Quantitative Chemically Specific Coherent Diffractive Imaging of Reactions at Buried Interfaces with Few Nanometer Precision

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Supporting Information

ABSTRACT: We demonstrate quantitative, chemically specific imaging of buried nanostructures, including oxidation and diffusion reactions at buried interfaces, using nondestructive tabletop extreme ultraviolet (EUV) coherent diffractive imaging (CDI). Copper nanostructures inlaid in SiO2 are coated with 100 nm of aluminum, which is opaque to visible light and thick enough that neither visible microscopy nor atomic force microscopy can image the buried interface. Short wavelength high harmonic beams can penetrate the aluminum layer, yielding high-contrast images of the buried structures. Quantitative analysis shows that the reflected EUV light is extremely sensitive to the formation of multiple oxide layers, as well as interdiffusion of materials occurring at the metal–metal and metal–insulator boundaries deep within the nanostructure with few nanometers precision.

KEYWORDS: Nanometrology, imaging, buried layers, chemical specificity, high harmonic generation, extreme ultraviolet

Probing and imaging reactions at interfaces buried beneath visibly opaque materials are a critical capability for nanoscience and nanotechnology. In order to understand and optimize advanced functional nanomaterials for next-generation energy and nanoelectronic devices, it is important to determine the physical size and nature of interfaces, if they degrade over time, and how heat, charge, and spins move through different interfacial morphologies. However, most imaging modalities cannot be used for nondestructive, subsurface (>50 nm) imaging.1 Visible microscopy and atomic force microscopy (AFM) only image the surfaces of metallic samples. Backscattered electron (BSE), scanning electron microscopy (SEM), and secondary electron SEM with secondary electrons scattered electron (BSE), scanning electron microscopy (SEM), (AFM) only image the surfaces of metallic samples. Backscattered electron (BSE), scanning electron microscopy (SEM), and secondary electrons scattered electron (BSE) can image buried features using high electron energies to provide increased penetration depth.2 However, these approaches also have limitations of decreased spatial resolution,3 charging of insulating samples, sample damage, and hydrocarbon buildup.4 Furthermore, SEM often produces a complicated mixture of morphology and compositional information, making quantitative image analysis difficult. Moreover, for BSE-SEM achieving elemental contrast for neighboring elements is often difficult because BSE efficiency is proportional to the natural logarithm of the atomic number.5

Various specialized imaging techniques have been employed for probing buried interfaces. Mode-synthesizing AFM and scanning near-field ultrasound holography can detect subsurface structures.6,7 However, these techniques are not easily extended to dynamic imaging, which requires a fast imaging modality. Three-dimensional structures have also been probed using large-scale synchrotron X-ray diffraction microscopy in a transmission geometry.8

Short wavelength extreme ultraviolet (EUV) and soft X-ray beams have unique potential for imaging reactions at buried interfaces because they can penetrate visibly opaque materials, provide chemically specific contrast, and also image nanoscale features. In particular, by combining coherent beams from either high harmonic generation (HHG)10 or X-ray free electron lasers (XFELs)11 with coherent diffractive imaging (CDI),12−16 it is now possible to achieve spatial resolutions that are comparable to the illuminating wavelength in the X-ray region for the first time.17,18 Accordingly, CDI has found a range of applications in transmission and reflection geometries19−21 to investigate nanoscale strain,22,23 semiconductor structures,19 and for biological imaging.24−26 Because no optical elements are needed between the sample and detector, coherent diffractive imaging is the most photon efficient form of imaging and can be nondestructive with no charging effects or resolution loss with depth.27 Moreover, the contrast mechanisms in EUV CDI are relatively straightforward and...
intrinsically high: amplitude images exhibit high sensitivity to material composition, while phase images are exquisitely sensitive to both material composition and topography. 

