Geckoprinting: assembly of microelectronic devices on unconventional surfaces by transfer printing with isolated gecko setal arrays

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Developing electronics in unconventional forms provides opportunities to expand the use of electronics in diverse applications including bio-integrated or implanted electronics. One of the key challenges lies in integrating semiconductor microdevices onto unconventional substrates without glue, high pressure or temperature that may cause damage to microdevices, substrates or interfaces. This paper describes a solution based on natural gecko setal arrays that switch adhesion mechanically on and off, enabling pick and place manipulation of thin microscale semiconductor materials onto diverse surfaces including plants and insects whose surfaces are usually rough and irregular. A demonstration of functional ‘geckoprinted’ microelectronic devices provides a proof of concept of our results in practical applications.

1. Introduction

Recent research in unconventional/flexible electronics and packaging reveals the possibility of electronic devices for use in diverse applications such as flexible displays [1–3], curvilinear imaging devices [4–6] or bio-integrated systems [7–9] that overcome the mechanical constraints—rigidity, planarity, brittleness and excess weight—present in conventional high-performance inorganic electronic devices [10–15]. A critical step in manufacturing these unconventional devices is to transfer the ultrathin, microscopic electronic devices, fabricated in releasable form on the original substrates, onto the unconventional target substrates [3,16–17]. Many of the methods for integrating the electronic devices onto the target substrates require glue, high pressure or high temperature [18–19], and these processing conditions can negatively impact the thermal or electrical resistance and/or induce mechanical or electrical damage in the devices and packaging.

Several promising strategies for avoiding these adverse effects when transfer printing the microelectronic devices involve the use of artificial controllable adhesives that rely on either the elastic recovery of soft elastomers [20] or on the direction-dependent mechanical behaviour of micropillars [20–22]. These two types of controllable adhesives were inspired by aphids and geckos, respectively. Although the natural adhesives, especially the gecko type, have motivated engineers to develop artificial smart/controllable adhesives [23–43] using relatively simple structures in diverse applications including climbing robots [44], bio-medical systems [45] and many others, none of these materials offers the same combination of remarkable properties that the natural gecko adhesive does [46–48]. So far, no report exists in which the sophisticated natural adhesives were used for any practical applications.

Here, we demonstrate the deterministic assembly of microscopic inorganic semiconductor materials using natural gecko adhesives harvested from the
toes of geckos as a tool. We describe the transfer printing of inorganic semiconductor materials without using glue, high pressures or high temperatures, along with instructions for the preparation of the natural gecko adhesives for use in this manner. Cost effectiveness in harvesting natural gecko adhesives is an important consideration for industrial use of the techniques. We also illustrate, using experimental measurements of the forces acting on the semiconductor materials, the mechanics of this transfer-printing technique. Finally, we explore the capabilities of these methods by providing demonstrations on the unconventional biological surfaces of plants or insects, by reporting on the durability of the natural gecko adhesives and by demonstrating their use in fabricating functional microelectronic devices.

2. Material and methods

2.1. Preparing setal stamps

We harvested the natural setal arrays without harm from the toes of live geckos using an x-acto knife with a single edge blade under a stereo microscope (Olympus SZ-7). After cleaning the glass plate (125 × 125 mm) with acetone and dropping a small amount of glue (Loctite 401 Flex Gel, Henkel Corporation) on the plate with an x-acto knife, we brought the setal array in contact with the glass plate. We waited for 90 min to dry the glue at room temperature before using the setal stamp. We can harvest 6 million setae from a single gecko that costs about US$15 per animal. Earlier studies indicate that each seta is durable enough to last for over 30,000 cycles and it does not degrade over at least 2 years [49]. Peeling the setal arrays from the toes does not hurt the live geckos at all and geckos regenerate new setae at the next molt in one or two months.

2.2. Preparing microscopic Si plates

We prepared suspended microscopic Si plates by successively forming the plates, sacrificial layers and breakable anchors on a silicon on insulator (SOI) wafer. The fabrication process began with the photolithographic masking of doughnut shapes (outer radius approx. 75 μm, inner radius approx. 20 μm) after cleaning the wafer with piranha solution (mixture of sulfuric acid and phosphoric acid, 3:1) for 30 min. Deep reactive ion etching (DRIE, Alcatel AMS200) removed the exposed Si layer (thickness approx. 10 μm), forming doughnut-shaped micro Si plates on the layer of insulator, i.e. SiO2. Another photographic patterning formed masks (outer radius approx. 95 μm), larger than the micro Si plates. Removing the exposed SiO2 layer using wet chemical etching in a buffered oxide etch solution for 10 min formed the larger sacrificial layers under the Si plates. We finally formed four anchors (size approx. 12 × 60 μm) for each micro Si plate with a photosist (PR, AZ2124). Although the anchors hold the micro Si plates even after removing the sacrificial layer in hydrofluoric (HF) acid for 75 min, they are easily broken when picking up the micro Si plates with the setal stamps. For further details, see the electronic supplementary material.

