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Sample Preparation for Total Reflection X-ray Fluorescence Analysis Using Resist Pattern Technique

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Abstract

A circular resist pattern layer with a diameter of 9 mm was prepared on a glass substrate (26 mm x 76 mm; 1.5 mm thick) for total reflection X-ray fluorescence (TXRF) analysis. The parallel cross pattern was designed with a wall thickness of 10 μm , an interval of 20 μm , and a height of 1.4 or 0.8 μm . This additional resist layer did not significantly increase background intensity on the XRF peaks in TXRF spectra. Dotted residue was obtained from a standard solution (10 μL) containing Ti, Cr, Ni, Pb, and Ga, each at a final concentration of 10 ppm, on a normal glass substrate with a silicone coating layer. The height of the residue was more than 100 μm , where self-absorption in the large residue affected TXRF quantification (intensity relative standard deviation (RSD): 12–20%). In contrast, from a droplet composed of a small volume of solution dropped and cast on the resist pattern structure, the obtained residue was not completely film but a film-like residue with a thickness less than 1 μm , where self-absorption was not a serious problem. In the end, this sample preparation was demonstrated to improve TXRF quantification (intensity RSD: 2–4%).

Keywords: TXRF, dried residue, self-absorption, quantification, resist pattern

1. Introduction

Total reflection X-ray fluorescence (TXRF) analysis is performed with small volumes of liquid samples dropped on sample carriers [1,2]. It is well known that the TXRF quantitative results critically depend on the shape of the dried residue. This residue shape critically depends on the surface chemical property of the sample carrier. Figure 1 shows microscope photos of droplets and dried residue on flat glass sample carriers with and without a silicone coating layer. On the glass substrate without the silicone layer, the dried residue showed uncontrolled heterogeneous shapes, such as ring-type residue. The silicone coating layer provided hydrophobicity on the substrate. As a

result, the liquid droplet shrank at the center during the drying process, leading to the dotted residue shown in the two right-side photos of Fig. 1. In these cases, the dotted residue is also mostly located around the center of the droplet. That means the position of the dried residue can be controlled in the sample preparation process. It has been reported that the position of the residue on the sample carrier is important to TXRF analysis [3]. Therefore, it will be useful for reliable TXRF analysis to control the position of the dried residue on a silicone-coated glass substrate.

This type of small dotted residue is desirable for TXRF trace analysis, especially for liquid samples with a low concentration matrix, such as tap water. The analyzed elements will be concentrated in the dotted residue and analyzed effectively with an internal standard technique in TXRF analysis. However, samples of highly concentrated liquids such as coffee, tea, fruit juice, blood samples, etc. will give residue with high bumps. Self-absorption in the resulting large residue will affect TXRF quantification.

Basically, self-absorption may be ignored by an internal standard technique. In this technique, both the analyzed and internal elements should exist homogeneously in the residue. However, if there is a low-Z element analyzed at the bottom of the thick residue, the internal standard technique will not work effectively for quantification. To resolve this situation, nano-droplet and pico-droplet techniques have been studied [4,5]. Since their multiple, small dried residues have quite low thicknesses (heights), the absorption effect will be negligible. However, these techniques require the preparation of special equipment such as a pico-droplet inkjet printer or nano-droplet dispensing device to obtain nano-pico droplets. A strong shading effect for normal residue made from μL droplets in TXRF has been reported by a study using a color X-ray camera (CXC) [6]. 2D distribution of XRF signals from nano droplets was obtained by the CXC under total reflection conditions. This result indicates that the shading effect still occurred for multiple droplets of a picoliter volume.

Alternatively, we consider thin film-like residue to be useful for TXRF analysis of especially highly concentrated liquid samples. In this paper, we propose a new sample preparation technique to get a thin film-like residue. For this sample preparation, a resist pattern layer is formed on a sample carrier using a semiconductor technique. If the thin film-like residue can be obtained, the self-absorption will be negligible, leading to reliable TXRF quantification.

