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SUBMICROMETER-SCALE ALL-SOFT ELECTRONICS BASED ON LIQUID METAL

Min-gu Kim, Devin K. Brown, and Oliver Brand
School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA, USA
Institute for Electronics and Nanotechnology, Georgia Institute of Technology, Atlanta, GA, USA

ABSTRACT

This paper presents a novel fabrication technique to create submicrometer-scale liquid metal (eutectic gallium-indium alloy, EGaIn) thin-film patterns for all-soft electronic devices. The proposed hybrid lithography process combines electron-beam lithography with soft lithography and enables high resolution and high density all-soft electronic passive components and microelectrode arrays. For the first time, submicrometer-scale EGaIn thin film patterning with feature sizes as small as 375 nm is demonstrated. Thanks to the intrinsic softness of EGaIn, the fabricated devices can endure mechanical strain >30%, while maintaining electrical functionality.

KEYWORDS

All-soft electronics, eutectic gallium-indium alloy, liquid metal, hybrid lithography, submicron resolution

INTRODUCTION

Soft electronic materials with associated manufacturing technologies [1-2] have enabled soft electronic devices for a variety of wearable sensing applications [3-5]. In this regard, the use of intrinsically soft, liquid-phase conductors opens the path for all-soft and highly deformable electronic devices without the use of rigid electronic components [6]. Among possible conductive liquid candidates, gallium-based liquid metal (eutectic gallium-indium alloy, EGaIn) is of particular interest because of its low melting temperature (<15 °C) and favorable electrical (= 3.4×10^6 S/m) properties [6, 7]. Also, thanks to the formation of a thin oxide layer (≈ 1-3 nm) on the EGaIn surface under atmospheric oxygen level, EGaIn structures maintain their mechanical shape on soft elastomeric substrates [6-8]. The moldable characteristics of EGaIn have enabled a range of patterning methods based on lithography-assisted fabrication [9-12], fluid injection [13, 14], as well as additive [15] and subtractive [16] processes (Figure 1). However, creating high-resolution (<2 µm) and size-scalable EGaIn thin-film patterns remains challenging [17, 18]. In particular, while micrometer-scale EGaIn thin-film patterning based on soft lithography was demonstrated [9, 19], scaling this process down to submicron features is difficult because of the high surface tension (= 632 mN/m) of EGaIn.

This paper presents a novel fabrication technique to create submicrometer-scale all-soft electronic devices based on EGaIn by combining electron-beam lithography (EBL) for micro/nanostructure fabrication and soft lithography for EGaIn stamping. The proposed hybrid lithography process enables high resolution and high density all-soft electronic passive components and microelectrode arrays. For the first time, submicrometer-scale EGaIn thin-film patterning with feature sizes as small as 375 nm is demonstrated.

HYBRID LITHOGRAPHY

Fabrication Process

Figure 2(a) shows the schematic illustration of the investigated hybrid lithography process by combining EBL and soft lithography for submicrometer-scale EGaIn thin-film patterning. The process starts with spin-coating a water-soluble sacrificial layer (poly(acrylic acid), PAA) and depositing a parylene-C film using a chemical vapor deposition (CVD) process on top of a Si wafer (Figure 2(a)-i). The parylene-C film is used as a barrier layer to protect the underlying PAA layer during the following EGaIn patterning and during the release of the fabricated soft electronic devices from the Si wafer after the soft material encapsulation process. For nano/microstructure fabrication, EBL was utilized to pattern a spin-coated poly(methylmethacrylate) (PMMA) film with a thickness of 1 µm. Alternatively, other lithography techniques able to pattern submicron features can be considered for this step. To enhance adhesion and uniformity of EGaIn on the parylene-C-coated substrate, a biphasic structure was adopted [20]. A thin Ti/Au layer (5nm/30nm in thickness) was deposited using an electron-beam evaporator on the patterned nano/microstructure to provide strong adhesion and uniform wetting during the EGaIn stamping process. In the next step, a flat PDMS stamp wet with EGaIn was gently pressed 2-3 times onto the Au-coated PMMA nano/micropatterns to transfer a thin EGaIn film. Thanks to the hydrophilic nature of Au, the stamped EGaIn was uniformly spread on the Au thin film and filled the concave nano/micropatterns with EGaIn up to the designed PMMA thickness. The stamped EGaIn on Au was then patterned using a PMMA lift-off process with acetone (Figure 2(a)-ii). Finally, the remaining EGaIn patterns were encapsulated with a soft elastomer (e.g. poly(dimethylsiloxane), PDMS), and the fabricated soft electronic devices were released by submerging the substrate into water. After etching the palylene-C layer using reactive-ion etching (RIE) in an oxygen plasma, the soft electronic devices were encapsulated with another soft elastomer for backside sealing (Figure 2(a)-iii).

