# Characterization of nanoscale multilayer structures upon thermal annealing

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## Abstract

Obtaining a high quality physical description of the layered structure of multilayer based optical coatings is an essential part of the optimization of their optical performance. Grazing incidence X-ray reflectivity (GIXR) is one of the most informative and easy-to-use non-destructive tools for the analysis of multilayer structures. The typical challenge of GIXR structural characterization is the reconstruction of the layered structure from fitting simulated data to experimental data. Here we present an example of the application of a newly developed, free-form, GIXR analysis to the characterization of heat induced structural changes in periodic La/B multilayers. This example shows that the developed algorithm is capable of reconstructing electron density profiles in cases where a classical non free-form approach generally fails.

## Introduction

Grazing incidence X-ray reflectivity (GIXR) is a widely used method to determine the structure of thin films and multilayered structures. The main method of the analysis of GIXR data is based on fitting of calculated reflectivity curves to the measured data, while varying layer thicknesses, layer densities, and the size of interfacial regions/roughnesses as fitting parameters[1]. Here we will discuss analysis of periodic multilayer structures of which each period consists of two layers. As long as the period of such multilayer structure can be modeled as a two-layer structure with small interfaces between the layers, this approach of data analysis works satisfactory. The analysis becomes much more complicated if the thickness of the interfaces is comparable to thicknesses of the layers and, moreover, the interface compositional profile is unknown and may strongly deviate from the error function profile that is generally assumed. Such a wrong assumption will lead to an incorrect model representation. For these cases we have developed a special free form approach to the analysis of GIXR curves when the period of the multilayer mirror is presented as a set of sublayers and the optical constant of each sublayer can be varied independently during the fitting procedure. Details of this algorithm and the fitting procedure will be published by A. Zameshin et.al. elsewhere[2]. Here we present an example of application of this newly developed algorithm to the analysis of structural changes in La/B multilayers upon thermal annealing at 400℃. This topic was previously investigated by S.L. Nyabero et.al. [3] , but no information about structural changes upon annealing was extracted due to the difficulty of classical model dependent interpretation of GIXR data.

### Parametrization of free form layer composition profile

The free form analysis of GIXR data results in a reconstructed optical constant (OC) profile consisting of many sublayers. To enable a quantitative comparison of different OC profiles, for example for a sample analyzed before and after annealing as presented in this paper, a parameterization of the profiles is suggested here. A useful parameterization should address the features that are present in all OC profiles for the same sample.

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One of the most important parameters of a multilayer OC profile is the optical contrast, which is critical for the performance of any multilayer mirror in a real application. The Michelson contrast is defined as:

$$C = \frac{\delta_{La} - \delta_B}{\delta_{La} + \delta_B}, \quad (1)$$

where $\delta_i = 1 - Re(n_i)$, where $n_i$ is the refractive index of the $i$-th layer.

The straightforward way to determine Michelson contrast $C$ is to define $\delta_{La}$ and $\delta_B$ as the respective maximum and minimum of the derived optical constant profiles. Minimum and maximum values of δ are very sensitive to the actual shape of the OC profile and may therefore not be representative for the optical performance of the multilayer. A better way to determine $\delta_{La}$ and $\delta_B$ is to calculate the averaged $\delta$ for La and B layers, and use them in eq. (1). To define the layers in a consistent way, we use k-means cluster analysis, using the $\delta$ of each sublayer as metrics. Figure 1 shows an example of a typical OC profile that can be obtained as the result of a free form analysis of a GIXR data. For a reasonably smooth profile, this analysis provides La-rich and B-rich clusters, as shown in fig. 1. From these clusters the average $\delta$ is obtained and used to determine $C$.

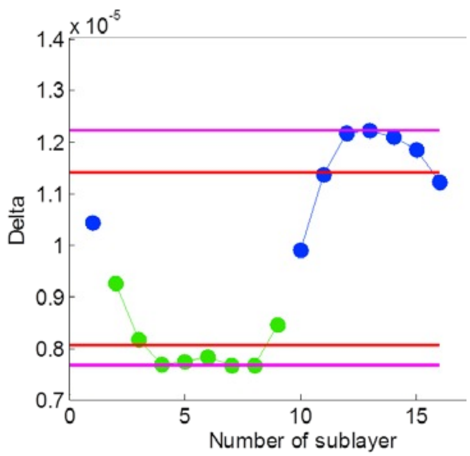


Fig. 1. An example of OC profile, represented by δ, obtained from a free form analysis of GIXR data from a La/B multilayer. The values of $\delta_{La}$ and $\delta_B$ as determined by maximum/minimum values of δ are depicted by pink lines. The values of $\delta_{La}$ and $\delta_B$ as determined via clustering analysis of the of δ profile are depicted by red lines. "La-rich" clusters are indicated by blue dots, "B-rich" clusters are indicated by green dots.

### Analysis of nanoscale-periodicity multilayer structures

As an example of the sensitivity and the analytical power of free form GIXR data analysis, we select a typical application case requiring high sensitivity, where standard analysis of GIXR data failed. We discuss the analysis of a periodic multilayer coating with 50 La/B bi-layers with period thickness of 3.9 nm, deposited by magnetron sputter deposition as described in ref [3]. GIXR data were measured using a PANalytical EMPYREAN X-ray diffractometer, using a parallel beam mirror to obtain high dynamic range. Figure 2 shows GIXR data measured just before (as deposited) and after thermal annealing. The thermal annealing was performed in an $N_2$ environment at atmospheric conditions at 400℃ for 10 hours.

