Low dose hard x-ray contact microscopy assisted by a photoelectric conversion layer

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Hard x-ray contact microscopy provides images of dense samples at resolutions of tens of nanometers. However, the required beam intensity can only be delivered by synchrotron sources. We report on the use of a gold photoelectric conversion layer to lower the exposure dose by a factor of 40 to 50, allowing hard x-ray contact microscopy to be performed with a compact x-ray tube. We demonstrate the method in imaging the transmission pattern of a type of hard x-ray grating that cannot be fitted into conventional x-ray microscopes due to its size and shape. Generally the method is easy to implement and can record images of samples in the hard x-ray region over a large area in a single exposure, without some of the geometric constraints associated with x-ray microscopes based on zone-plate or other magnifying optics. Copyright 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4802886]
FIG. 1. (a) Using a photoelectric conversion layer to enhance the sensitivity of the polymer film to hard x-rays. The resist polymer film is coated with a thin layer (50 nm) of gold. The gold layer effectively absorbs hard x-rays and releases secondary electrons into the underlying resist film. The resulting increase of secondary electrons in the resist film allows for dramatically decreased exposure time. (b) Comparison of profilometer scanned height profile of a 60 μm slit exposure of resist layers (ZEP520a) with and without gold coating. The plates were exposed to 17.5 keV x-rays at the APS 2-BM beamline for a total flux of $3.6 \times 10^{14}$ photons/mm$^2$. The pattern in the exposed area of resist is due to non-uniformities in the beamline intensity profile.

In the 1970’s Feder and co-authors discovered that when patterning the exposure of an x-ray beam on a resist polymer with a metal mask, the mask itself produced secondary electrons that exposed the resist beneath it, which blurred their desired lithographic pattern.\textsuperscript{18} Utilizing this effect, we propose a method to substantially lower the required exposure in hard x-ray contact microscopy by covering the resist film with a thin layer of gold or other high Z material (Figure 1(a)). This layer has a high coefficient of absorption for hard x-rays, and upon interaction with x-ray photons releases secondary electrons. Some of the electrons inevitably enter the resist layer and cause polymer chain scission. In effect, the high Z layer is a photoelectric conversion layer which increases the flux of secondary electrons in the underlying resist layer, thereby reducing the required dose. We used this method to image x-ray absorption gratings with a synchrotron source at 17.5 keV, as well as a compact, polychromatic x-ray tube.

To prepare the resist plate, a silicon wafer is primed with HMDS and spin-coated with 100-500 nm of ZEP520a, and then thermally evaporated with 50 nm of gold. Although e-beam deposition may seem favorable, the radiation produced during the process completely exposes the ZEP520a, making it unusable. Because electron penetration of gold ranges from 0 to 385 nm for energies of 0 to 17.5 keV, which is the range of photo electrons produced at the beamline, a thickness equal or less than 385 nm is required.\textsuperscript{19} To obtain a 50 nm or better resolution we deposited a 50 nm layer.
of gold. Due to the weak adhesion of the gold to the ZEP, a thin piece of adhesive tape is sufficient to lift off the gold from the ZEP after exposure. Standard chemical gold lift off procedures result in degradation and removal of the delicate ZEP layers and are unsuitable for this application.

Our process and needs are similar to those of x-ray lithography, except that lithography aims for binary-dose response, which results in high-contrast features that require a threshold dose to appear. For imaging applications, a more gradual dose response is preferable so that there is a greater dynamic range in the resultant radiograph. We chose the electron resist polymer ZEP520a (ZEON Corporation) for its high sensitivity compared to the traditional choice of poly methyl methacrylate (PMMA). The ZEP520a resist allows for many different development methods to adjust sensitivity and resolution. Because we require high sensitivity as well as a gradual dose response, we used a warm xylene protocol described by Yang and co-authors. They discovered that the dynamic range of the dose response (dose required to remove a certain thickness of resist) increased by two fold when the development temperature in xylene was raised from 20°C to 40°C, while the saturation dose decreased by 60–70%. Our development protocol consists of a 20 second dip in 40°C xylene, followed by a 20 second dip in 20°C xylene, a 20 second isopropyl alcohol rinse, and finally nitrogen air blow-dry.

