

# **Metal Free Seedless Adhesion of Au on Si Native Oxide**

Running title: Metal Free Adhesion of Au on Si Native Oxide

Running Authors: Lopez et al.

Gerald G. Lopez <sup>a)</sup>, Steven A. Wood, Meredith G. Metzler, Richard Grote, Lee  
Bassett

Singh Center for Nanotechnology, University of Pennsylvania, 3205 Walnut Street, Philadelphia,  
PA 19104

Andy Thompson

DisChem, Inc., 17295 Boot Jack Rd, Suite A, PO Box 267, Ridgway, PA 15853 USA

<sup>a)</sup> Electronic mail: [lopez@seas.upenn.edu](mailto:lopez@seas.upenn.edu)

The adhesion of gold to a silicon substrate in the absence of a seed layer, due to a lack of compatibility with a particular process, device constraints or basic redundancy, is an established and continuing difficulty in processing. As is widely known, Au adhesion is hindered by the oxygen present in the native oxide resting on the silicon substrate. Using a seed layer like Cr or Ti prior to deposition to promote the adhesion of Au is often used. This paper addresses this problem through an examination of the adhesion promotion properties of SurPass 4000 for sub-100 nm Au structures without the use of a metal seed layer. Patterns were exposed on 200 nm of ZEP520A from ZEON CHEMICALS on an

silicon substrate using an Elionix ELS-7500EX 50kV electron beam lithography tool at 1nA with a 60um final aperture and a 20nm beam step size, running at a 20MHz fixed clocked. All silicon wafers were treated with an O<sub>2</sub> plasma for 20 minutes prior to spin coating. After exposure, samples were then developed at 21°C using o-xylene for 70 seconds, then soaked in IPA for 30 seconds followed by a N<sub>2</sub> blow dry. A descum step followed using an O<sub>2</sub> plasma at 100 sccm at 100W for 5 seconds in an Oxford 80 PLUS RIE. Before the deposition of Au, each of the samples received varying treatments for adhesion. The control sample was left untreated, whereas the second sample had a 10nm Cr seed layer e-beam evaporated at 2 Å/sec onto the surface. Lastly, the third sample was soaked in SurPass 4000 for 2 minutes followed by an IPA rinse and N<sub>2</sub> blow dry. Using a load-locked Kurt J. Lesker Co. Model PVD75 with a 4 pocket e-beam hearth, samples were mounted to a carrier platen to evaporate 30nm Au (2.5 Å/sec) at a base pressure of 1 e-7 Torr. Metal lift-off was performed using 1165 stripper at 60°C for 60 minutes with no mechanical agitation. As expected, the lack of adhesion promotion treatment of the control sample results in an expected delamination of Au from the substrate. In contrast, the Cr treated sample exhibits excellent adhesion of Au given the presence of the Cr seed layer. Most importantly for the claims of this paper, the SurPass 4000 treated sample also exhibits adhesion of Au on Si in the absence of a metal seed layer. In the text that follows, we will discuss contact angle measurements and show discuss a possible application that could be enabled as a result of this finding.

## I. INTRODUCTION

The adhesion of gold to a silicon substrate in the absence of a seed layer, due to a lack of compatibility with a particular process, device constraints or basic redundancy, is

an established and continuing difficulty in processing. As is widely known, Au adhesion is hindered by the oxygen present in the native oxide resting on the Si substrate. It has been common practice to put a seed layer like Cr or Ti prior to Au deposition to prevent delamination of the Au thin film. Alternatively, if the native oxide is stripped using HF, gold is shown to adhere without the presence of an adhesion layer. However, it has been shown that gold diffuses into the silicon lattice when the native oxide is not present. This paper introduces for the first time the adhesion promotion properties of SurPass 4000 gold structures onto silicon without the presence of a metal seed layer. While previous studies have shown SurPass 4000 to be effective at improving adhesion between hydrophobic and hydrophilic material (solvent based resists on a range of substrate materials), this study also shows that SurPass 4000 treatment is also beneficial in improving adhesion between Si and Au where incompatible crystalline matrixes may cause adhesion failure due to compressive or tensile stresses.

In following section, the pattern design, data preparation and fabrication are discussed in detail along with contact angle measurements. Section III will discuss the results after metal-lift off and discuss a possible application that could be enabled as a result of this finding. Finally, in section IV, the paper will summarize the results and draw a conclusion with mentions of future work.

