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Depth Profiling of Nanometer Coatings by Low Temperature Plasma Probe Combined with Inductively Coupled Plasma Mass Spectrometry

Zhi Xing, Juan Wang, Guojun Han, Biekesailike Kuermaiti, Sichun Zhang,* and Xinrong Zhang

Department of Chemistry, Key Laboratory for Atomic and Molecular Nanosciences of the Education Ministry, Tsinghua University, 100084, Beijing, P. R. China

The development of material science increasingly calls for rapid characterization methods with low limits of detection and high spatial resolution. Here we report a depth profile analysis method for thin layer coatings by combining low temperature plasma (LTP) probe with inductively coupled plasma mass spectrometry (ICP-MS). The LTP probe with diameter of several tens of micrometers served as a tool for mass removal, which is generated by the discharge in a quartz capillary at ambient condition. The sample material is ablated by the LTP probe and converted into an aerosol, and transported by a carrier gas flow to the ICP-MS, where the decomposed and ionized aerosol particles are analyzed with high sensitivity. Scanning electron microscope (SEM) micrographs reveal that the trace after ablation by the LTP probe is a hole with a diameter less than 10 μm. A lateral resolution of approximately 200 μm has been achieved by analyzing an electron component with interval metal stripes. Depth profiling of a 100 nm single layer sample and a multiple layer sample (100 nm Al/250 nm SiO_2/100 nm Au/50 nm Cr) on a silicon substrate have been successfully performed at ambient condition. The present method offers unique advantages in terms of high spatial resolution, fast analysis speed and ease of implementation. It might be considered a complementary technique to existing depth profiling methods such as GD-MS/OES, AES, and SIMS. In addition, the simple-to-fabricate LTP probe is easily coupled to various other elemental analysis tools for thin layer or direct solid sample analysis in micro area.

The production control and quality assurance of thin layer coatings increasingly calls for rapid characterization methods with low limits of detection and high spatial resolution.[1−4] Various analytical techniques are available for depth profiling, providing different abilities to analyze thin layer samples. Depth profiling of a subnanometer to nanometer scale surface is usually accomplished by auger electron spectroscopy (AES)[5,6] and secondary ion mass spectrometry (SIMS).[7−10] AES is much less sensitive but shows comparatively little matrix effect and better suited for interfacial and multilayer profiling, while SIMS is suited for low-concentration delta layers and dopant profiles due to its high sensitivity. The main drawbacks of these techniques are the use of ultrahigh vacuum conditions and limitations in the analysis of thick layers (>10 μm).

Glow discharge (GD) optical emission (OES) or mass spectrometry (MS) is a complementary technique with high depth resolution (about 10 nm) that can be exploited for thin and thick layers (>100 μm) analysis.[11−15] GD-OES is an extremely rapid technique for depth profiling that has shown its potential for the quantitative analysis of many types of thin and ultrathin films.[11,14] On the other hand, GD-MS provides the potential for direct solid analysis because it offers the important advantages of isotopic information and lower limits of detection in comparison to OES.[15−19] The limitations of GD based thin layer analysis method are the restricted lateral resolution (approximately mm) and specific requirements on shape and dimensions of the sample due to the vacuum conditions.[14]

Laser-induced mass removal processes in combination with inductively coupled plasma mass spectrometry (ICP-MS) have

* To whom correspondence should be addressed. Phone: +86-10-6278-7678. Fax: +86-10-6278-2485. E-mail: sczhang@mail.tsinghua.edu.cn.

