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Chemical Lift-Off Lithography of Metal and Semiconductor Surfaces

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Abstract

Chemical lift-off lithography (CLL) is a subtractive soft-lithographic technique that uses polydimethylsiloxane (PDMS) stamps to pattern self-assembled monolayers of functional molecules for applications ranging from biomolecule patterning to transistor fabrication. A hallmark of CLL is preferential cleavage of Au-Au bonds, as opposed to bonds connecting the molecular layer to the substrate, *i.e.*, Au-S bonds. Herein, we show that CLL can be used more broadly as a technique to pattern a variety of substrates composed of coinage metals (Pt, Pd, Ag, Cu), transition and reactive metals (Ni, Ti, Al), and a semiconductor (Ge) using straightforward alkanethiolate self-assembly chemistry. We demonstrate high-fidelity patterning in terms of precise features over large areas on all surfaces investigated. We use patterned monolayers as chemical resists for wet etching to generate metal microstructures. Substrate atoms, along with alkanethiolates, were removed as a result of lift-off, as previously observed for Au. We demonstrate the formation of PDMS-stamp-supported bimetallic monolayers by performing CLL

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Author Contributions

All authors designed the experiments. KMC, DMS, CZ, TDY, and JNB carried out the experiments. All authors performed data analysis and interpreted the results. KMC, AMA, and PSW wrote the manuscript with input from all authors.

Supporting Information

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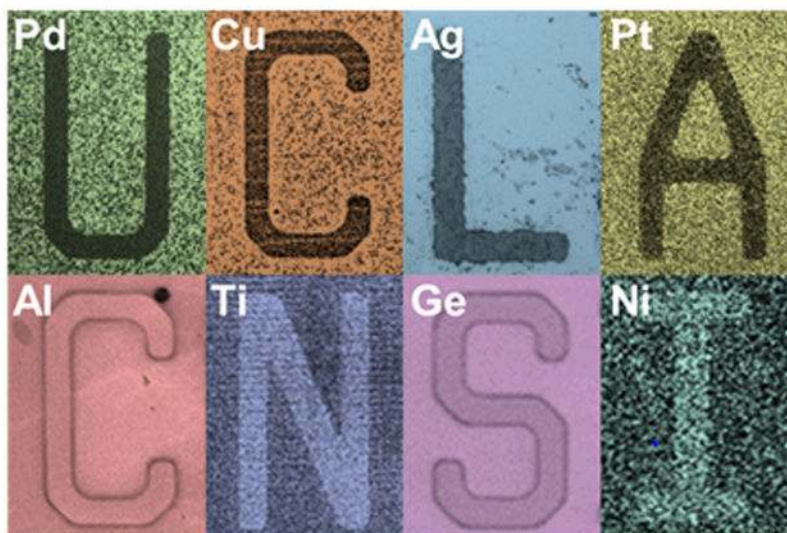
Additional methods, SEM images, atomic force microscopy characterization, and XPS sensitivity factors.

Notes

The authors declare no competing financial interests.

on two different metal surfaces using the same PDMS stamp. By expanding the scope of the surfaces compatible with CLL, we advance and generalize CLL as a method to pattern a wide range of substrates, as well as to produce supported metal monolayers, both with broad applications in surface and materials science.

Graphical Abstract



Molecular self-assembled monolayers (SAMs) on surfaces are versatile systems for investigating and tailoring surface, interfacial, and environmental interactions.¹⁻⁵ There are a variety of SAM molecules with differing head and tail group functionalities that can be tuned to bind (covalently and noncovalently) and to interact with specific surfaces, with alkanethiol monolayers on Au surfaces representing a commonly used and well-studied system.⁶⁻⁹ The patterning of alkanethiolate SAMs on metal surfaces imparts an additional level of control and dimension into these systems, which has led to a multitude of applications in surface science and nanotechnology.^{1,2,4,6,10-12}

