ANALYTICAL SCIENCE & TECHNOLOGY
(Journal of the Korean Society of Analytical Sciences)
Vol. 7, No. 4, 1994
Printed in the Republic of Korea

Measurment of Gold Coating Thickness by PIXE

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(Received Sept. 26, 1994)

양성자 유발 X-선 발생법에 의한 금 박막의 두께 측정

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(1994. 9. 26. 접수)

Abstract : The capability of PIXE (Proton Induced X-ray Emission) method for the precision measurement of coating thickness has been tested by measuring several gold coated copper plates. Two different experimental methods are applied and compared. The results are compared with those by the weight measurement and proton RBS (Rutherford Backscattering Spectrometry). The advantage of the method is that it can be also used for the nondestructive thickness measurement of thin layers on large-scaled samples or archeological samples which cannot be placed in a vacuum chamber.

요약 : PIXE(양성자 유발 X-선 발생) 분석법을 이용한 박막 두께 측정의 가능성을 알아보기 위하여, 구리판 위에 코팅된 금 박막 시료들을 이용하여 실험을 수행하였다. 두 가지 실험방법을 사용하여 분석을 하였으며, 결과를 비교하여 보았다. 또한 분석 결과의 정확성을 확인하기 위하여 무게측정 방법과 양성자 RBS 분석법에 의한 결과들과 비교하여 보았다. 이 분석 방법은 고고학 시료나 거대시료와 같이 진공 표적함에 집어 넣을 수 없는 경우에도 비파괴적으로 박막의 두께를 측정할 수 있는 장점을 갖고 있다.

Key words : PIXE, proton RBS, gold coating, nondestructive thickness measurement, stopping power, X-ray absorption.

1. Introduction

PIXE is widely used for the elemental analysis nowadays, but seldom for the nondestructive measurement of film thickness. For that purpose, RBS has been mostly used owing to its simple and absolute characteristics. But RBS has drawbacks in some circumstances especially when the mass of the substrate element is larger than that of the film element. PIXE can be used in such a situation since the elemental resolving power and detection limit is much better than RBS. Moreover PIXE can be used also in the atmosphere (External beam PIXE), which implies the ability of measuring large-scaled samples which cannot be placed in vacuum.

Several methods for the measurement of the film thickness by PIXE has been developed. For the re-

view of typical methods see ref. 1. The most widely used method is the simple estimation of the thickness by comparing the measured X-ray counts with that by the theoretical calculation with stopping power, ionization cross section and X-ray absorption tables.[2] Although the method is very simple because the measurement can be done at a fixed incident beam energy, one should fully rely on the theoretical calculation which could cause rather large systematic error. Using the calculated ionization cross section can be avoided, if one measures at various incident beam energies for a thick target and compare the yields with that of unknown film.[3] The range of thickness that can be measured by these techniques depends on the elemental composition of the film and beam energy but is roughly $0.1 \sim 10 \mu m$.

In this experiment, the above two methods were applied and compared for the thickness measurement of Au coatings on Cu plates. The method can be used for the nondestructive measurement of Au coating thickness of ancient remainings. The accuracy of the method is tested by comparing the result with that of the weight measurement and proton RBS. The experiment was done with KIGAM 1.7 MV Tandem van de Graaff accelerator.

2. Principle of the Methods

2.1. Method 1

The number of X-rays Y detected by a detector of efficiency ε for q incident particles of Energy E_i is given by

$$Y = \frac{\Omega}{4\pi} \cdot \varepsilon q N \int_{E_i}^{E_0} \frac{\sigma(E)}{S(E)} e^{-\mu t(E)\sec\theta} dE \qquad (1)$$

where N is the atom density of the target, Ω the solid angle of the detector, $\sigma(E)$ the X-ray production cross section at proton energy E, $S(E) = dE/dt$ the stopping power, E_0 the energy of protons after traversing the thickness t, μ the absorption cross section and θ the angle between the target surface normal and the detector. In principle, eq.(1) can be used directly for the determination of thickness using tabulated values of $\sigma(E)$, μ and $S(E)$, together with the absolute values of ε and Ω. But in most cases $\Omega\varepsilon$ is determined by measuring a very thin standard target where the change of cross section, energy loss and X-ray absorption can be neglected. In that case, the integral in eq.(1) diappears simply and $\Omega\varepsilon$ is easily obtained. By performing a numerical integration for a target with unknown thickness, E_0 can be calculated and thus thickness can be obtained. Another way is using a thick standard target where all the incident protons can be stopped. The thickness can be obtained by performing the two numerical integrations in the following equation :

$$\frac{Y}{Y_s} = \frac{\int_{E_i}^{E_0} \frac{\sigma(E)}{S(E)} e^{-\mu t(E)\sec\theta} dE}{\int_{E_i}^{0} \frac{\sigma(E)}{S(E)} e^{-\mu t(E)\sec\theta} dE}, \qquad (2)$$

where Y_S is the number of X-rays detected for the thick standard target.