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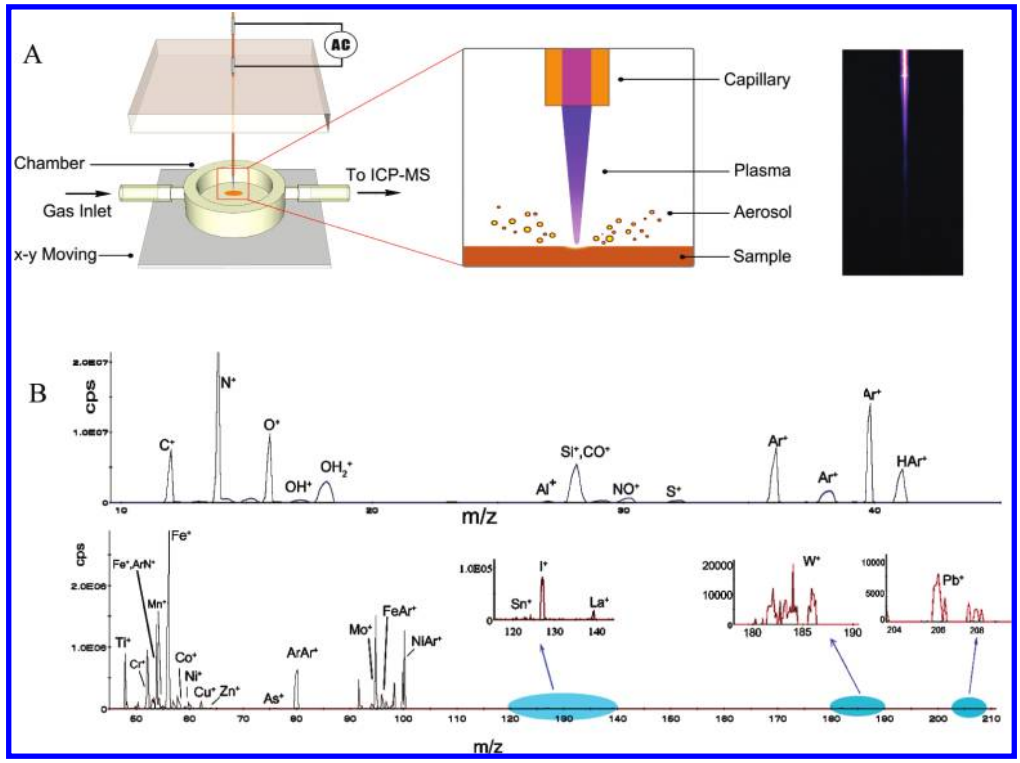

Figure 1. Schematic diagram of the LTP probe-ICP-MS system (A) and mass spectra of an alloy sample (GSBA68007-891) obtained by LTP probe-ICP-MS (B). Low mass range of *m*/*z* 9−45 (upper) and normal mass range of *m*/*z* 45−210 (lower).

recently been applied to depth profile analysis of different kinds of coated samples.[20−27] These techniques provide the advantages of minimum sample preparation, analysis of conducting and nonconducting samples of arbitrary structure, high spatial resolution (approximately μm), and the possibility of rapid, simultaneous, and multielemental analysis of solid samples. Recent reports on the depth-resolution in the order of hundreds of nanometer indicate a significant improvement of LA-ICP-MS in this field of application.[20−23] Furthermore, the capabilities of ultraviolet femtosecond laser ablation inductively coupled plasma mass spectrometry (UV-fs-LA-ICP-MS) for depth profile analysis of thin metal coatings has been recently evaluated by Pisonero et al.[24] However, the instrument setup is still complex, expensive, and not directly available to common ICP-MS instrument.

Herein, we propose a simple depth profile analysis method by combining low temperature plasma (LTP) probe removal processes with ICP-MS detection. The LTP probe with diameter of several tens micrometer served as a tool for mass removal, which is generated by a discharge in a quartz capillary at ambient condition.[28,29] We show that the LTP probe could ablate solid sample directly with high lateral and depth resolution. The depth profiling of single and multiple nanometer thin layer has been performed by combining LTP probe with ICP-MS. The present method is potentially a complementary technique for fast depth profiling of thin layer materials.