A brief qualitative comparison of both curves in fig. 2 shows some differences. The total reflection region is much lower before annealing. At very grazing incidence GIXR is sensitive to curvature of the sample that could originate from film-induced stress. During annealing the stress is relaxed and therefor the sample curvature reduces. In general, all Bragg peaks are slightly shifted towards a higher angles due to an apparent compaction of the multilayer period. In addition, the intensity of the Bragg peaks reduces faster as a function of reflection angle, and the intensities in between Bragg peaks have changed. All these changes are easily observed, but no direct conclusion can be made about the effects of thermal degradation on the structure of the multilayer without a detailed profile reconstruction.

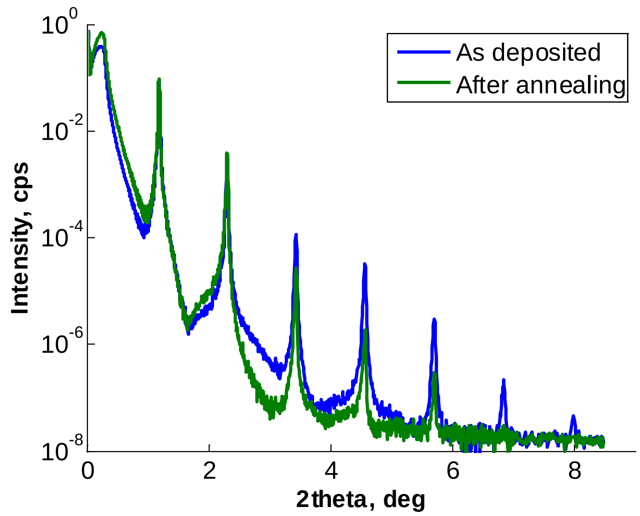


Figure 2. Comparison of GIXR curves for as deposited and annealed samples.

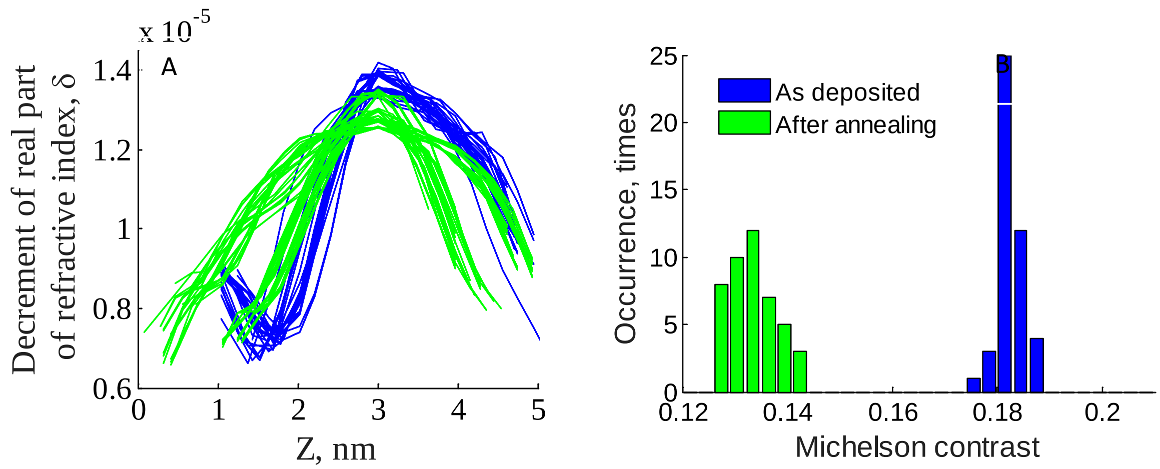


Figure 3 (A) Manifold of $\delta$ profiles obtained from free form analysis of the La/B multilayer before (blue) and after (green) annealing. Steps corresponding to different sublayers are smoothened for ease of visual comparison. (B) A histogram of Michelson contrast values obtained from the manifolds before and after annealing.

For each measured GIXR data set, the free form data analysis was performed several times, using different initial fit parameters. As a result we obtained a manifold of OC profiles that all describe a measured data satisfactory. These manifolds are presented in fig. 3A for the La/B multilayer structure before and after annealing. The optical contrast was calculated from eq. (1) for each OC profile, and the distribution of those is also shown in fig. 3B.

The GIXR analysis indicates that as a result of annealing the optical contrast of the multilayer is strongly decreased. The contrast values derived from the measurement before and after annealing are well separated, which allows one to confidently claim that the contrast of a multilayer is reduced after annealing. This conclusion coincides with the strong decrease of reflectivity of the multilayer at 6.8 nm wavelength, that was reported in ref [3]. A more detailed analysis of the manifold of OC profiles obtained from the form free fitting hints that during the annealing we can expect significant growth of interfaces that coincides with the assumption of formation of amorphous $LaB_6$ layers in multilayer after annealing.

Figure 3A also shows that the OC profiles obtained from the form free analysis, especially after annealing, cannot easily be parameterized by a standardly used two-layer model with simple interfaces, which explains the difficulties that Nyabero et all. faced in their analysis of GIXR data with a model dependent approach. The large difference in optical constant profiles within the manifold, equally well describing the same GIXR curve, can be explained by the fact that for analysis presented here we have taken GIXR curves measured with medium resolution, provided by a parallel beam mirror. This measurement scheme has been used because it provides higher count rates and is therefore more suitable for the in-situ measurement of fast changes in the reflectivity signal as investigated in ref [3]. In order to reduce the variation in the manifold from the free form analysis, a high resolution measurement of GIXR over a large dynamic range is actually preferred, but is beyond the scope of the work presented here.

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