2. Experiment

2.1. Resist pattern formation technique

The technique used for resist pattern formation is well known in the semiconductor industry. The general process of resist patterning can be described in four steps: 1) clean the Si wafer or substrate, 2) drop photoresist chemical material to spin-coat in a thin film on the Si wafer, 3) apply lithography with UV light on the resist film with a photo mask, and finally 4) remove the resist film. In our

experiment, a circular resist pattern film with a diameter of 9 mm was formed at the center of the slide glass substrate (26 mm x 76 mm, 1.5 mm thick) shown in Fig. 2(a). This diameter was chosen because the area analyzed by the TXRF instrument that we used was about 10 mm in diameter. We designed the resist pattern shown in Figs. 2(b) and 2(c). The parallel cross pattern was designed with a wall thickness of 10 μm , an interval of 20 μm , and a height of 1.4 or 0.8 μm . Due to a technical problem in adhesiveness, the resist pattern with a thin layer of 0.8 μm was deposited on only the Si wafer, while the resist pattern layer with a thickness of 1.4 μm was prepared on the glass substrate to compare the dried residue on normal glass substrates. We used normal slide glass with different surface treatments: 1) normal slide glass without any surface modification; 2) slide glass with the silicone coating layer having hydrophobic properties; 3) slide glass with the resist pattern with a film thickness of 1.4 μm ; and 4) Si wafer with the resist pattern with a film thickness of 0.8 μm . The Si wafer was cut with the same dimensions as the slide glass. The TXRF analytical results for the four types of substrates are summarized in Table 1.

2.2. TXRF instrument

A tabletop TXRF instrument, NANOHUNTER, produced by Rigaku Co. was used in this work. A Mo X-ray tube was operated at 50 kV and 0.6 mA. X-rays emitted from the Mo target were monochromatized by W/C multilayers, then Mo $K\alpha$ X-rays were irradiated on the surface of the sample at a glancing angle of 0.05 degrees. The thickness of the primary X-ray beam was about 100 μm . XRF was detected by a silicon drift detector (sensitive area: 7 mm^2 ; energy resolution: 150 eV at 5.9 keV). The analyzed area on the substrate was a circle about 10 mm in diameter. The measurement time for TXRF was 600 s.

2.3. Micro-XRF instrument and surface morphology observation

Micro-XRF imaging was performed using a commercial micro-XFF instrument, Horiba XGT-2700. A Mo tube was operated at 50 kV and 0.5 mA. The applied beam size was 100 μm , formed by a single capillary X-ray guide tube. The analyzed area of the sample was 5.12 mm x 5.12 mm. By scanning the sample, XRF elemental images were obtained.

The surface morphology was observed under a confocal laser microscope (Keyence, VK-8710). A laser (658 nm, 0.9 mW) was used in the operation of this microscope with a spatial resolution of 10 nm.

2.4. Sample solution

A standard solution containing Ti, Cr, Ni, and Pb was prepared with a final concentration of 10 ppm for each element in a Ga internal solution. Since this standard solution was a mixture of sulfuric and nitric acids, an S peak was observed in the TXRF spectrum. A 10 μL volume of solution was

dropped on the sample carrier using a micropipette. It has been reported that the TXRF intensity strongly depends on the relative position of the dried residue on the sample carrier [3]. Therefore, we carefully dropped the solution at the center of the sample carrier. The position of the droplet was adjusted to the center of the substrate by a blower during the drying process [3]. On the sample carrier having the resist pattern, the solution was just dropped at the center of the substrate. The droplets dried at room temperature (about 25°C).

3. Results and discussion

3.1. TXRF spectra

Figure 3 shows typical TXRF spectra taken for the sample carriers with and without the resist pattern layer before the sample was prepared. The blue and red spectra in Fig. 3 were measured for the substrates with and without, respectively, the resist layer. The resist layer drastically increased the Mo K α scattering peaks and Compton peaks. In addition, a strong S K α peak was observed for the spectrum with the resist layer. This S K α peak originated from the photosensitizer (diazonaphthoquinone sulfonic acid ester) included in the photolithography process. However, this resist layer did not increase the background intensity in the energy range from 4 keV to 15 eV shown in Fig. 3.

Figure 4 shows typical TXRF spectra obtained with dried residue. The blue and red spectra in Fig. 4 were measured for the substrates with and without, respectively, the resist layer. The existence of the resist pattern layer and the dried residue increased the background intensity with Mo K α and Compton scattering peaks; however, the XRF peaks were obtained with similar intensities even where the resist layer existed. That means the resist pattern film did not present a serious problem in the TXRF spectrum. In Table 1, the averaged intensities measured for the sum of Mo K α and Compton peaks are shown as 15, 16, 38, and 25 cps for the four substrates of glass, glass with the silicone layer, glass with the resist layer (height: 1.4 μm), and Si wafer with the resist layer (height: 0.8 μm), respectively. Reducing the thickness of the resist layer was found to reduce the scattering peak intensity.