## **II. EXPERIMENT**

In this section, the approach to test for metal free adhesion of gold on silicon is described in detail. A surface treatment experiment was designed to test the adhesion promotion of gold onto silicon. The details of the pattern design, data preparation, spin

coating, electron beam lithography process, surface treatment, metallization and lift-off are discussed. The results and discussion of the experiment follow.

## A. PATTERN DESIGN AND DATA PREPARATION

Three patterns were designed to test for Au adhesion onto native silicon oxide. All patterns span across a  $50\ \mu\text{m}$  by  $50\ \mu\text{m}$  square area. The first two patterns are hexagonal arrays of 40 and 100 nm dots. The third pattern is a line-space pattern that consists of 70 nm wide lines on a 400 nm pitch. Each pattern is treated with the same PEC parameters and shown in Table I using BEAMER from GenISys. Based on process characterization techniques demonstrated by Eichfeld<sup>1</sup> and Bickford<sup>2</sup>, the effective process blur of the e-beam lithography process is determined to be 66 nm.

TABLE I. The forward scattering and long range backscattering, the energy ratio of the long range to short range and the empirically determined effective process blur which are referred to as  $\alpha$ ,  $\beta$ ,  $\eta$ , and  $\text{blur}_{eff}$ . Based on process characterization techniques demonstrated by Eichfeld<sup>1</sup> and Bickford<sup>2</sup>, the effective process blur of the e-beam lithography process is determined.

<i>PEC Parameter</i>	Value
	5 nm
	$10\ \mu\text{m}$
	0.6
$\text{blur}_{eff}$	66 nm

The hexagonal array was designed such that a cell array, whose pitch in Y ( $Y_{pitch}$ ) is twice the pitch in X ( $X_{pitch}$ ), was referenced twice where the second reference (light grey) was offset by a half-pitch in X and Y compared to the first reference (dark grey) to create the final hexagonal structure. The  $X_{pitch}$  is 200 nm. When converted with BEAMER<sup>3</sup>, each structure is outputted with proximity effect correction and is centered about the 600  $\mu\text{m}$  writing field.

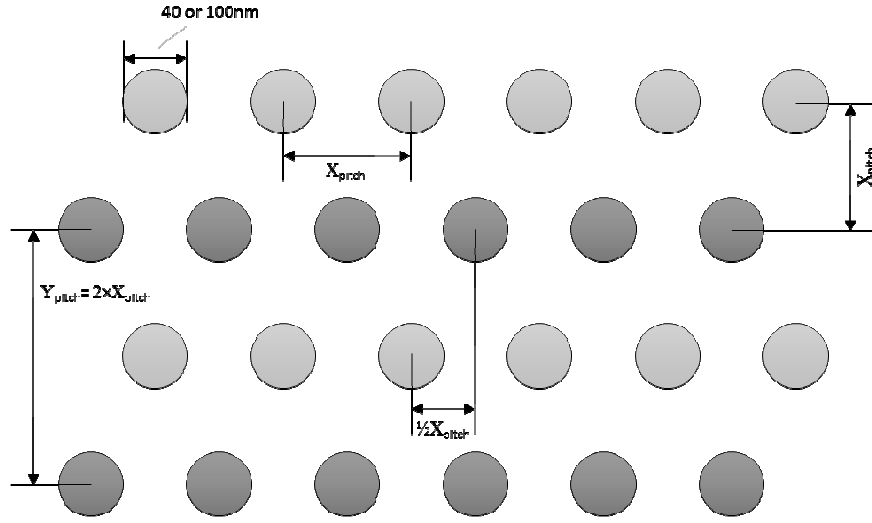


FIG. 1. The hexagonal dot array is designed by referencing the same unit cell twice. The unit cell array references a dot cell placing them on a  $Y_{pitch}$  that is twice the  $X_{pitch}$ . As illustrated, the first reference cell (the array of dark grey circles) is placed at origin and the second reference (the array of light grey circles) is offset by a half-pitch in X and Y to create the final hexagonal structure.

