Laser processing and printing of multilayer films for inexpensive and flexible microsystems

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Birck Nanotechnology Center

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Outline

Introduction

- Laser carbonization
 - Laser-induced porous carbon
 - Functionalization
- Laser ablation
 - Selective etching of multilayer films
 - CO₂ vs Nd:YAG
- Printed-electronics
 - Health-care
 - Precision agriculture
- Future work











Flexible electronics on arbitrary substrates

Food packaging



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Flexible electronics market : \$20.85 Billion in 2015



- Main *manufacturing and material supplier* companies for flexible and printed electronics.
- *<u>3,000 companies and organization</u>* work in this area and related areas



Materials

- Plastic substrates
 - Thermal budget
 - Chemical restrictions

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PDMS ^(a)	0.360- 1.24	Yes	Yes	Yes	Yes	Yes	-125	72000
Poly(vinyl alcohol) (PVA) ^(b)	49.5±3.2	Yes	Yes	No	Yes	No	85	9.03-4190
Whatman filter paper ^(c)	460-1700	Yes	No	No	Yes	Yes	-	989-8140
PTFE ^(d)	500	Yes	Yes	No	Yes	Yes	130	8.45
polylactide (PLA) ^(e)	1030- 4000	Yes	Yes	No	Yes	No	55-60	200**
PET ^(f)	2500	Yes	No	No	Yes	Yes	85	151
Polyimide ^(g)	3200	Yes	Yes	No	Yes	Yes	>400	417-5040
Parylene ^(h)	4000	Yes	No	No	Yes	Yes	80-100	9.25**









IEEE Review 2014



Fabrication methods

Conventional process



Direct process Transfer process

Low-cost scalable manufacturing





Inkjet printing

Laser-assisted deposition

- a. Environmentally friendly process
- b. Increased production speed
- c. Reduction in material loss
- d. Lower manufacturing costs
- e. Scalable manufacturing



Cleanroom assisted technology



D.H. Kim Adv. Mater. (2008)

- Great performance
- Wide range of applications
- Complex, expensive, and time consuming steps
- Incompatibility with large scale manufacturing



D.H. Kim Science. (2011)

M. Ying Nanotechnology. (2012)



Low-cost and Disposable

Smart packaging



Food-waste

1/3 of food produced in world1.3 billion tonnesWorth US\$990 billion

<u>Sources of food-waste</u> Improper **packaging 'Best before'** date has passed

Healthcare



<u>Chronic wounds</u> 6.5 Million infected in US \$25 billion to treat on an annual basis

Snowballing Threat

Aging population

Increasing numbers of **Obesity and diabetes**

Precision agriculture



Soil fertilizers

40-60% of crops are grown with the use of different fertilizers.

More than **50% synthetic** fertilizers.

<u>Problems of Overusing</u> Root Burn, Environmental Issues

Diminished Plant Health Pests and Diseases

Biology/drug discovery



Antibiotic-resistance **2 Million** infected in US **23,000** people die each year

Drug Development

\$2.6 Billion cost of developing a new drug
145% increase over the past decade



Printed Electronic

- Unique non-contact and mask-less patterning process extensive number of materials in a solution form:
 - Conductive polymers
 - Ionic conductors
 - CNT/graphene
 - Metallic nanoparticles
- Challenges:
 - High sintering temperatures at 200–350°C or required special functionalized substrates.
 - Nanoparticles agglomeration
 - Clogging of the equipment nozzle
 - Viscosity range of 8–15 cP
 - Conductive inks limited to costly noble metals e.g. silver and gold









Laser-Enabled Manufacturing











30W CO₂ Laser Engraver/cutter \$339.99

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Laser material processing



- Monochromatic light through an optical amplification process
- Commercial systems
 - 10.6 µm CO₂ laser (typical powers of 30–150 W) suitable for cutting polymers
 - **1.06 µm Nd:YAG fiber laser** (typical powers of about 40-90 W)
- Required ablation energy densities:
 - 10 to100 J/cm² for metals
 - 0.1 to10 J/cm² for organic materials



Flexible electronics





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Discovery Par

Laser carbonization





- Laser process yields porous carbon
- Maximum conductivity of ~0.02Mhos/sq with 6.75 W and 1.3 m/sec
- Optimal energy density (6200 J/m²)



