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X-Ray Calc: A software for the simulation of X-ray reflectivity

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ABSTRACT

X-Ray Calc is a fast and convenient tool for the simulation of X-ray reflectivity (XRR). The software was developed with the aim of simplification and acceleration of the XRR simulation through a user-friendly interface and optimized computation core. X-Ray Calc implements the recursive approach of calculation of XRR based on Fresnel equations and proposes special instruments for the modeling of periodical multilayer structures. X-Ray Calc computes XRR as a function of wavelength or grazing angle and can be used for the simulation of the performance of X-ray mirrors. Computer modeling and fitting to experimental grazing incidence X-ray reflectometry (GIXR) is a powerful tool. It could be used for a comprehensive analysis of the structure of single- and multi-component layered nanomaterials. This method allows for the obtaining of information about thickness, roughness, and density of individual layers in coatings by the fitting of the modeled GIXR to the experimental ones.

Code metadata

Current Code version	V86
Permanent link to code/repository used of this code version	https://github.com/ElsevierSoftwareX/SOFTX_2019_363
Legal Code License	GPL-3.0
Code Versioning system used	svn
Software Code Language used	Delphi
Compilation requirements, Operating environments & dependencies	Delphi 10.3 or above
If available Link to developer documentation/manual	
Support email for questions	oleksiypenkov@intl.zju.edu.cn

Software metadata

Current software version	2.4.3
Permanent link to executables of this version	https://github.com/OleksiyPenkov/X-rayCalc/releases
Legal Software License	GPL-3.0
Computing platform/Operating System	Microsoft Windows
Installation requirements & dependencies	
If available Link to user manual – if formally published include a reference to the publication in the reference list	https://github.com/OleksiyPenkov/X-rayCalc/tree/master/docs/pdf
Support email for questions	oleksiypenkov@intl.zju.edu.cn

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1. Introduction

Immediately after the discovery of X-rays, Rontgen tried to deflect, refract, or reflect them to explore the possibility of imaging devices [1]. Failing to observe any deflection, he stated that the refractive index of all materials is very small ($\sim 10^{-5}$). Later, by the discovery of X-ray diffraction from crystals, the method of deflecting X-rays was provided for the first time [2]. A new version of X-ray diffraction has evolved over the last 25 years with the building of well-defined artificial diffracting structures instead of natural crystals to manipulate X-rays. Usually, such artificial structures consist of periodically alternated nanolayers of two materials. Thus, the reflectivity of X-rays is amplified due to the multiplication of interfaces. Such structures are called *periodical multilayer X-ray mirrors* (PMMs). The invention of PMMs marked the beginning of X-ray optics [1].

Nowadays, X-ray optics has found applications in various fields of science and technology, such as deep space X-ray astronomy and lithography. For example, modern trends in the semiconductor industry require a reduction of the working wavelength of lithographical systems down to extreme ultraviolet (EUV) and beyond extreme ultraviolet (BEUV) [3,4]. The reflectivity of PMMS used in EUV/BEUV steppers is crucial for their performance. Since the nano-structure of PMMs is quite complicated, the design of effective PMMs requires special software tools [5–7]. In particular, such software should be able to precisely compute the interaction between X-rays and various combinations of air/solid and solid/solid interfaces.

Besides X-ray optics, X-ray reflectivity (XRR) has found another application in materials science. Grazing incidence X-ray reflectometry (GIXR) is a particular case of the utilization of XRR [8]. In this case, the reflectivity is measured in the grazing angle geometry using hard X-rays, usually at $\lambda = 0.154$ nm. Being accompanied by a computer simulation, GIXR becomes a powerful experimental tool for obtaining information about the structure of single- and multi-component layered nanomaterials [9–11]. Due to the layer thickness of 1–30 nm and the scattering of hard X-rays on interface boundaries of a layered structure, the formation of characteristic reflectivity patterns occurs in the area of grazing angles (0–5 degrees) (Fig. 1). A GIXR curve is sensitive to the number of layers and their thickness, materials, interface roughness, etc. Unfortunately, there is no analytical solution allowing one to gain all this information directly from the XRR curve. In other words, there is no direct solution to this problem. Nonetheless, the opposite problem can be solved with a computer simulation. In particular, it has been demonstrated that processes of materials growth and low-temperature diffusion could be investigated in detail by calculation of the theoretical GIXR curves and comparison with the experimental ones [10]. Parameters of the individual layers of the model multilayer structure, such as thickness, density, and roughness, were varied manually until the best match between the simulated and experimental GIXR curves was achieved.

