Investigation of sputtered gold layers on amorphous silicon subsrates with a polymer surface

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Abstract

The following report concerncs with gold layers on silicon substrates coated with a polymer. The growth of gold clusters in this system is already discovered by Grazing Incidence Small Angle X-ray Scattering (GISAXS). To get a reference to this measurements X-ray Reflectivity (XRR) data was taken from the same sample systems. This work deals with the evaluation of this XRR data.

Contents

1 Introduction

In the last years gold has become more and more importatt because of its unique optoelectronic, electrical and catalytic properties. Polysterene as a polymere with good isolation qualities is applied in many fields of the daily life. In fine mechanics and electronic technics it is used to build pasrts of boxes for television, radio-, foto and filming machines. Silicon is one of the most often used semiconducter in for example computer chips or solar cells. With all their different properties it is very interesting to investigate all of them together as one system.
In revious work of m. Schwartzkopf et al. the growing process of gold clusters on this system was investigated. As reference for layer thickness, density and roughness reflectivity data was taken.

2 Theory

2.1 Reflectivity

The sputtered goldlayer was investigated by x-ray reflectivity which is a common method to get information about thin surfaces, buried layers and thin film systems. A photon with a certain wavelength λ is scattered at the surface and the intensity reflected by the interfaces is measured under the same ange as the incoming angle of the x-ray beam. During the measurement the angle of the incoming and hence the outcomig beam is increased.

The consequtively discussed measurements were conducted at the DESY in Hamburg at beamline ? and at a Bruker d8 reflectometer at the institute ? in Garching. To get a deeper understanding in this methid some deeper theory is needed.

2.1.1 Index of Refraction

A light bea that crosses the interface of air or vacuum to a medium chenges it's direction. The explanation for this effect is the refractive index n, which depends on wavelength and material. For a smooth surface one part of the incoming beam is reflected, the other part is transmitted through the medium (??) The relation of refraction indices

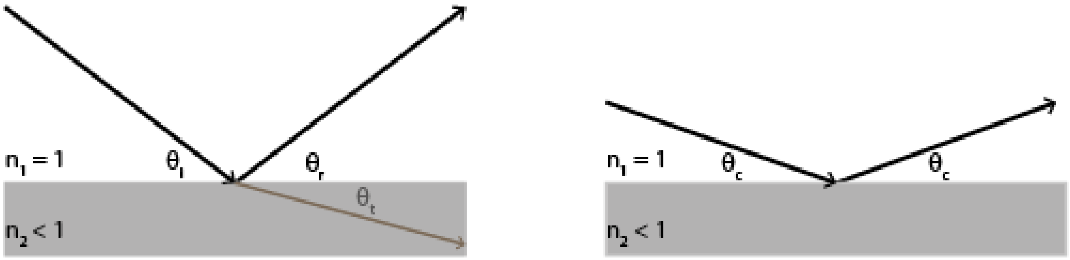


Figure 2.1: Reflekted and transmitted beam going from a medium with refraction Index n to a medium with refraction index $n < 1$ (left) and totalreflexion of the same beam at the incoming angle θ_c (right).

and angles is given by Snell's law (eqn. 2.1).

$$n_1 \cdot \cos\theta_i = n_2 \cdot \cos\theta_t \tag{2.1}$$

For x-rays the refraction index is given by:

$$n = 1 - \delta - \mathrm{i}\beta \tag{2.2}$$

Thereby $\delta = \frac{\lambda^2}{2\,\pi}\, r_e\, \rho_e$ and $\beta = -\frac{\lambda}{4\,\pi}\,\mu$ with the classical electron radius r_e, the wavelength λ, electron density of the material ρ_e and the linear absorption coefficient μ. the produkt from elektron radius and elektronen density $r_e \cdot \rho_e$ gives the socalled scattering length density (SLD) of the substrate. The real part δ of the refration index describes the dispersion, the imaginary part the exponential attenuation.
The refraction index is hence always smaller than one, what means that with equation (2.1) total reflexion occurs as long the angle θ_i of the incoming beam is under a certain critical angle θ_c.

2.1.2 Fresnel-Reflectivity

With increasing incomin angle the reflected intensity decreases. The relation of reflecetd to irradiated Intensity is called reflectivity:

$$R(\theta) = \frac{I(\theta)}{I_0}. \tag{2.3}$$

From the geometrical view of the wave vectors at an interface one can deduce the relatin between wavevectors $\vec{k}$ and momentumvector $\vec{q}$ (fig. 2.2).
If the reflected intetsity is always observed under the same angle as the incoming beam it is called secular reflectivity. Thereby it is recieved only infirmation perpendicular to the observed surface and no in-plane structure. This means for the momentumvector:

$$\begin{aligned}
\vec{q} &= (0,\ 0,\ q_z) && (2.4)\\
|q_z| &= \vec{k_i} - \vec{k_r} \\
&= 2|k|\sin\theta_i \\
&= \frac{4\,\pi}{\lambda}\sin\theta_i && (2.5)\\
\text{and hence} \qquad R(q) &= \frac{I(q)}{I_0} && (2.6)
\end{aligned}$$

