J. Synchrotron Rad. (1999). **6**, 185–187

Enhancement of the Refl-EXAFS sensitivity using the whispering gallery effect

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A new approach to enhancing the sensitivity for the reflection EXAFS signal is described. A method that uses the whispering gallery effect was realized in principle, implementing the optical guiding effect by a simple curved-mirror geometry. The multiple total reflection (MTR) phenomenon highly increases x-ray interaction with the waveguide surface and hence offers higher sensitivity compared to conventional (single reflection) REFL-EXAFS. The Ge K-edge REFL-EXAFS measurements were performed using both the MTR and conventional (single reflection) techniques for a GeO_2 3 Å thick film grown on a silica mirror. The MTR technique allows one to achieve about 20-fold gain in the signal-to-background ratio compared to the conventional technique.

Keywords: x-ray waveguides; thin films; grazing incidence XAFS.

1. Introduction

Early in 1954, Parrat pointed out the potential use of grazing incidence x-ray methods for the structural probes of surfaces and interfaces. In grazing incidence geometry, when the total external reflection of x-rays occurs at grazing angles below the critical angle θ_c, the dynamic interaction between incident and reflected beams leads to the formation of an evanescent wave penetrating a shallow depth of 20-50 Å. Since EXAFS is a powerful structural probe, efforts have been made to increase the surface sensitivity of this method. Since early 1980, the EXAFS philosophy has been applied to reflectance spectra (Barchewitz *et al.*, 1978; Martens & Rabe, 1980; Fox & Gurman, 1980; Heald, Chen & Tranquada, 1988), that is known as the REFL-EXAFS technique. This technique combines the advantages of high intensity with surface sensitivity.

However, a practical implementation of REFL-EXAFS was limited to concentrated samples due to a small signal-to-background ratio in measurements. Indeed, for a one-element mirror, with an experimental geometry suitable for extended energy scans ($\theta < \theta_c/2$), the reflectivity drop resulting from the absorption edge is usually not greater than 10-20%. This technique is almost improper to probe diluted samples and monolayer specimens. A very small quantity of the substance interacting with x-rays leads to a very small signal-to-background ratio in the reflectivity signal. Statistical fluctuations in the number of reflected photons become a principal source of noise and degrade the REFL-EXAFS sensitivity.

In our study, in order to gain the REFL-EXAFS sensitivity, we developed a technique that employs multiple total reflection (MTR) according to the principle of x-ray waveguide. Compared to single reflected x-rays, multiply reflected x-rays can interact with a larger amount of the surface layer, yielding an enhanced EXAFS signal. In our previous experiments, it was shown with a glass capillary that the sensitivity of REFL-EXAFS can be considerably improved by multiple total reflection of x-rays from the inner wall of the capillary. In particular, the submonolayer sensitivity of the MTR technique was demonstrated in XAFS measurements of Kr adsorbed inside the capillary (Chernov, 1996). However, capillary waveguides are rather specific objects to be used widely. This paper describes the usefulness of the MTR technique for examination of ultrathin films deposited on conventional wafers.

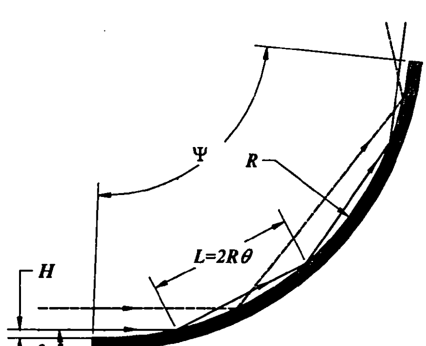

Figure 1
Schematic of the whispering gallery effect: grazing incident x-rays are captured by the concave mirror and propagate along the curved surface through successive reflections.

2. Whispering-gallery waveguide

The x-ray optical guiding effect can be obtained by employing a simple curved (and concave) mirror geometry. This type of x-ray waveguide using the whispering gallery (WG) effect was suggested by Vinogradov *et al.* (1982) to realize the transportation and deflection of x-ray beams. Fig. 1 illustrates the operation of the WG waveguide. A narrow x-ray beam falls tangentially on a cylindrical mirror of radius R and length L. In a ray-optical approach, the parallel incident beam can be divided transversely into an infinite number of rays. A ray can be efficiently transmitted through the waveguide if the reflections from the wall occur at angles less than the critical angle. Since the cylindrical shape of the waveguide retains grazing-incidence geometry, after a number of successive reflections ($n = 1+L/2R$), the ray can be deflected at a rather large angle Ψ.

The highest total reflectivity is achieved for low-absorbing materials of the waveguide and can be close to unity. In the hard x-ray region this condition is valid for light elements like C, Si and their compounds. Requirements for quality of the mirror surface in WG-waveguide applications are not stronger than for conventional x-ray mirrors. (Bukreeva *et al.*, 1995).

The incident beam is deflected effectively for its height less than $H_{max} = R\theta_c^2/2$. For a practical case, using $\theta_c = 0.2^0$ and R = 1m, the input beam height has to be as small as 5 µm. This highly reduces the input beam flux.