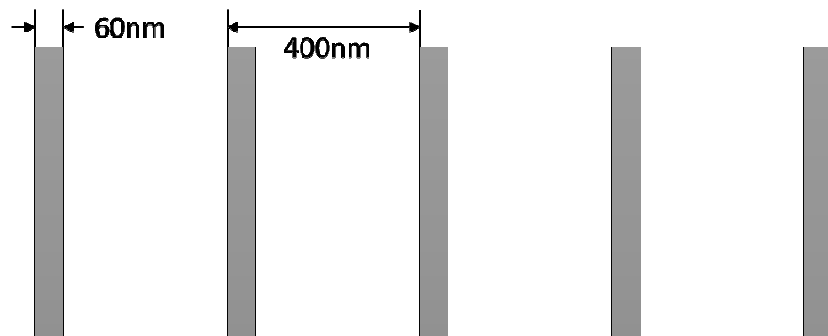


FIG. 2. The line-space pattern has 60 nm wide lines on a 400 nm pitch. After lift-off, measurement shows that the lines are roughly 65-70 nm wide.

## **B. FABRICATION**

The fabrication of the hexagonal dot arrays and line-space patterns was performed using e-beam lithography. The pattern was then transferred using metal lift-off in which three techniques were used to test for Au adhesion. The processes are described in the following subsections.

### **1. *Electron beam lithography***

All silicon wafers were treated with an O<sub>2</sub> plasma for 20 minutes prior to spin coating. Ellipsometry using a J.A. Woollam V VASE Spectroscopic Ellipsometer measured approximately 3 nm of native oxide on the wafers. For this study, dilutions of ZEP520A were conducted to optimize resist use. The authors found that an approximate dilution by weight of 5:6 ZEP520A to anisole yields roughly a 200 nm thickness when spun at 1000 rpm atop a Si substrate. The pattern is then exposed using a 20 MHz, 50 keV e-beam lithography system at 1 nA with a 60  $\mu$ m final aperture and a 20 nm beam step size. The process utilizes a 100  $\mu$ C/cm<sup>2</sup> base dose that is modulated across the pattern using PEC if applied. The use of a large beam step size is intentional in order to decrease the overall exposure time of the sample. After exposure, the sample develops in a bath of o-xylene for 70 seconds with an IPA rinse and N<sub>2</sub> blow dry. A descum step followed using an O<sub>2</sub> plasma at 100 sccm at 100W for 5 seconds in an Oxford 80 PLUS RIE.

