Theoretical characterization of reflector-assisted TXRF analysis

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The intensity enhancement phenomenon in reflector assisted TXRF has been investigated theoretically. Intensity enhancement effect was presented by focusing of primary and reflected X-ray beam to the sample. Proposed explanation behavior was compared with experimental results. Theoretical calculations are in a good qualitative agreement with experimental data. Based on proposed approach, the incident angle of primary X-rays can be evaluated in the experiment. [DOI: 10.1380/ejssnt.2006.579]

Keywords: X-ray scattering, diffraction, and reflection; Cobalt; Silicon; Computer simulations.

I. INTRODUCTION

Total reflection X-ray fluorescence (TXRF) is a powerful method for micro and trace analysis of the optically flat samples like Si wafers [1]. Since it was originally proposed in 1970’s [2, 3], this technique has been considerably improved. The main problem of micro and trace analysis is detection of low amount of trace elements on the substrate. To reduce the detection limit, one should find the way to increase the ratio of peak to background signal. This can be done either by increasing peak value and keeping background level as low as possible, or by decreasing background of the fluorescent X-rays. For this purpose monochromatic X-rays with more powerful intensity by synchrotron radiation have been applied for TXRF [4, 5].

Another way is to increase the primary X-rays by applying the focusing optics. The focusing equipment for primary X-ray beam is widely used to increase fluorescence intensity. Among them mono and poly-capillary lens [6, 7] and different type of beam guides have been proposed. Chebrukin and Shotyk [8] used a double plate sample carrier for focusing purposes. Sanchez et.al [9] reported low detection limit for reflector assisted TXRF analysis. V.K. Egorov and E.V. Egorov [10] made the fundamental study of the parallel type beam guide.

Strong angle dependency of X-ray fluorescence intensity is observed experimentally around critical angle in conventional TXRF by changing incident angle of primary X-rays [11, 12]. The results of angle-dependent TXRF have been explained by theoretical calculations [11]. The fundamental formate for angle dependency of XRF intensities have been described in detail elsewhere [11–15].

Reflector assisted TXRF systems are getting used for analyzing thin film sample. The advantage of reflector system is that the XRF signal intensity can be enhanced at certain conditions, as a result, this would improve detection limit. Peak appearance has been previously reported in a reflector angle \( \theta \) dependence of fluorescent intensity [16, 17]. Peak was also observed for angle dependency of fluorescent intensity of X-ray beam emitted by substrate, which is not the case for reflector-less condition. The incident angle \( \varphi \) influenced the position and the value of that maximum. In this work, we attempted to explain this phenomena form theoretical point of view.

II. BASIC EXPRESSIONS

Depending on the reflector angle, one of two types of reflection configurations can be considered as shown in Fig.1. Double reflection type (a) is always possible. Re-
reflectors is approached by X-ray beam with angle $\psi = \theta + \varphi$. In that case, the sample is approached by primary X-ray beam with incident angle $\omega = 2 \theta + \varphi$. Type (b) can be observed only in the case when reflector angle is higher than incident angle. In this case, the primary X-ray beam approaches reflector with angle $\psi = \theta - \varphi$. The reflected beam approaches the sample with angle $\omega = 2 \theta - \varphi$. Also in configuration type (b) the primary X-ray beam can reach the sample without reflection, as it is shown in Fig.1. Thus, the resulting fluorescence intensity would be a sum of intensities produced by primary and reflected X-ray beams. If the reflector angle is less than incident angle (reflection type (a) in Fig.1), primary X-Ray beam is cut by reflector and can not reach the sample. Because of the multiple reflections, the intensity of primary beam is reduced strongly. We would omit that case in further considerations if otherwise is not mentioned.