Molecular monolayers can be patterned *via* conventional lithographic techniques (*e.g.*, photolithography),^{13,14} but are more commonly patterned using low-cost and high-throughput soft-lithographic methods.^{2,3,15,16} Conventional soft lithography (*e.g.*, microcontact printing, μ CP), involves the additive patterning of SAM molecules onto surfaces by transfer of molecular inks *via* contact of patterned polydimethylsiloxane (PDMS) stamps with the corresponding surfaces.¹⁷⁻²² While μ CP has significantly advanced the field of SAM patterning, it is inherently limited in the resolution of features produced due to lateral diffusion of ink molecules during and after the patterning is performed.^{19,21-24} Advances in soft lithography have improved feature resolution^{12-14,25,26} (*e.g.*, polymer pen lithography²⁷ and microdisplacement printing).¹¹

In contrast to abundant additive patterning methods, chemical lift-off lithography (CLL) is a *subtractive* soft-lithographic strategy.^{28,29} Here, alkanethiol molecules, with exposed functional tail groups (*e.g.*, -OH, -COOH, -NH₂), in preformed SAMs are removed from Au

surfaces only in areas contacted by patterned PDMS stamps.²⁸⁻³⁰ Notably, as a result of the CLL process, Au atoms are transferred to the PDMS stamps.^{28,29,31} Chemical lift-off lithography enables high-fidelity patterning of SAMs over a wide range of feature sizes (nanometer to millimeter).^{28,29,32-34} This patterning process has inspired and enabled diverse applications including the patterning of bioactive molecules,^{30,32,35-39} supported gold monolayers,³¹ and the facile fabrication of field-effect transistor arrays.^{40,41}

Nonetheless, CLL has been primarily used to pattern alkanethiol monolayers on Au surfaces, with the patterning of other coinage, transition, and reactive metal, semiconductor, and metal oxide surfaces representing potentially unexplored areas of interest.^{28,42,43} The formation and patterning of alkanethiolate SAMs on other coinage metal surfaces (*e.g.*, Ag, Cu, Pd) have been previously demonstrated using μ CP.^{6,8,44-52} Alkanthiolate SAMs on transition and reactive metal surfaces are less studied as the reactivity of these surfaces typically leads to the formation of passivating metal oxide layers that hinders additive SAM patterning.⁵³⁻⁵⁷ For subtractive patterning, such as CLL, the entire substrate surface is first functionalized with a SAM, and thus passivated preventing surface oxide formation prior to patterning.²⁸ Straightforward and direct self-assembly and patterning of molecules on reactive surfaces may be beneficial for a variety of systems including the investigation of spin-selectivity in molecular assemblies on ferromagnetic surfaces,^{36,58} patterning of metal-oxide semiconductors for transistor and biosensor applications,^{41,59,60} and growth of two-dimensional materials (*e.g.*, graphene nanoribbons).^{61,62}

Herein, we extend CLL as a technique to pattern alkanethiolate SAMs on different coinage metals (Pt, Pd, Ag, Cu), transition and reactive metals (Ni, Ti, Al), and a semiconductor (Ge). Using the patterned monolayers as molecular resists, we demonstrate pattern transfer to underlying metal substrates *via* wet etching. In all cases, we show that corresponding supported (mono)layers of substrate atoms are removed during the CLL process. Moreover, we can form atomic blends of mixed metal monolayers on PDMS stamp surfaces. These findings illustrate that CLL is a versatile technique for economical and high-throughput patterning of a multitude of different material surfaces using straightforward alkanethiol self-assembly.

A schematic of the CLL process is shown in Figure 1. Patterned oxygen-plasma-activated PDMS stamps were brought into contact with SAMs of 11-mercapto-1-undecanol (MUO) on metal²⁸ or semiconductor surfaces. Stamp contact enabled removal of SAM molecules in the contacted substrate areas. We first investigated coinage metals besides Au used in our previous studies (*i.e.*, Pt, Pd, Ag, Cu). Self-assembled monolayers of alkanethiolates have been shown to form on other coinage metals;^{44-46,49,63,64} thus, we predicted that CLL could be used to pattern these additional metal surfaces.