EXPERIMENTAL SECTION

Instrument. An X Series ICP-MS was used for the present experiment (Thermo Fisher, U.S.). ICP-MS data were recorded in time-resolved analysis (TRA) mode (intensity vs time). The operating parameters of ICP-MS were as follows: RF power, 1200 W; gas flow rate of the plasma, 0.82 L/min; auxiliary gas flow rate, 0.70 L/min; cooling gas flow rate, 14 L min^{-1}. The LTP probe power supplies were purchased from Colona Co. Ltd. (Nanjing, China). The applied power in the experiment was about 30 W with a voltage of about 2.5 kV and a frequency of about 10 kHz. An auger electron spectrometer (AES, PHI 700, ULVAC-PHI, Japan) was used for the comparison purpose.

The LTP Probe-ICP-MS System. The schematic diagram of experiment setup is shown in Figure 1a. The photographs of experiment setup are shown in Supporting Information (SI) Figure S1. The ablation cell is the dominant part responsible for signal dispersion and a low-volume cell is crucial to provide optimum profile. The ablation cell is a polytetrafluoroethylene (PTFE) cylinder chamber (5 cm i.d., 5 cm height). The LTP probe consists of a fused silica capillary with a diameter of 150 μm and two aluminum foil electrodes separated about 10 mm and wrapped

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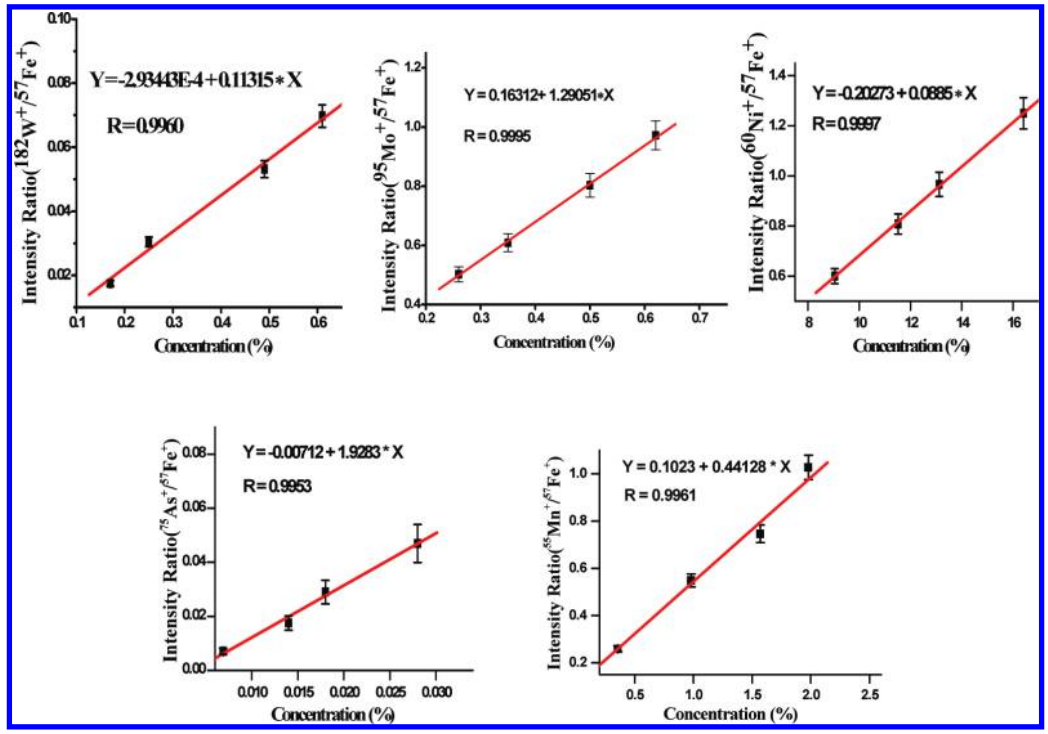

