Epitaxial lift-off of electrodedeposited single-crystal gold foils for flexible electronics

Naveen K. Mahenderkar,† Qingzhi Chen, Ying-Chau Liu, Alexander R. Duchild, Seth Hofheins, Eric Chason, Jay A. Switzer*

We introduce a simple and inexpensive procedure for epitaxial lift-off of wafer-size flexible and transparent foils of single-crystal gold using silicon as a template. Lateral electrochemical undergrowth of a sacrificial SiO₂ layer was achieved by photoelectrochemically oxidizing silicon under light irradiation. A 28-nanometer-thick gold foil with a sheet resistance of 7 ohms per square showed only a 4% increase in resistance after 4000 bending cycles. A flexible organic light-emitting diode based on tris(bipyridyl)ruthenium(II) that was spin-coated on a foil exploited the transmittance and flexibility of the gold foil. Cuprous oxide as an inorganic semiconductor that was epitaxially electrodeposited onto the gold foils exhibited a diode quality factor n of 1.6 (where n = 1.0 for an ideal diode), compared with a value of 3.1 for a polycrystalline deposit. Zinc oxide nanowires electrodeposited epitaxially on a gold foil also showed flexibility, with the nanowires intact up to 500 bending cycles.

Single-crystal silicon (Si) is the bedrock of semiconductor devices; its high crystalline perfection minimizes electron-hole recombination, and its dense SiO₂ native oxide minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays (1–5). Flexible devices and beautiful architectures have been produced using ultrathin foils of Si (6–8). Conductive polymers (9), carbon nanotubes (10), graphene (11), and metal nanostructures (12, 13) have been used as transparent and flexible substrates for flexible electronics. Ultrathin (5 to 30 nm) metal films (14, 15) have relatively high optical transmittance, flexibility, improved device efficiency, and low sheet resistance. However, they usually are grown by vacuum evaporation or sputtering, which gives a polycrystalline or textured deposit. Polycrystalline electronic materials suffer from electron-hole recombination and film grain boundaries (16). To expand the palette of electronic materials beyond planar Si, an inexpensive source of highly ordered material is needed that can serve as an inert substrate for the epitaxial growth of grain-boundary-free semiconductors, optical materials, and superconductors.

We show that wafer-size transparent and flexible single-crystal foils of gold (Au) can be produced by a simple and inexpensive lift-off procedure using single-crystal Si as the template for electrochemical epitaxial growth. The transparency of these single-crystal Au foils is exploited to fabricate a flexible organic light-emitting diode (OLED) based on tris(bipyridyl)ruthenium(II). The single-crystal nature of the Au is used to produce an inorganic diode based on epitaxial cuprous oxide (Cu₂O) that has more ideal diode characteristics than a diode based on polycrystalline Cu₂O.

Epitaxial lift-off of films on single-crystal substrates by dissolving a sacrificial adhesion layer can produce free-standing single-crystal foils (17). The epitaxial lift-off procedure for ultrathin single-crystal foils of Au electrodeposited onto Si(111) substrate is shown in Fig. 1. Electrodeposition of epitaxial Au on a Si(111) substrate was carried out using the method developed by Allongue and co-workers (18, 19). Previously, we showed that epitaxial electrodeposition of Au on Si(111), Si(100), and Si(110) substrates can serve as a proxy for bulk single-crystal Au (20). Single-crystal Si(111) with a 0.2° miscut toward [11̅2̅] and a resistivity of 1.15 ohm-cm was used as the substrate to grow the Au films (Fig. 1A). The deposition was performed at room temperature in a solution containing 0.1 mM HAuCl₄, 1 mM KCl, 1 mM H₂SO₄, and 0.1 M K₂SO₄ with a Si electrode that was prepolared at ~1.9 V versus Ag/AgCl before inserting it in the solution (Fig. 1B). Prepolaring the electrode inhibited the formation of an amorphous native oxide layer on the surface of Si and enabled epitaxial growth of Au.

