THIN FILM CHARACTERIZATION BY RESONANTLY EXCITED INTERNAL STANDING WAVES

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Abstract

This contribution describes how a standing wave excited in a thin film can be used for the characterization of the properties of the film. By means of grazing incidence X-ray reflectometry one can deduce the total film thickness. On the other hand in making use of a strong resonance effect in the electric field intensity distribution inside a thin film on a bulk substrate one can learn more about the internal structure of the film. The profile of the internal standing wave is proven by diffraction experiments. The most appropriate non-destructive technique for the subsequent thin film characterization is angularly dependent X-ray fluorescence analysis. The existence of the resonance makes it a powerful tool for the detection of impurities and of ultra-thin marker layers, for which the position can be determined with very high precision (about 1% of the total film thickness). This latter aspect will be discussed here on samples which had a thin Ti marker layer at different positions in a carbon film. Due to the resonance enhancement it was still possible to perform these experiments with a standard laboratory x-ray tube and with standard laboratory equipment, consequently this technique has thus the potential to become a powerful laboratory tool for marker or impurity detection in thin films.
1 - Introduction

It is well known that x-rays striking a solid surface at grazing incidence below a certain critical angle $\alpha_c$ are totally reflected [1]. This angle is approximately increasing with the element number, and is thus higher for metals than for organic materials. For a finite beam size one will then find a certain zone where incident and reflected beam overlap. In case the incident beam is a sufficiently coherent plane wave the interference between the incoming and the reflected beam will produce a standing wave field above the surface [2] with a node at the surface. The periodicity $D$ of this standing wave depends on the grazing incidence angle $\alpha$ and on the wavelength $\lambda$ of the x-rays:

$$D = \frac{\lambda}{2 \sin(\alpha)}.$$  \hspace{1cm} (1)

For a wavelength of $\lambda = 0.1$ nm (1.0 Å) and metal substrates (e.g. Ni) total reflection will occur only below $\alpha_c = 0.3^\circ$. Consequently the standing wavefields produced in this way do have periodicities exceeding 10 nm, which is large compared to interatomic distances.

![Figure 1: Path of all the reflected (R) and transmitted (or evanescent) beams for an x-ray beam being incident and refracted into a thin film. The subscript c refers to the critical angles of the respective interfaces, while $\alpha_j$ is the angle of grazing incidence onto those interfaces.](image)

If under this condition a film of a light element (e.g. of organic material) and thus with a smaller critical angle is deposited onto the solid surface, then the incoming beam still partly penetrates the film, which is illustrated in figure 1. However, it will still be totally
reflected from the underlying surface. This will give rise to the formation of a standing wave field in and above the film. Its periodicity can still be calculated by use of (1), however, in the film one has to put the appropriate angle $\alpha$ corrected for refraction. For X-rays the refraction reduces the angle of grazing incidence inside a film as shown in figure 1. With this corrected $\alpha$ being smaller than the one mentioned above and assuming a node at the film-reflecting surface interface one can easily identify reasonable film thickness (in the range 30 nm - 100 nm) in which the standing wave will have a second node at the interface air-film.

It was predicted by de Boer [3] and has already been observed by Wang et al [4] that under these conditions a considerable enhancement of the electric field intensity (much beyond the level of the incident field) can occur in the film. In performing an $\alpha$ scan below the critical angle of the substrate one finds the resonance any time the number of standing waves between the top two interfaces is an integer (resonance orders). At these positions the angularly measured reflectivity will display deep minima. During the $\alpha$ scan the fluorescence yield profile as a consequence of the photoelectric effect at any of the constituents of the film will even more obviously demonstrate the standing wave and resonance effect. With angularly dependent reflectivity and fluorescence measurements by use of a powerful synchrotron radiation source Wang et al [4] succeeded to precisely locate a submonolayer of a metal imbedded in a highly oriented Langmuir-Blodgett film of about 100 nm total thickness on a gold mirror surface. Here instead the potential applications of this method in the study of the composition of amorphous sputtered films with a conventional X-ray source are discussed. In particular, thin metal markers can be employed in the study of interdiffusion processes. The possibility to determine with high accuracy the position of a thin metal marker layer in a carbon film from fluorescence yield profiles, which has applications in polymer interdiffusion (see e.g. [5]), is discussed in detail.

