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Synthesis of Light emitting SiO_x Layers with calculable optical Properties – a first Step to controlled Integration of photoluminescence active Compounds in Silicon based Devices

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Abstract

Nowadays Silicon Rich Oxide (SRO) is an interesting candidate for an optoelectronic device due to its light emitting properties. Until now most experiments are try and error and no models exist to calculate the optical properties of this interesting class of material. The here investigated samples were synthesized by low pressure chemical vapor deposition (LPCVD) and their photoluminescence (PL) and their infrared absorption (IR) were investigated. All samples show an intense PL in the region of red light (~ 725 nm). The observed intensity increases with increasing layer thickness and decreasing Si excess. In the IR spectra a peak shift to higher wavenumbers at increasing layer thickness is found. Based on this data for the PL, as well as for IR a model has been developed which explain the observed results. With these models it is possible to predict and calculate the optical properties of SRO and therewith to design these materials with specific characteristics.

Keywords: Si nano crystals, nanostructured materials, luminescence, silicon rich oxide, IR spectroscopy

1. Introduction

An interesting candidate for light emitting devices which is currently attracting much attention are silicon nano crystals (Si nc), which can be obtained isolated in solution [1-2] or embedded in a SiO_2 (SiO_x x<2 (sub-stoichiometric silicon oxide)) [3-6] or other amorphous matrices. SiO_x is of special interest, because such systems are appropriate for the integration of optical and electronic data processing circuits on the same chip, so called optoelectronic circuits (OIC). Moreover the fabrication process is compatible with the present large scale integration technologies [7,8]. The Si nc in these systems have an enlarged band gap with respect to the bulk material and already at room temperature an intense visible photoluminescence (PL) is observed. The PL consists of intense emission peaks in the near infrared, visible and near ultraviolet regions. It was established that blue and green PL peaks are caused by various emitting centers in the silicon oxide, while the nature of the most intense PL peak in orange-red region is still discussed [9,10,11].

To obtain SiO_x a large variety of techniques has been proposed: ion implantation of Si into SiO_2 [12,13], magnetron sputtering of Si and SiO_2 [14,15], laser ablation of Si targets [3,16], molecular epitaxy, thermal evaporation of SiO [17,18], PECVD (Plasma Enhanced Chemical Vapor Deposition) and LPCVD. In our days many papers have been published describing different optical properties of SiO_x ($x<2$), depending on the synthesis technique and the reaction parameters [3-6,19-22]. Until now these experiments are try and error and it is not possible to predict the physical properties or to design these optical active films with certain characteristics. Another need for using this material for application is a fast, cheap and reliable method to check the quality of the devices in the production line.

In the here presented publication it is shown that both needs can be fulfilled. Firstly, a model has been developed, which makes it possible to estimate the PL depending on the reactant gases ratio and the layer thickness. Additionally this model allows a calculation of the maximal achievable PL for a certain stoichiometry. Secondly, we show how the thickness or the stoichiometry of samples can be checked quite easy with IR spectroscopy by evaluating the peak shifts using our second model.

2. Experimental

SRO films with different thicknesses were deposited on n type (100) Si wafers. A hot wall reactor was used as reaction vessel and the pressure was controlled by mass flow controllers and a pressure sensor. A silane (SiH_4) and nitrous oxide (N_2O) mixture at 700 °C was used with different partial pressure ratios (Ro) according to:

$$Ro = \frac{p[N_2O]}{p[SiH_4]}.$$

Samples with two different Ro and therewith different stoichiometry (Ro = 20 ($SiO_{1.38}$), Ro = 30 ($SiO_{1.58}$)) were synthesized. After deposition, SRO films were thermally annealed at 1100 ºC for 60 minutes in N_2 atmosphere.

PL at room temperature was carried out with a Perkin Elmer luminescence spectrometer model LS50B, which is controlled by computer. The samples were excited using 230 nm and 250 nm radiation. PL measurements were scanned between 400 and 900 nm (3.1–1.37 eV) with a resolution of 2.5 nm.