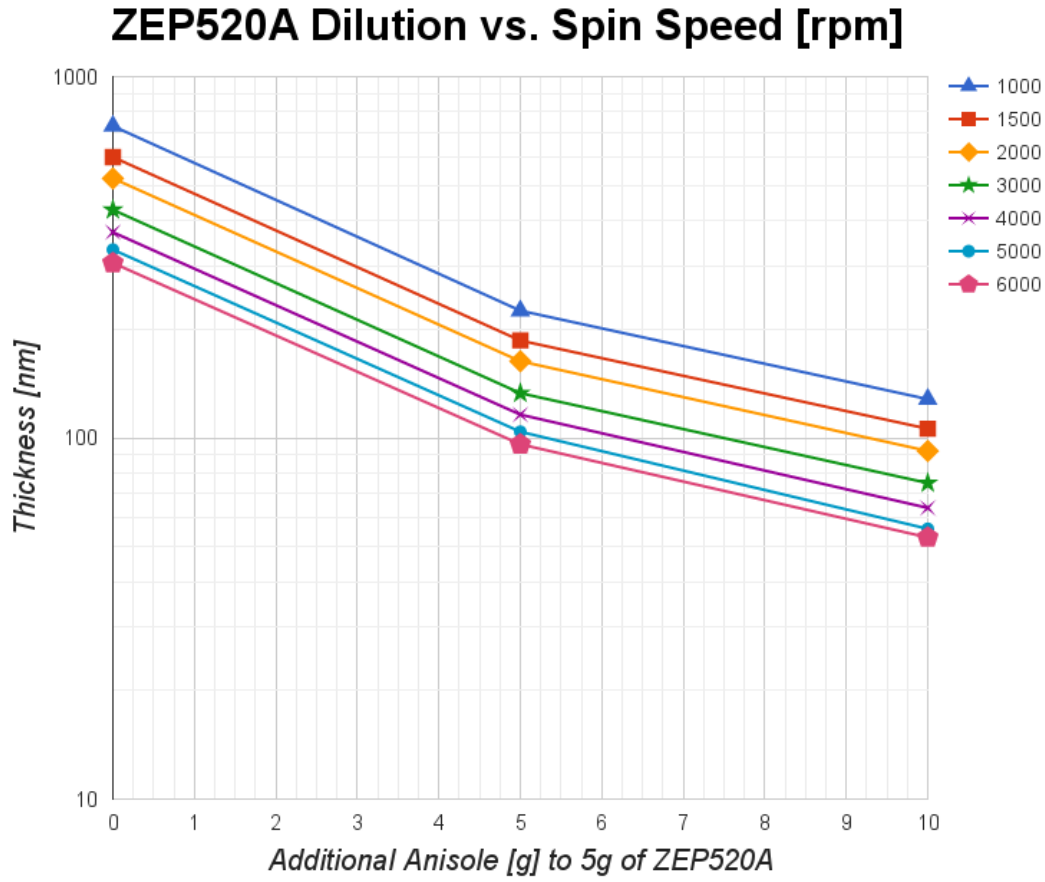


FIG. 2. (Color online) The dilution by weight of ZEP520A versus spin speed from 1000 to 6000 rpm was generated for this work. The aim of this chart is to provide approximate dilutions using anisole to acquire a specific resist thickness at any given spin speed. The lower rpm for a given thickness implies a higher dilution and less resist material, which means less consumable waste.

## 2. Surface treatment and contact angle measurements

The surface treatment after descum and before the Au deposition is what determines the adhesion of Au. For this experiment, three samples received a different surface treatment to test adhesion promotion. The first sample, the control, received no surface treatment. The second sample received a traditional seed layer of e-beam

evaporated Cr deposited at a rate of 2 Å/sec onto the surface. Final Cr thickness is 10nm. Finally, the third sample was soaked in SurPass 4000 for 2 minutes followed by an IPA rinse and N<sub>2</sub> blow dry. SurPass 4000 is a cationic charged water soluble compound that acts to improve adhesion by modifying the surface energy of the substrate for improved adhesion between otherwise incompatible materials.

Using a goniometer, contact angles measurements were performed on bare Si substrates after a 20 minute O<sub>2</sub> plasma. The impact on surface energy of the native oxide is compared between no treatment and treatment with SurPass 4000. In Fig. 2a, the contact angle for the control sample is shown. No surface treatment was applied to the control sample as it exhibits a contact angle of less than 5 degrees. The sample in Fig 2b was soaked in a bath of SurPass 4000 for 2 minutes followed by an IPA rinse and N<sub>2</sub> blow dry. The contact angle observed was 18 degrees which is a clear indication that there was a modification of the surface energy. Ellipsometry using a J.A. Woollam V VASE Spectroscopic Ellipsometer measured no detectable residue on the surface after SurPass 4000 treatment.

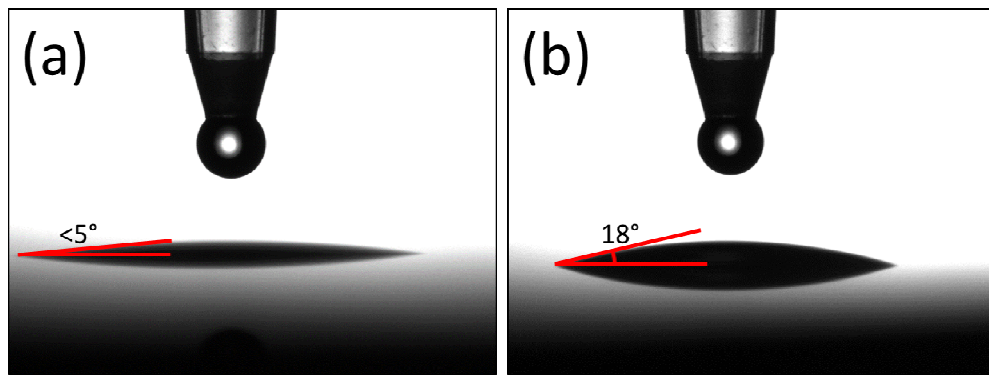


FIG. 3. (Color online) Contact angles were performed using a goniometer to compare the impact on surface energy of the native oxide. In (a), no surface treatment was applied to the control sample as it exhibits a contact angle of less than 5 degrees. The sample in (b)



was soaked in a bath of SurPass 4000 for 2 minutes followed by an IPA rinse and N<sub>2</sub> blow dry. The contact angle observed was 18 degrees which is a clear indication that there is a modification of the surface energy from treatment.