Figure 2. Calibration curves of ^{75}As, ^{182}W, ^{55} Mn, ^{95}Mo, and ^{60}Ni in standard alloy samples obtained by LTP probe-ICP-MS from a series of standard steel samples.

outside the capillary. The capillary was immobilized on the chamber cover. The ablation chamber was mounted on a 3-D moving stage, allowing the introduction of samples at random position. Argon carrier gas was passed through the cell to carry out the ablated aerosol particles. Helium gas was passed through the discharge capillary at a flow rate of 300 mL/min. An alternating voltage of several kilovolts (10 kHz) was applied to two electrodes to light and keep the plasma. The ablated analytes were introduced to the ICP torch via a silicone tube (6 mm o.d., 50 mm long) by the argon gas flow for analysis.

Standard Reference Materials and Samples. Standard reference materials (GSBA68001-891 to GSBA68007-891) were purchased from the National Institute of Standards and Technology (Beijing, China). High-purity aluminum materials (sheet) were purchased from National Research Center for Certified Reference Material (Beijing, China). A thickness standard sample consisting of a single tantalum layer (100 ± 5% nm) on a silicon substrate was used. An electron component with interval metal stripes and an Al/SiO_2/Au/Cr multiple thin layer on silicon substrate sample were obtained from the laboratories in this university.

Safety Consideration. The high-voltage power supply should be handled with extreme care to avoid electrical shock.

RESULTS AND DISCUSSION

The experimental setup and the configuration of LTP probe are shown in Figure 1A. The sample material is ablated by the LTP probe and converted into an aerosol, and transported by a carrier gas flow to the ICP-MS, where the decomposed and ionized aerosol particles are analyzed. The depth resolution may be affected by signal tailing induced by the aerosol transportation thorough the tube (sample material originating from different depths will enter the plasma simultaneously). However, in our design, the transportation tube is minimized to about 5 cm thanks to the small size of ablation cell. No signal tailing has been found in our experiment and the sorts of carrier gas do not affect the profile of the signals.

The complete elemental characterization of complex films and interface structures is influenced by different factors, including depth resolution, detection limits, accuracy, and precision for all elements. Therefore the acquisition of the mass spectra of an alloy sample (GSBA68007-891) is first studied with present method. The full range spectra have been obtained by the LTP probe coupled with ICP-MS (Figure 1B). Common elements, including Al, C, Si, Mn, P, S, Cr, Ni, Mo, W, Sn, Ti, Cu, Al, Co, Pb, and As, can be detected. The results indicated that the present LTP probe can effectively ablate solid samples as that of laser ablation or GD.

The quantitative analysis of some trace elements in the alloy sample has been performed based on the calibration curves generated by a series of standard steel samples. The calibration curves of ^{55} Mn, ^{75}As, ^{60}Ni, ^{95} Mo, and ^{128}W are shown in Figure 2. The quantitative analysis for ^{55} Mn, ^{75}As, ^{60}Ni, ^{95}Mo, and ^{128}W in the alloy sample of GSBA68007-891 were achieved. The contents of each element in the alloy sample (GSBA68007-891) are summarized in Table 1. Comparing with the certified values, the content of each element are well in agreement with the certified values.

Table 1. Results for the Analysis of GSBA68007-891 Alloy Sample (n = 6)

element	composition (n = 6) (mean ± SD) (%)	certified value (%)	deviation (±%)
Mn	0.352 ± 0.009	0.356	0.004
Ni	7.890 ± 0.967	7.820	0.070
As	0.024 ± 0.002	0.028	0.004
Mo	0.168 ± 0.001	0.17	0.002
W	0.181 ± 0.004	0.17	0.011