Monolayers on metal surfaces were imaged using scanning electron microscopy (SEM) after patterning by CLL. Scanning electron micrographs of Pt, Pd, Ag, and Cu surfaces contacted by “CNSI/UCLA” patterned PDMS stamps showed evidence of negative features in MUO monolayers corresponding to the features of the stamp (Figure 2A-D,S1). Features did not show evidence of broadening associated with lateral diffusion of MUO after patterning,²³ similar to the case of CLL on Au.³³

Patterned monolayers on metal surfaces after CLL act as molecular resists to facilitate fabrication of metal nano/microstructures *via* chemical wet etching.^{28,31,34,40,41} To demonstrate the functionality and resolution of the patterned SAMs, and to confirm that molecules were removed *via* CLL, we exposed patterned metal surfaces to chemical etchants selective for Pt, Pd, Ag, and Cu, respectively (see Methods).^{47,48,51,52,65,66} In all cases, metal regions were selectively etched in regions corresponding to areas of SAM removal by CLL, transferring the pattern of the monolayer to the metal substrate (Figure 2E-H). We expect that not all SAM molecules are removed *via* CLL (*ca.* 70% for Au),²⁸ however sufficient numbers of molecules were removed from all coinage metal surfaces to facilitate selective etching of underlying metals in the lifted-off areas.

Following the observations of coinage metal patterning, we explored extending CLL to transition and reactive metal surfaces (*i.e.*, Ni, Ti, Al), upon which alkanethiolate monolayers can be formed.⁵³⁻⁵⁵ To prevent formation of surface oxides, substrates were immersed into degassed ethanolic MUO solutions to form SAMs immediately after metal evaporation. Since CLL removes regions of preformed SAMs, transition metal surfaces can be patterned straightforwardly without additional surface treatments (*i.e.*, metal oxide etching).⁶⁷ Oxide etching roughens metal surfaces,⁶⁸ whereas other methods for patterning transition metals, such as SAM displacement, limit the types of molecules that can be patterned (*i.e.*, molecules that are easily displaceable).¹¹ Transition metal surfaces characterized using SEM indicated that SAMs on these surfaces were patterned using CLL (Figure 3A-C,S1).

We performed CLL on Ge surfaces, a semiconductor that can be functionalized with alkanethiols *via* covalent Ge-S bonds,⁶⁸⁻⁷¹ to extend the lithographic capabilities of CLL beyond metals (Figure 3D,S1). Direct patterning of molecules on semiconductor surfaces would foreseeably enable a myriad of applications for semiconductor device processing. For example, local work functions in patterned regions of semiconducting substrates might be tuned for band bending and alignment purposes.^{72,73}

We noticed that the contrast observed *via* SEM for the patterned SAMs appears to differ for the different surfaces in Figures 2 and 3. The levels of contrast in SEM for patterned SAMs is related to a variety of factors, including SAM densities and order, as well as the accelerating voltage and working distance of the electron beam during image acquisition.^{23,27,31} Given the rapidity of metal oxide formation, we expect that SAMs formed on reactive metal surfaces are not as highly ordered as on coinage metals; trace metal oxides on the former would affect SAM formation.^{46,53-57} Differences in SAM formation (*i.e.*, order and density), and thus differences in CLL yield, could contribute to observed differences in contrast. Additionally, formation of oxides in regions of removed SAM molecules after CLL could alter SEM contrast due to differential charging effects.⁷⁴⁻⁷⁶ Atomic-force microscopy images of patterned SAMs on Ge surfaces showed the expected topographies of monolayers of MUO (Figure S2),^{28,31} suggesting that the contrast observed for Ge *via* SEM is mainly an effect of surface compositional differences arising from the patterned SAMs and potentially differential charging effects on the semiconducting surfaces.