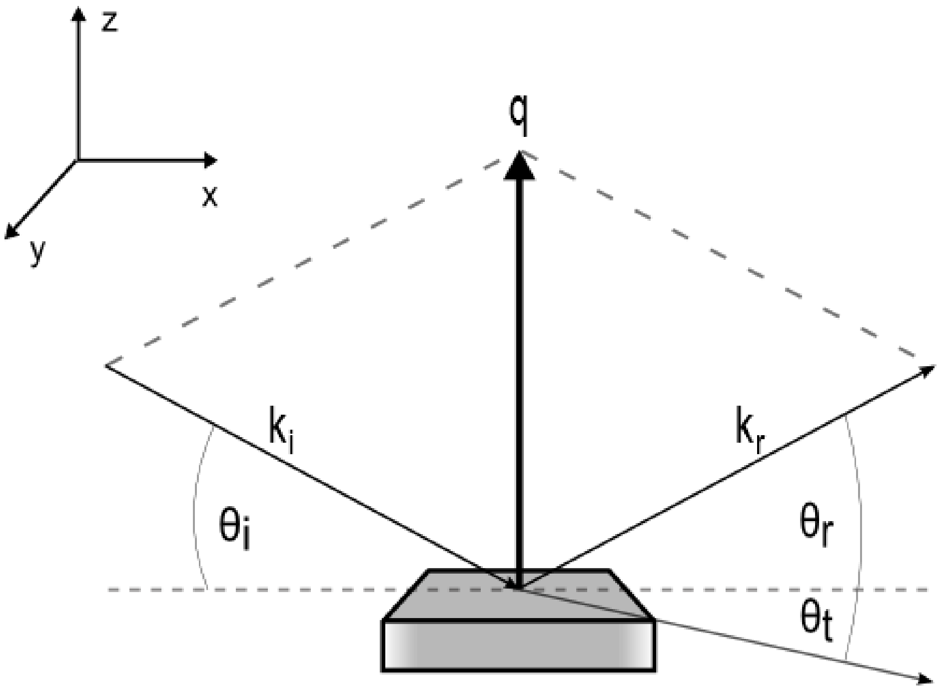


Figure 2.2: Reflectedr and transmitted wavevector on an interface

A propagating electromagnetic wave in the x-z-plane propagierende has a polarized E-Field in y-direction with the amplitude A which is described by the Helmholtz equation:

$$\begin{aligned}\vec{E}_{\mathrm{in}} &= A_{\mathrm{in}} \cdot \mathrm{e}^{\,\mathrm{i}\,(\omega\, t\, -\, \vec{k}_{\mathrm{in}}\, \vec{r})}\, \vec{e_y} \\ \vec{E}_{\mathrm{r}} &= A_{\mathrm{r}} \cdot \mathrm{e}^{\,\mathrm{i}\,(\omega\, t\, -\, \vec{k}_{\mathrm{r}}\, \vec{r})}\, \vec{e_y} \\ \vec{E}_{\mathrm{tr}} &= A_{\mathrm{tr}} \cdot \mathrm{e}^{\,\mathrm{i}\,(\omega\, t\, -\, \vec{k}_{\mathrm{tr}}\, \vec{r})}\, \vec{e_y} \qquad (2.7)\end{aligned}$$

The relation of the Amplitudes gives the Fresnel coefficients r for reflection and and t for transmission (eqn. 2.9)

$$r = \frac{\mathrm{A_r}}{\mathrm{A_{in}}} \qquad (2.8)$$

$$t = \frac{\mathrm{A_{tr}}}{\mathrm{A_{in}}} \qquad (2.9)$$

The product of r and t with their comlex conjugate gives the reflection and transmission coefficient:

$$\mathrm{R} = \mathrm{r} \cdot \mathrm{r}^* = \left| \frac{A_\mathrm{r}}{A_\mathrm{in}} \right|^2 \tag{2.10}$$

$$\mathrm{T} = \mathrm{t} \cdot \mathrm{t}^* = \left| \frac{A_\mathrm{tr}}{A_\mathrm{in}} \right|^2 \tag{2.11}$$

With consistency at the interface at z=0 and the time t=0 the reflectivity is given by:

$$\mathrm{R}(\mathbf{q}) = \frac{q_z^2 - 2\, q_z \sqrt{q_z^2 - q_\mathrm{c}^2} + q_z^2 - q_\mathrm{c}^2}{q_z^2 + 2\, q_z \sqrt{q_z^2 - q_\mathrm{c}^2} + q_z^2 - q_\mathrm{c}^2} \tag{2.12}$$

One can approximate for the reflectivity at vlues of $q_\mathrm{z} > 3 \cdot q_\mathrm{c}$:

$$\mathrm{R}(q_\mathrm{z}) = \frac{q_\mathrm{c}^4}{16 q_\mathrm{z}^4} \tag{2.13}$$

Figure 2.3 shows a theory curve and the q^{-4}-approximation of the reflectivity of smooth silicon.

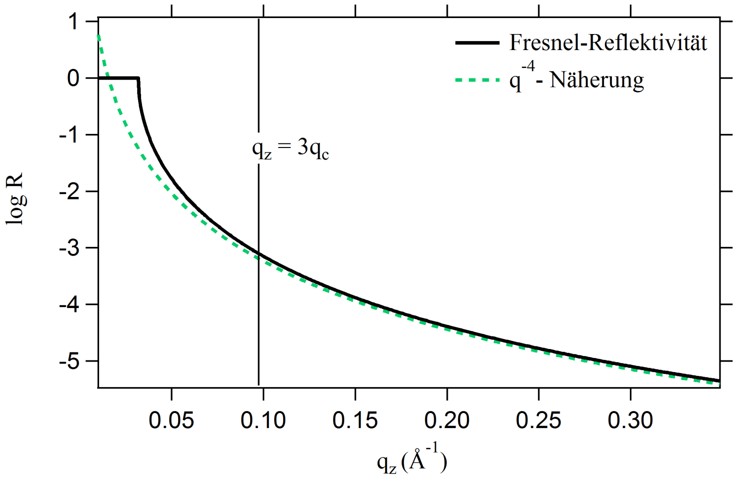


Figure 2.3: Reflectivity of smooth silicon. Starting from $q_\mathrm{z} > 3 \cdot q_\mathrm{c}$ the curve can be described by the q^{-4}-approximation.