Laser carbonization

- Smallest features
 - (width \times pitch = 90 μ m \times 120 μm) achievable with our laser system
- Partially oriented carbon flakes
 - \sim 70 nm wide
 - $\sim 2 \,\mu m$ length
- EDX spectra
 - 0.25 keV corresponding to high concentration of carbon material
- Raman spectra
 - G-band lattice stretching in C-C
 - D-band disorder and defects in the graphitic lattice
 - $I_{\rm D}/I_{\rm G}$ (~0.8) to quantify the amount of defects in the graphitic material
 - 2D-band layers of carbon
 - $(I_{2D}/I_G \approx 0.7)$ mostly three carbon layers



EDX spectra

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Transfer to PDMS



Piezoresistive strain sensor







(a)

- Unidirectional sensitivity
- (>20 MΩ) 100% longitudinal strain
- Gauge factor of 20,000 at 100% strain



Finger motion detection



- Sensors where attached to a latex glove using a cyanoacrylate adhesive (Loctite 420)
 - The bending angle of middle phalangeal joint was motion detection with stretchable carbon traces
 - R/Ro \approx 9 for a completely bent joint

Discovery Park

Surface wettability





Carbon and Silver composite



52 $\Omega/sq \rightarrow 0.02 \Omega/sq$



EDX mapping of silver and carbon

Laser Carbonized Polyimide



Ag/Carbonized Polyimide







Electromechanical properties





Wireless pressure sensor (C/Ag composite)





Wireless pressure sensor



Dip in phase for pressures ranging from 0 to 97 kPa.

Frequency decreases linearly with pressures up to 97 kPa with an average sensitivity of -26 kHz/kPa.

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Stretchable carbon-polyaniline composite





500 mg Polyaniline Emeraldine base dissolved in 5 mL of DMF

Structural parameters $r = 1 \text{ mm}, \theta = 120^{\circ}$ $W = 300 \,\mu\text{m} \text{ to } 1.2 \text{ mm}$ $60 \,\mu\text{m}$ trench around the perimeter

Electromechanical characterization



- Raman spectra before and after deposition of PANI
- PANI/C-PI composite after the protonation has an approximately 32 % lower resistivity (0.065 Ω.cm)



- Periodic out-of-plane deformation at the crests
- Micro-cracks proliferate at higher strains
- 300 µm serpentine traces:
 - Stable electrical resistance for elongation up to 100 % (less than 20% change in resistance)
 - 135 % Ultimate elongation

Stretchable pH sensor (C/PANI)



- Chronic wounds pH 7.15 to 8.9
- Susceptible to different infections such as staphylococcus



- Potentiometric pH sensor
 - PANI/C working
 - Ag/AgCl reference electrode
- PANI is the conductive filler, binding material, and pH-sensitive membrane
- Serpentine C/PANI traces serve as both the stretchable interconnect and the pH-sensitive electrodes.
- Solid electrolyte (KCL+Ecoflex)



Stretchable Potentiometric pH sensor



- Potentiometric measurement
- Protonation and de-protonation of PANI
- Linear sensitivity of -53mV/pH with stability

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Laser ablation and selective etching



Similar material

Multilayer film selective laser ablation

- Commercially available low-cost multilayer films
- Reduced cost of production by using readily available films
 - ITO-coated PET
 - Metalized paper
 - Vacuum deposited
 - Laminated





Laser patterning ITO-coated PET









Direct ablation of ITO film

- ITO material absorbs the fiber laser energy (1.06μm) ~103 times higher than PET polymer.
- Absorbed laser energy vaporizes the ITO.
- Significant concern was the color change of the substrate
- Chemical decomposition of the polymer substrate.
- Used for marking PET in industry









Indirect CO₂ laser patterning

Laser ablated area



Transparent pH monitoring system (ITO



- Laser-scrubbed using a CO₂ laser engraver to create isolated transparent electrodes
- Working electrode is prepared by electropolymerization of aniline
 - 0.1M aniline in 1M HCl
- NFC substrate containing the coil/antenna and interconnects
 - Double sided copper PCB



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pH monitoring on wound models

Microfluidic test setup



- 0.5 %w/v agarose gel prepared with pH 5 and 0.01%w/v phenol red
- pH 8 buffer solution was pump at constant flow (0.4ml/min).