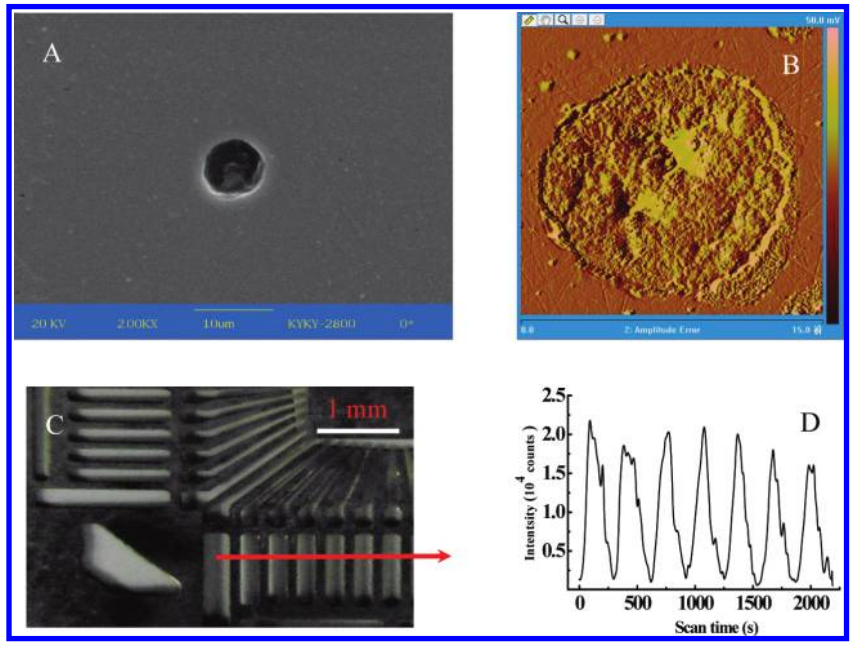

Figure 3. Characterizing the lateral resolution of LTP probe ablation. (A) SEM photograph of a crater on a Ta thin layer sample ablated by LTP probe for 30s. (B) Three-dimensional crater morphology of the crater obtained by AFM. (C) The photograph of circuit board with scale bar. (D) Profile of $^{97}Au^{+}$ signal (ion intensities versus time) of circuit board ablated by LTP probe and detected by ICP-MS.

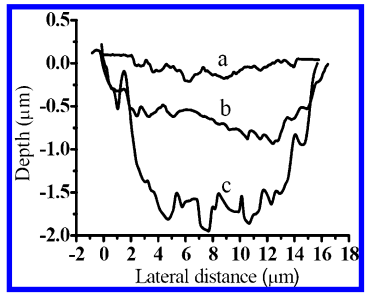

Figure 4. Crater profiles across the central part of the crater at increasing time. a, b, and c is the profile of crater with ablation time of 30, 90, and 240 s, respectively. The distance of the end of the capillary to the ablation surface is about 10 mm.

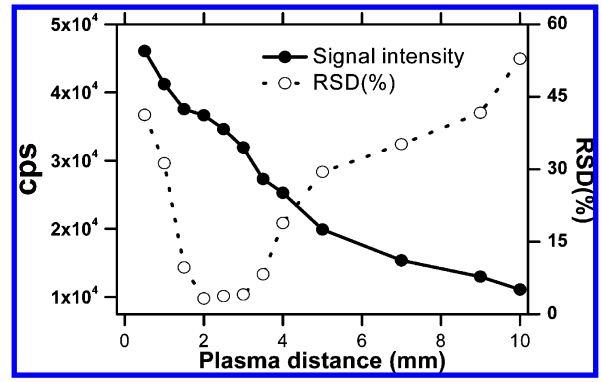

Figure 5. Average signal intensity (cps) and corresponding RSDs ($n = 11$) for ^{60}Ni as a function of the distance between the end of the capillary and the sample surface of a standard alloy (GSBA68006-891). The applied power was set at 30 W.