3. Experimental

To demonstrate the sensitivity gain provided by MTR, a 0.3mm-thick silica mirror covered with a monolayer of germanium oxide

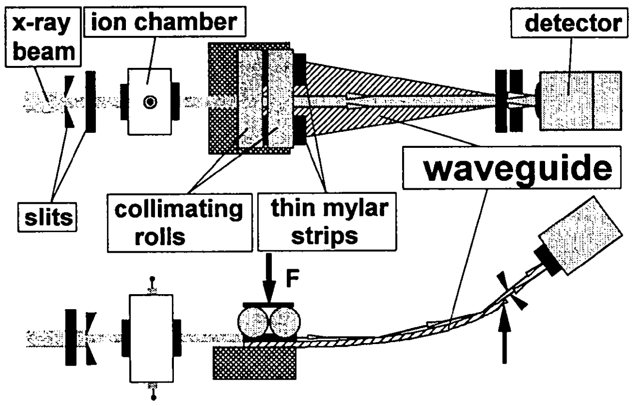

Figure 2
A schematic of the experimental setup for MTR REFL-XAFS measurements using the whispering-gallery waveguide.

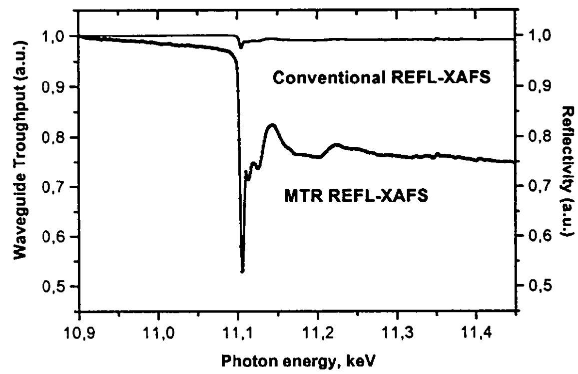

Figure 3
Comparison of the Ge K-edge reflectivity spectra taken by the conventional and MTR techniques for the silica wafer covered by a 3Å thick GeO_2 layer.

was prepared. Silica was chosen owing to easy polishing and the relatively low Z value. This provides a high transportation efficiency of the waveguide in the hard x-ray range. Silica wafer was polished to obtain a 3-5 Å roughness (Chkhalo *et al.*, 1995) and was shaped like a triangle. The wafer surface was chemically modified by Ge ions using a CVD technique and was then oxidized using an RF oxygen plasma source. The presence of a GeO_2 cap layer with a thickness of approximately 2-4 Å was supported by XPS measurements. Little growth of roughness after treatment, from 3-5 Å to 4-6 Å, was observed in x-ray reflectivity measurements.

XAFS spectra at the Ge K-edge were measured on the EXAFS beamline of the VEPP-3 storage ring (2 GeV and 120-90 mA) at SSRC (Novosibirsk). The synchrotron radiation was monochromatized using a channel-cut Si(111) monochromator. The energy resolution of the monochromator was estimated to be about 3 eV. A silica mirror was used to reject higher harmonics. A nitrogen-filled ion chamber to monitor incident beam was used in both REFL-EXAFS and MTR REFL-EXAFS measurements. An Ar-filled ion chamber and a fast scintillation detector were used for REFL- and MTR REFL-EXAFS measurements, respectively. Tungsten-carbide slits were used to reduce the monochromatic beam to a height of 50 μm and a width of 3 mm.

Fig. 2 shows a schematic view of the experimental arrangement used to realize the MTR REFL-EXAFS technique with the WG-waveguide. The triangle-shaped wafer with a length of 8 cm was mounted on a goniometer. The mirror tip was pushed by a screw to obtain the cylindrical waveguide with controlled radius of curvature. The base of the mirror was clamped to the goniometer holder by two rolls. The spring-loaded rolls were pressed against the mirror, while two thin strips were placed between the rolls and the mirror surface. A thin mylar film covered by a 1μm thick chromium layer was used for this purpose. To avoid the beam absorption, the strips were placed away from the mirror center. Two thin slits between rolls and the mirror surface formed a microcollimator. The collimator gap (~ 2-1 μm) was varied by the spring load. This design permits us to adjust a maximum grazing angle (θ_{in}) of the incident beam to approximately $\vartheta_c/2$, where ϑ_c is 0.16^0 for the SiO2 wafer at the Ge K-edge (11.103 keV).

The conventional REFL-EXAFS data were taken with the same sample. To prevent the wafer bending due to gravity, the wafer was attached to a flat mirror with a grooved channel for x-rays. To avoid signal distortions due to low-frequency modulations caused by the energy dependence of the penetration depth, the measurements were done far below the ϑ_c value at a grazing angle of 0.075 ± 0.02^0. The Ge K-edge fluorescence yield data were taken in the same geometry using a Stern/Heald/Lytle type detector. Scattered radiation was suppressed by a Ga-containing filter and collimated by slits.

