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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 × 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%).

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. Fig. 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 homogenously 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-

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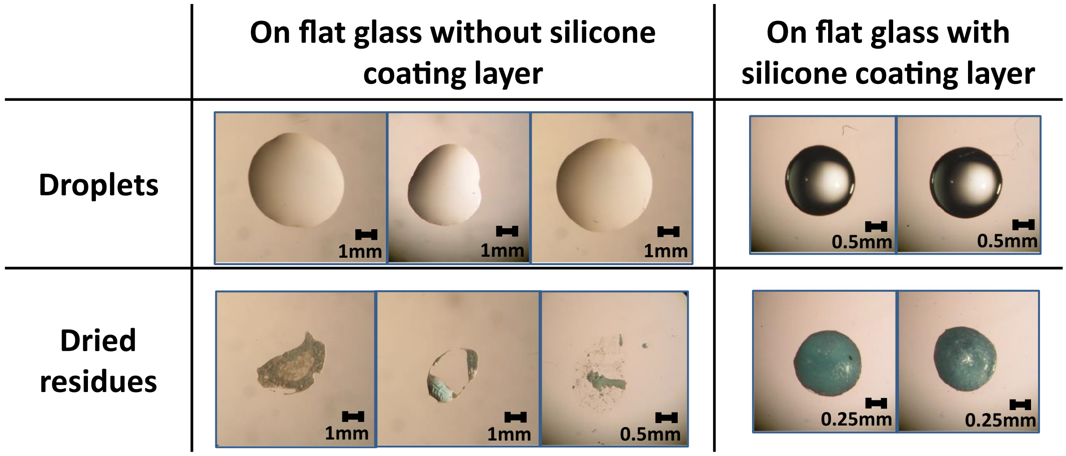

Fig. 1. Optical microscope images of droplets and dried residue on 2 types of glass substrates, one with and one without a silicone coating layer.

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 × 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 Fig. 2(b) and (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.

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 Kα X-rays were irradiated on the surface of the sample at a glancing angle of 0.05°. 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 × 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.

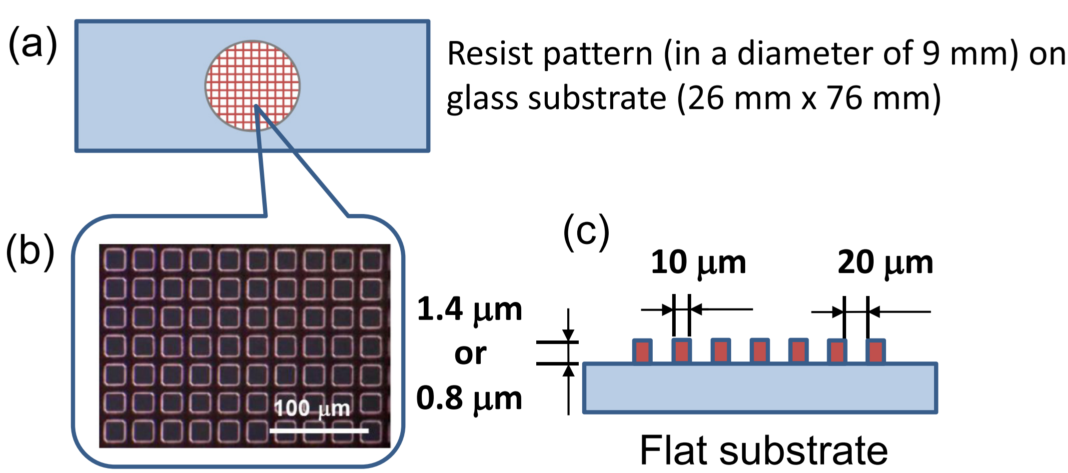

Fig. 2. (a) Schematic drawing of a resist pattern with a diameter of 9 mm prepared on the slide glass substrate (26 mm × 76 mm). (b) Optical microscope image of the parallel cross resist pattern. (c) Cross-sectional view of the resist pattern (wall width: 10 μm; interval: 20 μm; thickness: 1.4 μm or 0.8 μm).