We tested the efficacy of the photoelectric layer by exposing ZEP plates at a synchrotron beamline (2-BM, Advanced Photon Source, Argonne National Laboratory, USA) through a 60 μm slit at 17.5 keV for 1 and 3 minutes. The corresponding total photon flux was $1.2 \times 10^{14}$ photons/mm² and $3.6 \times 10^{14}$ photons/mm² respectively. After development, the plates were scanned with a Dektak-XT profilometer in the direction across the slit. The average profiles of 10 repeated scans are shown in Figure 1(b) for plates with and without the gold layer. The exposed section of resist demonstrates a non-flat profile due to the overall non-uniformity of the incident beam’s intensity. The average depth of the resultant impression was measured to be 6.2 nm on the blank uncoated ZEP versus 268 nm on the gold coated ZEP, which corresponds to sensitivity increase by a factor of approximately 43.2. This result is in alignment with D. Regulla et. al.’s finding that inclusion of a gold photoelectric conversion layer when exposing human lymphocyte cells to x-rays resulted in an increase in dose by a factor of 45.4.

An application of this method is the inspection of hard x-ray optical components that could not be fitted into zone-plate based x-ray microscopes due to size or geometry. We used this method to characterize a recently developed intensity grating of a silicon-tungsten multi-layer structure. The gratings are up to 2.5 cm squared in size and have an oblique incidence angle of 28°. This geometry hindered the placement of the gratings into x-ray microscopes using zone-plates. Contact microscopy was taken as the only practical technique to image the transmission pattern through these gratings. As illustrated in Figure 2, the gratings were placed in direct contact with the resist plate. To protect the delicate gold layer, the plate was coated with a few microns of Shipley’s SU-8 resist polymer. Exposure time was adjusted to compensate for the attenuation of the x-ray beam through the grating’s silicon substrate.

The radiographs produced of various absorption gratings show the efficacy of this method. Because ZEP is a positive resist, sections which have been exposed are removed in the development process; whereas, sections which are not exposed remain. The imaging results of a prototype multi-layer grating are summarized in Figure 3. Figure 3(a) shows the AFM scanned image of the resulting imprint from exposing the prototype grating on the APS 2-BM beamline. The exposure was at 17.5 keV with a total photon flux of $8.1 \times 10^{13}$ photons/mm². The corresponding height profile of the imprint is shown in Figure 3(b). A scanning electron micrograph (SEM) image of the cross-section of the multi-layer grating is shown in Figure 3(c). The tungsten layers appear bright in the SEM cross-section image, corresponding to stripes of low x-ray exposure and less resist removal in the AFM scan and in the height profile. The uneven thicknesses of the tungsten and silicon layers are clearly seen in both the contact micrograph and in the SEM cross-section image. These are due to calibration adjustments during the electron-beam deposition process.

The smallest grating period we have imaged with this method is approximately 200 nm. Figure 4 shows the results from a grating of multi-layer stacks with a period of 188 nm, using the same imaging conditions as in Figure 3. The period of the grating is equal to the sum of the thicknesses of a tungsten and a silicon layer. The layer thicknesses were controlled by the multi-layer
FIG. 2. The setup for contact microscopy of a multi-layer hard x-ray intensity grating. The multi-layer grating is placed in contact with the resist plate. The x-ray beam is oriented parallel to the layers. The silicon layers allow the x-ray to pass through, while the tungsten layers block the x-ray. The transmitted intensity pattern is recorded onto the plate. The period of the grating is set by the thickness the silicon and tungsten layers, and can be as small as 200 nm.

FIG. 3. (a) An atomic force microscopy scan of the imprint of a prototype tungsten/silicon multi-layer transmission grating on a gold-coated resist plate. The x-ray exposure was at 17.5 keV and a total flux of $8.1 \times 10^{13}$ photons/mm$^2$. The height scale of the surface profile is shown on the right. Bright stripes are areas of less resist removal, corresponding to lower x-ray intensity. The height profile across the fringes is graphed in (b). In an SEM cross-section image of one multi-layer stack in the grating, (c), the tungsten layers appear bright, while the silicon layers and the silicon substrate appear dark. The multi-layer structure matches the x-ray transmission pattern by the AFM scan.
FIG. 4. (a) An AFM scan of the imprint of a multi-layer transmission grating having a period of 200 nm. The imprint was created on a gold-coated resist plate with an x-ray exposure at 17.5 keV and a total flux of $8.1 \times 10^{13}$ photons/mm$^2$. The bright fringes are areas behind the tungsten layers having lower x-ray intensity, and correspondingly less resist removal. The height profile of resist surface is graphed in (b). (c) An SEM image of a cross-section of one multi-layer stack in the grating, showing bright tungsten layers interleaved with dark silicon layers. The irregularity of the top half of the stack is introduced in the sectioning process, and therefore is not present in the transmission image in (a). The large bright area over the stacks is a protective epoxy coating.