In case of layers on the substrate the beam is reflected at each interface. Because of the path difference of the reflected parts we get constructive and destructive interference which occurs as oscillations in the detected intensity (fig. 2.4). Those oscillations are called ”Kiessig-Fringes”. The oscillatin period depends on the layer thicknesses and the differences of the electron densities among themselves. An other effect which has

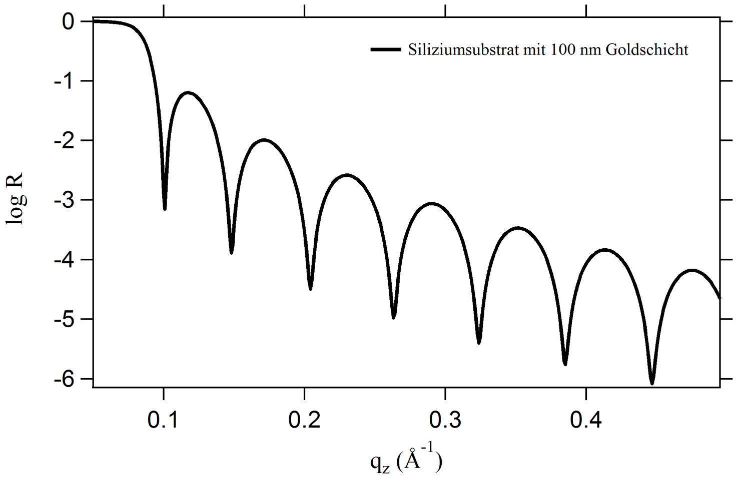


Figure 2.4: example for Kiessig-Fringes at a silicion substrate with a 100 nm gold layer

it's influence on the reflectivity signal is the roughness of the layer as it is shown in figure 2.5. With higher roughness the diffraction at the surface gets more diffuse and hence the intensity decreases. Summarized x-ray reflectivity gives infirmation about layer-thicknesses, electron densities of the layers and roughnesses.

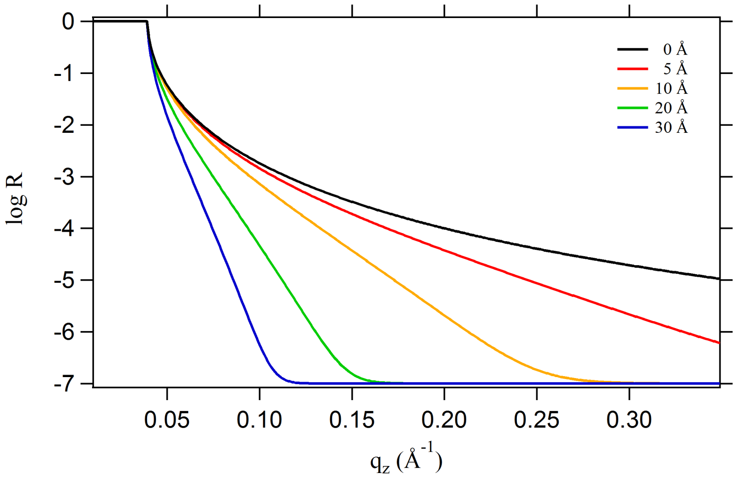


Figure 2.5: Reflektivity profiles of a TiO_2-substrate with different roughnesses.

2.2 Sample Preparation

The used samples were silicon substrates (100) with a layer of polysterene (PS) respectively a mixture of PS and Polymethylmethacrylat (PMMA) blocks . All of them were coated with a goldlayer by sputter deposition (fig. 2.6). For comparsion also one sample without a layer of PS or PMMA was directly coated by Glancing Angle Deposition with gold. The samples were measured directly after coating at the PETRA II synchrotron in Hamburg at 13 keV and for comparsion what happens over the time after about six month again with a lab source from the TU Munich at 8 keV. Except of the sample with only gold on silicon all the measured samlpes were coated for different times to get different layer thicknesses.

Figure 2.6: Layersystem of the coated samples. Left: Gold sputtered on PS, right: Gold sputtered on PS+PMMA

3 Results of the Measurements

3.1 Gold on Silicon

The reflectivitygraph of the silicon sample coated with gold is shown in figure 3.1. The coating time was 60 minutes. This sample was only measured with a lab source.

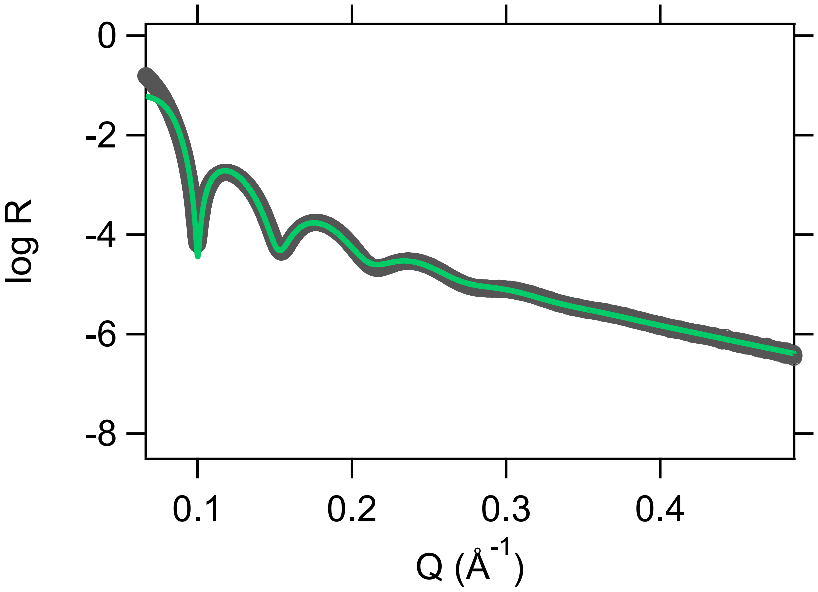


Figure 3.1: Reflectivitygraph of Silicon coated with Gold

Table 3.1: Values of the fitting parameters

	Thickness (Å)	SLD (10^{-6}Å^{-2})	σ (Å−)
Au	93.917	110.02	9.3267
SiO_2	10.424	18.17	2.453
Si	inf	20.2 (fixed)	2 (fixed)

The fittig parameters shows a deviation of the gold values to the theoretica values since the SLD for gold is 123 $\cdot 10^{-6}$Å^{-2}. The electron density of the layer hence is 17.265 g/cm^3 which means, the layer is only 89.45% gold. This shows a cartain porrousity of the gold layer. The missing 10.55% therefore come from the air over the goldlayer.

3.2 Gold coated on a silicon substrate with PS

The result of the porrous gold layer is now also used for all further samples. In this part the silicon were first coated by spin coating with a 100 nm layer of PS before they were given in the sputter chamber to coat them with gold. Thereby four different samples were sputtered for four different times to get different layer thicknesses. It was not known how the gold ayer interacts with the PS especially over the time. Therefore some different layer models were tried to find the best fitting model.