To analyze whether substrate molecules were removed during CLL for the metal and semiconductor surfaces investigated herein, similar to previously studied Au substrates,^{28,31} X-ray photoelectron spectroscopy (XPS) was performed on PDMS stamps post-CLL. In all cases, characteristic peaks corresponding to the metal or semiconductor substrate atoms were observed (Figure 4), demonstrating that layers of substrate atoms were removed by CLL from all surface types. In some cases, it appeared that layers greater than monolayer were removed (based on the differences in contrast observed in Figure 3, large signal-to-noise differences observed in the XPS spectra in Figure 4, and the relative elemental sensitivities given in Table S1), similar to transfer printing techniques demonstrated by Rogers and others.⁷⁷⁻⁸⁰

We previously hypothesized that removal of Au atoms during CLL was partly due to the formation of covalent linkages between the PDMS stamp and SAM molecules, as well as formation of Au-alkanthiolate complexes that weaken the bond strengths between the outermost Au substrate atoms and the underlying Au substrate atoms.^{28,31,81} For all elemental substrates tested in this report, the metal-sulfur bonds are stronger than the metal-metal bonds.⁸² The energetics of these systems suggest that contributions from differences in bond enthalpies play roles in the removal of the outermost layer(s) of substrate atoms, in addition to adatom formation observed in some monolayer systems.⁸³ In sum, CLL can be used as a facile top-down method of fabricating and patterning supported metal⁶² and semiconductor monolayer materials (*e.g.*, germanane)⁸⁴ on flexible and transparent polymer supports such as PDMS.

An advantage of soft lithography is the ability to perform multiple patterning steps to straightforwardly create complex multicomponent patterns.^{12,28,39,85} To demonstrate patterning of multiple metals onto the same PDMS support with CLL, we investigated the formation of bimetallic metal layers on PDMS stamps. Previous reports indicated that the PDMS is still activated after a single CLL step (and up to ~5 successive CLL steps using the same stamp on different surfaces), and that full monolayers of Au atoms were not removed onto the PDMS.^{28,31,42,86} Taking advantage of this fractional removal, we performed two successive CLL steps on two different metal surfaces (Au and Ag) using the *same* activated PDMS stamp (Figure 5A). X-ray photoelectron spectroscopy of the PDMS stamp after the sequential CLL process showed peaks corresponding to both Au and Ag, demonstrating the formation of mixed-metal monolayers supported on PDMS (Figure 5B-C). Atomically blended bimetallic monolayers represent a new class of materials with unexplored properties and potential applications (*e.g.*, catalysis),^{62,87} which can be fabricated straightforwardly using CLL.

In this study, SAMs of the same type of alkanthiolate molecule (MUO) were straightforwardly formed on different metal and semiconductor surfaces. Chemical lift-off lithography is not limited to the surfaces or SAM molecules studied herein;^{29,31} presumably, any surface that can be functionalized with molecular monolayers (*e.g.*, metals,^{67,88-90} semiconductors,⁹¹ transition metal dichalcogenides)⁹² could be patterned with CLL. Performing CLL with molecules containing additional functionalities within the alkyl backbone (*e.g.*, hydrogen-bonding interactions)⁹³ or functionalized cage molecules (*e.g.*, carboranethiolates),⁹⁴⁻⁹⁶ which form relatively defect-free monolayers and can have a range

of bond densities between the monolayer and substrate, may have significant effects on the overall efficiencies of CLL.

Monolayers formed on reactive metal surfaces are likely not well ordered due to trace metal oxide formation, yet they can be patterned with *via* CLL. Changing the head group functionality of the SAM molecules to something that binds favorably to surface oxides (*e.g.*, phosphonic acids)⁹⁷ can enable the direct patterning of metal oxide surfaces.⁴² However, CLL with these types of SAMs, in which the head group is not bound directly to the metal, would be hypothesized not to remove surface metal atoms in the process, but instead break the weakest bonds in the molecules constituting the SAM.⁴²

We previously investigated the nanoscale structure and function of supported Au monolayers on PDMS fabricated with CLL and showed that these Au monolayers are ultrathin and optically transparent, yet they retain the chemical functionality of Au.³¹ Accordingly, ultrathin monolayers fabricated from other metal and semiconductor surfaces may have chemical and physical properties that can be differentially exploited compared to bulk materials (*e.g.*, magnetism, Ni,⁹⁸ semiconductor, Ge).⁸⁴ Furthermore, functional metal monolayers could be used as supports for additional structural growth, enabling patterning of a diverse range of materials (*e.g.*, nanoparticles,^{99,100} surface-tethered metal-organic frameworks and multilayers,¹⁰¹⁻¹⁰³ and metal-organic chalcogenolate assemblies)¹⁰⁴ on flexible and transparent substrates. Capabilities to create bimetallic and multi-metallic layers and monolayers with CLL adds an additional level of control to the generation and tailoring of supported metal monolayers with designed properties.

