Fast fourier transform and multi-Gaussian fitting of XRR data to determine the thickness of ALD grown thin films within the intial growth regime

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While a linear growth behavior is one of the fingerprints of textbook atomic layer deposition processes, the growth often deviates from that behavior in the initial regime, i.e. the first few cycles of a process. To properly understand the growth behavior in the initial regime is particularly important for applications that rely on the exact thickness of very thin films. The determination of the thicknesses of the initial regime, however, often requires special equipment and techniques that are not always available. We propose a thickness determination method that is based on X-ray reflectivity (XRR) measurements on double layer structures, i.e. substrate/base layer/top layer. XRR is a standard thin film characterization method. Utilizing the inherent properties of fast Fourier transformation in combination with a multi-Gaussian fitting routine permits the determination of thicknesses down to \( t \approx 2 \) nm. We evaluate the boundaries of our model, which are given by the separation and full width at half maximum of the individual Gaussians. Finally, we compare our results from two layer stacks with data from X-ray fluorescence spectroscopy, which is a standard method for measuring ultra thin films.

Atomic layer deposition (ALD) is a key technology not only for the state-of-the-art semiconductor industry and nanoelectronics but also for photovoltaics, catalysis and battery development. The two most characteristic features of ALD are the conformity and self-limitation of the growth process. One approach to test the self limiting behavior is by validating the linear increase of the layer thickness with the number of ALD cycles. However, it is common for ALD processes to deviate from this linear dependence for very low cycle numbers. Often a Volmer-Weber type growth is observed in the first few cycles, different from the different surface chemistries of the substrate and the layer itself. Understanding the initial growth stage is crucial for applications that rely on the exact thickness of ultra thin films, in particular, for the use in tunnel junctions, solar cells or as building blocks for nanolaminates. The determination of low layer thicknesses within the initial stage is experimentally challenging and often involves the use of specific techniques and equipment, including X-ray fluorescence or various in-situ methods such as quartz crystal microbalance or vibrational sum-frequency. Herein, we propose an efficient way to determine the thickness of thin films down to 2 nm using X-ray reflectivity and fast Fourier transformation (FFT) enabling the investigation of the initial stage for various ALD processes. The analysis utilizes double layer systems in combination with the inherent properties of a Fourier transformation to not only detect oscillation frequencies related to the single layers but also linear combinations of those oscillations. This simplifies the evaluation of XRR measurements by either fully eliminating the need of modeling the XRR data itself, which is often ambiguous due to the large number of involved parameters, or, in case a full modeling is indispensable, by providing a reasonable set of starting parameters. We show the relevance of our approach as well as its limitation in the nm-regime. Furthermore, we compare our results for the substrate/Y\(_2\)O\(_3\)/Fe\(_2\)O\(_3\) layer system with X-ray fluorescence (XRF) data to validate our study. X-ray reflectivity (XRR) is commonly employed to determine the thickness of a thin film or a layer system. This approach is based on the path difference of X-rays scattered by different interfaces of the thin film sample. Figure 1 shows a simple layer system: a substrate with one thin film on top. Under the assumption that each layer is a homogeneous medium with a mean refraction index smaller than unity, the classical Snell’s law and the Fresnel equations can be applied to our system. The intensity of the reflected X-rays can then be expressed as a function of the Fourier transform of the electron density gradient normal to the surface. In the simplest case, the density change along the surface normal \( z \) at an interface of two materials is described by an error function (cp. Fig.1a)). Differentiation of the error function leads to a Gaussian which describes the density gradient. For a stack with a single layer on a substrate this is depicted in Fig.1a). A typical XRR measurement of one layer on a substrate, as is shown in Fig.1b), exhibits oscillations in
the reflected intensity which stem from the interference of X-rays reflected from the first and the second interface. The periodicity of these oscillations is proportional to the inverse of the layer thickness, whereas the amplitude of the oscillations depends on the density difference of the two adjacent layers. Hence, materials are best chosen with a density difference of at least 2% for straightforward evaluation. For data processing only incident angles larger than the critical angle of total reflection have to be taken into consideration. This critical angle was set to the point where the maximal intensity is reduced by a factor of 2, as is sketched by the dashed line in Fig. 1(b). The concept of applying an FFT to XRR data to determine the thickness is well known and often used but is mostly discussed in terms of single layers or multi-layer structures. The fundamental characteristic of an FFT is to decompose a function into its frequency components. As discussed previously, XRR data consist of different oscillation frequencies which correspond to specific layer thicknesses. For a single layer applying an FFT to the autocorrelation function of the electronic density derivative along z (cp. Fig. 1(b)) results in a spectrum which peaks at the thickness of the layer. In Fig. 1(c) this is illustrated for the data from panel b). To reduce spectral leakage a Hamming window was used on the data. Using the correct windowing function is especially crucial for the thickness determination of very thin films. After windowing the data was zero-padded to ten times its original length, which acts as an interpolation function on the FFT spectrum. The FFT was then performed on the windowed and padded data. Since the data sets are finite, the spectra have an $1/f^2$ background which is also sketched in Fig. 1(c). For very thin single layers the corresponding thickness peak is concealed beneath this background, prohibiting the extraction of the layer thickness.