2. Problems, background, and validation

Several commercial and open-source software packages for the simulation of XRR have been developed since the 1990s. For instance, one of the first software packages for XRR simulation was initially presented by D.L. Windt in 1998 (IMD—Modeling and Analysis of Multilayer Films) [12]. X-ray Calc was designed as a user-friendly and fast replacement of IMD. The first version of X-ray Calc was released in 2002 and was significantly upgraded in 2016 and 2020. Despite an almost 20-year history, X-ray Calc is still used in many laboratories. During the design of X-ray Calc, a particular focus was made on fitting the simulated and measured GIXR curves of PMMs. Because GIXR is an everyday instrument for laboratories developing X-ray optics, high computation speed and convenience of the software are crucial factors.

Just a computation of a single theoretical GIXR curve is not a very complicated task. However, it is not enough to compute a model GIXR curve to get information about the structure of the coating. Instead, the computed GIXR curve should be fitted to the experimental data by adjusting the model's parameters. A typical model for GIXR simulation may include tens of variables. A large number of variables makes the curve fitting time-consuming. Due to the complicity of the physical model and non-linear contribution of variables, fitting of GIXR curves was found to be less than suitable for automatization. In practice, an experienced operator performed high-quality fitting much faster compared to computer algorithms of optimization, such as the least-squares method. As a result, the further development of X-ray Calc was focused on the speed and convenience of the manual fitting of GIXR curves.

X-ray Calc implemented the recursive method of computation of XRR, which entirely considers the effects of dynamic scattering and absorption. In this method, the following equation is used for the calculation of the reflectivity coefficient for a multilayer structure having n layers as a function of the incidence angle θ [13,14]:

$$r\left(z_j\right) = \frac{r_j^F + r(z_{j+1}) \cdot e^{2i\chi_{j+1}l_{j+1}}}{1 + r_j^F \cdot r(z_{j+1}) \cdot e^{2i\chi_{j+1}l_{j+1}}},\ j = 0, 1, \ldots N \tag{1}$$

where l is the layer's thickness. The substitutional parameter χ is defined as follows:

$$\chi_j = k \cdot \sqrt{\varepsilon_j - sin^2\left(\vartheta\right)} \tag{2}$$

In Eq. (1), r_j^F is an amplitude refraction index for the jth interface, given by Fresnel's equation:

$$r_j^F = \frac{\chi_j/\eta_j - \chi_{j+1}/\eta_{j+1}}{\chi_j/\eta_j + \chi_{j+1}/\eta_{j+1}} = \frac{\eta_j^{-1}\sqrt{\varepsilon_j - sin^2\left(\vartheta\right)} - \eta_{j+1}^{-1}\sqrt{\varepsilon_{j+1} - sin^2(\vartheta)}}{\eta_j^{-1}\sqrt{\varepsilon_j - sin^2(\vartheta)} + \eta_{j+1}^{-1}\sqrt{\varepsilon_{j+1} - sin^2(\vartheta)}} \tag{3}$$

$$\eta_j = \begin{cases} 1 & for\ s\ polarization \\ \varepsilon_j & for\ p\ polarization \end{cases}$$

$\varepsilon_j = 1 - \delta + \mathrm{i}\cdot\gamma$ is a complex refractive index. It depends on the wavelength and is calculated by the following equation:

$$\begin{pmatrix} \delta \\ \gamma \end{pmatrix} = 0.54 \cdot 10^{-5} \cdot \frac{\rho}{\mu}\lambda^2 \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \tag{4}$$

where λ is the wavelength of X-ray radiation (in Angstroms), ρ is a density of a material, μ is atomic weight, f_1, and f_2 are real and complex parts of atomic scattering factor [13]. X-ray Calc has an embedded database of the scattering factors based on [15].