After the epitaxial growth of Au, lateral undergrowth of a sacrificial SiO₂ layer was achieved by photoelectrochemically oxidizing Si under irradition of light at +0.75 V versus Ag/AgCl in 0.5 M H₂SO₄ solution (Fig. 1C). Au/n-Si forms a Schottky (rectifying) junction, so irradiation of light is required to generate holes at the Au/n-Si interface to oxidize the Si. The epitaxy of the Au foil was maintained during the lateral undergrowth of SiO₂, analogous to the epitaxial lateral overgrowth process in silicon-on-insulator technology (21). A polymer adhesive (tape or hot glue) was applied to the Au surface as a support and facilitator for foil separation (Fig. 1D). The SiO₂ layer was etched using dilute (5%) hydrofluoric acid to detach the Au foil from the Si substrate (Fig. 1E); this enabled an effortless separation of the foil (Fig. 1F). Both the tape and hot glue have high optical transmittance in the visible range (400 to 800 nm) and are resistant to chemical etching procedures. After the foil separation, the Si substrate was etched using a 0.6 M KOH and 0.1 M I₂ solution to dissolve any residual Au and then reused. Because only a 2- to 3-nm-thick layer of SiO₂ is removed during each fabrication cycle without extensive roughening, the Si should be reusable thousands of times.

High-resolution transmission electron microscopy (HRTEM) was used to study the interfacial changes during photoelectrochemical oxidation of Si. The as-deposited 30-min film (i.e., 30 min of deposition time) did not show an interfacial SiO₂ layer between the Si(111) and Au(111), as seen by the abrupt transition at the interface in Fig. 2A. Electron diffraction patterns for the as-deposited layers of Au on Si showed a spot pattern with in-plane and out-of-plane order (fig. S1). After the photoelectrochemical oxidation of Si, an amorphous SiO₂ interface with a thickness of 2.45 nm was evident in Fig. 2B. Native oxide formation on the Si surface in ambient air is limited to 0.5 to 1 nm because of the dense pinhole-free oxide layer that protects the Si from further oxidation. However, during photoelectrochemical oxidation of Si, tunneling of electrons through the insulating oxide layer caused the SiO₂ layer to grow thicker. The tunneling of electrons completely ceased when the oxide layer reached a thickness of 2.0 to 2.5 nm and the photocurrent dropped nearly to zero (fig. S2). The electron diffraction pattern of Au on Si with an interfacial oxide layer showed a similar spot pattern, indicating that the epitaxy was maintained after the lateral undergrowth of SiO₂ (fig. S3). Both micrographs (Fig. 2, A and B) are viewed along the [11̅2̅] zone axis, and the measured d-spacings for Au and Si are consistent with bulk values.

Scanning electron microscopy (SEM) was performed to study the surface morphology and the initial nucleation and growth of Au foils. All of the foils for SEM were separated with an adhesive tape as the support layer. Figure 2C shows a segment of Au foil formed after 5 min with a fractal morphology that had been reported for evaporated ultrathin films of Au (22, 23). We attribute these fractal features to the diffusion-limited aggregation of Au on the surface of Si during the initial nucleation period. This Au foil has a coverage of 56% and appears to be at the percolation threshold thickness (5 to 6 nm), in
agreement with the results of Hövel et al. (24). Beyond the percolation threshold, the fractal features are interconnected in a large network mesh with electrical connectivity across the entire foil. Figure 2D shows Au foils deposited for 10 min with 70% coverage; Au foils deposited for 20 min and 30 min, respectively, are shown in Fig. 2, E and F. The applicability of Au foils as a substrate was shown by depositing and characterizing inorganic semiconductor thin film and nanowires. Cu$_2$O was electrodeposited on a 30-min Au foil (Fig. 2G) for study of the diode characteristics. Zinc oxide (ZnO) nanowires were electrodeposited on a 30-min Au foil (Fig. 2H) and were subjected to 500 bending cycles. The Au thickness on Si was measured from the interference fringes in the XRD pattern (Fig. 3B). Satellite peaks (Laue oscillations) around a Bragg peak caused by constructive and destructive interference of x-rays reflected from Si-Au and Au-air interfaces were used to precisely measure the Au thickness (19). Figure 3B shows Laue oscillations around the Au(111) peak for Au films on Si as a function of deposition time. The film thickness was determined from the satellite peak positions according to