Here, we demonstrate noninvasive, nondestructive imaging of the evolution of buried interfaces and reactions that occur at these interfaces using tabletop EUV CDI. Copper nanostructures inlaid in SiO$_2$ are coated with 100 nm of aluminum, which is opaque to visible light and thick enough that neither visible microscopy nor atomic force microscopy can image the buried interface. Short wavelength high harmonic beams can penetrate the aluminum layer, yielding high-contrast images of the buried metallic and insulating structures. Quantitative analysis shows that EUV light can not only detect but is extremely sensitive to multiple oxide layer formation as well as material interdiffusion that occurs at the Al–Cu and Al–SiO$_2$ boundaries deep within the nanostructure at the few nanometers level. We verify the presence of interdiffusion at the metal–metal interface using destructive Auger electron spectroscopy (AES) sputter depth profiling.

Key to our new ability to nondestructively image buried interfaces is the use of ptychographic CDI, which uses redundant information from multiple diffraction patterns recorded with overlapping fields of view to robustly reconstruct both the amplitude and phase of an object. Ptychographic CDI has been implemented in a high-NA reflection geometry using HHG illumination with the amplitude of the reconstructed images yielding the relative reflectivity (or transmissivity) between different regions of a sample. The results presented here required a modification of ptychography that returns absolute reflectivities simply by measuring the flux of the beam. This new approach called reconstructed absolute phase-diverse transmissivity/reflectivity CDI (RAPTR-CDI) allows us to nondestructively detect the formation and evolution of interfacial diffusion and oxidation layers at the Al–Cu and Al–SiO$_2$ boundaries.

**Experiment.** The experimental setup is illustrated in Figure 1. Bright, phase-matched, fully spatially coherent high harmonic beams were generated by focusing a Ti:sapphire laser beam (23 fs, 1.5 mJ, 785 nm pulses at 5 kHz) into a 5 cm long waveguide filled with Argon gas at 49 Torr. Harmonics around the 27th order (29.1 nm) were reflected from two superpolished silicon substrates set at Brewster’s angle to reflect the HHG beam while rejecting the residual laser light. Two 200 nm-thick Al filters were used to block any remaining fundamental laser light. The HHG beam was then passed through an iris to induce a hard edge on the beam incident on the sample. Two narrow-bandwidth multilayer mirror sets at 12° and 47.7° and with a bandpass of ∼1 nm were used to select the 29.1 nm harmonic light. An ellipsoidal mirror focused the HHG beam to a ∼16 μm diameter spot, which was incident on the sample at 57.8° from the normal. A 2048 × 2048 Princeton Instruments (PI-MTE) CCD, placed a distance of 3.85 cm downstream of the sample and normal to the undiffracted beam, was used to collect the light diffracted from the sample.

The two samples (provided by SEMATECH) imaged in this work were cleaved from a damascene-style wafer consisting of Cu structures inlaid in SiO$_2$. The wafer was polished flat using chemical mechanical planarization (CMP). After exposure to atmospheric conditions for 14 months, repeating patterned cells were cleaved such that essentially identical areas of interest would be present on two samples. One sample was then coated with 100 nm of Al using an Edwards Cryo 304 electron-gun physical vapor deposition system, while the other was left uncoated for comparison.

For both samples, the object and probe were computationally reconstructed using a combination of ptychography algorithms. The diffraction patterns were interpolated onto a linear spatial frequency grid using tilted plane correction and then reconstructed with RAPTR-CDI, including position correction. The multilayer mirrors allowed small amounts of adjacent harmonics to leak through, broadening the total fractional bandwidth of the illumination and degrading the fidelity of the reconstructions. For this reason, the corrected positions were next fed into a multicolor ptychographic information multiplexing algorithm. By using this multicolor
algorithm, noise due to the presence of adjacent harmonics could be filtered out so that only 29.1 nm light contributed to the reconstructed images. The multicolor algorithm significantly improved the image fidelity over single color ptychography (see Supplementary Figure S1).