The recursive calculation starts from the substrate (j = N). Values of $r(z_j)$ are consequentially calculated on each interlayer interface. The reflectivity of the whole structure is calculated as $R = |r(z_0)|^2$. Thus, Eqs. (1)–(4) allow computing refraction of X-rays for arbitrary layered structures for any wavelength and incident angle.

Therefore, by specifying a wavelength and perform the above calculation for all values of the incidence angle, we obtain the $R(\theta)$ curve(s), represented in Fig. 1. Similarly, $R(\lambda)$ curve can be computed for a fixed value of the incidence angle.

Various structural imperfections, such as interface roughness, affect the XRR, but Eq. (1) describes the refraction of an ideal structure. To implement the effects of interface roughness in the model, the rough interface with a sudden change of dielectric constant is replaced by an interlayer of thickness 2σ [12,16].

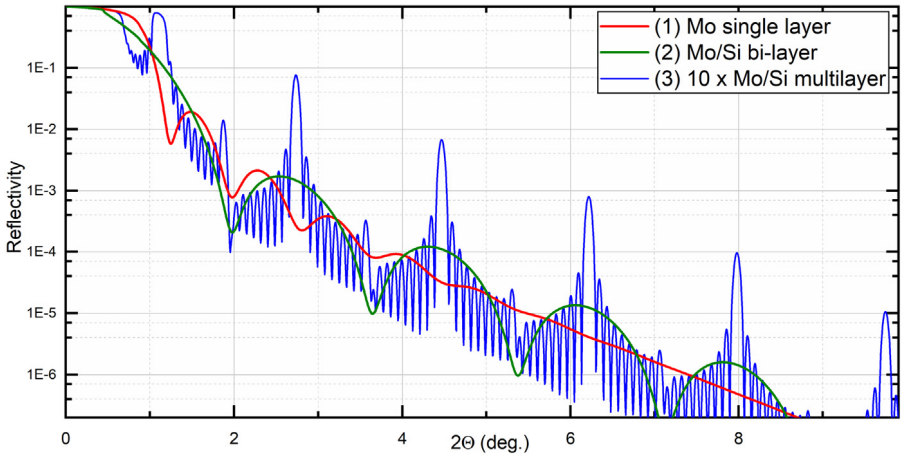

Fig. 1. Computed GIXR curves at $\lambda = 0.154$ nm for different kinds of coatings on a Si wafer. 1 — Single 10 nm thick Mo layer. 2 — Bi-layer Mo/Si coating having layer thicknesses of 5 nm; 3 — Periodical multilayer coating having 10 pairs of 5 nm thick Mo and Si.

Inside this layer, the dielectric constant gradually changes according to a particular function. For instance, if the roughness distribution as described by the Gaussian function, the variation of dielectric constant inside the thin interlayer is represented by the error function (the so-called Debye–Waller factor [17]):

$$r(\vartheta) = r_0(\vartheta) \cdot f(\vartheta) = r_0(\vartheta) \cdot \exp\left(-\frac{16\pi^2\sigma^2 sin^2(\vartheta)}{\lambda^2}\right) \quad (5)$$

where R_0 is the reflectivity of the ideally smooth interface calculated by Eq. (1).

Besides the error function, the linear-gradient function, step function, or sinus also could be used, as f(θ) in Eq. (5), to describe the profile of the dialectic constant at the interface [12,16]. It should be noted that this mathematical model cannot distinguish interface roughness and a concentration gradient. The blur of dielectric constant on rough interfaces causes reducing refraction on each interface and the overall refraction. The role of roughness increases with rising incident angle.

The precision of the simulation by X-ray Calc was validated by comparison with the IMD software [12]. XRR curves were simulated by both software packages for several identical structures. In both cases, the same database of X-ray scattering factors was used. A point-by-point comparison of results revealed the minimal divergence (below 0.5%). The observed difference might be attributed to the accumulation of rounding errors.

3. Software description

The software was coded in Delphi. It consists of a single .exe-file and provides a convenient windows interface for work with structure models, calculations, and experimental XRR curves (Fig. 2). The software operates with so-called Projects. The Project is a single file comprising an unlimited number of theoretical models and experimental curves grouped in folders.