$$t = \frac{(L_2 - L_1) \lambda}{2(\sin \theta_1 - \sin \theta_2)} \quad (1)$$

where $t$ is the film thickness, $L_1$ and $L_2$ are the Bragg peak order (numbering of peaks in Fig. 3B), $\lambda$ is the x-ray wavelength (0.15418 nm), and $\theta_1$ and $\theta_2$ are the satellite peak angles. The calculated thicknesses from the Laue oscillations for the corresponding deposition times are listed in Fig. 3B. A linear dependence of thickness with time was observed (Fig. S4). Figure 3C shows the XRD pattern of a segment of Au foil and electrodeposited Cu$_2$O and ZnO on Au foil. Both the Au foil and the electrodeposited Cu$_2$O had a strong [111] out-of-plane orientation. The thickness of a 10-min deposition of Au on Si agreed closely with that of Au foil measured using Laue oscillations (fig. S5). The ZnO also grew epitaxially on Au foil but showed a strong [0001] out-of-plane orientation because of its hexagonal crystal structure.

The in-plane orientation and the epitaxial relation of the Au on Si, Au foil, Cu$_2$O, and ZnO was determined with x-ray pole figures. In a pole figure, planes other than those parallel to the substrate surface are probed while tilting and rotating the sample through a series of tilt and azimuthal angles (fig. S6). Figure 3D shows a (220) pole figure of Si(111), with three spots separated azimuthally by 120° at a tilt angle of 35.5°, corresponding to the three-fold symmetry of the (111) plane. A (220) pole figure of Au(111) on Si(111) is shown in fig. S7 with three spots expected at a tilt angle of 35.5°; however, there are also an additional three spots separated azimuthally by 60°. The two sets of spots on the (220) pole figure of Au correspond to the 180° in-plane rotation of parallel and antiparallel domains. Figure 3E shows a (220) pole figure of Au(111) foil, with the six spots at a tilt angle of 35.5° separated azimuthally by 60°. This pattern shows that the Au maintained its high in-plane and out-of-plane order after the foil separation. Figure 3F shows a (220) pole figure of Cu$_2$O(111) electrodeposited on Au(111) foil with the expected six spots at a tilt angle of 35.5°. Figure 3G shows a
spacings of the plane parallel to the substrate. Au on Si has a lattice mismatch of -24.9%, which is too high to produce epitaxial deposits. Therefore, the epitaxy in the Au-Si system can be explained by the formation of coincidence site lattices (CSLs), in which four unit meshes of Au coincide with three unit meshes of Si (20). These CSLs lower the mismatch from -24.9% for a single unit cell to +0.13% for the CSL (fig. S8). Similarly, the lattice mismatch for ZnO on Au was minimized from +12.7% to +0.16% for the CSL (fig. S9). The lattice mismatch for Cu2O on Au is +4.7%, which is low enough to produce cube-on-cube epitaxial films with reasonable in-plane and out-of-plane strain in the material (fig. S10).

High optical transmittance and low sheet resistance are imperative for Au foils to be used as flexible and transparent substrates. Figure 4A shows the photograph of a wafer-size Au foil with a diameter of 50.8 mm. Figure 4B shows the optical transmittance of Au foils as a function of thickness. All of the foils showed a maximum in transmittance around 500 nm and the peaks slightly red-shifted with an increase in thickness. The sheet resistance, in terms of ohms per square, for all of the foils (measured with a four-point probe) increased along with transmittance as the Au foil thickness decreased. A 7-nm-thick Au foil showed the highest transmittance at 85%, and the 28-nm-thick foil showed the lowest at 25%. The maximum transmittance (~500 nm) as a function of thickness is in close agreement with previous studies on evaporated gold thin films (25).

The endurance of the Au foils as a function of sheet resistance was measured by subjecting the foils to as many as 4000 bending cycles (Fig. 4C). Bending cycles for all of the foils were performed with a steel rod as a guide with a radius of curvature of 3 mm. The sheet resistance of 28-, 16-, and 11-nm-thick Au foils increased by 4%, 6.3%, and 34%, respectively, after 4000 cycles of bending.