3.2. Morphology of dried residue observed under optical microscope

Optical microscope images of droplets on the four types of substrates are shown in the top row of photos in Fig. 5. On the slide glass without the silicone coating, a large circular droplet with a diameter of about 4 mm was observed. However, on the slide glass with the silicone coating layer, the size of the droplet was small at 2–3 mm due to the hydrophobic surface property. On the substrate with the resist pattern layer, a large, almost square droplet was observed. The size of the droplet on the resist layer (thickness: 0.8 μm) was slightly larger than that on the resist layer with a thickness of 1.4 μm . The largeness of the droplet seems to depend on the thickness of the resist

pattern layer.

After the samples dried at room temperature, 25°C, optical microscope images were taken of the dried residue, which are shown in the middle row of photos in Fig. 5. The dotted residue was obtained on the substrates without the resist pattern layer, as shown in the two leftmost photos in the middle row of Fig. 5, because the droplets shrank to a small volume during the drying process. On the resist layer substrate, large film-like residue was obtained as shown in the two rightmost photos in the same row of Fig. 5. It was also found that the thinner resist layer (0.8 μm) gave a film-like dried residue larger than the dried residue on the thicker resist layer (1.4 μm). The parallel cross pattern in the resist layer disrupted the shrinking process of the droplet, leading to the formation of the thin layer type of residue.

The bottom row of Fig. 5 shows enlarged photos of the film-like dried residue on the two substrates. It seems that a homogeneous, thin layer type of residue was obtained, though small dots were observed in the bottom right photo in Fig. 5.

The typical dried residue was observed under the confocal laser microscope. This instrument gave 3D images of the surface morphology of the solid samples. Figures 6(a) and 6(b) show photos of the residue on the substrate with the silicone coating layer and substrate with the resist pattern layer, respectively. Figure 6(a) shows the confocal laser microscope image with the surface morphology at the red line and a 3D image on the right side. The diameter of the residue was about 0.9 mm. The residue showed bumps with a maximum height of 91 μm on a plateau of 33 μm . Since the thickness of the primary X-ray beam was about 100 μm , the top of the residue might not have been effectively irradiated by the primary X-ray beam. The self-absorption in the residue would also be considerably large for TXRF quantification. On the substrate with the resist pattern layer, thin flat residue was obtained as shown in Fig. 6(b). The surface morphology at the red line is shown by the white line. The thickness was evaluated to be 0.65 μm .

3.3. Elemental mapping of dried residue

XRF elemental mapping was performed by the micro-XRF instrument. Figures 7(a) and 7(b) show S $K\alpha$ and Ti $K\alpha$ images, respectively, obtained for the residue on the four types of substrates. The sulfur originated from a H_2SO_4 acid standard solution, while the Ti originated from the Ti standard solution. The total measurement times for both the substrates with and without the resist layer were 36,000 s and 3,600 s, respectively. Since the intensity of S and Ti on the substrate with the resist layer was too weak, a longer measurement time was necessary. These XRF images clearly show the shapes of the dried residue. The diameter of S $K\alpha$ from the residue on the normal slide glass was 710 μm , and it was 620 μm in the Ti image. This difference is due to the dependence of the X-ray beam size on the energy of X-rays. It suggests that higher-energy X-rays were focused at the center of the beam, while the lower-energy X-rays were broader at the edge of the beam. Similarly, a dotted type

of XRF image was observed for the residue on the glass with the silicone coating layer. In this image, the color bar indicates 1,019 cps for red, the maximum color.

In contrast, large, almost square film types of S K α XRF images were observed for the residue on the glass and Si wafer with the resist pattern layer, as shown in Fig. 7. The size of the residue was 4.3 mm x 4.3 mm in the S K α image at the far right in Fig. 7(a). This result agrees with the optical microscope images in Figs. 5 and 6. Since the volumes of the droplets on the four substrates were the same (10 μ L), the total XRF intensities shown in Fig. 7 should have also been the same, even when the residue areas were different. That suggests that the thicknesses of the dried residue are different. The color red on the S K α image in the rightmost map in Fig. 7(a) indicates 245 cps, though the color red indicates 1,019 cps for the glass substrate without the resist layer. This means that the thickness of the residue was reduced by the resist pattern layer. Unfortunately, Ti images were not visible due to weak XRF intensities. In addition, several concentrated points (diameter: 150–300 μ m) were found in the rightmost S and Ti images of the residue in Fig. 7.