The software allows for control of all the parameters of computation, such as wavelength, the number of points in the computed curves, and the range of grazing angles. Reflectivity could be calculated as the function of an incident angle or wavelength. The main plot allows one to overlay several computed and experimental curves and visually compare the degree of matching. For convenience, vertical scales can be switched between linear and logarithmic, and the individual regions of the plot can be zoomed.

The "Fitting" floating window provides quick access to the parameters of the structure to manually fit the computed curve to the experimental one without switching to the structure tab. The result of the calculation can be exported as an ASCII or graphic file. Experimental data can be loaded to the Project from an ASCII file or pasted from the clipboard. X-ray Calc provides necessary tools for the experimental data, such as sorting and normalization.

Besides compact representation of periodical structures, the software provides special extensions for models such as gradients. The gradient extension allows for implying the gradual changing of parameters of the model — for instance, thickness. It can be used to model some physical effects, like drifting of the deposition rate during the manufacturing of a coating or increasing of the interface roughness due to columnar growth.

X-ray Calc supports multicore CPUs that significantly reduce computation time. The typical time for simulation of GIXR was from 0.05 to 0.25 s for 16 and 4 cores CPU, respectively. The computation was performed for PMM consisting of 300 stacks having 4 layers each, and the GIXR curve had 3000 points. Such a high computation speed allows for performing the manual curve fitting in real-time.

4. Illustrative examples

The first example demonstrates the predicted effect of structure on the XRR of Mo/Si PMM at the wavelength of 13.5 nm (Fig. 3A). Three models were compared. The first model represented the ideal case and consisted of smooth layers of Mo and Si. The second model described the rough structure where the interface roughness was introduced. The third model represented the real structure and was based on experimental facts and knowledge about Mo/Si multilayers [18]. In this case, Mo and Si layers were separated by asymmetrical interlayers that consisted of molybdenum silicide.

The second example is an experimental XRR curve for Co/C periodical multilayer structure (Fig. 3B) [19]. The XRR curve was recorded in θ–2θ geometry with a monochromator. $Cu_{k\alpha}$ X-ray source was used ($\lambda = 0.154$ nm). The coating had 29 pairs of carbon and cobalt layers deposited by magnetron sputtering onto a Si wafer. The initial thickness of the layers (3 nm) was defined based on the deposition rate and deposition time. Then the parameters of the model were manually adjusted to obtain the best match between experimental and calculated curves, as shown in Fig. 3 .

The model structure of the coating is shown in Table 1. The correctness of this model is discussed in [18]. It can be seen that the thickness of the carbon layer is 20% larger compared to the initial input. Additionally, cobalt layers have lower density compared to reference values. The observed reduction of

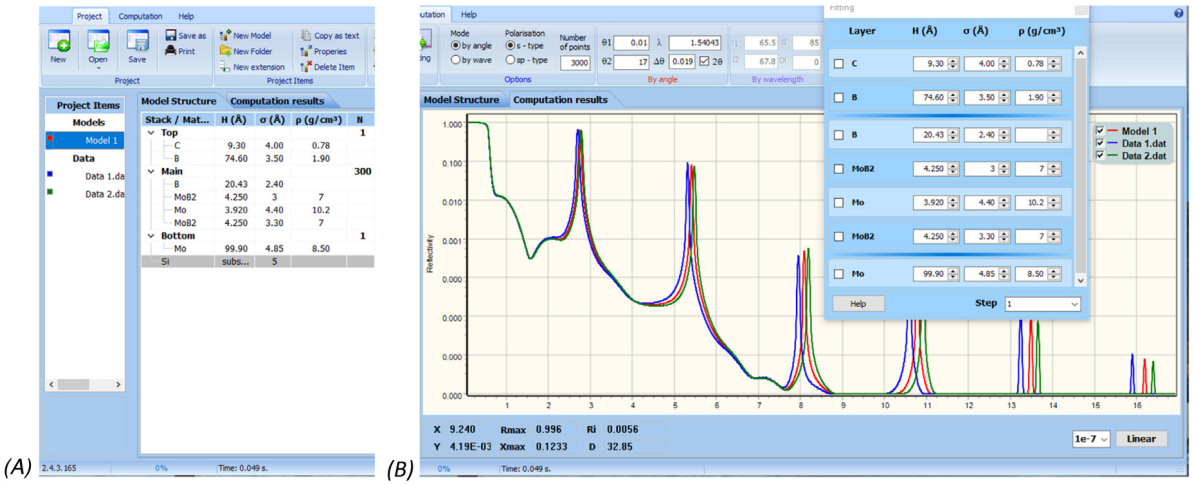

Fig. 2. (A) Main window with active "Model Structure" tab. (B) "Computation Results" tab with experimental and computed XRR curves. The "Fitting" window is used for quick adjusting of the parameters of a model.