- In-vitro wound model with Staphylococcus epidermidis
- Change in pH 6.9 to 8.7 over 10 hours

Metallized films

- Manufacturing process
 - Physical vapor deposition (25 to 500nm Aluminum)
 - Lamination (5 to 20µm Aluminum)
- Substrates
 - Plastic films (polypropylene, nylon, and PET)
 - Paper
- Cost of metal
 - Aluminum 0.99 USD/lbs
 - Copper 2.60U SD/lbs
 - Silver 1,203 USD/lbs
 - Gold 90,290 USD/lbs

Comparison of Metallised PET and aluminium foil

	Moisture (g/m².day)	Oxygen (mL/m².day)	UV light (%transmittance)
PET film, 12.7μm	31	465	91
Metallized PET	0.8	1.2	5
Aluminium foil 6µm	0	0	0

Physical vapor deposition





Lamination





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Metallized paper-Laser ablation

Indirect - CO₂ Laser ablation

- CW wave
- Minimal selectivity
- Color change
- 174mJ/cm² threshold energy for electrical isolation.
- Average decrease of 3.9 mg (~44.3%) in mass



Direct - Nd:YAG Laser ablation

- Pulsed mode
- High selectivity
- Wider optimal setting of laser power and speed
- Minimal weight loss of less than 0.1mg (1.15% of original weight)





Surface analysis



- CO₂ laser ablated samples
 - Destruction within natural microstructure of the paper.
- Nd:YAG laser ablated samples
 - Retention of highly porous fibrillary structure in the paper substrate

Mechanical and Surface wetting analysis





Paper-based humidity and temperature sensor



- Food waste in United States is **30 to 40% of the food supply.**
- Moisture in inappropriate amounts can reduce the shelf life of many foods and drugs.
- Moisture balance is important in achieving optimum wound healing conditions
- Laser ablated metalized paper



Paper-based sensors

Humidity sensors Temperature sensors RTD1 RTD3 $R = R_{ref} \left[1 + \alpha \left(T - T_{ref} \right) \right]$ $C = \varepsilon_r \varepsilon_o A/d$ IDE2 IDE3 IDE1 RTD4 RTD2 Temperature coefficient dielectric constant of the material of the material a starter and a feature STREET, SHOT RTD4 IDE 3 with Nd:YAG laser IDE 3 with Nd:YAG laser Theoretical 180 0.6 A RTD3 - IDE2 with Nd:YAG laser IDE2 with Nd:YAG laser Measurements 150 160 RTD2 10 - IDE1 with Nd:YAG laser - IDE1 with Nd:YAG laser RTD1 Sensitivity(ΔR/ΔT) Capacitance(pF) ଖ ଟି ପ୍ରି ¹⁴⁰ Capacitance(pF) Resistance (80 20 0.0 -20 20 40 60 80 10 20 30 40 50 60 70 80 10 20 30 40 20 40 100 120 0 Temperature(°C) RH(%) RH(%) Resistance (Ω) Range -20 to 80 °C $S = \Delta R / \Delta T = \alpha R_{ref}$ Region II (68-85 %RH) Region I (2-68 %RH) RTD1 \rightarrow 0.102 $\Omega/^{\circ}C$ Capillary condensation effect IDE1 \rightarrow 2.5 fF/%RH RTD2 \rightarrow 0.186 $\Omega/^{\circ}C$ $IDE2 \rightarrow 45.7 \text{fF}/\% \text{RH}$ Maximum change at 85% RH RTD3 \rightarrow 0.29 $\Omega/^{\circ}C$ $IDE1 \rightarrow 471\%$ IDE3 → 83.2 fF/%RH IDE2 → 1740% RTD4 \rightarrow 0.451 $\Omega/^{\circ}C$ IDE3 → 1804%

R. Rahimi, et al. ACS applied materials (2018)



Laser ablating laminated AI foil

• Aluminum foil

PARCHMENT SIDE

PAN LINING PAPER

Revnolds Wrap

FOIL SIDE

- Thickness \rightarrow 10 μ m
- Nd:YAG laser abation
- Parchment paper substrate
 - Thickness \rightarrow 67 μ m
- High electrical conductivity
 - Inductors and Antennas



Laser welding conductive layers





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XPS and SEM Surface analysis Before After laser ablation



- Complete removal of conductive Al metal
- Al₂O₃ NP on laser ablated surface



- 140 µm electrode width
- 180 µm spacing



Wireless humidity sensor



Intelligent packaging

- Ultra low-cost of manufacturing
- Chipless wireless monitoring

Coffee package filled with N₂ gas

- Laminated polyethylene bag
- 3MHz drift with defected package
- Less than 0.2MHz change with well sealed package



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Chronic Wound Therapy

Current wound dressings

Smart wound dressing approach



- Qualitative assessment of the wound with require extensive professional attention
- Treatments: moisture control and antibiotics.