This issue can be solved by using systems with more than one layer. In the same fashion as for single layer systems, the FFT has been applied to multilayer systems. In the simplest case these consist of two deposited layers, i.e. substrate/base layer/top layer. For a two layer configuration, three peaks are expected in the FFT spectrum, which correspond to the thicknesses of the base layer, the top layer and the combined thickness of both layers. This characteristic can be used to determine the thickness of ultra thin layers for which the thickness extraction is usually not straightforward. As mentioned before, for single layers ($d \leq 5$ nm) the peak in the FFT spectrum is often concealed by the $1/f^2$ background. By using a two layer system, however, the thickness information of the thin layer is also contained within the combined thickness of both layers. Therefore, by evaluating the combined peak as well as the base layer peak the thickness of the (ultra) thin top layer can be extracted. The applicability of this evaluation method is independent of the explicit stacking order of the individual layers.

We applied the aforementioned evaluation method to determine the in-situ ALD growth of Fe$_2$O$_3$ on Y$_2$O$_3$ in the initial stage regime. Therefore, a series of samples featuring a constant Y$_2$O$_3$ base layer and different Fe$_2$O$_3$ top layers has been grown on Si/SiO$_2$ substrates with 100 nm thermal oxide. The base layer always consists of 100 cycles of Y$_2$O$_3$, which resulted in a mean thickness of $(7.7 \pm 1.5)$ nm. Subsequently, different cycle numbers of Fe$_2$O$_3$ were deposited in-situ to form the top layer, resulting in a substrate/Y$_2$O$_3$/Fe$_2$O$_3$ layer stack. The FFT data of a typical sample (i.e. Y$_2$O$_3$ on Fe$_2$O$_3$) can be found in Fig. 2(a). It shows two peaks as well as a shoulder in the $1/f^2$ background indicating a third peak. To extract the individual layer thicknesses from the experimental data, we used a multi-Gaussian fit, which is given by Eq. 1. The fit function consists of the sum of three Gaussian functions plus the $1/f^2$ background.

$$f_{\text{fit}}(x) = \sum_{i=1}^{3} a_i \cdot \exp \left[ -\ln 2 \cdot \left( \frac{p_{0,i} - x}{w_i/2} \right)^2 \right] + a_N \cdot \frac{1}{x^\alpha} \quad (1)$$
Here, $a_i$ describes the amplitudes of Gaussians 1, 2 and 3 and $a_N$ gives the amplitude of the $1/f^\alpha$ noise. The maximum peak positions of the Gaussians are given by $p_{0,i}$ and the full width at half maximum values by $w_i$. Additionally the relation $p_{0,2} = p_{0,3} - p_{0,1}$ was introduced to account for the correlation of the maxima positions (i.e. the layer thicknesses). The fit to the data in Fig. 2a) using Eq. (1) is given by the yellow line. Panel b) shows the individual Gaussians remodeled with the parameters extracted by the fit. Although Gaussian 2 ($p_{0,2} = 3.7 \text{ nm}$) is mostly concealed beneath the $1/f^\alpha$ background (dashed orange line), it can still be resolved by our fitting procedure using Gaussian 3 ($p_{0,3} = 11.0 \text{ nm}$) and Gaussian 1 ($p_{0,1} = 7.3 \text{ nm}$), as is portrayed in Fig. 2b). Please note that the thickness determination of a single layer with $d = 3.7 \text{ nm} (= p_{0,2})$ would not be possible, since in that case the information would be hidden under the $1/f^\alpha$ background. For using a double layer system, however, the thickness information of layer 2 is also contained in the peak of the sum of the layers enabling us to extract the thickness of layer 2 although it is concealed by the background.

To elucidate the boundaries of our multi-Gaussian approach we designed a model two layer system. Figure 3 shows the modeled FFT spectrum consisting of two separate Gaussians (1 and 2) representing the thicknesses of the two individual layers, while Gaussian 3 represents the sum of the thicknesses of the individual layers. The maximum positions $p_{0,i}$ ($i = 1, 2, 3$) of Gaussian 1, Gaussian 2, and Gaussian 3 define the layer thicknesses of layer 1, layer 2 and the sum of layers 1 and 2, respectively. The amplitudes and widths of the Gaussians were chosen to represent results of fitting the experimental data. The different panels show the change of the spectrum for several spacings of the maximum values of Gaussian 3 and Gaussian 1, which is $p_{0,2}$. For spacings $p_{0,2} \geq 2 \text{ nm}$, which are depicted in panels a) to c), Gaussian 1 and Gaussian 3 can be readily distinguished. A single Gaussian fit to the conjunction of Gaussian 1 and Gaussian 3 in the transient regime, i.e. panels b) and c), would lead to a substantial systematic error. For a separation of $p_{0,2} \leq 1 \text{ nm}$, however, the individual determination of both of the peaks is no longer unambiguously possible (cp. panel d). In this case representing the data by a single Gaussian fit is possible, in contrast to panels a) to c). Please be reminded, that the spacing between Gaussian 1 and 3 (i.e. $p_{0,2}$) describes the layer thickness of layer 2. Gaussian 2 is concealed beneath the $1/f^\alpha$ background for $p_{0,2} \leq 5 \text{ nm}$, so the determination of the thickness of layer 2 is only indirectly possible by using Gaussian 1 and Gaussian 3. Therefore, the minimum layer thickness that can be resolved with our setup using the multi-Gaussian fitting method lies between $1 \text{ nm} - 2 \text{ nm}$. Experimentally this lower boundary depends on the width of the individual Gaussians, which in turn depend on a collection of parameters arising from the specifics of the X-ray reflectometer used and the samples themselves.
ference fringes as well as enhancing the general intensity decay. This further reduces the possible resolution of the FFT by reducing the length of the data set.