To evaluate the sensitivity of LTP probe-ICP-MS, the limit of detection (LOD) of As, W, Mn, Mo, and Ni in the alloy sample are investigated. Considering the effect of the matrix, high purity Al is regarded as the blank for the detection of these elements. The limits of detection (3σ) are 26, 30, 35, 64, and 87 ng g^{-1} for As, W, Mn, Mo, and Ni, respectively. The relative standard deviation (RSD) are 4.5, 6.3, 8.4, 9.6, and 9.8% for As, W, Mn, Mo, and Ni ($n = 11$), respectively. Thus, the present technique shows sufficient sensitivity and reproducibility to analysis trace elements in solid samples.

The resolution of present method is characterized in the subsequent phase. The resolution is related to the size of LTP probe, which is mainly determined by the inner diameter of capillary. For this reason and based on our previous experience, a capillary with an inner diameter of 150 μm is selected. Under optimized conditions, the conical plume vertically impacts the surface of the samples. A thin layer of Ta on silicon has been ablated with the LTP probe. Scanning electron microscope (SEM) micrographs reveal that the trace after ablation is a hole with a diameter less than 10 μm (Figure 3A). The crater morphology obtained by using AFM is shown in Figure 3B. It is apparent that the crater has a flat bottom and a steep wall. An electron component with interval metal stripes (Figure 3C) is selected to evaluate the lateral resolution of present LTP probe. The distance of adjacent Au strips is about 200 μm. The profile of the signal (^{97}Au) shows flustration and baseline separation has been achieved between the signals from adjacent strips (Figure 3D). The results indicate that the lateral resolution of the probe is approximately 200 μm. However, this is not the full potential of present method because the diameter of the crater is about 10 μm and the signal intensity is at 10^4 counts level. Therefore, the resolution of present method has much room to be improved by analyzing suitable samples.

Information about the crater geometry obtained by using AFM is shown in Figure 4. The profiles across the central part

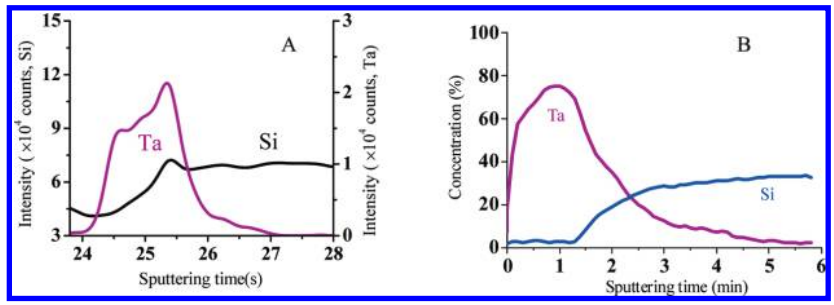

Figure 6. Qualitative depth profile of a thin Tantalum layer (100 nm) on a silicon substrate. (A) Profiles obtained by LTP Probe-ICP-MS (the data were acquired with 100 ms for Ta and 100 ms for Si, and the profiles were fitted in Origin 8.0). (B) Profiles obtained by AES.

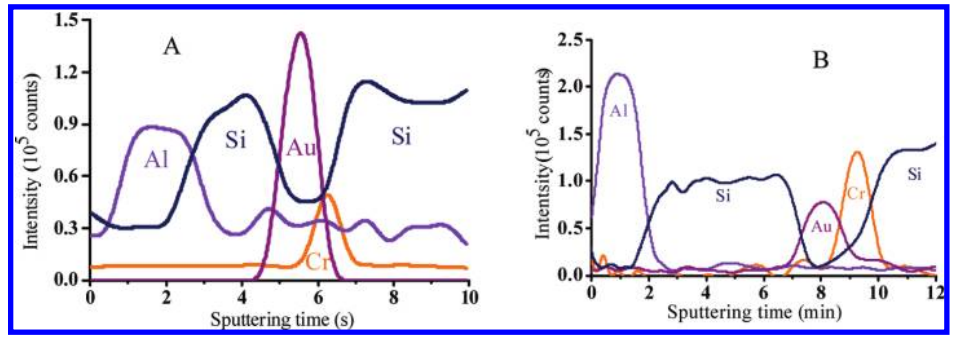

Figure 7. Qualitative depth profiles of an Al/SiO_2/Au/Cr multiple thin layers on silicon substrate. (Al 100 nm, SiO_2 250 nm, Au 100 nm and Cr 50 nm). (A) Profiles obtained by LTP Probe-ICP-MS (the data were acquired with 100 ms for each element, and the profiles were fitted in Origin 8.0); (B) Profiles obtained by AES.