2.2. Method 2

It is immediately noticed that the accuracy of the method 1 depends exclusively on the theoretical values of σ, μ and S. A way of not using theoretical σ can be provided by sacrificing the experimental simplicity. Since the only information we need for the thickness determination is the energy of protons E_0 after traversing the film thickness Δt, we can use a thick standard sample and reduce the incident beam energy until we find the beam energy E_0 satisfying the following condition :

$$Y(E_i) = Y_s(E_i) - Y_s(E_0) \qquad (3)$$

It is of course assumed that the X-ray absorption in the unknown target is neglected. But in

most cases, films are not so thin as the X-ray absorption can be neglected, and therefore, we still need to correct for the amount of the absorption of X-rays in the film. Then eq.(3) is modified as

$$Y(E_i) = Y_s(E_i) - Y_s(E_o) \cdot e^{-\mu \cdot \Delta t \cdot \sec\theta} \tag{4}$$

where Δt is the thickness of the film which corresponds to the energy difference $E_i - E_0$. The advantage of the method is that μ can be measured very precisely if needed. Therefore, since we need to use only stopping power S as theoretical value, the accuracy is expected to be more precise than that of method 1.

3. Experimental

3.1. Sample Preparation

The sample used in this experiment is described in *Table* 1. Thin film standard is the product of Micrometer, USA and the thick sample is the product of Reactor Experiments, Inc., USA. All other samples were vacuum evaporated Au on Cu plates. The plates were polished with 0.3μm α-alumina before evaporation. The size of the evaporated Au was 1.27cm in diameter. The amounts of evaporated Au were accurately measured by a micro-balance with a precision of 50μg which corresponds to the thickness of about 0.02μm. Since the range of 2.4 MeV proton in Au is 39mg/cm^2 all the protons are expected to stop within the thick sample.

3.2. PIXE and Proton RBS Measurement

For PIXE measurement, 2.4 MeV proton was used. The beam diameter on the target position was about 5mm in diameter. In order to ensure the homogeneous irradiation of the target surface, the beam was intentionally broadened by the magnetic quadrupole triplet and then again scanned through the surface of the sample by a electrostatic raster scanner. The whole vacuum chamber was used as a Faraday cup. The absolute integrated dose was registered with a precision current integrator. The measurement was done with a total dose of 0.3μC except 2.4μC for the thin standard. A Si(Li) detector of resolution 175eV for 5.9keV was used for the X-ray measurement. In order to keep the system dead time low, a 456μm thick aluminum filter was placed in front of the detector. *Fig*. 1. shows the X-ray spectra of the thick standard sample and sample No. 1. It can be clearly seen that Cu X-ray does not show up for the thick sample. The cross section of L_α X-ray is larger than that of L_β X-ray, but since we used a very thick absorber, the ratio is reversed in the spectrum. For the thickness measurement, each 9.716keV L_α, 11.442keV L_β and 13.382keV L_γ X-rays was used. The mass absorption coefficients of these lines in Au are 128.3, 84.6 and 129.1 cm^2/g, respectively.[4] The number of L_β X-ray count from the thick target measured as a

Table 1. Samples used in this experiment

	sample description	thickness, mg/cm^2 (μm)
standard samples	thin (on 3.5 μm mylar)	0.045 ± 0.002 (0.023)
	thick	50 ± 1 (26)
test samples	No. 1	1.76 ± 0.05 (0.91)
	No. 2	3.47 ± 0.05 (1.80)
	No. 3	7.20 ± 0.05 (3.73)
	No. 4	14.39 ± 0.05 (7.46)