3.4. TXRF quantitative results

TXRF quantitative results for the four types of substrates are shown for five elements (Ti, Cr, Ni, Ga, and Pb) in Table 1. The intensities shown for Ti K α , Cr K α , Ni K α , Ga K α , and Pb L α in Fig. 4 were measured in a measurement time of 600 s. In this table, n indicates the number of repeat measurements for each substrate. The sum intensities of Mo K α and Compton scattering are also shown in the far left column: 15 cps for the glass substrates, 16 cps for the glass with the silicone layer, 38 cps for the glass with the resist layer (height: 1.4 μ m), and 25 cps for the Si wafer with the resist layer (height: 0.8 μ m). In addition, the background intensities at the XRF peaks of the five elements are shown in the far right column. It was found that the resist layer increased scattering intensities; however, the background intensities beneath the XRF peaks did not increase significantly even on the sample carriers that had the resist layer.

Table 1 shows the averaged intensities and relative standard deviation (RSD) of intensities for the XRF peaks of the five elements. In addition, concentration values that were calculated with the standard addition technique are shown in ppm. For the glass substrates with and without the silicone layer, the calculated RSD values were large. Such large RSD would be due to the uncontrolled shapes of the residue. As already mentioned, the self-absorption effect will significantly affect TXRF quantitative results, especially for the dotted or bumpy residue. However, the concentrations of some elements were close to the expected concentration of 10 ppm. This result indicates that the standard addition technique corrected the quantitative results.

In the substrates with the resist pattern layer, the intensity RSD values were drastically improved; Table 1 shows that they were 2–6%. This is because the existence of the parallel cross resist pattern made it possible to obtain the thin film-like residue. Self-absorption decreased in the thin layer.

Finally, the evaluated concentrations for the five elements were close to the expected 10 ppm. In particular, the Si wafer substrate with the thinner resist pattern layer provided better quantitative results.

It may be a concern if the addition of the resist layer absorbed the primary X-rays and X-ray fluorescence. With the model shown in Fig. 8, we calculated how much of the X-rays would be absorbed in the resist layer. We assumed that the primary X-rays of Mo K α would be absorbed by the resist layer (density: 1.25 g/cm³ for phenolic resin) in a total pass of 3 mm, because the diameter of the resist layer was 9 mm, the wall width was 10 μ m, and the interval was 20 μ m. In our results, 80.6% of the primary X-ray beam would still be present at the end of the resist layer, meaning only 19.4% would be absorbed while traveling across the resist pattern. The absorption of S K α (2.31 keV) X-rays in the resist layer with a thickness of 1 μ m was also considered. It was evaluated to be 97.3% at the end after absorption. Therefore, the resist layer would not have a significant influence on the absorption of fluorescent X-rays.

4. Conclusions

To achieve reliable TXRF quantitative results, we attempted to make a film-like dried residue. For this purpose, we used a resist pattern layer having a parallel cross structure on a glass or Si substrate. A circular resist pattern layer with a diameter of 9 mm was prepared on the glass substrate (26 mm x 76 mm, 1.5 mm thick) for TXRF analysis. The parallel cross pattern was designed with a wall thickness of 10 μ m, an interval of 20 μ m, and a height of 1.4 or 0.8 μ m. This additional resist layer did not significantly increase the background intensity on the XRF peaks in the TXRF spectra. The standard sample solution was prepared with Ti, Cr, Ni, Pb, and Ga, each at a concentration of 10 ppm. A 10 μ L volume of the standard solution was dropped on both the normal glass substrates and the resist pattern substrates. The height of the residue was more than 100 μ m on the normal glass, where self-absorption in the large residue affected TXRF quantification. The intensity RSD was 12–20%. In contrast, the resist pattern substrates provided a thin layer type of residue, less than 1 μ m thick, leading to improvement of TXRF quantification (intensity RSD: 2–4%). From a small-volume droplet cast on the resist pattern structure, the obtained residue was not completely film but a film-like residue.

We calculated the absorption of X-rays in the film under total reflection conditions. This absorption effect will be experimentally confirmed in the future. Moreover, the resist pattern will be optimized for further improvement of TXRF analysis. In parallel, other types of material instead of the resist pattern layer and other preparation procedures will be considered and attempted.