Infrared measurements were done using a FTIR BRUCKER Vector 22 spectrometer. The scanned range was between 350 cm^{-1} and 3500 cm^{-1} with 2.5 cm^{-1} of resolution.

The thickness and refraction index of the SRO films were measured using a Gärtner L117 ellipsometer with incident laser wavelength of 632.8 nm.

3. Results

3.1 Photoluminescence:

In Fig 1a-b the PL spectra for Ro = 20 and Ro = 30 for different layer thicknesses are shown. In general, the PL spectra consist of one broad band, peaked at 1.7 eV (725 nm) called Red band (R-Band). As expected the observed PL intensity increases with increasing layer thickness. The intensity for Ro = 20 compared to Ro = 30 is around 2-3 times higher. Interestingly the increase of the PL intensity with increasing thickness strongly depends on the stoichiometry in the investigated samples. For Ro = 30 an almost linear increase is found (Fig. 1b), while the PL intensity of the silicon richer Ro = 20 (Fig. 1a) sample seems to reach a maximum. For Ro = 20 no significant change in the intensity between a layer thickness of 197.5 nm and 485.2 nm is observed, whereas a change from 107.4 nm to 197.5

nm leads to a doubling of the intensity in the PL. All samples were excited with 230 nm and 250 nm wavelength but no significant change in the results for these experiments was found.

3.2 Infra Red spectroscopy:

In Fig. 2a and 2b the IR transmittance spectra for Ro = 20 (a) and Ro = 30 (b) are shown in the region from 350 cm^{-1} to 3500 cm^{-1}. In all spectra three modes are observable which are related to the presence of amorphous SiO_2. The first mode occurs around 480 $cm-^{1}$ and can be assigned to the Si-O rocking mode, the second, less intense, mode around 820 cm^{-1} is related to the Si-O bending mode. The most intense mode is the TO mode (transverse optic mode) around 1076 cm^{-1}, which is associated with the asymmetric stretch motion of the bridging oxygen atom. As shown in Fig.2 the peak position of the TO mode shifts with increasing film thickness to higher wavenumbers. Additionally a shoulder around 1200 cm^{-1} occurs for thicker samples. As expected the peak intensities increase almost linear with the layer thickness of the SiO_x films. For an accurate determination of the peak position, the TO mode and the shoulder were fitted separately using Gaussian profiles.

4. Discussion

To understand the PL and its emission process in these systems several factors have to be considered. The first factor influencing the optical properties is the synthesis technique. The results of the here investigated samples for example differ with results where other deposition methods were used [3]. Also important is the origin of the PL, but especially for the intense PL in orange-red region the model of excitonic recombination in quantum confined Si nc does not explain experimental results satisfactorily and other radiative channels are still discussed [5,9-11,21,22]. In the here presented results, the peak position of the R-band does not change significantly, so it can be assumed that for all experiments the mechanisms of the PL, the radiative channels and the emission centers, are the same. For further discussion the kind of micro structure (emission centers) responsible for the PL is assumed to be unchanged by the reactant ratio of the investigated thin films. While the radiative channels are the same, the number of channels or number of defects seem to depend on the stoichiometry, explaining the different intensities for Ro = 20 and Ro = 30. For a homogenous composition, which has been observed by TEM spectroscopy, one would expect a linear increase of the intensity with the layer thickness. The data for Ro = 30 could satisfy this expectation on the first look, but for Ro = 20 no linear trend is observed. To explain this non linear trend, absorption effects must be considered. Recently we published the absorption coefficients of different Ro for different excitation wavelengths [23]. Taking those results in consideration we propose the following model to calculate the PL intensity for different Ro in dependence of the layer thickness:

According to *Lambert Beer* Law the incoming excitation beam with wavelength λ_{ex} and initial Intensity I_0 will reach the emission centers found at depht d_i with the following intensity:

$$I_{ex} = I_0 e^{-\alpha_{ex} d_i} \quad (1)$$

where α_{ex} is the absorption coefficient of the film with the stoichiometry Ro for the excitation wavelength λ_{ex}.