3.2.1 Different fitting models

To find the right fitting model the datasets of only the sample with the thickest gold layer was used. According to sputtering rate and sputtered time the thickness should be about 8 nm.

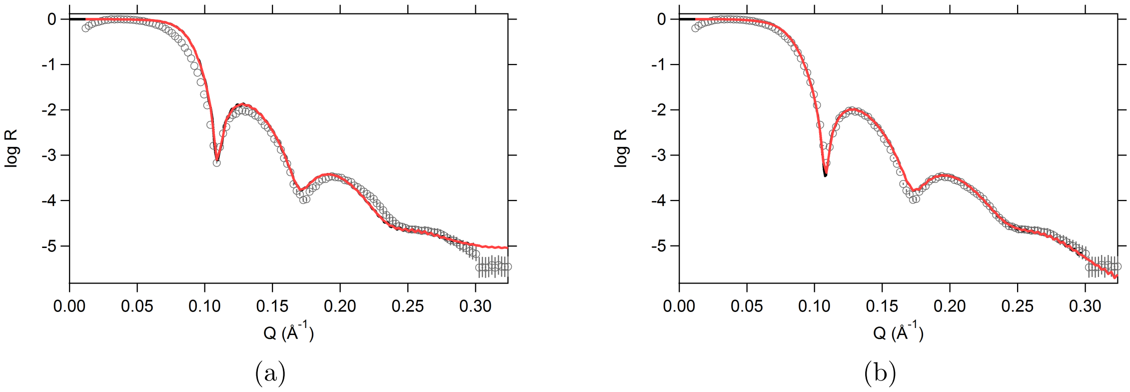
3.2.1.1 3-Layer-System

The first step was a three-layer-model only with the native oxide layer of the silicon, PS and gold. The figures 3.3 and 3.3 show the reflectivitygraphs of both measurements, (3.3(a)) with fixed SLDs, (3.3(b)) with fitted SLDs.

Table 3.2: Values of the fit parameters for a three layer system at the 13 keV measurement

	Thickness (Å)		SLD (10^{-6}Å^{-2})		σ (Å−)	
	theory	fit	theory	fit	theory	fit
Au	83.054	80.068	123	109.6	10.876	10.347
PS	1365.7	1355.6	9.61	18.252	7.7691	6.3842
SiO_2	15.74	14.018	18.9 (fixed)		11.245	1.9359
Si	inf		20.1 (fixed)		2(fixed)	

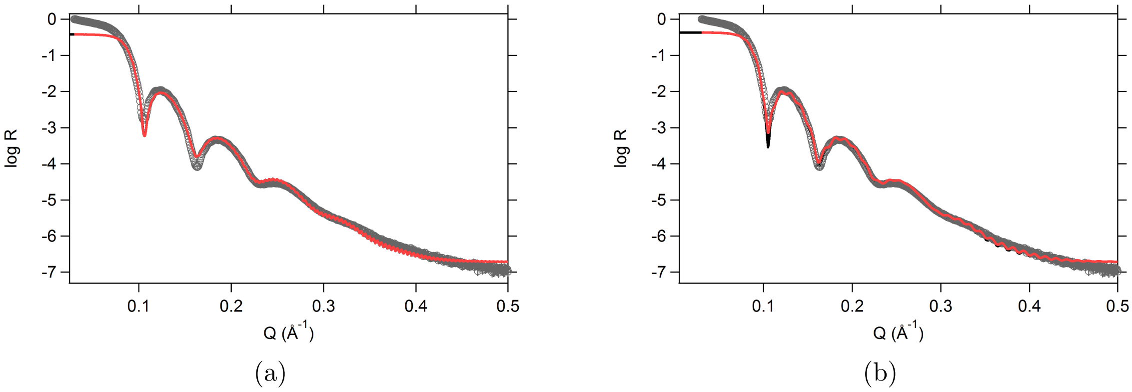
Tabular 3.2 shows the values for the fiting parameters of the 13 keV measurements directly after coating, tabular 3.6 for the later measuremants at 8 keV. One sees clearly,



(a)

(b)

Figure 3.2: Reflectivitygraph (13 keV) of Silicon with PS six months after coating with a 8 nm gold layer fitted with the 3 layer model. Left with theory values right with fitted values of the SLD.



(a)

(b)

Figure 3.3: Reflectivitygraph (8 keV) of Silicon with PS directly after coating with a 8 nm gold layer fitted with a 3 layer model. Left with theory values right with fitted values of the SLD.

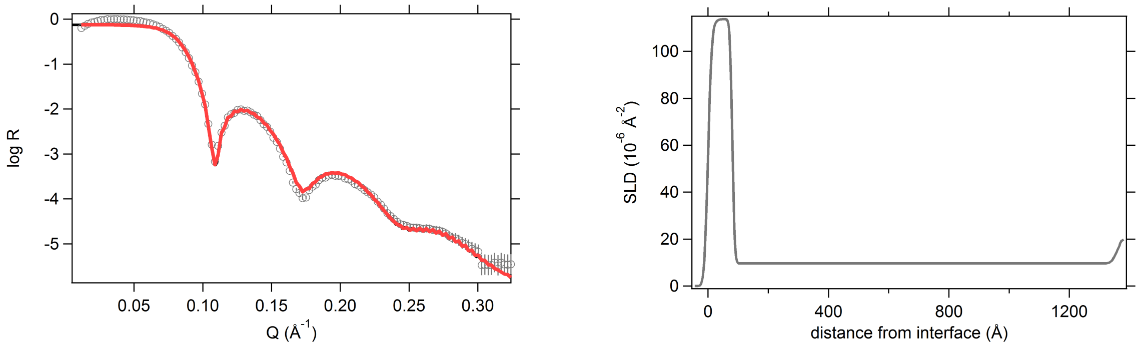
that the curve doesn't fit well with theory values. Are they open the result is a gold layer with a lower and a PS layer with a higher density than the theory values. This leeds to the ssumption of a porrous gold layer. For the investigation of the denser PS layer an other layersystem is needed.