Collectively, we demonstrate CLL as a patterning technique that can be used to pattern SAMs on a variety of metal and semiconductor surfaces. Here, high-fidelity patterns of SAMs were generated on coinage, transition, and reactive metal, and semiconductor surfaces beyond Au. Patterned substrates were used as molecular resists for chemical wet etching to produce three-dimensional features. For all surfaces tested, XPS revealed the removal of corresponding substrate atoms during the CLL process. Moreover, reactive and reusable PDMS stamps enable the formation of bimetallic monolayers supported on PDMS by performing two sequential CLL steps on different substrates. Thus, we extend CLL to pattern a variety of surfaces straightforwardly with applications towards the fabrication and study of new materials and systems.

■ Experimental Methods

Materials

Prime quality 4" Si{100} wafers (P/B, 0.001-0.005 Ω -cm, thickness 500 μ m) were purchased from Silicon Valley Microelectronics, Inc. (Santa Clara, CA, USA). Sylgard 184[®] silicone elastomer kits (lot #0008823745) were purchased from Ellsworth Adhesives (Germantown, WI, USA). 11-Mercapto-1-undecanol was purchased from Sigma Aldrich.

Chemical Lift-Off Lithography

Metal and semiconductor surfaces were prepared *via* electron-beam evaporation (Kurt J. Lesker Company, Jefferson Hills, PA or CHA Industries, SOLUTION, Fremont, CA) onto Si

substrates. Self-assembled monolayers of MUO were formed on metal surfaces *via* immersion in 5 mM ethanolic solutions for 24 h. For reactive metal surfaces (*e.g.*, Cu, Ni, Ti, Al), substrates were immersed in degassed MUO solutions immediately after metal evaporation to minimize metal oxide formation. For Ge, SAMs were formed *via* immersion into a 1:1 (v/v) ethanol:water solution of MUO. Chemical lift-off lithography was performed as previously reported,^{28,31} where surfaces were contacted with patterned or featureless oxygen-plasma-activated PDMS stamps for 24 h, after which the stamps were removed. To form supported bimetallic monolayers, featureless PDMS stamps were brought into contact with functionalized Au surfaces for 1 h and then functionalized Ag surfaces for an additional 1 h immediately after lift-off from Au surfaces.

Scanning Electron Microscopy

Scanning electron microscopy images were obtained using a Zeiss Supra 40VP scanning electron microscope with an InLens secondary electron detector. Surfaces were imaged immediately after CLL. Accelerating voltages were adjusted for each metal surface to produce optimal contrast: 1 kV for Ni, Ti, and Al; 1.5 kV for Pt; 2 kV for Pd, Ag, and Cu; and 3 kV for Ge. Working distances were optimized for each image. Modulating accelerating voltages and working distances affect the contrast observed for patterned SAMs.²³ Images were processed *via* polynomial background subtraction using Gwyddion¹⁰⁵ and contrast limited adaptive histogram equalization in MATLAB.¹⁰⁶

Metal Etching

Patterned metal surfaces were etched with corresponding chemical wet etchants: Pt with concentrated *aqua regia* (3:1 v/v 12.1 M HCl:15.6 M HNO₃) for 20 min,⁶⁶ Pd with a solution of 0.2 M K₂Cr₂O₇ and 0.5 M HCl in 40% aqueous H₃PO₄ for 6 min,¹⁰⁷ Ag with an aqueous 25 mM FeNO₃ solution for 15 min,⁵¹ and Cu with an aqueous 12 mM FeCl₃ solution for 30 s.⁵²