### **3. *Metallization and lift-off***

All samples received gold evaporation at the same time. Using a load-locked Kurt J. Lesker Co. Model PVD75 electron beam evaporator with a 4 pocket hearth, samples were mounted to a carrier platen for evaporation of 30 nm of gold at a rate of 2.5 Å/sec and at a base pressure below 1 e-7 Torr. Metal lift-off was performed using approximately 100 mL MicroChem 1165 stripper of MicroChem 1165 Stripper heated in a water bath to 60°C. The samples were placed in the solvent for 60 minutes without agitation. Afterwards, the samples were thoroughly rinsed with acetone, methanol and isopropanol and dried with an N<sub>2</sub> gun.

## **III. RESULTS AND DISCUSSION**

### **A. *Key Observations Post Gold Lift-Off***

For this experiment, three silicon wafers received a different surface treatment to test adhesion promotion of gold onto silicon. The first sample, the control, received no surface treatment. As shown Fig. 4, delamination of the gold patterns without any prior surface treatment to promote adhesion occurred during lift-off. The second sample received a traditional seed layer of e-beam evaporated Cr deposited at a rate of 2 Å/sec onto the surface for a final thickness of 10nm. The results are as expected in Fig. 5 where all the patterns exhibit adhesion to the surface. Finally, the results for the third sample,

which was soaked in SurPass 4000 for 2 minutes followed by an IPA rinse and N2 blow dry, is shown in Fig. 6. The patterns exhibit adhesion to the surface and look similar to Fig. 5. As mentioned in the previous section about fabrication, agitation was not applied during lift-off as the mechanical vibration caused delamination for the SurPass 4000 treated sample.

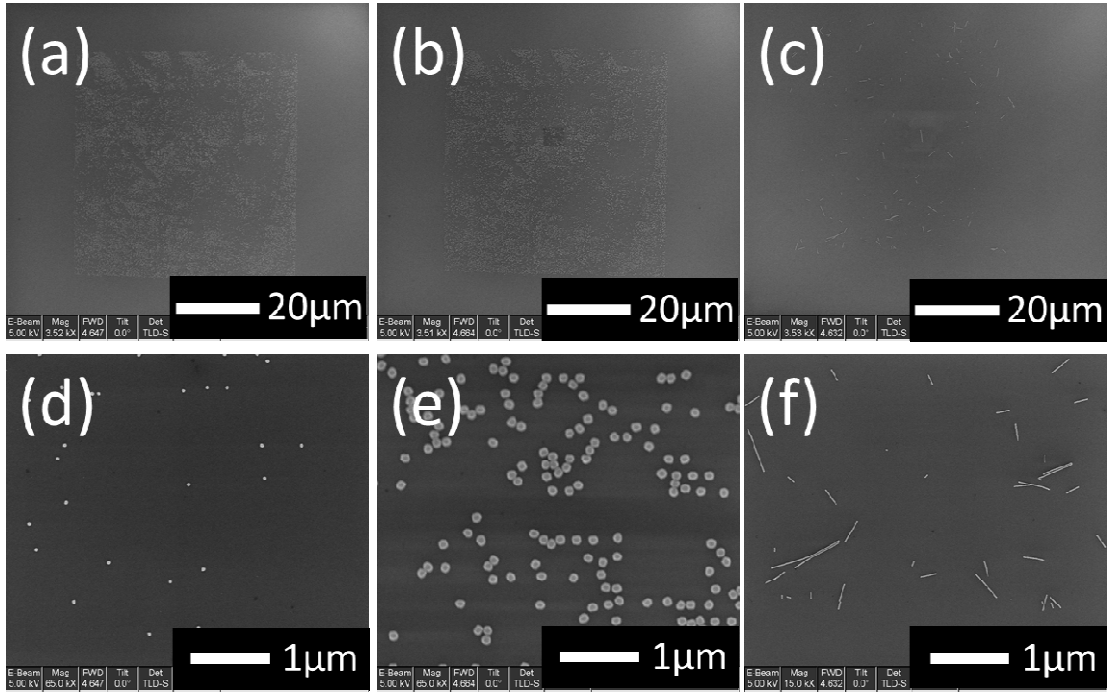


FIG. 4. As expected, the lack of adhesion promotion treatment of the control sample results in an expected delamination of Au from the substrate. The zoom-out view of the 40 nm dots, 100 nm dots and 70nm lines are shown in (a), (b) and (c), as well as their zoom-in view in (d), (e) and (f), respectively.