3.2.1.2 4-Layer-System

The four layer system consists of a porrous gold layer on top as seen before, an interdiffusion layer from PS mixed with embedded gold, pure PS and the silicon oxide. The figures 3.5 and 3.5 schow the fits with this system (3.15(a)) and the density profile in z-direction (3.15(b)).

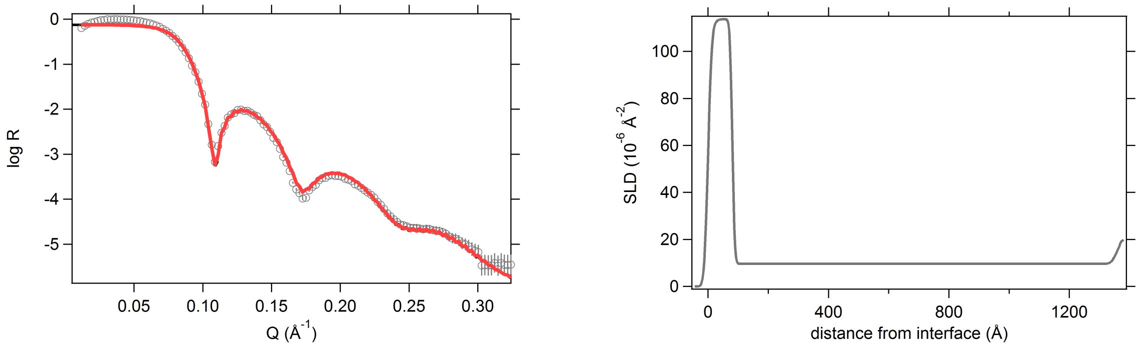
Table 3.3: Values of the fit parameters for a three layer systemat the 8 keV measurement

	Thickness (Å)		SLD (10^{-6}Å^{-2})		σ (Å−)	
	theory	fit	theory	fit	theory	fit
Au	88.638	87.484	123	116.29	6.1533	6.0566
PS	1331.9	1420.8	9.61	18.311	9.3669	9.0379
SiO$_2$	23.343	9.3642	18.9 (fixed)		14.874	2.5594
Si	inf		20.1 (fixed)		2(fixed)	



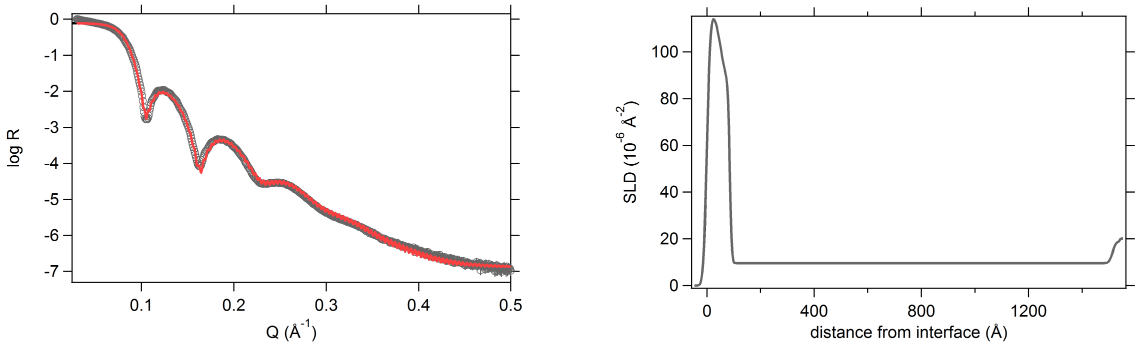
(a) (b)

Figure 3.4: Reflectivitygraph (8 keV) of Silicon with PS directly after coating with a 8 nm gold layer fitted with a 3 layer model. Left with theory values right with fitted values of the SLD.



(a) (b)

Figure 3.5: Left: Reflectivitygraph (13 keV) of Silicon with PS directly after coating with a 8 nm gold layer fitted with a 4 layer model. Right: SLD profile.



(a)

(b)

Figure 3.6: Left: Reflectivitygraph (8 keV) of Silicon with PS directly after coating with a 8 nm gold layer fitted with a 4 layer model. Right: SLD profile.

Table 3.4: Values of the fit parameters for a four layer system at the 13 keV measurement directly after coating

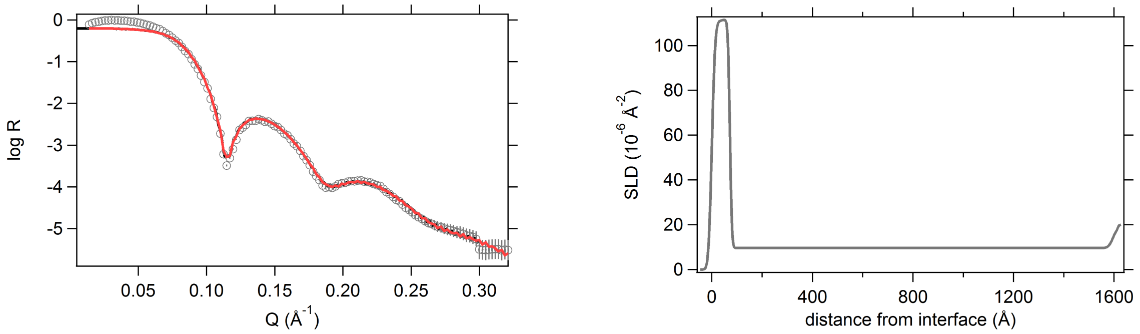
	Thickness (Å)	SLD (10^{-6}Å^{-2})	σ (Å−)
Au	24.688	111.47	9.7247
Au+PS	56.021	113.75	10.267
PS	1275.5	9.61 (fixed)	6.3741
SiO_2	11.336	18.9 (fixed)	13.393
Si	inf	20.1 (fixed)	2 (fixed)

Table 3.5: Values of the fit parameters for a four layer system at the 8 keV measurement six months after coating