In this lecture all the aspects of a standing wave inside a thin film will be discussed with experimental data from our most recent experiments [6-9].
2 - Theory: Standing wavefield in thin film systems

2.1 - Standing wavefield intensity in thin film systems

In order to calculate the electric field distribution above and inside a thin film system one first needs to calculate its reflectivity. Parratt [10] presented as first a model for doing this. Here instead the subsequent and equivalent treatment of Stern will be presented [11]. Any single layer (index \( j \), see figure 1) can be characterized by its complex dielectric constant

\[
\epsilon_j = \epsilon_{1,j} + i\epsilon_{2,j}
\]

which can be derived from atomic scattering factors tabulated for photon energies from 10 eV to 30 keV [12].

From this the wavevector in any layer can be defined with \( \epsilon_0 = 1 \) (vacuum) as

\[
k_j = (2\pi/\lambda) \sqrt{\epsilon_j - \epsilon_0 \cos^2 \alpha}
\]

which allows to calculate the Fresnel reflection coefficient at any interface \( (j \rightarrow j+1) \) as

\[
r_{j,j+1} = (k_j - k_{j+1})/(k_j + k_{j+1}).
\]

The reflection coefficient of a system comprising the two interfaces \( (j-1 \rightarrow j) \) and \( (j \rightarrow j+1) \) separated by the distance \( d_j \) is then given by

\[
r_{j-1,j} = (r_{j-1,j} + r_{j,j+1} \exp(2id_jk_j))/(1 + r_{j-1,j} r_{j,j+1} \exp(2id_jk_j))
\]

For the lowest interfaces with \( j+1 \) being the substrate (as shown in figure 1) the \( r \) values behind the equal sign are calculated by use of (4), for eventually remaining layers to the surface these equations are then applied recursively. The resulting reflectivity is calculated by

\[
R = r_{0,1}^* r_{0,1}
\]

where the asterisk denotes the complex conjugate. The electric field intensity at the surface \( (z = 0) \) instead is \( E^2(\alpha,z=0) = |(1 + r_{0,1})|^2 \). Requesting continuity of the intensity at all the interfaces one can calculate the electric field or the standing wave intensity through the layer system.

The electric field calculations for a thin film by use of equations (2) to (6) show that a resonance effect only occurs when the film has a lower electron density than that of the underlying reflecting surface. Part of the results presented here are for a carbon film 98.5 nm thick on an opaque Ni layer investigated at 5.414 keV (Cr K\( \alpha \)) photon energy. The theoretical depth dependence of the electric field intensity normalised to the incident intensity in such a film is presented in figure 2 for the first three resonance orders. Note
the strong enhancement (a factor 30) of the field intensity for the first order. The behaviour at the critical angle for a carbon film (0.324°) is also shown; in this case the field intensity above the surface is close to the absolute maximum value of 4. Obviously the enhancement decreases with order number but remains still high even for the third order with a value exceeding 10. The intensity maxima occur at different sample depths as we vary the angle of incidence. This means that one could use this effect in order to determine in a non-destructive manner the position of a marker placed inside the sample.

![Diagram](image)

Distance to air-film interface [nm]

Figure 2:
Calculated electric field intensity versus depth in a 98.5 nm thick carbon film on a Ni substrate for 5.414 keV photon energy [12] and for grazing incidence angles of 0.331°, 0.3485° and 0.3765° corresponding to the first three resonance orders. The curve for 0.324° presents the field for the critical angle of the carbon coating.

It is worth to remark that neither marker nor sample need to be crystalline. The only limitation to the technique is that the overlayer must have a lower electron density than the reflecting surface, therefore it is particularly suitable to study polymer samples.
The intensities and the shape of the standing waves presented in figure 2 cannot be monitored directly, and thus in order to verify its exact shape the following secondary effects created by it have to be measured.