Comparable is the emission progress; the emitted light with the wavelength λ_{em} and Intensity I_{em} will reach the detector with following intensity I_{obs}:

$$I_{obs} = I_{em} e^{-\alpha_{em} d_i} \qquad (2)$$

where α_{em} is the absorption coefficient for the emission wavelength. The intensity of the excitation beam and the intensity of the emission centers of certain depth in the film are linked by:

$$I_{em_i} = C_{eff} I_0 e^{-\alpha_{ex} d_i} \qquad (3)$$

in which the conversion efficiency C_{eff} is:

$$C_{eff} = n_i c_{eff} \qquad (4)$$

where n_i is number of emission centers at certain depth and c_{eff} the conversion rate of one emission center. The observed intensity coming from the emission centers of depth d_i can be described as:

$$I_{obs} = C_{eff} I_0 e^{-\alpha_{ex} d_i} e^{-\alpha_{em} d_i} = C I_0 e^{-d_i(\alpha_{ex} + \alpha_{em})} \qquad (5)$$

The total observed emission at the wavelength λ_{em} from a film with the thickness *d* is then given by:

$$I_{\lambda_{em},obs} = C_{eff} I_0 \int_0^d e^{-x(\alpha_{ex} + \alpha_{em})} dx = \frac{C_{eff} I_0}{\alpha_{ex} + \alpha_{em}} \left[1 - e^{-d(\alpha_{ex} + \alpha_{em})}\right] \qquad (6)$$

According to eq.6 the maximum intensity which can be observed from a film with unlimited thickness d_∞ is:

$$I_{\lambda_{em},obs_{\max}} = \frac{C_{eff} I_0}{\alpha_{ex} + \alpha_{em}} \qquad (7)$$

and the percentage of the maximum possible intensity reached after certain thickness *d* can be calculated by:

$$\% I_{\lambda_{em},obs_{myx}} = \left[1 - e^{-d(\alpha_{ex} + \alpha_{em})}\right] \times 100 \qquad (8)$$

In Fig. 3a and Fig. 3b $\%I_{\lambda_{em},obs_{myx}}$ calculated with eq. 8 over *d* for Ro = 20 and Ro = 30 is compared with the observed PL (scaled). It is clearly shown that the intensity I_{em} is growing with the layer thickness, as described with our model, proving that it is possible to calculate the PL for a certain reactant ratio and layer thickness with accuracy.

As expected the stoichiometry has a significant influence on the absorption properties, which is already indicated by the value of the absorption coefficients (for Ro = 20 $\alpha_{250\ \mathrm{nm}}= 4.8\cdot10^{4}\ \mathrm{cm}^{-1}$ and for Ro = 30 $\alpha_{250\ \mathrm{nm}}= 9\cdot10^{3}\ \mathrm{cm}^{-1}$ [23]). While for Ro = 30 after a 500 nm only 40 % of the possible maximum intensity in the PL is reached, for Ro = 20 already more than 80 % of the maximum is reached. An important consequence of these results for application is that due to absorption effects (here especially for Ro = 20) a maximum PL (calculable with eq.7) is reached after a certain thickness and by further increasing no significant change is observed PL will be found.

Another possibility is to fit the data of the PL with eq. 6 (Fig. 3c). As result from these fits it is possible to compare C_{eff}, from the term:

$$\frac{C_{eff}I_0}{\alpha_{ex}+\alpha_{em}}$$

In our case the intensity I_0 is the same for all experiments, the absorption coefficients are known, so a direct comparison of C_{eff} for the different stoichiometries Ro = 20 and Ro = 30 is possible. As described above it is highly likeable, that the mechanism and type of emission centers responsible for the PL are identical. In this case c_{eff} in eq. 4 should be constant. This gives the interesting opportunity to compare the relation of the density of emission centers in the different samples. In our case in films with Ro = 20 the density of emission centers is 3.6 times higher than in films with Ro = 30, showing that by varying the reactant ratio a broad intensity spectra can be reached.