4. Results and discussion

In Fig. 3, the reflectance signal taken in MTR geometry is compared with that of the conventional (single-reflection) mode. As is evident from the figure, the MTR mode has a superior sensitivity compared to the single-reflection geometry. The reflectivity drop at the Ge K-edge taken with the WG waveguide shows an approximately 20-fold gain. The total reflection coefficient after a number of successive single reflections is the product of their coefficients. To calculate the magnitude of the drop in reflectance T_m for the MTR case, one needs to know the

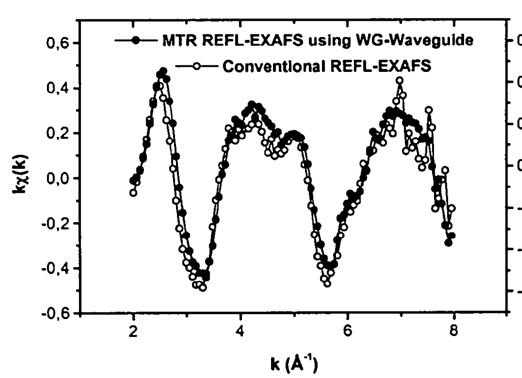

Figure 4
EXAFS oscillations extracted from MTR and conventional REFL-EXAFS spectra.

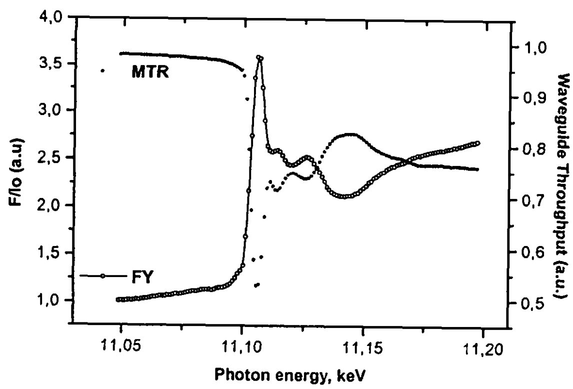

Figure 5
Comparison of near-edge absorption data from the Ge K-edge taken by FY and MTR techniques for the silica wafer covered by a 3Å thick GeO_2 layer.

number of reflections at a given θ_{in} angle. (It is easy to show that the overall signal drop accumulated by rays entering below this angle has almost the same magnitude.) For a small drop T_l in the reflectance of a single-reflection event, one can use the relationship $T_m = mT_l$ to calculate the T_m. For our case (R = 1m, H = 1μm, $\theta_{in} \approx 0.08^0$, the «working» length of the WG waveguide L = 70 mm, and the distance between reflecting points l = 2.6 mm), the number of reflections equals 25. A minor discrepancy between calculated and experimental values is attributed both to simplifying theoretical assumptions and to experimental imperfection.

In Fig. 4, the normalized k^1-weighed EXAFS oscillations of both the MTR and conventional modes are shown. Good agreement, both in the shape and amplitude of modulations, proves that MTR information is similar to that obtained by the conventional mode. It is of interest that the spectrum taken by a conventional technique is distorted by glitches in a high k-range, whereas the MTR REFL-EXAFS spectrum is not affected. This may be due to a higher contrast of MTR REFL-EXAFS.

To maximize the REFL-EXAFS sensitivity, a crucial point is the magnitude of the drop-to-background ratio. Conventional REFL-EXAFS measurements are not of good quality because of statistical noise of the background photons. Moreover, in practice, the systematic errors of experiment, e.g., monochromator glitches, significantly degrade the quality of REFL-EXAFS spectra. Therefore, a quantitative analysis for conventional REFL-XAFS technique can be hardly made for submonolayer samples. The MTR technique permits the accumulation and enhancement of the reflectance features and, hence, can be used for studies of submonolayer samples.

In Fig. 5, the Ge K-edge spectrum taken with the WG waveguide is compared with that of the fluorescence yield (FY) technique. About 20 individual 0.5h. -spectra were accumulated to achieve a sufficient signal-to-noise ratio. Clearly, the fine features of the FY and MTR signals are similar, demonstrating that MTR REFL-XAFS provides the same information as FY XAFS. At first sight, fluorescence detection seems to be favorable because the FY spectrum has higher contrast compared to the MTR spectrum. However, for our experimental conditions, the output flux obtained by MTR (~ 10^5 ph./s) was higher than that for the conventional FY technique (~10^4 ph./s). This difference is explained by a low fluorescence detection efficiency. If this is a concern, then the MTR technique is a better choice.

The results presented in this paper show that the modified REFL-EXAFS technique can provide new possibilities for a structural study of deposited monolayers and adsorbed molecules. Substantial improvements of this method can be expected with the use of third-generation SR sources. Their high brightness allows the employment of ordinary-sized wafers at reasonable output fluxes. This technique seems to be promising in the studies of ultrathin films deposited on single-crystal wafers, where the conventional fluorescence-yield XAFS is strongly affected by the Bragg reflections from the wafer.

Discussions with S.K. Kim, N.V. Kovalenko, A.V. Vinogradov, and K.V. Zolotarev are greatly appreciated. This work was partially supported by the Russian Foundation for Fundamental Research under Contract 97-02-18454.

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(*Received 10 August 1998; accepted 21 December 1998*)