The intensity of X-rays, reflected from the mirror, would be reduced by the reflectivity coefficient $R$. It depends on the angle between the mirror and incident X-ray beam. The reflectivity coefficient $R$ is a decreasing function of incident angle, with the steep drop in its behavior around critical angle. A typical shape of reflectivity coefficient as a function of incident angle is presented in Fig.2. The calculation was made for a Si substrate and monochromatic X-ray beam of Mo Kα line (17.44 keV). For condition mentioned above, critical angle is observed around 1.78 mrad.

As it is well known, the TXRF intensity $I$ is increasing with incident angle $\varphi$ for all type of substrate at least until the critical angle. For quite thick sample, it continues to grow even for higher angles. The example of calculated angle dependency of fluorescence intensity $I(\varphi)$ of Co Kα line from Co layer of different thicknesses on a Si substrate is presented in Fig.3. We calculate X-ray intensity $I$ with a laboratory-made three-media model described in [12]. As a result of reflection, original intensity of impinging X-rays would be reduced at least by a factor of $R(\varphi) R(\psi)$ for type (a) or by a factor of $R(\psi)$ for type (b). Fluorescent intensity for type (b) is a sum of intensities produced by primary and reflected X-ray beams as it is clear from Fig.1(b).

The X-ray fluorescence intensity $I_R(\theta, \varphi)$ as a function of reflector angle for certain incident angle $\varphi$, is given by equations (1a) and (1b) for reflection type (a) and (b) respectively.

$$I_R(\theta, \varphi) = R(\varphi) R(\theta + \varphi) I(2 \theta + \varphi) \quad (1a)$$

$$I_R(\theta, \varphi) = I(\varphi) + R(\theta - \varphi) I(2 \theta - \varphi) \quad (1b)$$

Here the X-ray intensity $I$ can be taken from TXRF calculation without reflector [12]. For both cases the function $I_R(\theta, \varphi)$ has a term that is produced by multiplication of growing $I$ and decreasing function $R$. As a result, it has a maximum at certain angle. The example of calculation of TXRF intensity of Co Kα line as a function of reflector angle $\theta$ for different incident angle $\varphi$ is presented in Fig.4. The calculations were performed for Co
The intensity dependence estimated with equation (1b) demonstrates peak position shift to higher reflector angle with increasing incident angle. Also the value of the peak is increased when angle $\phi$ is increased. Moreover, equation (1b) suggests that the incident angle $\phi$ should be equal to reflector angle $\theta$ at the position of a steep growth of intensity when the focusing by type (b) begun to work. This feature of reflector assisted TXRF can be employed as an independent way to verify the incident angle.

### III. COMPARISON WITH EXPERIMENT

To confirm our theoretical approach, we measured angle dependency of X-ray intensities with different incident and reflector angles and for different samples. The experimental setup has been described previously [16, 17]. Mo K$\alpha$ (17.44 keV) from Mo X-ray tube was used for TXRF measurement. X-ray generator was operated at an applied voltage of 30 kV and an anode current of 20 mA. The thin film samples were prepared in the Institute of Materials Research (IMR) at Tohoku University with multi-ion vapor deposition system. The round spot of 5 mm diameter of Co layer of 6 different thicknesses (1 nm, 5 nm, 10 nm, 30 nm, 60 nm and 100 nm) was deposited on Si substrate for each sample.

The sample was placed at the center of rotation of the goniometer. The incident angle $\phi$ of the primary X-ray beam was varied by inclining the goniometer. The reflector has a dimension of 90x30 mm. One edge of the reflector was fixed at the center of rotation of goniometer to focus primary X-ray beam to the analyzed position. Another edge of the reflector was placed on two bars connected to an additional $z$-stage. The angle $\theta$ between the reflector and the sample surface was varied by changing $z$-position of that stage. The detailed description of reflector configuration can be found in previous publications of our group [16, 17].