In the IR spectra for all films the vibrational frequency of the TO is shifted to lower wavenumbers compared with bulk α-SiO_2 (1090 cm^{-1}), a discrepancy which is known for thermal grown silicon oxides, in which the TO modes typically appear around 1076 cm^{-1} [4,5,24,25], comparable with the here presented results. Besides this discrepancy, which has not been discussed in detail, a significant blue shift occurs in our films with increasing layer thickness (Fig.4). Two factors have to be taken into consideration to explain this observation. The first one is the presence of defects which come along with the presence of sub-stoichiometric silicon oxide. At least two different defect structures are associated with these shifts in IR in literature. The first ones are the so called dangling bonds or *E`* centers (O≡Si·) [26], the second ones are oxygen-deficient centers (or neutral oxygen vacancy (NOV)) O≡Si-Si≡O [27]. It has been shown for pure SiO_2 films that these defects exist in the interface between the Si substrate and the grown SiO_2 film and that in ultra thin films (< 10 nm) they cause a shift to lower wavenumbers. For SRO it can be assumed that the amount of suboxide is much higher than in pure SiO_2 films, because the defect containing interlayers between Si/SiO_2 do not only occur at the boundary of the substrate with the film but also around Si agglomerates (like Si nano crystals), which are distributed within the film. Based on this assumption, the difference in the peak position between different Ro can be explained. For Ro = 20 the values for the peak position for the same layer thickness compared with Ro = 30 are ~ 2 cm^{-1} lower. Taking the higher Si excess of Ro = 20 into consideration, the amount of Si agglomerates and therewith the ratio of defects/SiO_2 is higher, which causes a shift to lower wave numbers compared to Ro = 30.

Also previous reported IR shifts caused by annealing can be explained in this way. It is known that annealing leads to a healing of defect structures, meaning that the amount of defects in annealed samples is significant lower which leads to a shift towards higher wavenumbers (blue shift).

While a different ratio of defects/SiO_2 of a defect rich suboxide layer can explain a peak shift for different concentration in the Si excess, it does not explain the correlation between peak shift and layer thickness (Fig. 4). As the ratio of defects/SiO_2 is constant in a film independent of its thickness, no peak shift should be expected at varying the thickness.

Excluding defects as reason for thickness depending peak shift other possibilities must be considered. The absorption frequency (ω) in the central and noncentral force approximation of TO mode is given by Eq. 3

$$\omega_{TO} = \left[\frac{2}{m_0} \left(\alpha \sin^2 \frac{\Theta}{2} + \beta \cos^2 \frac{\Theta}{2} \right) \right]^{\frac{1}{2}} \qquad (9)$$

where Θ is the Si-O-Si angle between adjacent SiO_4 tetrahedra, m_0 is the mass of the oxygen atom and α and β are the central and noncentral force constants. As clearly seen in Eq. 3 no dependence of the layer thickness is given which could explain the peak shift in TO Mode (Fig. 2).

Martinet and Devine [28] explained a peak shift in SiO_2 films with comparable thicknesses to the here presented samples using a classic approach for a multiple reflection of beams incident on a thin film. In this approach the different transmission coefficients at the boundaries SiO_2/air and $SiO_2/Si_{substrate}$ and the thickness dependency are considered (for more details compare with [27]) and it has been shown that the overall transmission coefficient is correlated with the layer thickness *d*. Under the assumption that the excess Si is even distributed in the SiO_2 forming a homogenous layer with consistent transmission coefficient, which has been proven by TEM measurements, and that the amount of defect free SiO_2 in the matrix is huge compared with the one in the sub-oxide layers, the model from Martinet and Devine can be used as basic principle to explain the observed peak shift in our samples.