2.2 - Diffraction pattern created by standing wave field

If one terminates the thin film system abruptly the standing wave between the vacuum-film and film-substrate interfaces will be the source for an exiting beam. The standing wavefield is coherent and thus diffraction phenomena are to be expected. Due to the variation of the field over the aperture the diffraction pattern will be different to the classical Fraunhofer diffraction case with constant intensity in an aperture. And more importantly it will here vary with the number of standing waves. This has first been observed by Feng et al [13]. Far away from the terminal the intensity distribution \( I(\Theta_o) \), where \( \Theta_o \) is the observation angle in the plane containing incident and reflected beam, can be calculated as [13]

\[
I(\Theta_o) = C \int_{-\infty}^{\infty} \left( \int_{-\infty}^{\infty} E(\alpha, z) e^{i z K \sin(\Theta)} \, dz \right)^2 g(Q_o - Q) \, d\Theta
\]

(7)

C is a constant, \( E(\alpha, z) \) is the field amplitude of the standing wave in the film and \( z \) is the coordinate between the interfaces. \( K = 2\pi / \lambda \) is the absolute value of the vacuum wavevector and \( g(Q_o - Q) \) refers to the aperture in front of the detector, which is usually a rectangular function, defined as \( g = 1 \) only when \( |Q_o - Q| \) is smaller than the half acceptance angle of the detector aperture as seen from the source. In measuring the intensity distribution under these conditions for known values for the film thickness one can thus investigate the electric field distribution in the standing waves.

2.3 - X-ray fluorescence yield due to a standing wavefield

At a certain point in the film instead the electric field distribution can be measured by introducing a marker as a probe into the system. As one alternative one can then measure the photo electron yield of electrons with energies characteristic for the marker layer. However, with the electrons undergoing many inelastic collision processes in the film, this technique is rather insensitive for deep embedded markers. X-ray fluorescence photons of appropriate energy on the other hand will be able to exit even from very deep
zones. In this case the photoelectric effect gives rise to the experimentally observable fluorescence yield and is proportional to the electric field intensity at the position of the probe atom. For a probe atom distribution \( \rho(z) \) the fluorescence yield \( Y \) is given by

\[
Y(\alpha) = \int E^2(\alpha, z) \rho(z) \, dz. \tag{8}
\]

3 - Experiment

3.1 - Sample production

A number of samples were prepared by sputter deposition in the multilayer laboratory of the SINCROTRONE TRIESTE. The substrates were float glass of 75 x 25 x 4 mm with a surface flatness of about \( \lambda/10 \) peak-to-valley in any square of size 10 mm. Their surface microroughness is of the order of 0.7 nm rms. The sputtering was achieved by use of a triode assisted and magnetically confined plasma in a low pressure Ar atmosphere (p=0.1 Pa) \[14\]. Without breaking vacuum we could exchange up to three different targets (in our present case C, Ni and Ti or Cr). The distance between these targets and the sample was 180 mm. The sputtering rates were adjusted to relatively low rates of less than 1 nm/min for all materials. From previous X-ray specular reflectivity measurements we found that under these conditions the different materials form smooth interfaces.

3.1.1 - Samples for diffraction experiments

One sample had a 137 nm carbon film enclosed between an opaque layer of 22 nm of Cr as the substrate and 4.4 nm Cr as a semitransparent cover. In order to form an aperture at the carbon layer end another 20 nm of Cr were added over the last 2 mm.

3.1.2 - Samples for fluorescence measurements

In three other samples instead Ti markers of 0.2 nm and 0.5 nm thickness were included in the carbon film at different positions, but leaving the C/Ti/C system total thickness always at the same value of 98.5 nm. One sample (nicti2) had 0.5 nm Ti in the
center, while the others had 0.2 nm Ti at 2/3 (nicti3) and 1/3 (nicti4) of the total system thickness, starting from the substrate.

3.2 - Experimental setup

Even though the setups for the two types of experiments which will be discussed in the following were realized in two different laboratories, they are very similar, and thus the general concept is presented in only one scheme (figure 3).

3.2.1 - Experimental setup for diffraction experiments

This set of experiments was performed at the microfocus beamline BL1 at the high brightness undulator ID13 at the European Synchrotron Radiation Facility (ESRF), which has a vertical electron beam divergence of only $\sigma_y = 8.2 \ \mu\text{rad} (0.0005^\circ)$. The first undulator harmonic tuned to a photon energy of 13 keV was further monochromatized by a channel cut Si(111) crystal monochromator [15]. No focusing was applied to the beam, which was simply taylored by a double slit system to dimensions of 65 $\mu$m height and 0.6
mm width at the sample position. Here the sample had its surface in the horizontal plane and it was aligned by use of a two-circle goniometer (for pitch and roll adjustment), which was mounted onto translation slides for height and lateral motions. At about 170 mm from the sample end a PIN-diode (the lower D in figure 3) with a 0.1 mm high aperture (or 0.034°) was mounted onto a vertical translation slide.