2.3. Apparatus for transfer printing

We built a manual transfer-printing apparatus consisting of a four-axis microstage, setal stamp holder, multi-axis force sensor and stereo microscope. The target and original substrates are placed on the four-axis microstage, which provides three-dimensional translation and one-dimensional rotation for positioning the Si plates relative to the setal stamp. The multi-axis force sensor (ATI technology) is mountable on the four-axis microstage when force measurement is required. The custom-built setal stamp holder has a through hole (size approx. 25 × 25 mm) at the centre to provide microscopic view of the setal stamp and Si plates with the microscope installed over the setal stamp holder. A vacuum chuck and two-axis tilt stage in the setal stamp holder fixes the setal stamp in place and provides parallel alignment with the substrates on the four-axis microstage. The set-up, including the force sensor and microscope, enables real-time monitoring of forces and microscopic visual inspection during the transfer-printing procedure.

2.4. Transfer-printing micro Si plates

After parallelization using the tilting stage, we placed the microscopic Si plates anchored on the original substrate on the four-axis microstage. After positioning the Si plate under the setal stamp, we moved the Si plate upward to make contact with the setal stamp. Then, we dragged the setal stamp horizontally on the Si plate (about 100 μm) in the proximal direction. Dragging 100 μm is enough to engage adhesion, because a single seta reaches its maximum adhesion with additional 20 μm displacement on the surface after fully straightening the seta with 20 μm displacement [48]. Retracting the setal stamp while dragging away from the microstage broke the anchors and picked up the Si plate. We dragged the setal stamp during retraction to make the retraction angle shallow because natural gecko adhesives maintain adhesion when retraction angle is less than 30° from substrates [46–48]. We replaced the original substrate with the various receiver substrates to transfer-print the Si plate. In the same manner as for picking up, we brought the Si plate, which the setal stamp was holding, into contact with one of the receiver substrates and dragged the setal stamp in the opposite direction to the attachment direction (about 100 μm) to release adhesion. Finally, retracting the setal stamp from the receiver substrate completed the transfer-printing process. We monitored the forces in real time and saved the collected data using a DAQ board (National Instrument, USB-6341) for post-processing.

2.5. Preparing 2J solar microcells

The 2J solar microcells were fabricated by sequential chemical wet etching of the tandem structures consisting of GaInP (bandgap approx. 1.8 eV) and GaAs (bandgap approx. 1.4 eV) on a GaAs wafer with hydrochloric acid (HCl, 35%, OCI Company Ltd) and phosphoric acid (H3PO4, 85%, OCI Company Ltd), as described elsewhere [50]. Electron beam evaporation of Ti (20 nm) and Au (60 nm) formed top and bottom contacts on the n and p regions, respectively. For the vertical-type solar microcells, we formed the p contact on the backside of the microcells after flipping the microcells with a smooth PDMS surface. A gentle sprinkling of acetone from a squeeze bottle released the solar microcells on the backside of a Si wafer, and the cells were then ready to be picked up with the setal stamp. We characterized the electrical performance of the solar microcells under 1 sun conditions using a full spectrum solar simulator (Sol3A Class AAA solar simulator, Oriel Instruments) and a DC sourcemeter (2400, Keithley).

3. Results and discussion

One of the remarkable capabilities of a tokay gecko (Gekko gecko; figure 1a), is the ability to hang suspended on a smooth glass surface. The legs pull together towards the centre of the animal, establishing the shear forces on the toes required to generate adhesive forces. The hanging weight beside the gecko in the image indicates the direction of gravity. Figure 1b shows the underside of the gecko’s toes, bearing leaf-like lamellae, each covered with hierarchical micro and nanoscale hairs
called setae [47], attached to an optically transparent glass surface. Macroscale manipulation such as uncurling and curling of the toes switches adhesion on and off, respectively. Uncurling the toes makes contact and engages adhesion. Curling mechanism of toes when the gecko detaches its adhesive toes from the glass surface.

As it is challenging to make hierarchical structures similar to those of the natural setal arrays of geckos, we harvested the toes when the gecko detaches its adhesive toes from the glass surface.