- Chemical (pH, O₂, biomarkers)
- Physical (moisture, temperature, strain, blood flow)
- Oxygen
- Antibiotics
- Growth factor
- Electromechanical stimulation

Patch with pH sensing and drug delivery





phase



pH Sensor and Drug delivery



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Oxygen in Wound Healing





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WESTERN MICHIGAN

- Impaired vasculature susceptible to tissue hypoxia.
- 5 to 20 mm Hg in chronic wounds
- 30 to 50 mm Hg in normal tissue
- Oxygen is critical element for sustaining all phases of wound healing



SCHOOL OF MEDICINE

INDIANA UNIVERSITY



NEXTELEX

Substrate and interface films

Parchment paper substrate

Flexible

- Inexpensive
- Available in rolls (for R2R) Gas permeable



G. Chitnis et al. *Lab Chip*, 2011, 11, 61–5.



Generation via catalysis



Sensing via phosphorescence

Ru(dpp)₃Cl₂



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Unit cell and *in-vivo* studies

- Number of Ru layers = 1
- Number of $KMnO_4$ layers = 3
- Number of unit cell patches per sheet = 30



Printed unit cell array





Mouse (diabetic) with patch and 14 day O_2 treatment vs. Integra alone

Patches on wounds



Wound area calculations vs. time







Screen printed pH sensor array on naner



- 4-10 pH with sensitivity of -51 mV/pH
- Response time 24s for the for pH 6–8



Carbon

Polyethylene/paper

Ag/AgCI

Polyethylene/paper



Moisture sensor for wound dressing





- Moist wounds heal 2-3 times faster
- Wounds that are too moist can become macerated, which can lead to further skin breakdown.





- Non-contact Capacitive moisture measurement
- Wireless low-power Bluetooth interface





Smarter Agriculture

- Accurate measurement (such as N, P and K)
 - Adjust fertilizer application rates
 - Improve agricultural production
 - Excessive use of fertilizers causes contamination (groundwater)
- Real-time, in-field and nondestructive measurement

Reduce operational expense
 Increase testing throughput















Printed silver electrode



ISE Working electrode







Printed electrodes

Strip coating membranes



Roll-to-roll fabricated Nitrate Sensors





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• Future work

- 1) Textile-Based Wearable Electronics
- 2) Smart Functional and Biodegradable Films
- 3) Scalable manufacturing of hybrid systems











- Natural feeling and Breathable
- Functional materials:
 - Threads, Micro-tubes, fiber optics, inks and therapeutics.
- Screen printing and Embroidery
- Monitoring
 - EKG, Pressure ulcers, Gesture recognition
 - Aortic waveform, Tissue oxygen
 - Cystic fibrosis, Pneumothorax, Pulmonary blood flow (Perfusion)







Embroidery, weaving and screen printing



Electrical impedance tomography



②Smart Functional and Biodegradable Films



Electro-spray nanofibers



Scale-up Laser processing

EASTM/



Filters/Energy storage

- Water purification
- Energy storage (e.g. Super capacitors, batteries)
- Food packaging with Nano materials
- Biodegradable films and Sensors
- Physiologically relevant films for tissue engineering and drug discovery
- Non-woven dressing with functional nano materials and hydrogels (e.g. AgNP, ZnO)







Hydrogel Electronics

Biodegradable Electronics!

③Scalable manufacturing of hybrid systems

Scale-up Laser processing (LasX)



Drug delivery and pharm



Micro-fluidics /lab-on-chip

- Scale-up processing techniques with roll-to-roll laser system (LasX)
- Identifying Scale-up challenges
- Inexpensive Nano carbon-based Biosensors
- Hybrid electronics for food/therapeutics packaging
- Combat the spreading of the counterfeiting of drugs





Smart food/drug packaging



Soil microbial activities



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ichael and kay Birck













Thank you for your attention! Questions?