### 3.2.1 - Experimental setup for fluorescence measurements

The experimental setup for the X-ray fluorescence measurements instead was based on a double-axis diffractometer with vertical axes. The X-ray beam from a standard sealed tube with Cr anode (E=5.414 keV, 0.015 mm (H) x 8 mm (V) line focus, and a voltage and current setting of 35 kV and 26 mA) was monochromatized by a Si(111) crystal. After the monochromator a slit limited the beam size impinging on the sample to about 0.03 mm (H) x 5 mm (V). The FWHM (full width half maximum) beam divergence was evaluated to be about 0.015°. The reflected beam intensity and the fluorescence signal were measured simultaneously in a θ-2θ scan. The sample was moved in steps of (1/400)°. The reflected intensity was measured with a NaI(Tl) scintillation detector (the upper D in figure 3) whose window was covered by a slit with an acceptance angle of 0.25° in order to block the scattered intensity. The fluorescence was measured with an energy dispersive Si(Li) detector with a large collection area of 80 mm² (diameter 10.1 mm), placed with its active surface at a distance of 9 mm from the sample surface. For the angles of interest the X-ray footprint (F in figure 3) has dimensions of 6 mm (H) x 5 mm (V) at most, therefore no correction for geometrical fluorescence losses was needed. The total intensity detected by the Si(Li) detector was always quite low, so that no dead-time correction needed to be applied.

### 4 - Discussion

#### 4.1 - Diffraction experiments

In order to successfully perform this experiments it is necessary that the standing wave travels laterally in the thin film to its end as does a standing wave in an optical waveguide. The possibility to make also X-rays travel in a thin film waveguide was first proposed and verified by Spiller and Segmüller [16] already in 1974. Due to the
absorption of x-rays in any material efficient traveling will only be found in light materials and for photon energies larger than 10 keV. Only very recently Lagomarsino et al [8] and shortly after Feng et al [13] could detect a wave exiting from the thin film end using powerful synchrotron radiation from the ESRF. The latter measured also the first diffraction profiles of this beam [13]. Here are presented the results of a more detailed study which we performed [9].

Figure 4 compares the reflectivity of the sample for 13 keV photon energy (measured in the part with the semitransparent Cr layer) with a simulation based on equations (2) to (6) assuming the substrate to be SiO₂. From the measured modulation the geometrical parameters of the structure have been derived, resulting in 22 nm Cr in the base layer, 136.9 nm for the carbon guiding layer and 4.4 nm for the semitransparent Cr cover layer. For these parameters we find good agreement with the measurement if we assume a surface and interface microroughness of 0.8 nm rms. In addition the source divergence of σ_y' = 8.2 μrad is included into the calculations and the fact that at angles below 0.2° the substrate did not completely intercept the incident beam. Without these

![Figure 4](image_url)

Comparison of the measured angularly dependent reflectivity R of the thin film structure (dots) with the calculations (solid line), which are for 4.4 nm Cr cover layer on top of 136.9 nm C on 22 nm Cr on SiO₂ with 0.8 nm rms interfacial roughness and a beam divergence of σ_y' = 8.2 μrad. The photon energy is 13 keV. At angles below 0.2° losses due to intensity not hitting the sample anymore were considered.
latter corrections the calculated reflectivity would increase towards smaller angles while in the first three narrow reflectivity minima it would always be smaller than $R=0.1$. In this case one finds 11 reflectivity minima below the critical angle of the substrate Cr at $0.25^\circ$.