By comparison the influence of the two factors leading to a phase shift (first the concentration of the Si excess, second the layer thickness) is more or less equal. Reducing the Si excess (for the same layer thickness) from 5.6 % (Ro = 20) to 3.4 % (Ro = 30) leads to a blue shift of 1.7 cm^{-1} while doubling the layer thickness from 1000nm to 2000 nm is accompanied with a blue shift of 1.8 cm^{-1}.

Summarizing the results it is possible to calculate a peak position in the here investigated range by using equation 10:

$$\omega_{d,Ro} = \left(P_{SiO_2} - \phi_{Ro}\right) + dB \quad (10)$$

where ω_{d,R_o} is the peak position depending on layer thickness *d* and Ro, P_{SiO_2} the peak position for a “pure” SiO_2 film, ϕ_{Ro} a constant for the peak shift caused by Si excess and *B* constant scaling factor for the layer thickness, depending on the Ro. An interesting feature of this formula is, that ϕ_{Ro} is related to the ratio of defects/SiO_2, which gives the possibility to compare the defect density of different samples, synthesis techniques or thermal treatments simply by IR spectroscopy. A larger ϕ_{Ro} implies a larger ratio of defects/SiO_2.

With the here developed models SRO get more interesting for applications; firstly, its predictable and calculable PL makes it possible to design thin films with specific optical characteristics and secondly, with simple IR spectroscopy it is possible to monitor the synthesis process easily.

5. Conclusion:

Based on experimental data from PL and IR spectroscopy, we were able to develop two models. The first one explains the intensity development in the PL for samples with different stoichiometries and different thicknesses. Even if the origin of the PL is still discussed, the model explains the correlation of film thickness and PL, taking absorption processes into consideration. Furthermore, this model allows calculating the maximum PL reachable for every stoichiometry. Also the comparison of the conversion efficiency between different samples is possible. The second model explains the shift in the TO mode found in the IR spectra. Considering defects and different transmission coefficients at the boundaries SiO_2/air and $SiO_2/Si_{substrate}$ it is possible to calculate the shift in IR spectra for different film thicknesses and stoichiometries. With this two models SRO deposited by LPCVD are much more predictable; a first step towards the design of optical active layer was done, bringing this class of material closer to application.

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Figures:

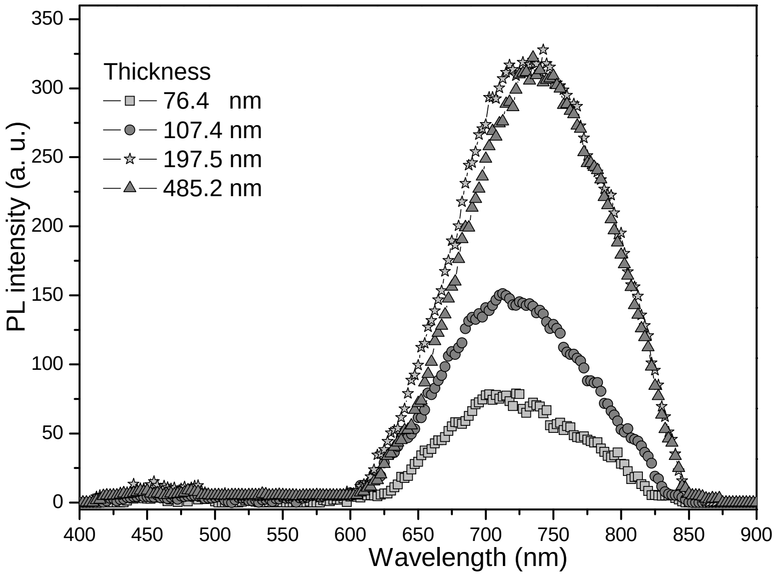


Fig. 1a: PL spectra of Ro = 20 for different layer thicknesses

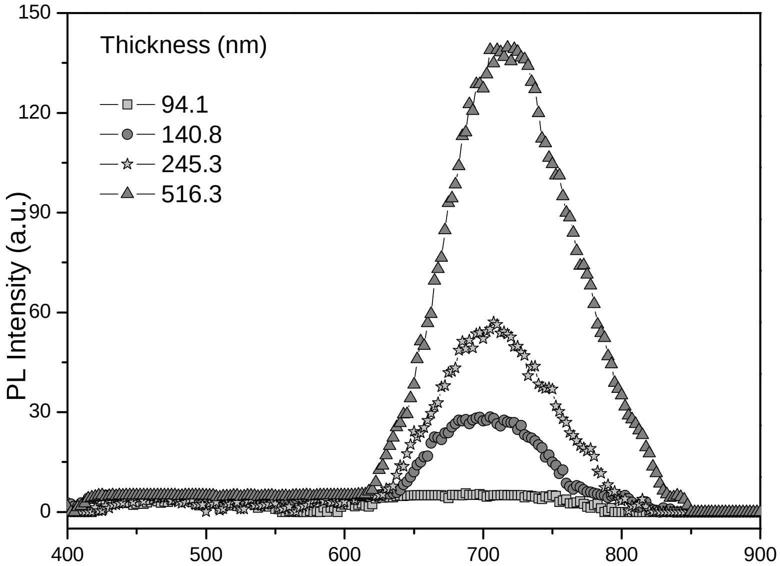


Fig. 1b PL spectra of Ro = 30 for different layer thicknesses

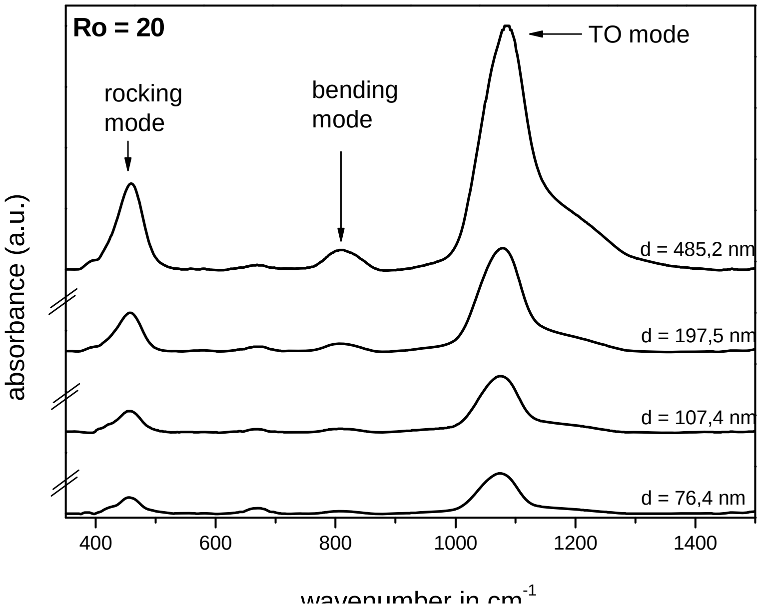


Fig 2a: IR spectra for Ro 20 for different layer thicknesses

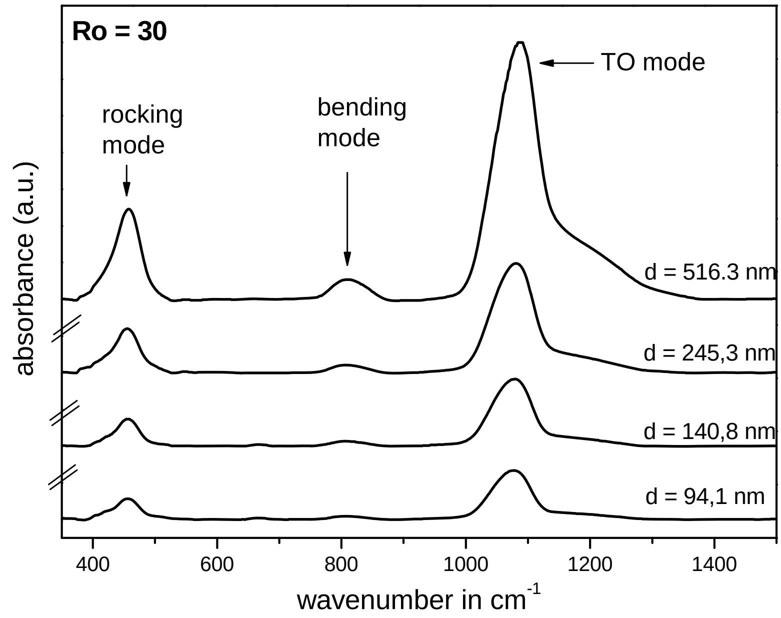
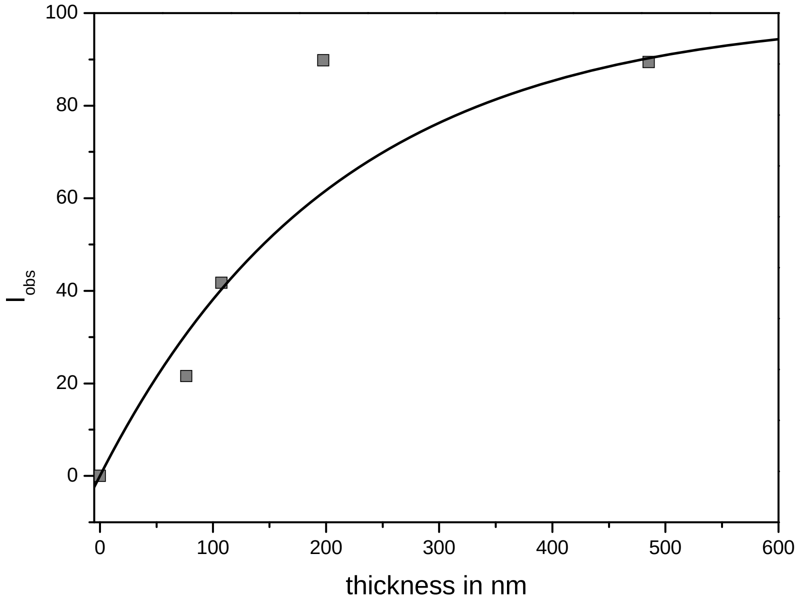