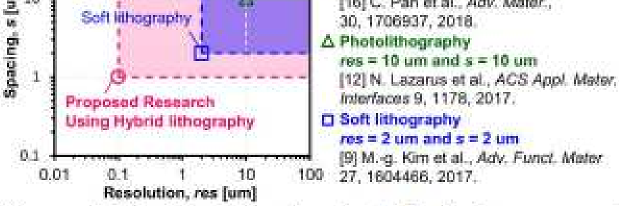

Figure. 1: Liquid metal patterning technologies: comparison of resolution (line width) and line spacing of conventional liquid metal patterning techniques as well as proposed hybrid lithography for submicron resolution.

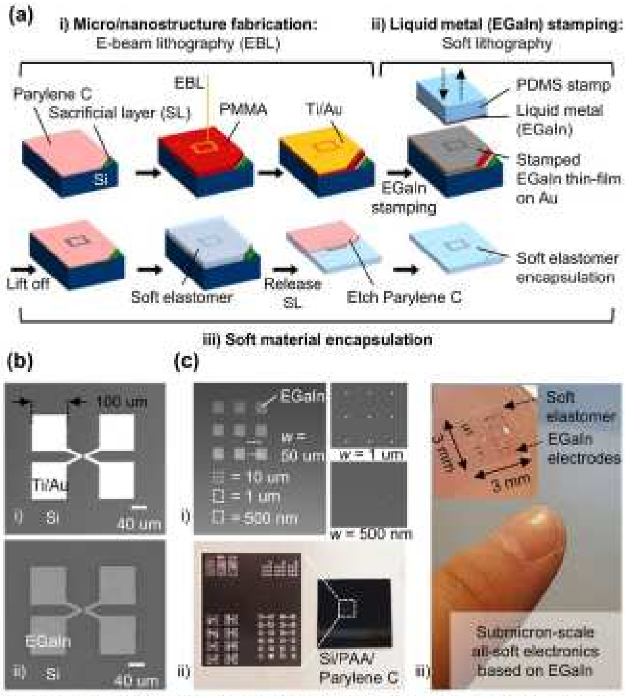

Figure 2: (a) Fabrication process for submicron-scale liquid metal (EGaIn) patterning by combining electron-beam lithography (EBL) and soft lithography; (b) Patterned i) Au and ii) EGaIn on Au thin film; (c) i) Patterned EGaIn dot array with dot dimensions ranging from 50 µm down to 500 nm and ii)-iii) soft material encapsulation and release process of the patterned EGaIn structures.

The stamped EGaIn on Au thin film showed uniform wetting characteristics and could be successfully patterned using the PMMA lift-off process without structural deformation. Figure 2(b) shows the i) patterned Au thin film after the lift-off process without EGaIn stamping and ii) the stamped and patterned EGaIn on the Au thin film, demonstrating EGaIn patterning capability using the PMMA nano/microstructures patterned using EBL. Figure 2(c) shows the soft material encapsulation and release process of patterned EGaIn structures. Figure 2(c)-i shows a patterned EGaIn dot array with dot dimensions ranging from 50 µm down to 500 nm in diameter. Similarly, EGaIn electrodes were patterned on the parylene-C layer, then encapsulated with PDMS and released from the Si wafer. Finally, Figure 2(c)-iii shows a fabricated submicron-scale, all-soft electronic device based on EGaIn and PDMS attached to the tip of a fingernail. The thickness of the soft elastomer is adjustable by selecting a proper target spin speed. The tested PDMS thickness was ≈ 50 µm, providing conformal wrapping capability on non-flat surfaces for skin-mountable, bioelectronics applications.