deposition protocol. In this sample, the cross-section SEM images showed irregularities in the top half of the multi-layer structure (Figure 4(c)). It was uncertain whether these were actual defects in the multi-layers, or simply artifacts at the cleaved surface which were introduced in the sectioning process. The question was resolved by the contact radiograph of the transmitted intensity through the grating, which showed uniform fringes throughout the height of the multi-layer stack (Figure 4(a)). The defects in the cross-section images were therefore the result of the sectioning process.

With the addition of the gold photoelectric layer, we were able to image the transmission pattern of intensity gratings with a compact x-ray tube. The x-ray tube had a nominal focal spot size of 100 μm, operating at 70 kVp and 32 Watts. The grating-resist plate assembly was placed at 37 mm distance from the focal spot of the x-ray tube. In a 20 hour period, the accumulated level of exposure was approximately $4 \times 10^{13}$ photons/mm$^2$ after accounting for attenuation through the silicon substrate. This is approximately half the level of exposure on the synchrotron beamline described above. Figure 5(a) shows the resultant imprint of the exposure on the resist plate. The depth of the features in the developed resist film is also approximately half of those obtained on the synchrotron beamline and illustrated in Figures 3 and 4. The period of the grating is the thickness of a tungsten-silicon bi-layer, which is 561 nm for this sample. When compared to imprints obtained from the synchrotron beamline and shown in Figures 3 and 4, the edges of the intensity fringes are less sharp, due to the blurring effect from the size of the focal spot of the x-ray tube.

Two factors enter into the consideration when deciding the thickness of the gold layer. Increasing the thickness up to the penetration depth of the secondary electrons in gold will deliver more secondary electrons to the resist layer, while on the other hand the diffusion of electrons in the gold layer blurs the image features and lower the spatial resolution. With our 17.5 keV x-ray exposure the maximum penetration depth of the secondary electrons in gold is approximately 380 nm. We chose a 50 nm gold thickness for sufficient resolution for the grating samples.
FIG. 5. (a) Atomic force microscopy scan of the imprint of a multi-layer transmission grating having a period of 561 nm. The imprint was created on a gold-coated resist plate using a compact x-ray tube operating at 70 kVp and 32 Watts. The total photon flux was $4 \times 10^{13}$ photons/mm$^2$, accumulated over a 20 hour period. The height profile of resist surface is graphed in (b). When compared to images from the synchrotron beamline in Figures 3 and 4, the extent of the focal spot of the x-ray tube blurred the edges of the intensity fringes. An SEM image of the cross-section of one of the many multi-layer stacks in the grating is shown in (c).

There may exist other materials that make for more productive photoelectric conversion layers than gold. For example, cesium iodide (CsI) may produce more secondary electrons in the lower part of the electron energy spectra than gold. The challenge for CsI and such alkali halides lies in producing a layer comparable in smoothness and uniformity to gold, given the granular structures they tend to form in coating processes.

In conclusion, x-ray contact microscopy is a simple method to obtain radiographic images at the resolution of tens of nanometers with minimal sample preparation. By using hard x-rays of photon energies above 10 keV, the capability of the technique is expanded to imaging denser samples, making it available to a broader range of samples. By using a gold photo-electric conversion layer we showed that the required exposure dose and time can be reduced by over a factor of 40. This method allowed hard x-ray contact microscopy to be performed with a compact x-ray tube in a bench-top setup. X-ray contact microscopy is particularly useful for samples that cannot be fitted into zone-plate based microscopes either due to size or geometry. It can also record a projection image over a large area in one exposure. These qualities combined with the penetration power of hard x-rays provide an effective solution for the inspection of certain samples such as the x-ray gratings we demonstrated above.

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