Figure 5 presents in an angle dependent scan the correlation between the reflectivity and the intensity diffracted from the end of sample. Both spectra were measured with the PIN diode at fixed positions and without any aperture in front of it, however, for the latter spectrum the dominating reflected beam was blocked by

![Figure 5](image)

**Figure 5:** Comparison of the measured angularly dependent reflectivity $R$ of the film waveguide structure (top) with the measured intensity $t$ exiting at the film waveguide end tangentially to the guide surface (bottom). Both spectra are normalised to the incident signal and are taken at 13 keV photon energy. The line connects the measured points as a guide for the eye.
Position in C film [nm]  Detector position [mrad]

$E/E_0$  Signal [arb. units]

- $TE_0$
- $TE_1$
- $TE_2$
- $TE_3$
- $TE_4$
appropriate means (B in figure 3). The observed correlation between reflectivity minima and thus the positions of integer numbered resonantly enhanced standing waves and the exiting diffracted intensity presents nicely the fact that only in this condition appreciable intensity is deposited into the film. Due to the analogy with optical waveguides the standing waves are here denoted as TE_0 to TE_4, which corresponds to the first 5 exitable modes of the film resonator. For each of these modes the diffraction patterns observable far from the film waveguide end were measured and are compared to the simulations according to equation (7) in figure 6 (right side). The zero position angle corresponds to the direction of the incident beam and thus the structure moves to higher angles with increasing mode number. The calculations take care of the fact that the standing wavefield of a guided mode does not have the nodes exactly at the carbon/chromium interfaces but that the electric field is partly penetrating into the chromium boundary layers, as is shown in figure 6 (left side), which presents the simulated electric field amplitude between the interfaces for the different modes. The calculations also consider the detector box function g(\Theta_0 - \Theta) with (0.1 mm /169 mm) = 0.59 mrad acceptance. As far as the positions of the peaks and the number of secondary maxima between the major peaks in figure 6 (right side) is concerned experiment and simulation are in good agreement. This verifies firstly that the source is a standing wave with locally fixed field amplitude which otherwise varies through the film thickness. Secondly it proves unambiguously the model of the integer numbered standing waves in the thin film in condition of a reflectivity minimum (the integer refers to the field intensity, which is E² and has thus twice the number of oscillations of the field amplitude E). Small discrepancies between experiment and theory are of unrelated origin and their discussion goes thus beyond the scope of this presentation. They are discussed elsewhere [9].
4.2 - X-ray fluorescence experiments

While the previous experiments could prove the existence and the shape of the standing wave in a thin film, they are not able to verify the absolute value of the electric field enhancement. This instead can be done with angularly dependent fluorescence experiments. These experiments were performed with 5.414 keV photon energy and slightly different total film thickness.

Figure 7a shows the angular dependence of the reflectivity obtained for sample nicti3 (dotted line). The solid line is the result of the simulation calculated considering all interfaces, including the presence of 0.2 nm Ti at 2/3 of the total carbon thickness. The Ti affects the standing wave very little and thus the reflectivity behaviour below the critical angle of the substrate Ni is once more dominated by the total carbon layer thickness. Due to the smaller total thickness one now finds only 8 reflectivity minima below the critical angle of the substrate. The measured reflectivity curves for the other two samples nicti2 and nicti4 are almost identical, verifying the idea that the thin Ti layer has little effect, and are thus not discussed any further. The angular positions of the features in the simulation agree with those in the experimental data, confirming the C/Ti/C system thickness of 98.5 nm in all samples. An increase in the carbon absorption coefficient, motivated later, will improve the agreement for the signal at the first reflectivity minima. However, the simulations were not corrected accordingly because the total carbon thickness and the Ti position derived from feature positions are unaffected.

In order to measure the above mentioned correlation between the modulation in the reflectivity minima and the electric field enhancement an isotropically distributed marker is needed. Sputtered films always contain sporadic inclusions of the sputtering gas, which in this case was argon. The angularly dependent Ar Kα fluorescence (2.957 keV photon energy) exhibited the same modulation for all samples and thus once more only the data for nicti3 are presented in figure 7b. The measured data were corrected for the illuminated area and normalized to the calculations just below the critical angle of Ni at around 0.6°, where the resonance enhancement levels off. The simulation has been carried out taking into account an interface roughness of 0.7 nm rms and a beam divergence following a gaussian distribution with standard deviation $\Sigma=0.005^\circ$. The Ar fluorescence presents an oscillatory behaviour with the maxima corresponding to the reflectivity minima, as is evident comparing figure 7a and figure 7b. This proves the existence of the resonance effect. The agreement between theoretical and experimental
Figure 7:
Comparison of the experimental data (points connected by broken lines as guide for the eye) and the calculations (solid line) for 5.414 keV photon energy versus the grazing incidence angle for the following aspects (the calculations [12] are always for the model parameters presented in the insets
with 0.7 nm rms interface roughness and beam divergence $2\Sigma=0.01^\circ$
normalized for an incident beam of unity intensity):
a) reflectivity of nicti3 (0.2 nm Ti at 2/3 carbon thickness, closer to the surface)
b) Ar fluorescence intensity of nicti3
c) Ti fluorescence intensity of nicti2 (0.5 nm Ti at 1/2 carbon thickness)
d) Ti fluorescence intensity of nicti3
e) Ti fluorescence intensity of nicti4 (0.2 nm Ti at 1/3 carbon thickness, closer to the substrate).