It is challenging to make hierarchical structures similar to those of the natural setal arrays of geckos, we harvested natural setal arrays from the toes of geckos, speculating that they have a potential for use in the micro-assembly of electronic devices onto unconventional (e.g. biological) surfaces without liquid adhesives, high pressures or high temperatures. Gluing is associated with high electrical or thermal resistance, and high pressures or temperatures limit the type of target substrate or change the electrical properties of the microelectronic devices. Figure 1d shows an optical microscope image of the setal array glued on transparent glass permanently with cyanoacrylate superglue (Locktite 401 flex gel). The inset shows a magnified scanning electron microscopy (SEM) image of the setal array. We call the prepared setal array a 'setal stamp' because we employ the array to pick up and place microscopic Si plates for transfer printing onto various surfaces. The size of the array is usually around 0.35 \times 0.40 \text{ mm}. Further details are given in the Material and methods.

With the setal stamps, we conducted transfer printing of microscale silicon devices with the manipulation, similar to geckos when attaching and detaching their toes to surfaces. Figure 2 illustrates the transfer-printing procedure using the setal stamp for microscopic silicon plates prepared on SOI wafers by simulating the uncurling and curling mechanism. Silicon is the most used semiconductor material in electronic devices, and transfer printing Si plates is one of key technologies in integrating high-performance inorganic electronic devices onto unconventional substrates. The micro Si plates (outer radius approx. 75 \mu m, inner radius approx. 20 \mu m and thickness approx. 10 \mu m) prepared for transfer printing using the setal stamp are in a raised configuration supported by four breakable PR anchors (size approx. 12 \times 60 \mu m, thickness approx. 1.8 \mu m). Wet chemical etching removes the buried insulator layer (SiO₂, thickness approx. 1 \mu m) in HF acid for 75 min after vertical etching through the top Si and insulator layer with DRIE and wet chemical etching, respectively, to define lateral dimensions of the micro Si plates and the underlying insulator in doughnut shapes. (See Material and methods for details.) Although soft elastomeric stamps (e.g. polydimethylsiloxane or PDMS) can pick up these types of Si plates easily, transfer printing the Si plates onto non-adhesive surfaces is challenging because adhesion between the PDMS stamp and thin micro Si plate is relatively high.

Transfer printing using natural gecko adhesives begins by bringing the Si plate and setal stamp into contact, as shown in figure 2a, after aligning and positioning them on the four-axis microstage and the setal stamp holder. See the electronic supplementary material for details on this set-up. Figure 2b illustrates the attachment step, dragging the setal stamp horizontally in the proximal direction to engage adhesion. Retracting the stamp vertically during dragging picks up the Si plate, as illustrated in figure 2c. After replacing the original substrate with a target receiver substrate, the setal stamp holding the Si plate is brought into contact with the receiver substrate. The stamp is then dragged horizontally in the distal direction, in the opposite direction to that used to engage the array; this minimizes the adhesion between the setal stamp and micro Si plate, as illustrated in figures 2d,e. Retracting the setal stamp in this configuration leaves the Si plate in place, completing the transfer printing process, as shown in figure 2f. Figure 2g–h shows SEM images of the Si plate temporarily anchored to the original substrate, and the setal stamp after picking up the Si plate from the original substrate. Figure 2i shows the micro Si plate after completion of the transfer onto a receiver substrate, silicon in this case.

Reliable transfer printing of the thin microscale Si plates is attributed to the controllable adhesive forces of the setal stamps. Figure 3 shows the adhesive forces at the interfaces of the micro Si plates, measured separately for each interface on the custom-built measurement apparatus consisting of a multi-axis force sensor, four-axis microstage, setal stamp holder and stereomicroscope. (See the Material and methods for details about the apparatus.) We conducted separate measurements to compare the forces at the interface between the Si plate and setal stamp \( F_{(N\text{-setae}, \text{proximal})} \), and the interface between the Si plate and anchors \( F_{(N, \text{proximal})} \), and the interface between the Si plate and anchors \( F_{(N, \text{proximal})} \) during the approach–engage–retract procedure as shown in figure 3a,b. We used the superscripts ‘N’ and ‘S’ to note normal and shear forces acting on the Si plate, and ‘proximal’ and ‘distal’ to note the direction of horizontal dragging the setal stamp with respect to the Si plate,
respectively. Figure 3c illustrates the configuration of the force measurement between the Si plate and setal stamp during the approach–engage–retract procedure on the Si plate whose sacrificial layer is not removed. Delamination occurs between the Si plate and setae. Because the Si plate (contact area approx. 0.109 mm²) is larger than the anchored Si plate (contact area approx. 0.016 mm²), we scaled the force F_{N, proximal, Si–setae} down proportionally (0.016/0.109 = 0.15) for comparison with the force F_{N, proximal, Si–anchor}. The maximum normal adhesive force is 3.24 mN as indicated by the black solid line in figure 3c. Figure 3b illustrates the measurement of the force between the Si plate and anchors (F_{N, proximal, Si–anchor}) during the approach–engage–retract procedure on the anchored Si plate whose sacrificial layer is removed. Breakage occurs between the Si plate and anchors. The gravitational contribution has been ignored as it amounts to only a small contribution to the net force (approx. 3.65 nN). The normal and shear forces required to break the anchors are too small to quantify with the force sensor, but the upper bounds of these forces are readable (less than 0.63 mN). Two separate measurements indicate that F_{N, proximal, Si–setae} is greater than F_{N, proximal, Si–anchor}, enabling picking up the Si plate from the original substrate.

