrix assisted pulsed laser evaporation direct write, Navy Case Number 78,117, Patent Issued.
- [6] R.A. McGill, R. Chung, D.B. Chrisey, P.C. Dorsey, P. Matthews, A. Pique, T.E. Mlsna, J.L. Stepnowski, *IEEE Trans. on Ultrasonics, Ferroelectrics, and Frequency Control* 45 (1998) 1370.
- [7] A. Pique, D.B. Chrisey, B.J. Spargo, M.A. Bucaro, R.W. Vachet, J.H. Callahan, R.A. McGill, T.E. Mlsna, *Advances in laser ablation of materials*, MRS Proc. 526 (1998) 421.
- [8] J. Bohandy, B.F. Kim, F.J. Adrian, *J. Appl. Phys.* 60 (1986) 1538–1539.
- [9] J. Bohandy, B.F. Kim, F.J. Adrian, A.N. Jette, *J. Appl. Phys.* 63 (1988) 1158–1162.
- [10] I. Zergioti, S. Mailis, N.A. Vainos, C. Fotakis, S. Chen, C.P. Grigoropoulos, *Appl. Surf. Sci.* 127–129 (1998) 601–605.
- [11] F.J. Adrian, J. Bohandy, B.F. Kim, A.N. Jette, P. Thompson, *J. Vac. Sci. Technol. B* 5 (1987) 1490–1494.
- [12] I. Zergioti, S. Mailis, N.A. Vainos, P. Papakonstantinou, C. Kalpouzos, C.P. Grigoropoulos, C. Fotakis, *Appl. Phys. A* 66 (1998) 579–582.
- [13] H. Esrom, J.-Y. Zhang, U. Kogelschatz, A. Pedraza, *Appl. Surf. Sci.* 86 (1995) 202–207.
- [14] M. Pimenov, G.A. Shafeev, A.A. Smolin, V.I. Konov, B.K. Bodolaga, *Appl. Surf. Sci.* 86 (1995) 208–212.
- [15] Matrix assisted pulsed laser evaporation direct write, Navy Case Number 79,702, Patent Pending.
- [16] D.B. Chrisey, A. Pique, R.C.Y. Auyeung, R.A. McGill, R. Chung, S. Lakeou, P. Wu, J. Fitz-Gerald, H.D. Wu, M. Daignan, *Surface Engineering: Science and Technology I*, in: A. Kumar, Y.-W. Chung, J.J. Moore, J.E. Smugeresky (Eds.), *The Minerals, Metals, and Materials Society*, 1999, pp. 143–154.