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy of PDMS surfaces post-CLL was carried out using an AXIS Ultra DLD photoelectron spectrometer (Kratos Analytical Inc., Chestnut Ridge, NY) and a monochromatic Al K_α X-ray source with a 200 μm circular spot size in ultrahigh vacuum (10⁻⁹ Torr). High-resolution spectra of Au 4f, Pt 4f, Pd 3d, Ag 3d, Cu 2p, Ni 2p, Ti 2p, Al 2p, and Ge 3d regions were acquired at a pass energy of 20 eV using a 300 ms dwell time. For all scans, 15 kV was applied with an emission of 15 mA. An average of 30 scans were collected for each of the high-resolution spectra. Note, all spectra were collected under charge neutralization conditions (*i.e.*, electron flood gun)⁵⁸ to prevent charging of sample surfaces. Charge neutralization results in shifts of binding energy values.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. General scheme for chemical lift-off lithography. An oxygen-plasma-activated polydimethylsiloxane (PDMS) stamp is brought into contact with a metal or semiconductor surface functionalized with a self-assembled monolayer (SAM), in this case, 11-mercapto-1-undecanol. Lift-off of the PDMS stamp removes SAM molecules only in the contacted regions, patterning remaining SAMs on the substrate surfaces.

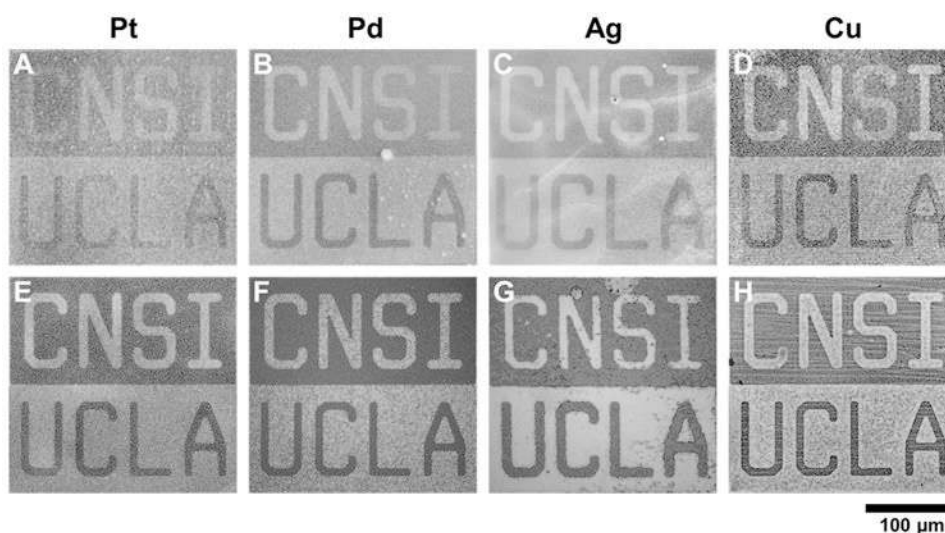


Figure 2. Chemical lift-off lithography (CLL) of coinage metal (Pt, Pd, Ag, Cu) surfaces. Metals are ordered in terms of increasing reactivity from left to right. **(A-D)** Representative scanning electron microscopy images of patterned self-assembled monolayers (SAMs) of 11-mercapto-1-undecanol (MUO) on metal surfaces after CLL. Monolayers were patterned such that MUO molecules remained in the “CNSI” letter regions and in the regions surrounding the “UCLA” letters. **(E-H)** Representative optical microscopy images of metal surfaces after chemical wet etching using the patterned SAMs as molecular resists.