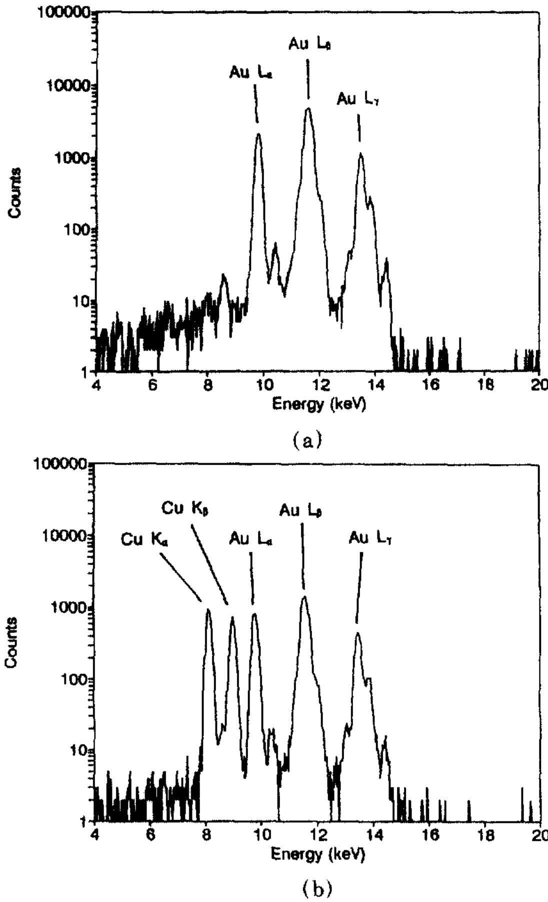

Fig. 1. PIXE spectra of (a) the thick and (b) the 0.91μm Au film on Cu substrate.

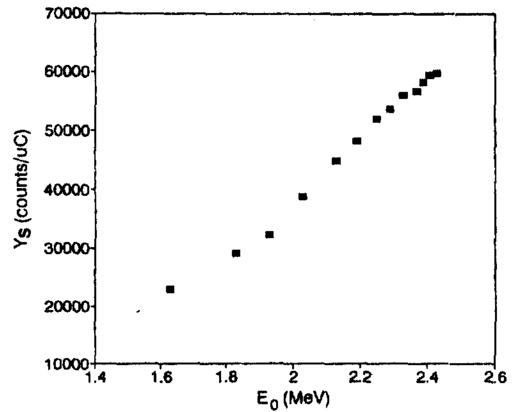

Fig. 2. Thick target yield of Au L_β measured as a function of incident proton energy E_0.

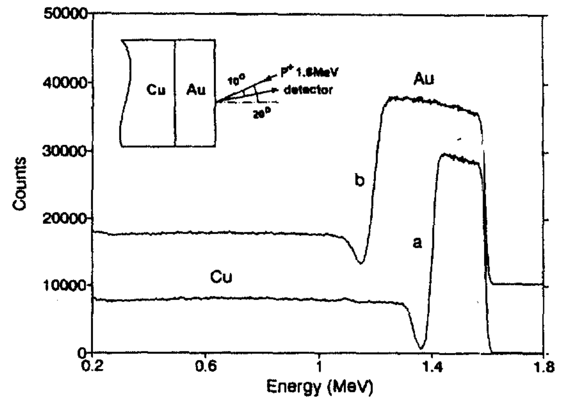

Fig. 3. Proton RBS spectra of (a) 0.91μm and (b) 1.80μm Au film on Cu substrate.

function of incident beam energy for the method 2 application is shown in *Fig*. 2 as an example.

In order to ensure the quality of the samples and to compare its result with the PIXE measurement, proton RBS was performed for the samples Nos. 1 and 2. 1.6 MeV proton beam was irradiated on a circle of 2mm beam diameter on the targets. The total dose amounts to 2μC. The backscattered protons were detected with a PIPS (Passivated Ion-implanted Planar Silicon) detector with a resolution of 14keV for 5.5 MeV alpha particles at 170°. *Fig*. 3 shows the energy spectra of the backscattered protons for the samples. It is seen that the Au film is well separated from the Cu substrate which enables the direct estimation of the film thickness from the low and high energy edges. To check the thickness nonuniformity along the radial direction, which might occur in the process of vacuum evaporation, three points (4mm up,

Table 2. Thickness nonuniformity measured by proton RBS. (unit : μm)

Position at target	sample No. 1	sample No. 2
Up	0.88	1.86
Center	0.91	1.79
Down	0.93	1.73
Average	0.91	1.79

center and 4mm down) on the target surface were analyzed. The RUMP program[5] was used for the analysis of the spectrum. The results are shown in *Table* 2. As can be seen the nonuniformity is less than 4%. Since the beam size is 5mm around the target center for PIXE, the nonuniformity can be considered to be negligible.