Characterization of Patterned EGaIn Structures

EGaIn lines with different widths, fabricated using the hybrid lithography technique with a 1 µm-thick PMMA layer, were investigated to highlight the uniform and sharp-edge patterning capability. Figure 3(a) shows SEM images of patterned EGaIn lines with line widths from 500 nm to 10 µm, as well as a 3D profile of a 500 nm wide line. Thanks to the uniform and strong adhesion between Au and EGaIn, the stamped EGaIn film uniformly spread and filled the concave nano/microstructures. When the remaining PMMA film is removed during the lift-off process, any EGaIn on the top of it is lifted-off and washed away together with the PMMA layer. After the lift-off process, EGaIn remains only on top of the Au regions that were in direct contact with the underlying parylene-C layer (i.e., the areas opened during the PMMA development process). The patterned EGaIn lines show sharp edges without EGaIn aggregation or loss during the lift-off process, as shown in the 3D profile of the patterned 500 nm line (Figure 3(a)). The measured EGaIn thickness of ≈ 918 nm is slightly smaller than the PMMA thickness, which was 1 µm in this study. Because of the use of a soft and deformable PDMS stamp for EGaIn transfer, the stamped EGaIn can be uniformly spread on the Au thin film and does not cover all PMMA edges, which makes the lift-off process possible. This result indicates that the EGaIn thickness can be controlled by controlling the thickness of the PMMA film.

Figure 3(b) shows the measured cross-sectional area of the patterned EGaIn structures, measured using profilometry, as a function of the measured line width. The measured cross-sectional area of patterned EGaIn matched well with the designed value, which also confirmed that the EGaIn was uniformly patterned without EGaIn aggregation or loss during the lift-off process. As a result, the measured resistance of patterned lines matched well with the calculation. Figure 3(c) shows the measured resistance of the EGaIn lines as a function of the patterned EGaIn line width for lines with 200 µm length. The measured resistance scaled linearly with 1/width with <12% deviation compared to calculated values based on the bulk resistivity of EGaIn, indicating that the electrical properties of EGaIn dominate the electrical characteristics of the patterned EGaIn structures even in the presence of the Ti/Au adhesion layer [16].

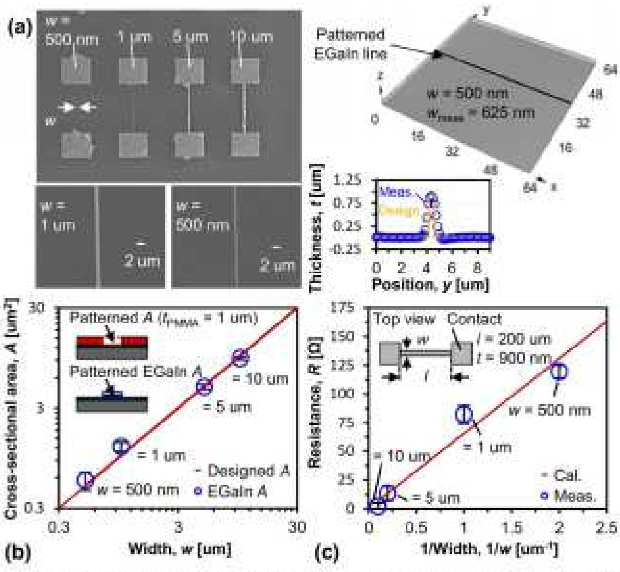

Figure 3: (a) SEM images of patterned EGaIn lines with widths from 500 nm to 10 µm with a measured 3D profile of 500 nm line; Calculated and measured (b) cross-sectional area and (c) resistance of patterned EGaIn lines as a function of designed line width.