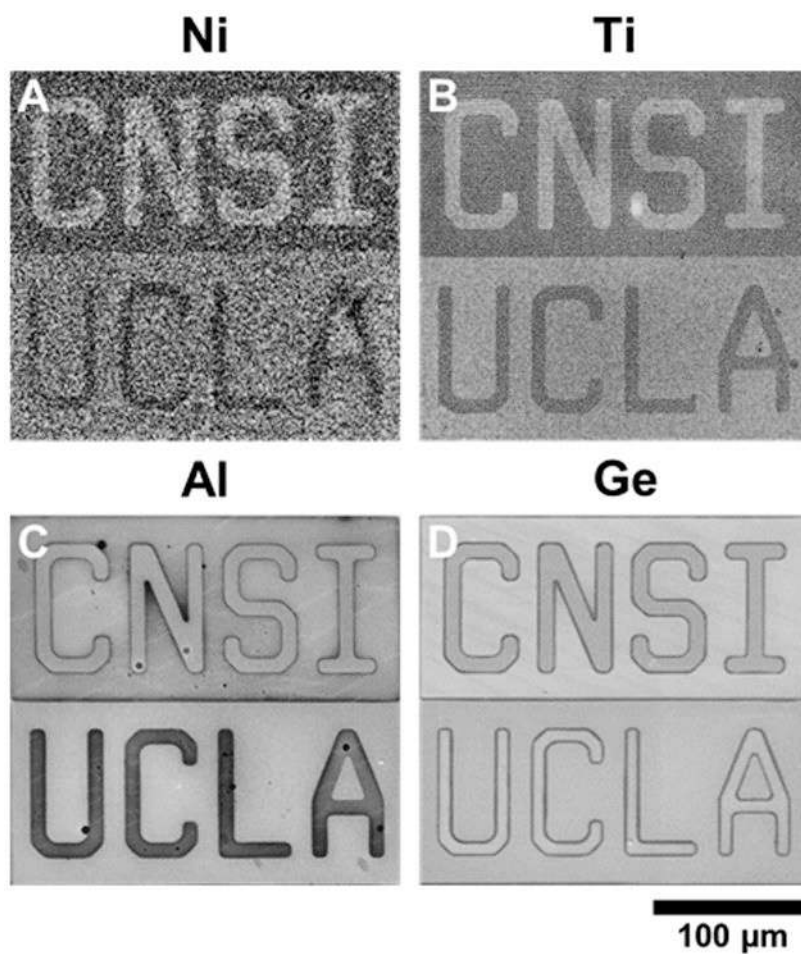


Figure 3. Chemical lift-off lithography (CLL) of transition or reactive metal and semiconductor surfaces. (A-D) Representative scanning electron microscopy images of patterned self-assembled monolayers of 11-mercapto-1-undecanol on the metal surfaces (Ni, Ti, Al) and a semiconductor surface (Ge) after CLL. Stamps with the same features as Figure 2 were used.