4. Results and Discussion

The methods 1 and 2 as described in the chapter 2 are tested. For the method 1, the calculation was done using both thin and thick targets as standard. The CONCAL program[6] was used for the numerical integration of eq.(1). The program uses the X-ray production cross sections in ref.7 and stopping powers in ref.8 but does not take the secondary effect such as self excitation into consideration. The results are summarized in *Table* 3. The two values by thin and thick standard targets are practically identical, implying that the matrix correction, i.e., the numerical integration of eq.(1) is very precise. But they show about 15% deviation from the real value.

For the method 2, three X-ray lines were used separately in the calculation. The correlation between the incident beam energy difference $E_i - E_0$ and the absorption corrected normalized X-ray count $Y_N(E_i) = Y_s(E_0)/Y_s(E_i) \cdot e^{-\mu \cdot \Delta t \cdot \sec\theta}$ is depicted in *Fig.* 4. At any given X-ray count of unknown sample $Y(E_i)$, the thickness of the Au film can be calculated using the relation $\Delta t = (E_i - E_0)/S(E)$ and the modification of eq.(4) :

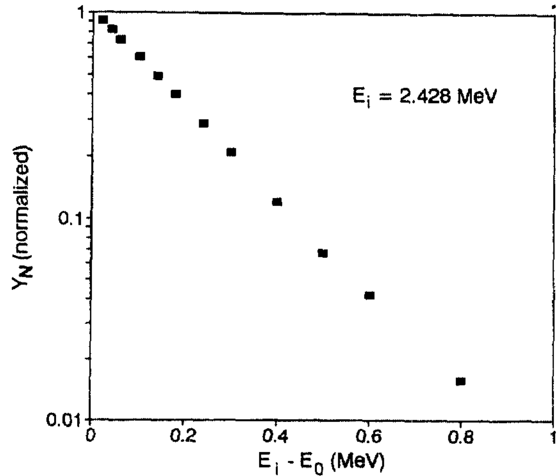

Fig. 4. The absorption corrected normalized X-ray count Y_N measured as a function of the energy difference $E_i - E_0$.

$$\frac{Y_s(E_i) - Y(E_i)}{Y_s(E_i)} = \frac{Y_s(E_o)}{Y_s(E_i)} \cdot e^{-\mu \cdot \Delta t \cdot \sec\theta} \qquad (5)$$

The results are shown also in *Table* 3. In the table, the results by proton RBS and by weight measurements are practically same and the values can be considered to be correct. Comparing with

Table 3. The results of the PIXE thickness measurement with 2.4 MeV proton beam. See the text for the description of the methods. The errors for PIXE and RBS measurements are about 5% and by weight, about 1%.

(unit : μm)

sample \ method	PIXE Method 1		PIXE Method 2			by RBS	by weight	by L_γ / by weight
	by thin standard	by thick standard	by L_α	by L_β	by L_γ			
No. 1	1.06	1.04	1.11	1.12	1.04	0.91	0.91	1.14
No. 2	2.04	2.00	2.12	2.22	2.08	1.79	1.80	1.15
No. 3	4.72	4.64	4.78	4.75	4.35	—	3.73	1.16
No. 4	not measurable		not measurable			—	7.46	

these values, the results by PIXE yield 15 to 25% larger. The results by thin and thick standard targets are practically same, implying that the matrix correction, i.e., the numerical integration of eq.(1) is very precise. The results of the Method 2 are slightly different among them. The reason may be the self excitaiton of L_α by L_β and L_β by L_γ which is not compensated in our calculation. Accordingly the results for sample No. 3 show the largest deviation from the true value. Since L_γ has no self excitation effect, the values by L_γ is considered to be the most correct. The ratios of the result by L_γ to that by weight in *Table* 3 show that the deviations for three samples are almost constant. The results by PIXE method gives about 15% more thickness than the real values regardless of the sample thickness. The reason for this discrepancy is not very clear, but should be corrected for when measuring an unknown sample. Further investigation is needed also for other films rather than Au in order to reveal this discrepancy.

Since the measured Au X-rays are severely absorbed in Au and the aluminum filter, the thickness of the sample No. 4 was not measurable. The X-ray count of No. 4 was same with that of thick standard sample. It may be also measured with a thinner absorber foil, if the dead time caused by high counting rate can be tolerated.

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