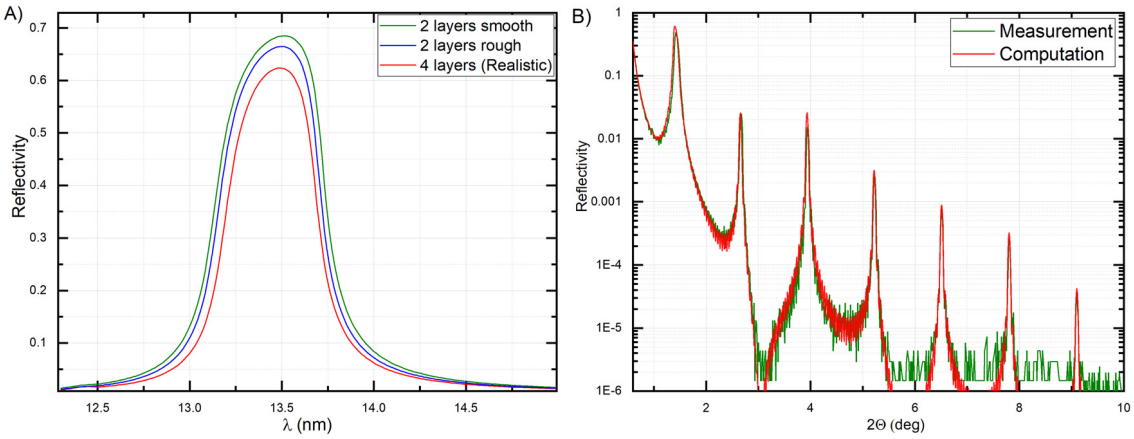

Fig. 3. (a) Computed XRR curves for Mo/Si X-ray mirrors having a different structure compared to functions of the wavelength; $\theta = 85°$. (b) Result of the manual curve fitting. Measured and computed GIXR curves for Co/C periodical multilayer structure; $\lambda = 0.154$ nm.

Table 1
Model parameters for XRR simulation for Co/C periodical multilayer structure (Fig. 3b).

Stacks	N	Layers						
		Material	Thickness (nm)	StD	Roughness (nm)	StD	Density (g/cm^3)	StD
Top	1	Carbon	5.22	0.5	0.8	0.2	2	0.1
Main	29	Cobalt	3.05	0.1	0.35	0.1	8	0.1
		Carbon	3.76	0.1	0.25	0.1	2	0.1
Substrate	–	Silicon	–		0.5	0.2	3.2 (Ref.)	–

density is physically meaningful, which was attributed to diffusional mixing between carbon and cobalt that occurred during the deposition [20]. Cobalt layers have a higher roughness that can indicate asymmetrical intermixing.

5. Impact

The effectiveness of X-ray Calc for simulations of GIXR has been demonstrated in various studies. For instance, it was used for the evaluation of structural and phase transformations in nanolayers of cobalt [20] and characterization of the structure of C/Si bilayer coatings [21]. In the case of periodical structures, precise measurement of layer thicknesses in wear-resistant coatings [19] and Sb/B_4C PMMs [22] was performed. The reliability of the simulations and correctness of the models are correspondingly discussed in the papers mentioned above.

6. Conclusions

In this paper, X-ray Calc software is described. It is a powerful tool for the computer simulation of XRR with the aim of characterization of the structure of coatings. The software was created for the efficient manual fitting of experimental GIXR curves. Simple installation, high calculation speed, and a user-friendly interface help to broaden this useful method among the research community. Future development of the software will

include the development of automatic fitting procedures, which will expand the application potential.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.softx.2020.100528.

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