The force measurement on the micro Si plate by dragging horizontally in the distal direction, i.e. in the opposite direction to engaging, is illustrated in figure 3d. Although it is difficult to directly measure the normal adhesive force between the microscopic Si plate and the receiver substrate F_{N, Si–Si}, we know this force is at least 3.24 mN because once the transferred plate is placed on the receiver substrate it is almost impossible to detach it again using the setal stamp as illustrated in figure 3e. The force measured during the approach–release–retract procedure F_{N, distal, Si–setae} is always negative, a compressive force (approx. ~0.85 mN) as indicated with the black line in figure 3e. Although the microscopic Si plate makes contact with the receiver substrate, the positive F_{N, distal, Si–Si} is always greater than the negative F_{N, distal, Si–setae}, enabling the successful placement of the Si plate on the receiver substrate. We prepared smooth PDMS stamps (size approx. 640 × 640 µm, height approx. 180 µm) to compare with the setal stamps for transfer printing. The adhesive stress (approx. 189.6 kPa) of the smooth PDMS stamp is similar to that of the setal stamp (approx. 3.24 mN over 0.016 mm² = 202.5 kPa), enabling easy pick-up of the micro Si plates. However, owing to the lack of releasing mechanism of the smooth PDMS stamp, it was unsuccessful to transfer-print the micro Si plates onto the receiver Si substrate in the experimental set-ups. More details of the comparison are given in the electronic supplementary material.

The controllable adhesive characteristics of the setal stamps enable deterministic transfer printing of the micro Si plates even on unconventional surfaces. The images in figure 4 show the capability of the setal stamps to transfer-print the micro Si plates onto various surfaces including smooth Si, rough Si and some biological surfaces. Figure 4a shows stacked Si plates, printed vertically. The magnified image in figure 4b clearly shows triple layers of Si plates, vertically aligned and printed using the setal stamps. Figure 4c shows an array of Si plates, laterally aligned and printed to write letters of ‘GIST’ on a transparent glass surface. The orthogonal lines in the image are on the back surface of the glass and are used as alignment marks for transfer printing. Transfer printing on a rough surface is also possible, as shown in figure 4d.
backside of the silicon wafer (root mean square roughness approx. 0.34 \( \mu \text{m} \)) has much less contact area with the micro Si plate than the smooth silicon substrate, switching off the adhesion by dragging the setal stamp releases the micro Si plate on the rough substrate.

The highly controllable adhesive characteristics of the stamp enable transfer printing even on the unconventional surfaces such as biological surfaces, e.g. the leaves of plants and the backs and wings of insects as shown in figure 4e–j. These biological surfaces are more irregular than the backside
of a silicon wafer. Figure 4e shows the Si plate printed on the leaf of a plant (Farfugium japonicum, figure 4f). The surface of the leaf is much rougher (RMS roughness approx. 13.42 μm) than the back of the Si wafer. Figure 4g shows the micro Si plate transfer-printed on the back of an insect (Zophobas morio), whose back has pits (average period: 300–500 μm) and tiny hairs (length approx. 3 μm). The inset shows a magnified image of this surface. See the electronic supplementary material for detailed images of the surface. Printing on a very thin wing (thickness approx. 750 nm) whose surface has low density of sharp pillars (length approx. 9 μm, density approx. 0.0026 μm^{-2}) is also possible, as shown in figure 4i, although bumps, pits or pillars on these surfaces reduce contact area significantly, switching off the stamp adhesion using external manipulation releases the microscopic plates. It is also possible to pick up and place the Si plate repeatedly on these unconventional surfaces. See the electronic supplementary material, video. Although the setal stamps enable transfer-printing of microelectronic devices onto diverse substrates, the efficiency to integrate a large area array of electronic devices is still limited because of transfer printing one by one. In its current state, the reported technique could be used for unconventional electronics that require a small number of microelectronic devices, for example, flexible electronics for advanced therapeutic or diagnostic uses, fabricated in forms that are implantable or attachable to biological systems including the human body. Small numbers of microelectronic devices transfer-printed on soft substrates are enough to sense or signal to biological systems. Examples include sensors for instrumented balloon catheters [51], photo detectors for wearable proximity sensors [52] and micro-LEDs for implantable ontogenetic light sources [53].