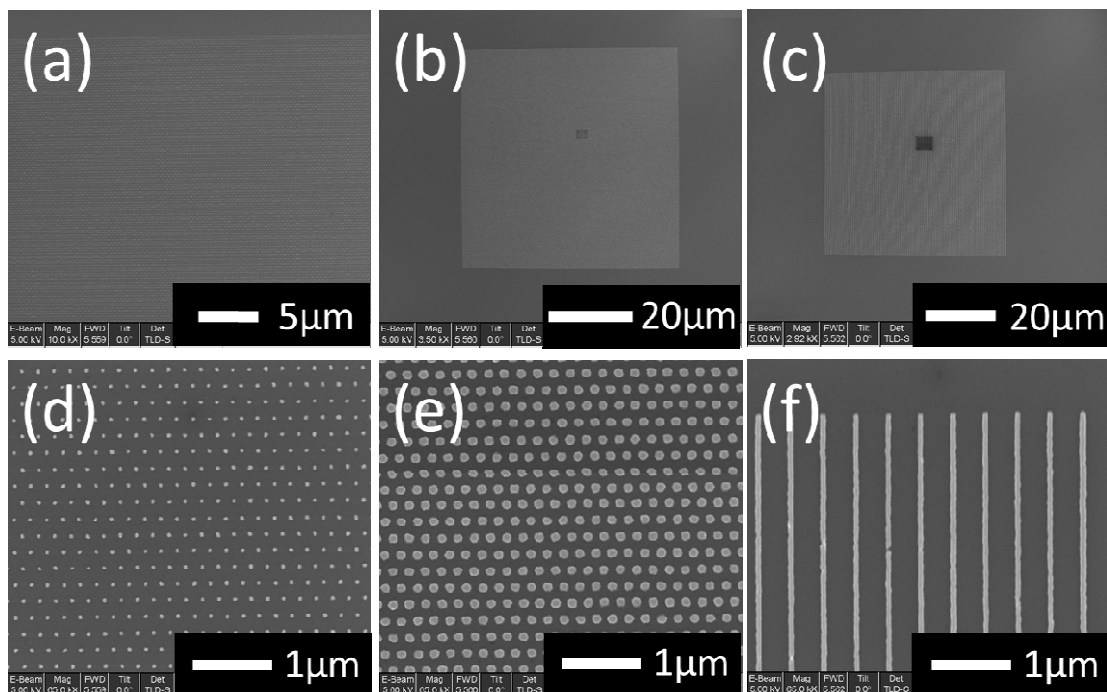


FIG. 5. In contrast to the control sample that exhibits delamination of the gold from the silicon substrate, the Cr treated sample exhibits excellent adhesion of Au given the presence of the Cr seed layer. The zoom-out view of the 40 nm dots, 100 nm dots and 70nm lines are shown in (a), (b) and (c), as well as their zoom-in view in (d), (e) and (f), respectively.