	Thickness (Å)	SLD (10^{-6}Å^{-2})	σ (Å−)
Au	51.516	117.02	10.271
Au+PS	34.13	86.351	17.788
PS	1427.8	9.61 (fixed)	5.691
SiO_2	26.611	18.9 (fixed)	10.087
Si	inf	20.1 (fixed)	2 (fixed)

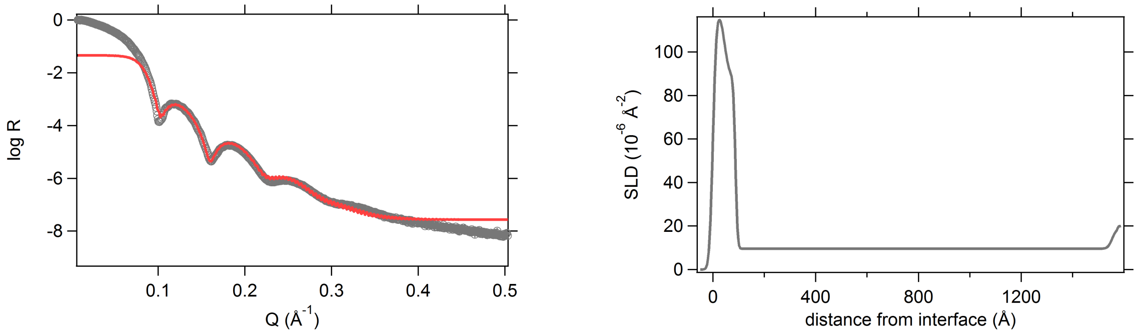
3.2.2 4-Layer-system on samples with different sputtering times

With the four layer system were fitted the other three datasets for the samples with 6 nm, the 4 nm and the 2 nm gold layer.



(a) (b)

Figure 3.7: Left: Reflectivitygraph (13 keV) of Silicon with PS directly after coating with a 6 nm gold layer fitted with a 4 layer model. Right: SLD profile.



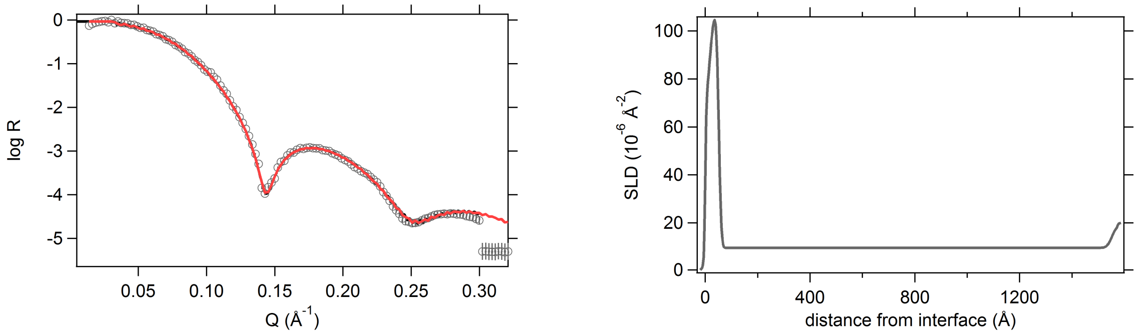
(a) (b)

Figure 3.8: Left: Reflectivitygraph (8 keV) of Silicon with PS six mnths after coating with a 6 nm gold layer fitted with a 4 layer model. Right: SLD profile.

In all cases a layer thicker than calculated from the sputtering rate was measured. Also the values for the densities were alway below the theory values for the prticular material.

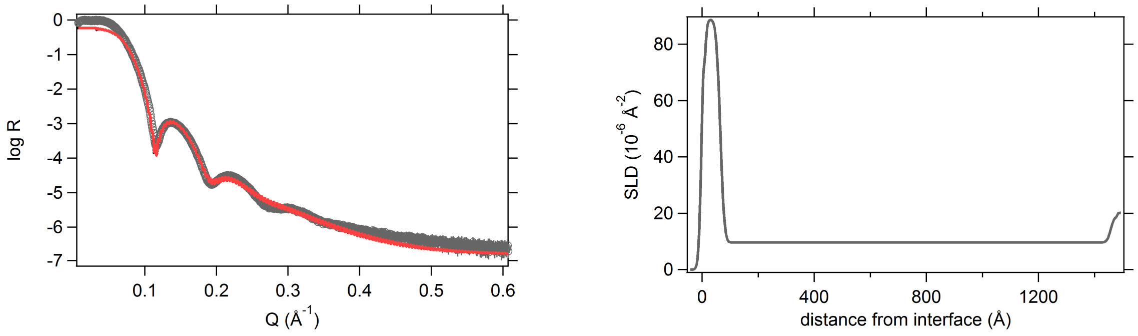
Table 3.6: Fit parameters of the 6 nm sample for a four layer system at the 8 keV and 13 keV measurement

	Thickness (Å)		SLD (10^{-6}Å^{-2})		σ (Å−)	
	13 keV	8 keV	13 keV	8 keV	13 keV	8 keV
Au	19.568	46.023	109.22	118.52	10.162	10.94
Au+PS	52.481	41.729	111.48	88.657	14.378	14.948
PS	1524	1466.7	9.61 (fixed)		14.415	6.8098
SiO_2	18.505	20.897	18.9 (fixed)		14.874	13.558
Si	inf		20.1 (fixed)		2(fixed)	



(a) (b)

Figure 3.9: Left: Reflectivitygraph (13 keV) of Silicon with PS directly after coating with a 4 nm gold layer fitted with a 4 layer model. Right: SLD profile.