Resolution and Spacing of Hybrid Lithography

Figure 4(a)-(b) show fabricated EGaIn test patterns to evaluate the lateral resolution and achievable line spacing of the hybrid lithography technique. With 1 µm PMMA thickness, designed line widths down to 500 nm with 1 µm spacing exhibit ≈ 900 nm EGaIn thickness. However, in the case of 100 nm designed line width, the patterned EGaIn line collapsed downward after the lift-off process, resulting in a 375 nm line width with 350 nm thickness. Because the measured cross-sectional area of the patterned EGaIn line matched well with the designed value, it is concluded that the high aspect ratio (AR) >10 of the initial design is responsible for this structural instability, while the amount of EGaIn transferred is as designed. From this observation, the aspect ratio is considered one of the most important factors determining the structural stability of the patterned EGaIn lines and further scaling down to 100 nm can likely be achieved by decreasing the PMMA thickness so that AR <2. In this study, with the 1 µm PMMA thickness, submicrometer-scale EGaIn features as small as 375 nm and with a minimal spacing of 1 µm were achieved, resulting in the highest resolution EGaIn patterning technique to date (see Figure 1).

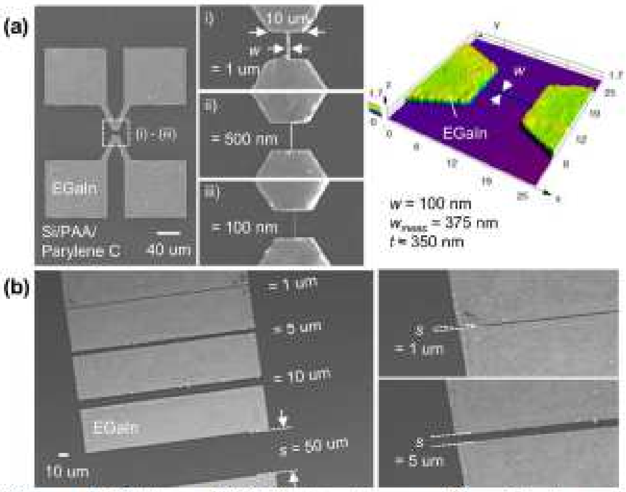

Figure 4: Patterned EGaIn structures on Si wafer to evaluate (a) lateral resolution with i) 1 µm, ii) 500 nm and iii) 100 nm line width and (b) 1 µm to 50 µm line spacing.

HIGH-RESOLUTION AND HIGH-DENSITY SOFT ELECTRONICS

To highlight the high-resolution patterning capability, all-soft passive electronic devices, such as soft resistive sensor arrays (Figure 5(a)) and soft interdigitated capacitors (Figure 5(b)), were demonstrated. Figure 5(a) shows high-resolution EGaIn-based soft resistors with i) 500 nm and ii) 1 µm line width. A soft resistive sensor array was patterned on a parylene-C layer (Figure 5(a)-iii), then encapsulated with soft elastomers and released from the Si wafer. Soft material encapsulation with PDMS ($E \approx$ 600-800 kPa) was demonstrated to provide an all-soft, resistive sensing platform, as shown in Figure 5(a)-iv. Considering the size of a single biological cell, the demonstrated submicrometer-scale EGaIn patterning capability, which is compatible with soft, bio-compatible materials, may enable novel, all-soft biological sensing platforms to investigate cell mechanobiology and provide critical information for disease, management, and therapy. Figure 5(b) shows an example of a high-resolution, soft interdigitated capacitor. Interdigitated capacitors with 5 µm line width and line spacing and up to 90 interdigitated electrodes (IDEs) were demonstrated by utilizing the hybrid lithography technique. Figure 5(b)-ii shows the measured capacitance as a function of frequency up to 1MHz for capacitors with different number of IDEs. The measured capacitance with 10 IDEs was 0.2 pF and linearly increased to 1.1 pF for the capacitor with 90 IDEs. Finite element simulations to determine the capacitance of the interdigitated capacitors were conducted using COMSOL Multiphysics (COMSOL Inc., Burlington MA) using an electrostatic physics model. Thereby, the measured capacitance as a function of the number of IDEs agrees well with the simulated values with < 15% deviation.