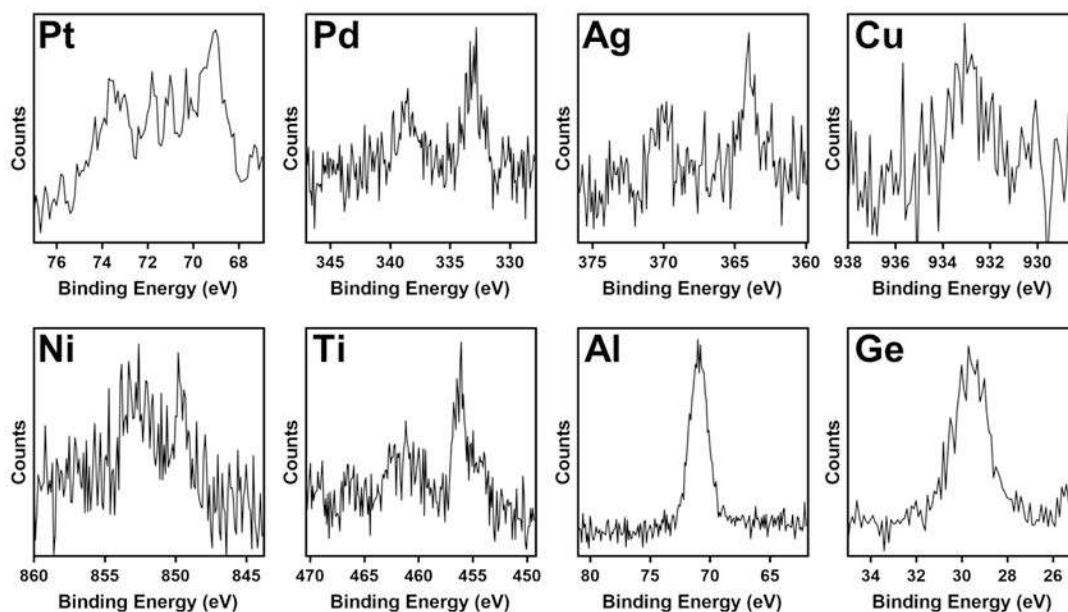


Figure 4.

X-ray photoelectron spectroscopy (XPS) analysis of featureless polydimethylsiloxane (PDMS) stamps after a chemical lift-off lithography on Pt, Pd, Ag, Cu, Ni, Ti, Al, and Ge surfaces. Featureless PDMS stamps and XPS were used to investigate the presence of corresponding substrate atoms on the PDMS stamps, demonstrating that layers of substrate atoms are removed in the lift-off process, either nominal monolayers, or in some cases, potentially thicker layers.

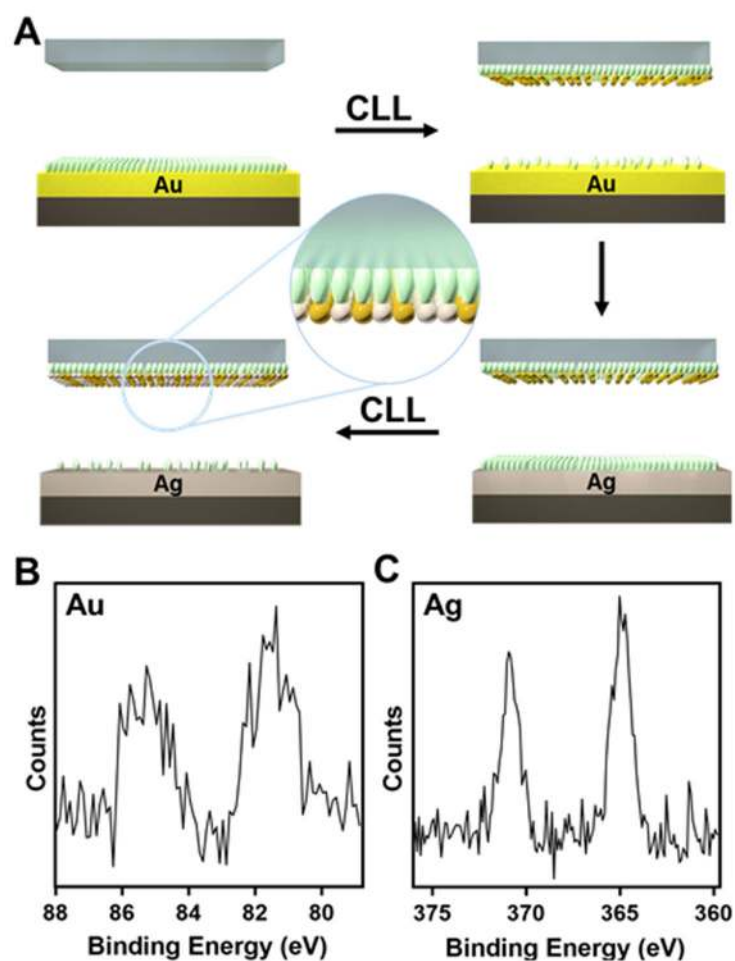


Figure 5. Sequential chemical lift-off lithography (CLL) of two different metals (Au, Ag) onto the same polydimethylsiloxane (PDMS) stamp. (A) Schematic illustration of the sequential CLL process. (B,C) X-ray photoelectron spectra of the PDMS stamp after the sequential CLL process showing characteristic peaks of both metals on the same stamp, demonstrating that both metals are “lifted-off” onto the PDMS stamp forming a supported mixed metal monolayer.