In order to use RAPTR-CDI to characterize the absolute reflectivity of the buried metal–metal and metal–oxide interfaces at 29.1 nm, we measured the flux of the HHG beam before each ptychography scan. We recorded images of the beam reflected from a gold mirror, then used the exposure time and reflectivity of gold to calculate the number of available photons incident on the sample in units of detector counts. The reflectivity of the gold mirror was taken to be 27.9% with the surface roughness assumed to be that of sibling silicon substrates used in ref18. Then, in RAPTR-CDI the probe is normalized to the measured power in each iteration. The absolute value squared of the complex amplitude of the reconstructed object is therefore equal to the reflected intensity from the sample at every pixel. Because the sample reflectivity is spatially varying, masks for the features and substrates (Supplementary Figure S2) were used to select regions free from contamination. We segmented the RAPTR-CDI reconstructions to calculate the average absolute reflectivities reported in Figure 3. We also scaled the multicolor reconstructions such that the mean reflectivity of the masked regions agrees with that of the RAPTR-CDI images. The scaled multicolor reconstructions for both samples are shown in Figure 2.

**Chemically-Specific Imaging of Buried Metal–Metal and Metal–Oxide Interfaces.** To highlight the extreme sensitivity of EUV light to interfacial reactions and chemical composition, we compare our multicolor CDI amplitude images (which have been normalized to the measured RAPTR-CDI reflectivities) to visible microscopy (Figure 1) as well as secondary electron SEM and AFM (Figure 2). The SEM (FEI Nova NanoSEM 630) with an Everhart-Thornley secondary electron detector and an accelerating voltage of 18 kV shows contrast on both samples (Figure 2c, d). The contrast on the coated sample is due to a combination of morphology on the surface of the Al as well as the chemical difference between the underlying features and substrate. This elemental contrast is detectable because the Everhart-Thornley detector also captures SE-II electrons generated from backscattered electrons reflected from the underlying structures. This means that the coated SEM image includes a complex mixture of height and material information that is not easily decoupled.

The AFM (Digital Instruments MAAFM-2) only shows surface topography. The coated features are visible on the top surface because Al deposition is slow (5 Å, or approximately two atomic layers, per second), causing each layer to acquire the underlying topography. However, the AFM’s accuracy in the vicinity of surface contamination is significantly degraded.

![Figure 2](image-url)
due to the much higher aspect ratio of the contamination than the nearly flat features.

The EUV ptychography amplitude reconstruction (Figure 2f) is the only image that definitively visualizes the buried features, as confirmed by the amplitude contrast between the Cu features and substrate. Indeed, if the EUV nanoscope were only imaging the top surface of the aluminum, then the absolute reflectivity image in Figure 2 would appear featureless and the reconstruction would be phase-only. Instead, EUV light penetrates through the Al to reveal the buried structures. Because the penetration depth of Al at 29.1 nm exceeds 400 nm, 80% of the light is transmitted through 100 nm of Al.

Quantitative Detection of Oxidation and Diffusion at Buried Interfaces. In order to compare our experimental reflectivity measurements to our theoretical calculations, we numerically modeled the multilayer stacks representative of both samples, including changes in the stacks resulting from oxidation and interdiffusion at all the interfaces (top and buried). We then calculated the complex reflectivities of these stacks. For these calculations, we used methods derived from ref 41, which solve Maxwell’s equations directly in the multilayer stack. We confirmed our predictions with IMD,40 a software program that uses the Fresnel equations to calculate the complex reflectivity for a stack of materials at EUV/X-ray wavelengths.42,43 Our multilayer stack method and IMD agree to within 0.3% reflected intensity and 5° reflected phase, which would correspond to a 0.38 nm height difference in a height map (see Figure 4).

The four distinct areas, coated features, coated substrate, uncoated features, and uncoated substrate, are modeled as