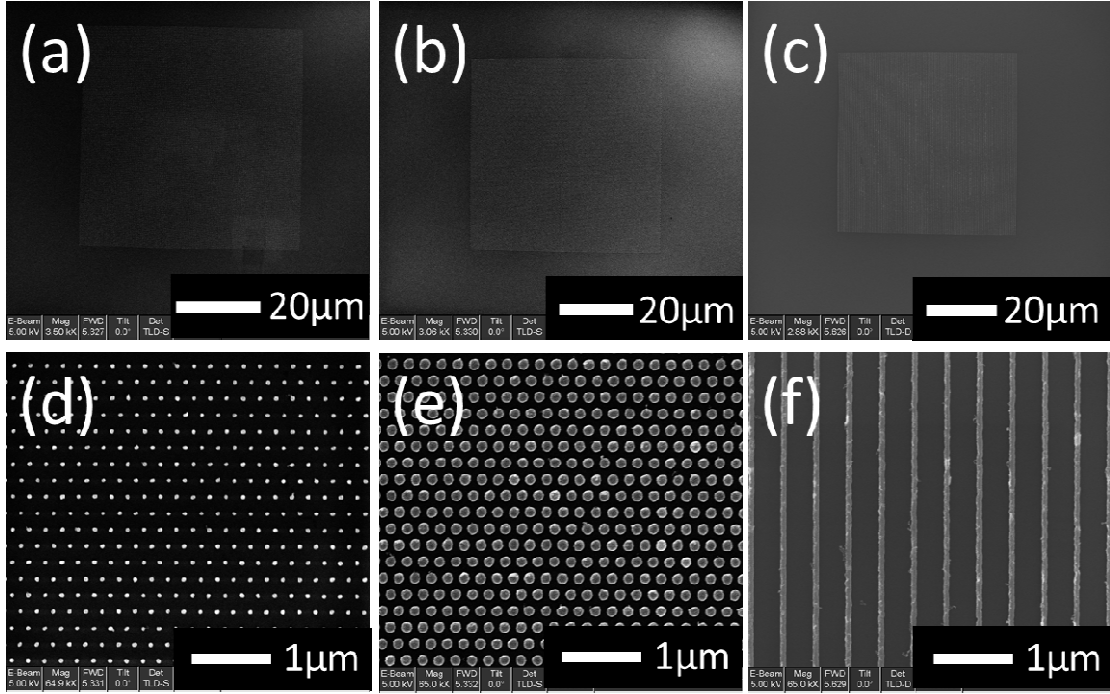


FIG. 6. Similar to the Cr treated sample, the SurPass 4000 treated sample also exhibits adhesion of Au on Si but in the absence of a metal seed layer. The zoom-out view of the 40 nm dots, 100 nm dots and 70 nm lines are shown in (a), (b) and (c), as well as their zoom-in view in (d), (e) and (f), respectively.

## ***B. Surface Plasmon Optical Losses with and without Metal Seed Layer***

The effects of a metal seed layer on surface plasmon propagation losses are illustrated in Fig. 7. Our calculations show that the surface plasmon mode supported by a 20 nm Au film on an  $\text{SiO}_2$  substrate increases by a factor of greater than 3.5 across the near-infrared with the addition of a 5 nm adhesion layer of Cr or Ti. Compared to a 25 nm Au film, the mode supported by a 20 nm Au film with 5 nm adhesion layer is increased by a factor

greater than 5. Though our calculations are limited to planar films, the large increase in optical loss due to the adhesion layer is also expected for photonic crystal and metamaterial structures that utilize Au for optical confinement. As a result of this simulation, future work points towards implementation of metal free seedless adhesion of gold onto SiO<sub>2</sub> to enhance the performance of plasmonic devices.