features is good, mainly for the angular positions of the resonance peaks. The perturbation of the electric field due to the Ti marker reduces in particular the first order resonance theoretically by a factor 2 compared to figure 2. A further reduction is introduced by the limited beam divergence.

![Graph](image)

Figure 8:
Comparison of the reflectivity (curve B, broken line referring to right scale) and the total photo electron yield (curve A, solid line referring to left scale) measured versus the angle of grazing incidence at a photon energy of 8.045 keV for sample nicti2.
Also the total photo electron yield can approximately be considered to arise from an isotropically distributed marker. Experiments of this kind have been performed at the sample nicti2 (with the Ti in the center) by Pelka et al [7] with Cu Kα radiation of 8.045 keV photon energy and are presented in figure 8. As expected the reflectivity curve (dashed line) is almost identical to that in figure 7a with 8 reflectivity minima observed below the critical angle of Ni at 0.45°. It should be noted that these experiments were performed with smaller divergence of the incident beam and thus the first two reflectivity minima are better separated and consequently are relatively deeper. As a consequence also the first two maxima in the total electron yield are better separated and thus now higher. However, for the other aspects the spectrum shows the same correlation with the reflectivity as does the Ar fluorescence yield and supports thus the resonance enhancement. While the Ar fluorescence above the critical angle of Ni does not undergo a significant change the total electron yield now reflects the fact that in Ni relatively more electrons than in carbon are produced per incident photon. Consequently here the signal is dominated by electrons originally produced beneath the carbon film in the nickel substrate.

In figures 7c-7e the Ti fluorescence for the three different positions of the Ti marker in carbon is shown. The measured angular dependences agree well with the calculations based on the above mentioned theory and on the sample structure. The feature positions and shapes in the spectra allow us to unambiguously derive the positions of the marker layer. Figure 7c is for sample nicti2 (Ti in the center of C) where, according to figure 2, only the odd resonance orders will excite the fluorescence. And indeed the existence of nodes of the standing wave at this position for even numbered standing waves is very obvious from the almost complete absence of any Ti fluorescence signal at the corresponding angles in figure 7c. Consequently one finds then only five fluorescence maxima instead of the eight maxima observed in the same angular range for the Ar fluorescence. The other two samples have the Ti marker at symmetric positions with respect to the center of the carbon film, i.e. at 2/3 and 1/3 of the total thickness. At these positions the 3rd and the 6th orders of the standing wave pattern have nodes (field minima), resulting indeed in very low Ti fluorescence signals at the corresponding points (0.375° and 0.5°) in figure 7d and 7e. No further coincidence between fluorescence maxima or minima is found for spectra 7d and 7e, which arises from the production mechanism of the standing wave pattern. In increasing the angle of incidence the standing
wave pattern does not remain symmetric with reference to a point in the film center, instead, it will always have a node at the Ni surface. With increasing angle the periodicity decreases and thus the moving standing wave pattern resembles very much a compressing spring fixed at one end. Obviously a larger number of distinct oscillations passes at the Ti marker farther from the reflecting surface (nicti3), compared to the marker closer to the Ni surface (nicti4). This is clearly shown in both the experimental and simulated curves in figures 7d and 7e. With the boundary condition: node at the Ni surface, an antinode of the standing wave pattern can only exist either at the 1/3 position or at the 2/3 position, but not simultaneously at both positions, resulting in the absence of further maximum and minimum coincidences.