Figure 3. Uncovering oxidation and interdiffusion at buried interfaces. (a–d) Stacks used to model the reflectivity of different parts of the coated sample and its surface roughnesses, σ. (a) Feature and (b) substrate stacks used in the full diffusive model. Neglecting this diffusion (stacks (c) and (d)) yields predicted reflectivity values very inconsistent with the reconstructed reflectivities, shown by the crosshatched bar in (e). Inset (e) shows how the modeled reflectivity values compare to the experimental values from the RAPTR-CDI reconstruction. (f) Auger electron spectroscopy sputter depth profile of a coated sample feature, confirming a diffusive region between the Al and Cu. (g) Uncoated feature and (h) substrate stacks. In this case, the full model is diffusionless. (i) Comparison of modeled and experimental reflectivity of the uncoated sample. Because the primary sources of uncertainty in these calculations arise from the oxide layer thicknesses, which are intrinsically difficult to quantify, we omit error bars from our model results.
The results for the experimental versus modeled coated sample feature reflectivity are shown in Figure 3e. We initially used a simple model with 100 nm of Al deposited on the same stacks used for the uncoated sample. This model led us to predict $R_{\text{features}} = 5.6\%$ and $R_{\text{substrate}} = 3.8\%$. However, these values are significantly higher than both of our experimental measurements (which were $R_{\text{features}} = 2.0\%$ and $R_{\text{substrate}} = 2.7\%$). Furthermore, the reconstruction displays a contrast inversion in the coated sample image, in which the coated Cu features are less reflective than the coated substrate, whereas they were more reflective in the uncoated sample (Figure 2e,f) and in the simple model for the coated sample. Adding an Al$_2$O$_3$ layer on top of the Al layer could not resolve this contrast inversion, nor could assuming that the Al scavenged O from the copper oxides to form Al$_2$O$_3$ at the interface, which is an energetically favorable reaction because $2\text{Al} + 3\text{CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu}$ corresponds to $\Delta H^\circ = -1207.52$ kJ/mol.44

The unexpected observation of this relative contrast inversion led us to hypothesize that diffusion occurred at the Al–Cu boundary, forming an interdiffusion layer that decreased the reflectivity at the interface (Figure 3a).35 We confirmed the presence of this diffusion layer on the coated features using AES sputter depth profiling, a destructive technique that requires ion sputtering through the sample to obtain Auger electron spectra at every relevant interface (Figure 3f). This technique revealed a 40 nm diffusive region at the interface. In the feature regions, we calculated stoichiometrically plausible percent compositions for Al, Cu, Al$_2$O$_3$, CuO, and Cu$_2$O from the elemental composition provided by the AES at each depth. We tested two diffusive models, one in which Al$_2$O$_3$ is the only oxide at the Al–Cu interface and one in which there is a mixture of Al$_2$O$_3$, CuO, and Cu$_2$O at the interface. We find that the model that assumes Al captures all of the O from the copper oxides at the boundary fits well with our measured reflectivity (Figure 3e). For the coated substrate (Figure 3b), we initially used the same stack as in the full model of the coated features for the top 50 nm of the sample (including a 3 nm diffusive Al$_2$O$_3$ layer at the surface), followed by an abrupt Al–SiO$_2$ interface at a depth corresponding to 100 nm of deposited Al. However, this resulted in a reflectivity twice as bright as we observe experimentally. We resolved this discrepancy by incorporating 26.5 nm of Al$_2$O$_3$ at the Al–SiO$_2$ interface with diffusion modeled by convolving the depth profile with a Gaussian of full width 6 nm. Because this Al$_2$O$_3$ layer corresponds to Al scavenging O from SiO$_2$, we incorporated the corresponding amount of liberated silicon in a layer below the Al$_2$O$_3$. This modification produced agreement between the experimental reflectivity (2.66%) and the model (2.57%). We were unable to experimentally confirm the presence of the diffusive Al$_2$O$_3$ layer at the interface because SiO$_2$ is nonconductive, preventing a reliable AES depth profile. However, there is experimental evidence in the literature indicating that Al can scavenge oxygen from SiO$_2$ when deposited via e-beam evaporation.45