Figure 4k shows the results of durability experiments performed on the setal stamp (size approx. 72.543 μm²), conducted on a clean silicon substrate mounted on a multi-axis force sensor that monitors the normal and shear forces during mechanical cycling. See the electronic supplementary material for details. Although there is variation in shear and normal forces (shear force: 47.86 ± 6.2 mN, normal force: −7.72 ± 1.24 mN, in mean ± s.d.), there is no continuous decrease of the forces over 400 cycles. Negative normal forces indicate normal adhesion forces. Tearing of the specimen occurred at the interface between the lamellar backing strip (thickness: 2–6 μm) and the glue holding it onto the transparent glass plate after more than 400 cycles. We anticipate that the addition of supporting layers for the thin lamella material or further development in the gluing technique will improve the durability of the setal stamp.

Figure 5 demonstrates the use of the natural setal stamps for assembling functioning microelectronic devices, e.g. solar microcells, on unconventional substrates. Figure 5a shows a lateral-type dual-junction GaInP/GaAs solar microcell (size approx. 760 × 760 μm, thickness approx. 6.7 μm), printed on a leaf (Kerria japonica), roughness approx. 4.23 μm RMS, figure 5b. See Material and methods for preparation of the solar microcells. The current–voltage characteristics of the solar microcells printed on the leaf, shown in figure 5c are almost identical to those of the solar microcells on the original GaAs wafer (efficiency approx. 19.3%, fill factor approx. 0.80). We characterized the electrical properties by directly probing the top(n-) and bottom(p-) contacts (width approx. 40 μm) with sharp probe tips as illustrated by black needles in figure 5a, while illuminating the
solar microcells on the leaf under the full spectrum solar simulator (SoLa3A Class AAA solar simulator, Oriel Instruments). The probe tips are wired to the DC sourcemeter (2400, Keithley). Figure 5d shows a schematic illustration of the transfer printing of a vertical-type solar microcell whose bottom contact faces down. The bottom contact makes direct contact with the dry metal line (Au), as shown in figure 4e, after transfer printing without using any glueing layers. Figure 5f confirms an electrical connection between the bottom contact and the dry electrical line (Au) by probing the top contact and the electrical line (Au in figure 5c) because the electrical characteristics of the vertical-type solar microcells (efficiency approx. 19.7%, fill factor approx. 0.82) are almost identical with those of the lateral-type solar microcells on wafer. Although the solar microcells are unencapsulated for imaging and probing, encapsulation techniques such as parylene deposition can provide stronger bonding and environmental protection for the printed micro devices.

4. Conclusion

The results reported here for transfer printing microscopic Si plates and other functioning semiconductor materials onto unconventional substrates, including the surfaces of plants and insects, using natural gecko adhesives provide reliable options for the integration of microelectronic devices without using glue, high pressure or high temperature. The deterministic assembly of ultrathin microelectronic devices without damaging them or degrading their performance is critically important in developing unconventional electronics. Measurements of the forces acting on the micro Si plates reveal that mechanically controllable adhesion of the setal stamps enables stable transfer printing onto unconventional surfaces, such as the surfaces of plants or insects, as well as smooth or rough Si surfaces. Although picking and placing microelectronic devices one by one limit the use of the technology to the applications that require few microelectronic devices. More refined apparatus that can pick and place multiple microelectronic devices at the same time, incorporating higher resolution force sensors, will provide efficient means of automatic transfer printing for more practical manufacturing process.

Use of animals in this study was approved by GIST and L&C IACUC. (GIST-2012-19, ACUP-2008-001)

Acknowledgements. We thank Dr. J. Puthoff at Lewis & Clark College for helpful comments. We also thank Prof. K. Lee and Dr Y. Jeong for help using facilities at the Research Institute for Solar and Sustainable Energies.

Funding statement. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (nos. 2013042560, 2013007512). K.A. acknowledges support from the National Science Foundation of the USA (NSF-IOFS-0847953 and Special Creativity Award to K.A.).

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