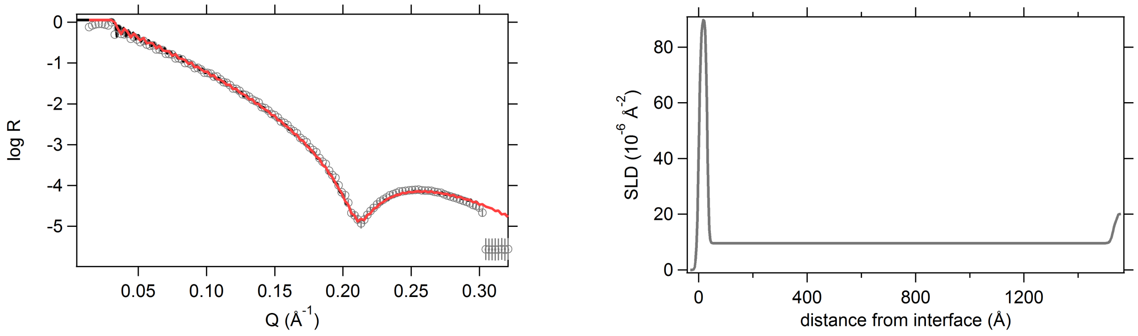


(a) (b)

Figure 3.10: Left: Reflectivitygraph (8 keV) of Silicon with PS six mnths after coating with a 4 nm gold layer fitted with a 4 layer model. Right: SLD profile.

Table 3.7: Fit parameters of the 4 nm sample for a four layer system at the 8 keV and 13 keV measurement

	Thickness (Å)		SLD (10^{-6}Å^{-2})		σ (Å−)	
	13 keV	8 keV	13 keV	8 keV	13 keV	8 keV
Au	16.372	29.795	62.383	73.85	3.4156	11.298
Au+PS	35.17	36.452	110.87	87.613	14.504	2.5954
PS	1500.7	1593.3	9.61 (fixed)		7.563	11.224
SiO_2	21.638	14.806	18.9 (fixed)		14.713	7.5519
Si	inf		20.1 (fixed)		2(fixed)	



(a)

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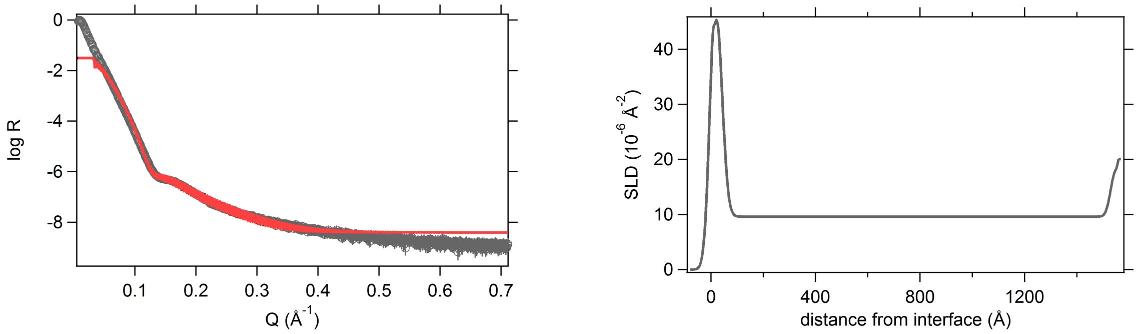
Figure 3.11: Left: Reflectivitygraph (13 keV) of Silicon with PS directly after coating with a 2 nm gold layer fitted with a 4 layer model. Right: SLD profile.



(a)

(b)

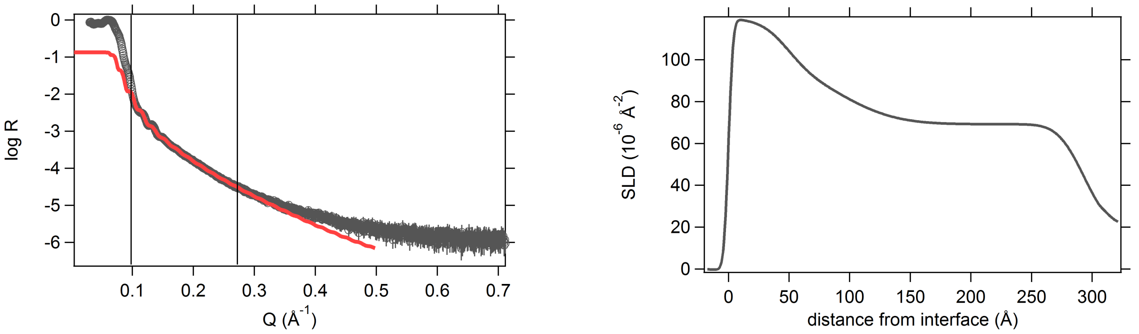
Figure 3.12: Left: Reflectivitygraph (8 keV) of Silicon with PS six mnths after coating with a 2 nm gold layer fitted with a 4 layer model. Right: SLD profile.

Table 3.8: Fit parameters of the 2 nm sample for a four layer system at the 8 keV and 13 keV measurement

	Thickness (Å)		SLD (10^{-6}Å^{-2})		σ (Å−)	
	13 keV	8 keV	13 keV	8 keV	13 keV	8 keV
Au	7.0545	29.795	84.116	73.85	6.4078	11.298
Au+PS	24.328	36.452	91.494	87.613	10.323	2.5954
PS	1498.1	1593.3	9.61 (fixed)		5.1666	11.224
SiO_2	15.316	14.806	18.9 (fixed)		8.9209	7.5519
Si	inf		20.1 (fixed)		2(fixed)	

3.3 Gold coated on a silicon substrate with PS and PMMA

After investigating the gold layers on Silicon with PS the PS was mixed in a relation of 50:50 with PMMA. PS and PMMA arrage in blocks as seen in figure 2.6 on the right. To fit reflectivity data from a system like this is very difficult since we get no information parallel to the surface. In this case there is on the one hand the bigger roughness due to the blocks and the smaller roughness of the material itself. With reflectivity one gets only information of the integer roughness what may give a wrong result. Figure 3.13 shows the data fitted in between the vertical lines. The thickness if the PS-PMMA-layer is about 100 nm, the gold layer shall be about 10 nm.