To investigate how sensitive the reflectivity in the EUV spectral range is to interdiffusion of layers, we modeled our final coated sample stacks with the same amount of material as in our full model but without any diffusion (Figure 3c,d). The theoretical reflectivities of these diffusionless models are shown by the red crosshatched bars in Figure 3e. The dramatic disagreement with our measurements indicates that RAPTR-CDI is highly sensitive to diffusion. Our final diffusive reflectivity models (green-striped bars) are compared to the experimentally measured reflectivities (gray bars) in Figure 3e. The uncertainty in the experimental measurement includes uncertainty in the gold mirror reflectivity and the standard deviation from the mean reflectivity due to spatial variation in the reconstructed reflectivity.
In the case of the uncoated sample, we estimated that the Cu features form a native oxide bilayer upon exposure to the atmosphere consisting of 4.8 nm CuO atop 7.4 nm Cu₂O, based on a study of copper oxide growth at ambient temperatures indicating a ratio of 0.65 = d_{CuO}/d_{Cu₂O}. The model is displayed in Figure 3g. We calculated the total oxide thickness by assuming that the sample was polished flat during chemical mechanical planarization and the average feature height measured by the AFM is all due to oxide growth. This total thickness agrees with the amount of oxide indicated by the AES measurement of the coated features. In our uncoated sample model, the substrate is SiO₂ alone (Figure 3h). These relatively simple modeled stacks for the uncoated sample lead to agreement with the measured reflectivity of the uncoated sample (Figure 3i), providing a good check that the RAPTR algorithm produces accurate and reliable results.

High-Resolution Surface Topography from Phase Reconstructions. In addition to the chemical composition discernible from the amplitude of the reconstructions (Figure 2), the phase of the reconstructions contains both material and height information. By subtracting the phase of the complex reflectivity predicted by our modeled feature and substrate stacks from the reconstructed phase images, we can generate height maps showing the surface topography of the samples. In the case of the coated sample, the phase of the exit surface wave accounts for phase changes within the stack, and the height map therefore shows the top surface topography as opposed to the buried surface. We compare these height maps to AFM height maps in Figure 4. There is good agreement between the height maps generated from ptychography and AFM, validating our RAPTR-CDI method for imaging buried nanostructures.

Conclusions. We demonstrated a unique and powerful new capability for quantitatively imaging the evolution of buried interfaces at the nanometer-level, with chemically specific contrast, through metal and oxide layers that are opaque to visible light, AFM, and SE-1 SEM. This allowed us to nondestructively detect the evolution of interfacial diffusion and multiple oxidation layers between the Al coating and the buried Cu features and SiO₂ substrate. We also validated our findings using AFM, SEM, Auger electron spectroscopy, and values from the literature. This work required the development of a new technique we call RAPTR-CDI, which is a modified ptychography algorithm that yields absolute reflectivities by normalizing the probe at every iteration to the correct measured flux incident on the sample. This enables exquisite sensitivity to multiple interfaces simultaneously, even those buried deep within the sample.

In the future, we can extend this work by imaging interfacial charge, energy, and spin transport, examining the effect of increased temperature on interlayer diffusion, and using a comb of harmonics spanning an absorption edge to simultaneously image through multiple layers. Studying these physical properties will aid in the design of next-generation energy-efficient photovoltaics, thermoelectrics and nanoelectronic devices. RAPTR-CDI also opens the door to fully quantitative material characterization combined with EUV imaging, that is, imaging reflectometry, by performing angle-resolved measurements with the sample placed on a tilt stage. This would allow for highly sensitive metrology of thick samples inaccessible to visible ellipsometry. The technique could further be extended to perform high-throughput buried layer imaging by using multiple EUV beams to achieve a wide field of view. In the future, this technique coupled with the fast temporal resolution of high harmonics can be harnessed for imaging dynamically functioning interfaces.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b01864.

Sample fabrication, details, and values of the reflectivity model calculations, details of the height maps, further information about the reconstructions, and masks used to obtain experimental reflectivity values (PDF)

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Notes
The authors declare the following competing financial interest(s): H.K. and M.M. have a financial interest in a laser company, KMLabs, that supplied some equipment used to perform these experiments.

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ABBREVIATIONS

CDI, coherent diffractive imaging; HHG, high harmonic generation; SEM, scanning electron microscope; SE-Ⅱ, secondary electron II; AFM, atomic force microscope; EP, electroplate; CVD, chemical vapor deposition; CMP, chemical mechanical planarization; RAPTR, reconstructed absolute phase-diverse transmissivity/reflectivity; NA, numerical aperture

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