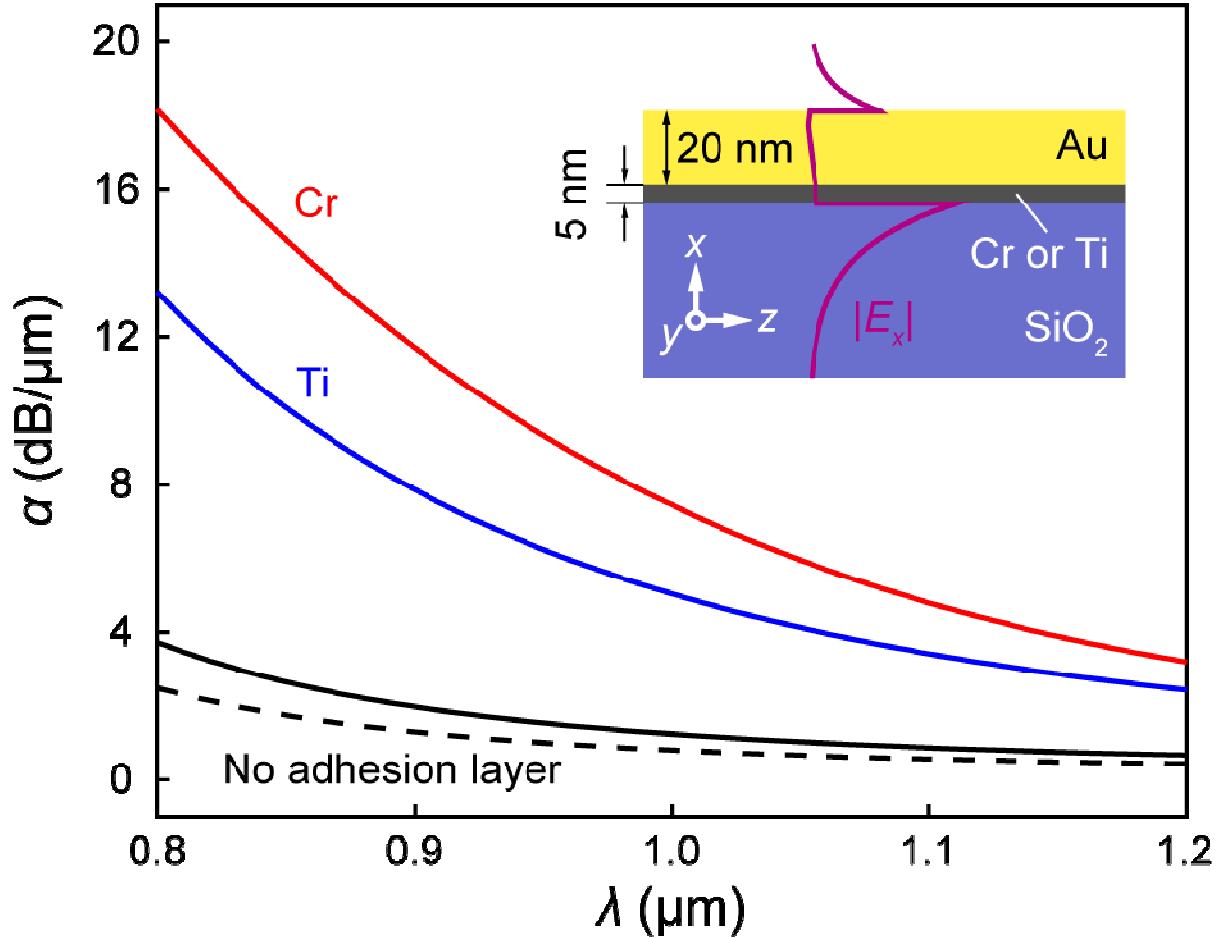


FIG. 7. (Color online) Comparison of surface plasmon propagation loss as a function of wavelength with and without an adhesion layer calculated using the finite-element method with material parameters from Ref. 4. Propagation loss with no adhesion layer is calculated for 20 nm (solid black curve) and 25 nm (dashed black curve) Au thicknesses.

(inset) Dimensions and field profile for the surface plasmon mode (evanescent decay lengths are not to scale).

## IV. SUMMARY AND CONCLUSIONS

Successful metal free seedless adhesion of gold onto a silicon native oxide was demonstrated for features down to 40 nm. Surface treatment impacts the adhesion as well as careful processing during lift-off without agitation. No surface treatment results in delamination of the metal thin film. Using a traditional method with Cr as a seed layer, gold was able to adhere to the silicon surface without issue. Finally using SurPass 4000, a cationic charged water soluble compound, adhesion was achieved by modifying the surface energy of the substrate. Using simulation, removing the metal seed layer could improve the efficacy of plasmonic devices that currently use a metal seed layer.

## ACKNOWLEDGMENTS

*The authors would like to thank Professor Jonathan Spanier and Dominic Imbrenda of Drexel University in Philadelphia, PA for use of the Carl Zeiss Supra 50. Lastly, the authors are eternally grateful to Professor Shu Yang and Gaoxiang Wu of the University of Pennsylvania for use of the goniometer for contact angle measurements.*

<sup>1</sup> C. M. Eichfeld and G. G. Lopez, Journal of Vacuum Science & Technology B, 32, 06F503 (2014).

<sup>2</sup> J. R. Bickford, G. G. Lopez, N. Belic, and U. Hofmann, Journal of Vacuum Science & Technology B, 32, 06F511 (2014).

<sup>3</sup>BEAMER (2016), <http://www.genisys-gmbh.com>.

<sup>4</sup>A. D. Rakić, A. B. Djurišić, J. M. Elazar, and M. L. Majewski, Applied Optics, 37, 5271 (1998).