of crater are lowered with ablation time of 30, 90, and 240 s. All craters have a concave shape with flat bottom. Ideally, the crater produced by LTP probe should have a flat bottom with straight vertical walls that reaches to the same depth as the bottom. However, in practice, this shape is rarely obtained. For increasing the ablation time, the formation of microstructures inside the crater resulted in a stronger surface roughness. Our experiments demonstrated that crater geometry and surface roughening of the bottom of the crater originated during the ablation process currently represent the main limiting factors for depth profiling of LTP probe. Further optimization of the working condition of LTP probe is still needed for improving the depth resolution.

The distance of the capillary to sample surface is critical to the sputter rates as monitored by the signal intensity. Therefore, the effect of the distance between the end of the capillary and the sample surface was investigated. As shown in Figure 5, the signal intensity decreased as the distance varied from 0.5 mm to 10.0 mm. A distance of 5.0 mm was chosen as compromise of sensitivity and ablation rate.

The qualitative depth profiling of a standard sample, consisting of a single Ta thin layer of 100 nm ±5% on a silicon substrate, has been performed to demonstrate the ability of present technique. A typical qualitative intensity-time profile is shown in Figure 6A. The ablation of 100 nm Ta thin layer takes about 3 s indicating an ablation rate of 33 nm per second. Comparing with the results obtained by AES, it can be observed that the profiles are very similar (Figure 6B). It should be indicated that the ablation speed of present method (about 33 nm/s) is much faster than that of AES (about 20 nm/min). The sorts of carrier gas have little effect on the profile since the ablation cell is small and connected to the end of ICP torch with only 5 cm interval.

The depth profiles of an Al/SiO_2/Au/Cr multiple thin layer on silicon substrate has also been performed. The total thickness of the coating is about 500 nm with Al layer 100 nm, the intermediate SiO_2 250 nm, Au layer 100 nm and Cr layer 50 nm thick. Figure 7A shows the profiles of each layer, which is similar to the profiles obtained by AES (Figure 7B). Inside each layer, the signal from the materials layer is up to 10−150 times higher than the signal corresponding to the adjacent layers. It is apparent that the different layers are properly resolved both near the surface and deeply embedded in the matrix. Even Cr layer with a thickness of 50 nm give clear profile indicating the depth resolution of present method is smaller than 50 nm. However, the baseline for Al and Si is much higher than that of Au due to the spectral interference at low mass end of ICP-MS spectra and further experiment is needed to improve the depth profiling of thin layers of light elements.

CONCLUSION

In summary, the combining of LTP probe with ICP-MS can effectively create a powerful analytical tool for multidimensional mapping in thin layer material characterization. The advantages of present method for the analysis of thin layer samples are high spatial resolution, fast analysis speed and ease of implementation. Further studies about the depth resolution and the characteristics of present method are still needed to pave the way to real application. Although depth-profiling with LTP probe-ICP-MS has not been optimized to its full potential, but it might be already considered complementary to other depth profiling methods. In addition, the simple experiment setup of LTP probe is easily coupled to various elemental analysis tools for thin layer or direct solid sample analysis in micro area.

Therefore, the present method will be a useful tool to assist material development and promote the development of other scientific area.

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SUPPORTING INFORMATION AVAILABLE

Photographs of the experimental setup, Optimization of parameters for LTP probe-ICP-MS system, and a discussion on the studies on the memory effect. This material is available free of charge via the Internet at http://pubs.acs.org.

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