One important point is the accuracy in the determination of the marker position and of the total film thickness. This point is discussed by use of figures 9 and 10. As far as the reflectivity is concerned the total thickness C/Ti/C determines the position of the minima below the critical angle of the Ni underlayer. The comparison of the experiment with the calculations in figure 9 results in a total thickness (best representation is curve 9a) of 98.5 nm ± 1 nm for sample nicti3. Here the Ti thickness and position are not affecting the angular positions of the minima. Figure 10 shows the comparison of the measured Ti fluorescence profile of sample nicti2 with the calculations (best representation is curve 10c with the Ti between 65.53 nm (below) and 32.77 nm of C (above)), in which the total thickness is kept at the value of 98.5 nm. Also in this case we find an accuracy of ± 1 nm. Here not only the structure positions but also the structure shapes, which undergo appreciable variations with changing Ti position can be used for the determination of this position. For the other samples the comparison results in the same accuracy. This means that the total thickness and also the position of the marker layer can be determined with an accuracy of ± 1% of the total system thickness, which is only slightly worse (factor 2) than what has been found in synchrotron radiation experiments at Langmuir-Blodgett films of almost the same thickness [17].

In figures 7b and 7c-7e the agreement between the experimental and the simulated curves is very good concerning the angular position of the resonance peaks, but some discrepancies exist in the intensity, mainly for the first two maxima. One possible cause is the presence of the Ar atoms in the carbon matrix. Due to the much higher absorption coefficient of Ar with respect to C, even 0.5% of Ar is enough to increase the film absorption by about 35%. This reduces theoretically the resonance enhancement in the first orders, thus a significant improvement in the agreement between experiment and
theory has to be expected. However, the Ar content has not been included in the calculations due to its unknown concentration in the carbon film. On the other hand, after careful calibration measurements, the resonance effect could even become a non-destructive tool for the quantitative determination of the gas content or other contaminant content in sputtered or otherwise produced thin films.

Figure 9:
Comparison of the measured reflectivity (sample nicti3, points connected by broken lines as guide for the eye) and the calculations (solid line) for 5.414 keV photon energy versus the grazing incidence angle for the following total film thickness (the calculations [12] include always 0.2 nm of Ti at 2/3 of the total film thickness, 0.7 nm rms interface roughness and beam divergence $2\Sigma=0.01^\circ$):
a) for 98.5 nm, b) for 99.5 nm and c) for 97.5 nm.
For clarity curves b and c have been displaced by 0.15 up and down, respectively.
Figure 10:
Comparison of the experimental fluorescence profiles (sample nicti2, points connected by broken lines as guide for the eye) and the calculations (solid line) for 5.414 keV photon energy versus the grazing incidence angle for the following C layer thickness underneath a 0.5 nm thick Ti layer (the calculations [12] are always for the total film thickness of 98.5 nm, for 0.7 nm rms interface roughness and beam divergence $\Sigma=0.01^\circ$): 
a) for 51.0 nm, b) for 50.0 nm, c) for 49.0 nm, d) for 48.0 nm, e) for 47.0 nm. With the exception of curve c, the curves have been displaced in the ordinate for clarity.

5 - Conclusion

It has been shown that a standing wave can be formed by x-rays incident at very grazing angles onto a thin amorphous low Z film on a totally reflecting mirror. In varying the angle of incidence and thus the profile of the standing wave field in the film the
presence of an isotropically distributed contaminant and the position of a thin metal marker layer could be derived from x-ray fluorescence measurements in a non-destructive way. The position of the marker layer and the total film thickness could be determined in a comparison to model calculations with an accuracy of 1% of the total thickness. Due to the resonance enhancement of the standing wave field these experiments could be performed with standard laboratory equipment. The same type of experiments was previously made at the most powerful synchrotron radiation sources and on highly oriented Langmuir-Blodgett films [4,17] deposited onto polished mirrors. The prototype experiments presented here instead were carried out on amorphous sputtered films deposited onto float glass slides. Consequently thin film characterization by resonantly enhanced internal standing waves in amorphous material has the potential to become a powerful laboratory tool. Fluorescence spectra of the presented quality require about 10 hours of data collection time. The extension of this technique to the study of dynamical processes will require more flux and should be possible with powerful wigglers/undulators at the existing third generation synchrotron radiation facilities.

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\[ \varepsilon = 1 - (r_0 \lambda^2/\pi) \sum_n n_p (f_{1,p} - i f_{2,p}), \]

where \( r_0 \) is the classical electron radius and \( n_p \) is the number of atoms of element \( p \) per unit volume with scattering factors \( f_{1,p} \) and \( f_{2,p} \).