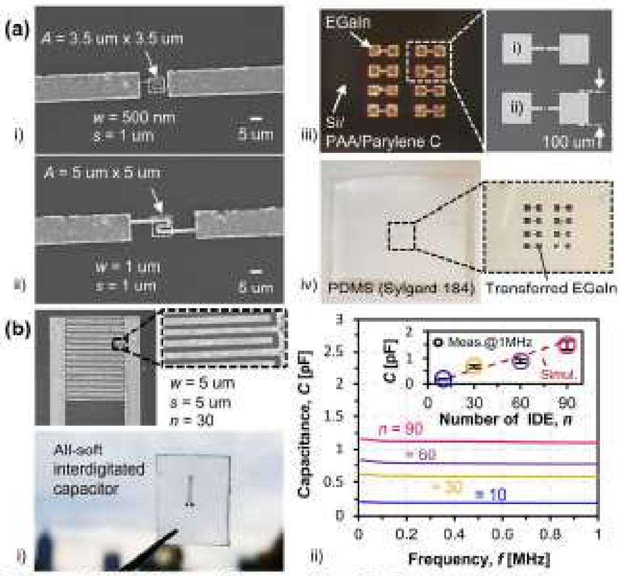

Figure 5: High-resolution all-soft electronic components based on EGaIn: (a) all-soft resistive sensors with i) 500 nm and ii) 1 µm line width, iii) all-soft resistive sensor array on a silicon wafer, and iv) encapsulation with soft elastomer and release from the silicon wafer; (b) i) Fabricated all-soft interdigitated capacitors with 5 µm line width and spacing and ii) measured capacitance as a function of frequency and simulated and measured capacitance as a function of the number of IDE.

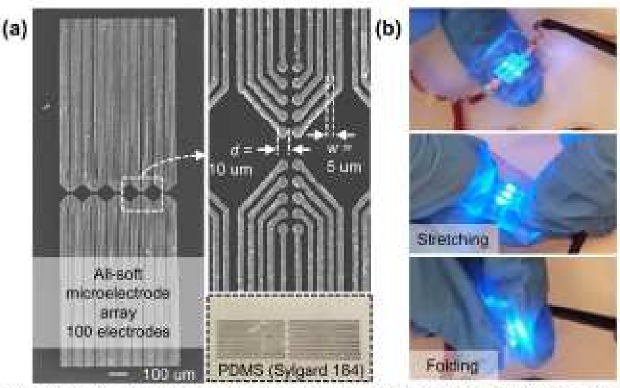

Figure 6: (a) All-soft microelectrode array (sMEA) with 100 electrodes, each 10 µm in diameter with 5 µm wide interconnections; (b) Fabricated soft circuit with embedded LEDs under mechanical stretching (≈ 30%) and folding deformation.

In addition, an all-soft microelectrode array (sMEA) with 100 sensing electrodes, each 10 µm in diameter with 5 µm wide interconnections, was demonstrated to highlight the high-density fabrication capability, as shown in Figure 6(a). Finally, to demonstrate the flexibility and stretchability of the fabricated soft devices, commercial LEDs were integrated with a soft circuit and subjected to stretching and folding deformation (Figure 6(b)). Thanks to the intrinsic softness of EGaIn, the fabricated devices can endure mechanical strain > 30% as well as folding deformations while maintaining electrical functionality.

CONCLUSION

This paper presents a novel fabrication technique to create submicrometer-scale EGaIn patterns on soft polymeric substrates for all-soft electronic devices. The hybrid lithography process combines electron beam lithography with soft lithography and enables high resolution and high density all-soft electronic passive components and microelectrode arrays. For the first time, we demonstrated submicrometer-scale EGaIn thin-film patterning with feature sizes as small as 375 nm using the presented hybrid lithography process. The fabricated soft electronic devices, such as microelectrode arrays and resistor arrays, can endure mechanical deformation, while maintaining electrical functionality. Considering the high-resolution and high-density EGaIn patterning capabilities, the proposed fabrication technique shows potential for soft and integrated biological sensing applications.

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CONTACT

M. Kim, e-mail: mgk@gatech.edu
D. K. Brown, e-mail: devin.brown@ien.gatech.edu
O. Brand, e-mail: oliver.brand@ece.gatech.edu