The measured normalized intensity of Co K$\alpha$ line as a function of incident angle $\phi$ is presented in Fig.5. The measurements were performed for all layer thicknesses without reflector. The corresponding calculated data showed in Fig.3 are in a good agreement with measured curves shown in Fig.5. The critical angle for ultra thin Co layer sample (1nm) is much lower than for thicker samples. This phenomenon occurs because for that sample the peak position is determined only by the transition of X-rays on the sample surface. For thicker samples fluorescent X-rays produced by Co atom from deeper layers significantly contribute to total intensity and this caused the shift of peak position to higher angles.

The normalized intensity measured by reflector assisted TXRF analysis for 10 nm Co layer on a Si substrate sample is presented in Fig.6 as a function of reflector angle for Co K$\alpha$ line.
different incident angle $\varphi$. The experimental data in Fig.6 demonstrate a good qualitative agreement with calculated data in Fig.4. The position of the peak on reflector angle dependency shifted to higher values and the peak intensity increased. The higher incident angle $\varphi$ of primary X-ray beam, the higher the angle $\omega$, which is the incident angle of the reflected primary X-ray beam, as shown in Fig.1. As a result, the X-rays can penetrate deeper and produce more fluorescent X-rays.

IV. RESULTS AND DISCUSSION

It is important to know the value of incident angle $\varphi$ in TXRF measurements. But it is difficult to decide this value in experiment only. The drastic increase of the intensity of fluorescent X-rays was observed at certain angle. This result fit well with calculation. As it was predicted, the position of the peak corresponds to the value of the incident angle. For example: curve obtained for incident angle $\varphi$ of 2.67 mrad (▼ in Fig.6) has a local maximum at reflector angle $\theta = 2.77$ mrad; curve obtained for $\varphi = 3.54$ mrad (uencia in Fig.6) has a local maximum at reflector angle $\theta = 3.61$ mrad. As we wrote before, this feature can be used for independent evaluation of the incident angle.

The model we have developed is very simple and semi analytical. It does not take into account all possible parameters which can influence reflector assisted TXRF. In the frame work of this approach, some quantitative discrepancy with experimental data could not be explained. However, good qualitative agreement suggests that this approach is promising for further development.

To show the intensity enhancement effect, we have calculated the value of “maximum enhancement coefficient” $K_{enh}(\varphi)$ as a function of incident angle. This coefficient was defined as a ratio of peak value of the intensity $(I_R(\theta, \varphi))^{max}$ of Co K$\alpha$ line with reflector for given incident angle to the corresponding value with the same incident angle without reflector from Fig.5.

$$K_{enh}(\varphi) = \frac{(I_R(\theta, \varphi))^{max}}{I(\varphi)}$$

The corresponding results for 5 nm Co layer sample are shown in Fig.7. As one can see from the figure, the lower incident angle, the higher the enhancement coefficient. As it is shown in Fig.1, flux of primary X-rays is increased by reflector: the direct X-ray beam and reflected X-ray beam. In addition, for lower incident angle $\varphi$ the reflected primary X-ray beam approaches the sample at higher angle $\omega$ at its optimum position. It should be noted that angle $\omega$ of reflected primary X-ray beam is still less than peak position for reflector-less measurement – the critical angle for total reflection. As a result primary X-rays can go deeper to the sample and produce more intense fluorescent X-rays.

The X-ray spectrum for reflector assisted TXRF measured at incident angle $\theta$ of 2.67 mrad and the reflector angle of 3.33 mrad for Co 10 nm layer on Si substrate sample is presented in Fig.8. The background level for Co K$\alpha$ line is about 1 % of the peak value. We can assume that in spite of the deeper penetration of primary X-rays in the reflector assisted TXRF analysis the increase of background level is negligible compare to reflector-less case.

V. CONCLUSION

The theoretical explanation of the intensity enhancement of reflector assisted TXRF analysis has been proposed. Data obtained in an analytical approach were compared with experiment. Good qualitative agreement was observed between experimental data and theoretical approach. Proposed explanation gave us an independent way to evaluate incident angle.

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