We used the multi-Gaussian fitting routine to examine the layer stack series mentioned previously, i.e. substrate/Y$_2$O$_3$/Fe$_2$O$_3$. We compared our multi-Gaussian approach with the results of XRF measurements on the same samples. The thicknesses of the Y$_2$O$_3$ base layer extracted by both techniques are given in Fig. 4a). The corresponding thicknesses of the Fe$_2$O$_3$ top layer are depicted in panel b). From the XRF measurements the number of atoms per area can be determined. A calibration by means of uniform films was done for the number of Fe atoms, whereas a drop casting method was used for the calibration of the Y atoms. The thicknesses determined by XRF measurements are shown as squares while the evaluation of the same samples by XRR utilizing the introduced multi-Gaussian fitting of the FFT spectra are depicted as triangles. The dashed gray line in panel a) gives the mean base layer thickness.

In summary, we have proposed a way of utilizing the inherent properties of the FFT to determine layer thicknesses down to 2 nm from data acquired by XRR. Using bilayer structures consisting of substrate/base layer/top layer enables us to calculate the top layer thickness from the peak stemming from the combined thickness of base and top layer and the base layer peak. Using a Hamming window on the data as well as zero padding the data prior to the FFT is crucial to get the correct layer thicknesses, especially for very thin top layers. We describe the FFT spectrum using a multi-Gaussian fit. This approach is limited by the ability to distinguish between one Gaussian versus the superposition of two Gaussians, yielding a lowest layer thickness of 2 nm for our samples and FWHM of the XRR peaks. We used the multi-Gaussian fitting approach to determine the initial stage of in-situ ALD grown of Fe$_2$O$_3$ layers on Y$_2$O$_3$ and compared the results to XRF data, showing a good congruence of the layer thicknesses. Our approach is not only limited to ALD but can also be used for any kind of thin film deposition technique. Furthermore, it enables the evaluation of in-situ as well as ex-situ grown samples, providing a wide area of application. Using the presented evaluation could help a wide variety of researchers to better understand the initial stage of their (ALD) processes using customary equipment and a simple analysis procedure.

$$t_{layer} = \frac{\text{# atoms}_{XRF}/A_{XRF}}{\text{# atoms}_{unit\ cell}/V_{unit\ cell}}$$

A tooling factor of 1.37 [0.41] was determined by least square fitting for the Y$_2$O$_3$ [Fe$_2$O$_3$] layer to achieve the best possible agreement between XRF and XRR values. Both evaluation techniques result, within the margin of error, in the same layer thicknesses of top and base layer, corroborating the validity of the multi-Gaussian fitting routine for this layer system (cp. Fig. 4a) and b)). Both evaluation methods suggest a growth delay of the Fe$_2$O$_3$ top layer between 50 and 100 cycles, while the Y$_2$O$_3$ base layer stays constant, as expected. Both, top and base layer thicknesses are in good agreement for the two different evaluation methods.

In summary, we have proposed a way of utilizing the inherent properties of the FFT to determine layer thicknesses down to 2 nm from data acquired by XRR. Using bilayer structures consisting of substrate/base layer/top layer enables us to calculate the top layer thickness from the peak stemming from the combined thickness of base and top layer and the base layer peak. Using a Hamming window on the data as well as zero padding the data prior to the FFT is crucial to get the correct layer thicknesses, especially for very thin top layers. We describe the FFT spectrum using a multi-Gaussian fit. This approach is limited by the ability to distinguish between one Gaussian versus the superposition of two Gaussians, yielding a lowest layer thickness of 2 nm for our samples and FWHM of the XRR peaks. We used the multi-Gaussian fitting approach to determine the initial stage of in-situ ALD grown of Fe$_2$O$_3$ layers on Y$_2$O$_3$ and compared the results to XRF data, showing a good congruence of the layer thicknesses. Our approach is not only limited to ALD but can also be used for any kind of thin film deposition technique. Furthermore, it enables the evaluation of in-situ as well as ex-situ grown samples, providing a wide area of application. Using the presented evaluation could help a wide variety of researchers to better understand the initial stage of their (ALD) processes using customary equipment and a simple analysis procedure.

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