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Captions

Table 1

TXRF intensity, RSD, concentration, and background intensity measured for 4 types of substrates: 1) normal glass; 2) glass with a silicone coating layer; 3) glass with a resist pattern layer (height: 1.4 μm); and 4) Si wafer with a resist pattern layer (height: 0.8 μm). The sample solution was a 10 μL volume of a standard solution containing Ti, Cr, Ni, Ga, and Pb, each at a concentration of 10 ppm.

Figure 1

Optical microscope images of droplets and dried residue on 2 types of glass substrates, one with and one without a silicone coating layer.

Figure 2

(a) Schematic drawing of a resist pattern with a diameter of 9 mm prepared on the slide glass substrate (26 mm x 76 mm). (b) Optical microscope image of the parallel cross resist pattern. (c) Cross-sectional view of the resist pattern (wall width: 10 μm ; interval: 20 μm ; thickness: 1.4 μm or 0.8 μm).

Figure 3

Typical TXRF spectra with (blue) and without (red) the resist pattern layer before the sample was prepared.

Figure 4

Typical TXRF spectra with (blue) and without (red) the resist pattern layer after the sample was prepared (dried residue obtained).

Figure 5

Optical microscope images of droplets and dried residue on 4 types of glass substrates: 1) glass; 2) glass with the silicone coating layer; 3) glass with the resist pattern layer (height: 1.4 μm); and 4) Si wafer with the resist pattern layer (height: 0.8 μm). The bottom two photos show enlarged images of dried residue on the resist pattern layer. The sample solution was a 10 μL volume of the standard solution containing Ti, Cr, Ni, Ga, and Pb, each at a concentration of 10 ppm.

Figure 6

Surface morphology images taken with a confocal laser microscope. (a) Sample with dried residue on normal glass. The maximum height was 91 μm . (b) Sample with dried residue on glass with the

resist pattern layer. The thickness of the dried residue was about 0.65 μm . 3D images are also shown on the right side. The sample solution was a 10 μL volume of the standard solution containing Ti, Cr, Ni, Ga, and Pb, each at a concentration of 10 ppm.

Figure 7

XRF elemental images of S $K\alpha$ (a) and Ti $K\alpha$ (b) for the dried residue on 4 types of substrates. The sample solution was a 10 μL volume of the standard solution containing Ti, Cr, Ni, Ga, and Pb, each at a concentration of 10 ppm. The analyzed area of the sample was 5.12 mm x 5.12 mm.

Figure 8

Schematic drawing of the resist pattern structure showing X-ray absorption in the resist material.

		Intensity (cps)	Intensity RSD	Concentration (ppm)	Background intensity at the peak
1) Glass n = 10 MoK+Comp.: 15 cps	Ti	1.6	4.5	8.7	0.20
	Cr	2.8	12.7	8.8	0.20
	Ni	7.5	17.0	10.0	0.11
	Ga	11.0	15.7	-	0.11
	Pb	2.1	3.5	4.5	0.06
2) Glass with silicone n = 10 MoK+Comp.: 16 cps	Ti	1.5	18.2	6.5	0.18
	Cr	2.7	20.8	6.9	0.20
	Ni	8.5	16.7	9.3	0.12
	Ga	13.4	17.2	-	0.14
	Pb	3.1	12.3	5.3	0.06
3) Glass with resist h = 1.4 μm n = 7 MoK+Comp.: 38 cps	Ti	1.8	6.0	9.6	0.24
	Cr	3.0	2.9	9.6	0.26
	Ni	7.9	6.3	10.5	0.12
	Ga	11.0	5.6	-	0.21
	Pb	4.8	2.5	9.9	0.08
4) Si wafer with resist h = 0.8 μm n = 6 MoK+Comp.: 25 cps	Ti	1.7	2.2	9.8	0.19
	Cr	2.7	2.5	9.8	0.21
	Ni	6.9	3.7	10.4	0.13
	Ga	9.7	4.1	-	0.13
	Pb	4.2	4.4	9.8	0.07

Fig.1

Fig.2

Fig.3

Fig.4

Droplets

Glass

Glass with
silicone layer Glass with resist
 $h = 1.4 \mu\text{m}$ Si wafer with resist
 $h = 0.8 \mu\text{m}$ *Dried at room temperature*

Dried residues

(a)

Height: $91\ \mu\text{m}$

(b)

Thickness: $0.65\ \mu\text{m}$

Fig.7

Fig.8