To evaluate the flexibility and transmittance of Au foils for light emission, we spin-coated an OLED based on tris(bipyridyl)ruthenium(II) (26, 27). The complex showed strong photoluminescence with an excitation wavelength of 455 nm and an emission of bright red-orange color around 660 nm (26). The complex was dissolved in a 3% (w/v) polyvinyl alcohol solution, spin-coated onto a 28-nm-thick Au foil, and dried in air. An indium/gallium (InGa) eutectic was used.
as a back contact as a low-work function metal, whereas the Au foil acted as a high-work function contact. Figure 4D shows the current-voltage response of Au foil/Ru(bpy)$_3$$_2$InGa junction with a diode (rectifying) behavior. The inset in Fig. 4D shows a flexible Au foil with electrogenerated chemiluminescence from the OLED at an applied forward bias of 6 V.

To study the single-crystal nature of Au foils, we prepared an inorganic diode by using electrodeposited Cu$_2$O on Au foil. InGa eutectic was used to make a rectifying contact to the p-Cu$_2$O, and the Au foil substrate served as the ohmic contact. Polycrystalline Cu$_2$O was electrodeposited on a stainless steel substrate from the same deposition solution at low overpotentials to produce a sample with a random orientation. Cu$_2$O on both the Au foil and the stainless steel were deposited for a constant charge density to maintain similar responses for a Cu$_2$O diode on Au foil and stainless steel with a polycrystalline powder pattern is shown in Fig. S11. Defects or grain boundaries in a material increase the probability of electron-hole recombination and lower the overall efficiency of the diode or solar cell. In a single crystal, an ideal diode quality factor (n) of 1 indicates diffusion-controlled currents with no electron-hole recombination in the material, but in polycrystalline materials, n varies from 2 to 7 (28, 29). The n value for polycrystalline Si also increases with decreasing grain size (29). Figure 4E shows current-voltage responses for a Cu$_2$O diode on Au foil and stainless steel. The epitaxial Cu$_2$O had an n of 1.6, whereas the polycrystalline Cu$_2$O had an n of 3.1 (Fig. 4F). The higher value of n for polycrystalline Cu$_2$O is consistent with previous results for films of Cu/Cu$_2$O Schottky diode solar cells (30).

Single-crystal Au foils offer the order of traditional semiconductors such as Si wafers without the constraint of a rigid substrate. The foils are flexible and optically transparent, and show promise for producing flexible and wearable displays, solar cells, and sensors. The epitaxial growth of Cu$_2$O and ZnO that we have demonstrated can be applied to a wide range of inorganic semiconductors such as CdSe, CdTe, and ZnSe for use in flexible solar cells. Because ZnO is both a wide-bandgap semiconductor and a piezoelectric material, it should be possible to produce pressure-sensitive “electronic skin” and LEDs based on the ZnO/Au system (31, 32). Also, Au is hypoallergenic and could serve as a platform for wearable sweat sensors for continuous health monitoring (5). Although this work focused on the production of ordered substrates for flexible electronics, the processing method can be used to provide an inexpensive source of large metallic single crystals. These could serve as ordered substrates for photovoltaics, high-temperature superconductors, stress-free microelectromechanical systems (MEMS), catalysts, underpotential deposition, self-assembled monolayers, and molecular electronics.

REFERENCES AND NOTES

ACKNOWLEDGMENTS
The material is based on work supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Sciences and Engineering, under grants DE-FG02-08ER46518 (J.A.S.) and DE-SC0008799 (E.C.). All data are presented in the main paper and supplement.

SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/355/6330/1203/suppl/DC1
Materials and Methods
Figs. S1 to S11
References (33–36)
12 December 2016; accepted 13 February 2017
10.1126/science.aam5830
Epitaxial lift-off of electrodeposited single-crystal gold foils for flexible electronics
Naveen K. Mahenderkar, Qingzhi Chen, Ying-Chau Liu, Alexander R. Duchild, Seth Holheins, Eric Chason and Jay A. Switzer

Science 355 (6330), 1203-1206.
DOI: 10.1126/science.aam5830

Lifting off gold films
A method for growing and removing single-crystal gold films can be used to create a flexible and transparent substrate for devices. Mahenderkar et al. grew gold films on the face of a silicon wafer and then used photoelectrochemistry to undergrow a sacrificial silicon dioxide layer. This layer allowed the gold film to be peeled off with adhesive tape. A 28-nm-thick gold foil showed a minimal increase in sheet electrical resistance after 4000 bending cycles. Flexible films of single-crystal cuprous oxide and of zinc oxide nanowires were then grown on the gold foils. Science, this issue p. 1203