(a)

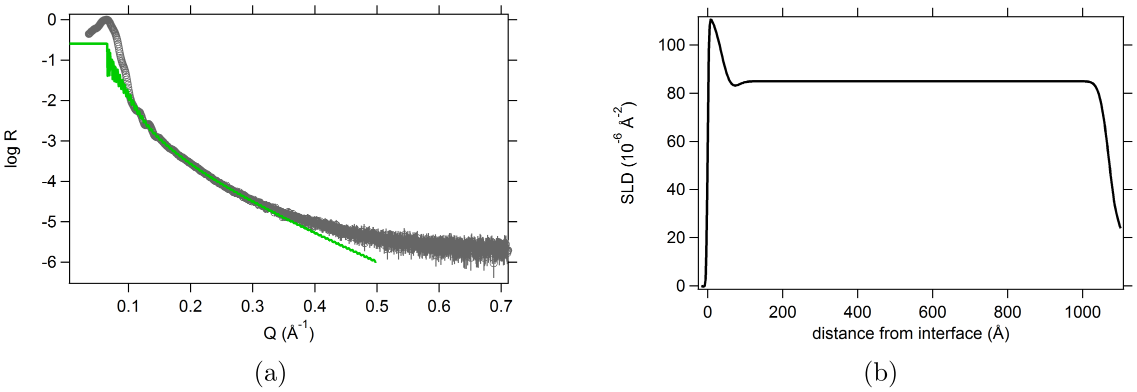
(b)

Figure 3.13: Left: Rflectivity signal of a silicon wafer coated with a mixture from PS and PMMA sputtered with a gold layer. Right: SLD profile.

Table 3.9: Fitting parameters for a gold layer on silicon with PS+PMMA

	Thickness (Å)	SLD (10^{-6}Å^{-2})	σ (Å−)
Au	48.184	120.26	3.0837
Au + PS + PMMA	37.051	102.49	15.81
PS + PMMA	208.17	61.52	40.303
SiO$_2$	15	18.9 (fixed)	17.13
Si	inf	20.1 (fixed)	2 (fixed)

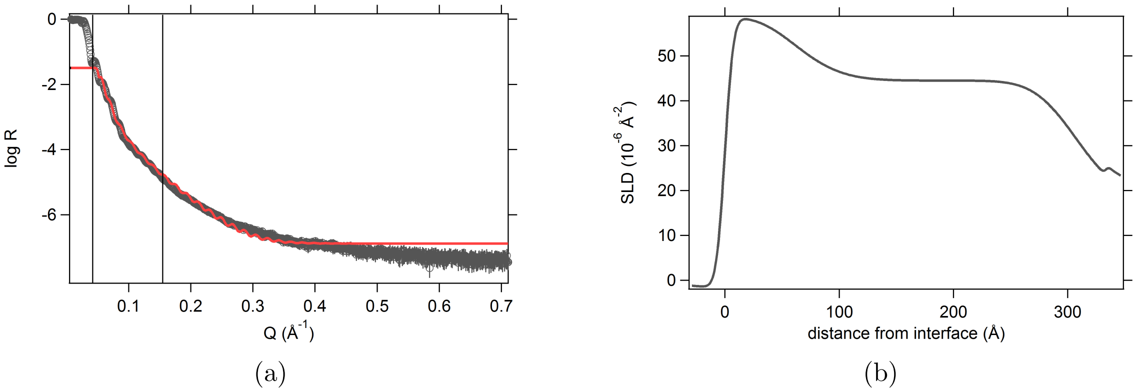
Also here an interdiffusion layer is assumed. As one can see, the fitted layerthickness of the PS-PMMA-layer is abou 21 nm which is five times smaller than it should be. Figure 3.14 shows the same data with a theoretical curve where this layerthickness is fixed on 100 nm. As one can clearly see this curve does not fit the data anymore. Figure 3.15 shows the date from a sample with the same system but sputtered for a shorter time.



(a) (b)

Figure 3.14: Left: Reflectivity signal of fig. 3.13 and theory curve with fixed PS-PMMA-layer thickness of 100 nm. Right: SLD profile.

The layer thickness of the gold layer should be around 1 nm, the thickness of the PS-PMMA-layer again 100 nm. From the values in tabuler 3.10 one can see, that the same problem with fitting the PS-PMMA-layer occurs: the theory curve only fits for a layer thickness which is five times smaller than it should be.



(a) (b)

Figure 3.15: Left: Rflectivity signal of a silicon wafer coated with a mixture from PS and PMMA sputtered for 10 minutes with gold. Right: SLD profile.

Table 3.10: Fitting parameters for the gold layer on silicon with PS+PMMA

	Thickness (Å)	SLD (10^{-6}Å^{-2})	σ (Å−)
Au	14.894	60.164	5.9477
Au + PS + PMMA	17.471	82.068	29.615
PS + PMMA	274.68	44.517	42.037
SiO_2	26.283	18.9 (fixed)	29.026
Si	inf	20.1 (fixed)	2 (fixed)

4 Interpretation

The four layer system shows a very well fitting curve for the reflectivitygraphs. The sputtered gold sinks consequently in the much less dense PS. In case of the first sample measured directly after coating the gold layer plus the interdiffusion layer is about 8 nm as it should be respectively to the sputtering rate. For the older sample it is 85 nm. For the other samples the fit parameters show also thicker layers, which can be explained by more sinking of the gold layer with the time. Also the samples with the mixture from PS and PMMA n silicon could be described with the four layer fitting system.

The most important result hence is the existence of an interdiffusion layer between the gold and the ps/PS+PMMA layer. The values for layerthickness of this additional layer under the gold are always higher than the goldlayer itself. The gold is therefore not only sputtered on the surface but it sinks into the less dense layer below. That this layer has to be a mixture of gold and PS/PS+PMMA is shown by the SLD whicht is always somewhere inbetween the high SLD of Gold and the low SLD of PS. In addition the value of 34,12 nm as thickness for the interdiffusion layer for the 8 nm sample was also measured with a GISAX measurement of the same sample.

Why the values for the layerthickness of the PS+PMMA-layer are wrong by a factor f five is not exactly clear until now. The most obvious explanation are the different roughnesses as mentioned before. To get better results for those two samples measurements with different methods are neccessary. A good method could be GISAX as it is a method that shows also inplane structures parallel to the surface. Also measurements with atomic fource microscopy would be very interesting to show the roughness caused by the blocks of PS and PMMA.