Fig 2b: IR spectra for Ro = 30 for different layer thicknesses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I_{obs}
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100
200
300
400
500
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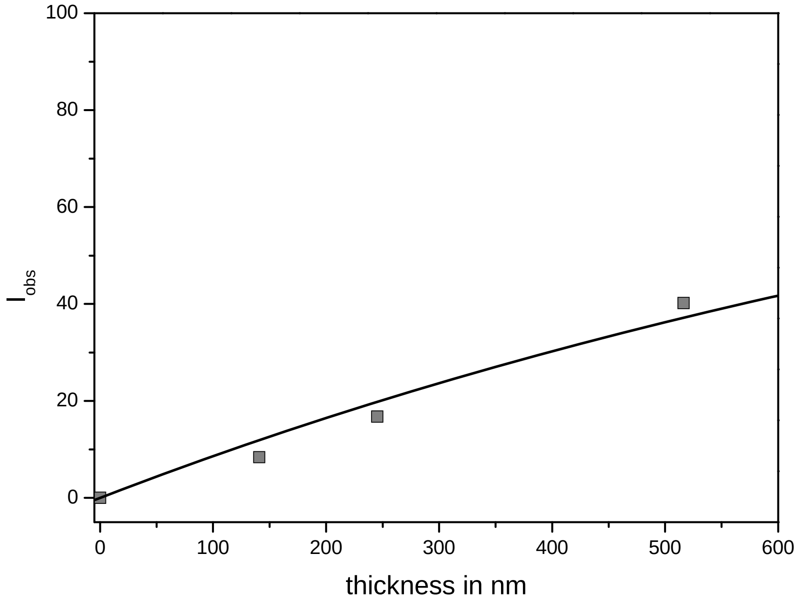
thickness in nm

Fig. 3a: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thickness in nm

Fig 3b:

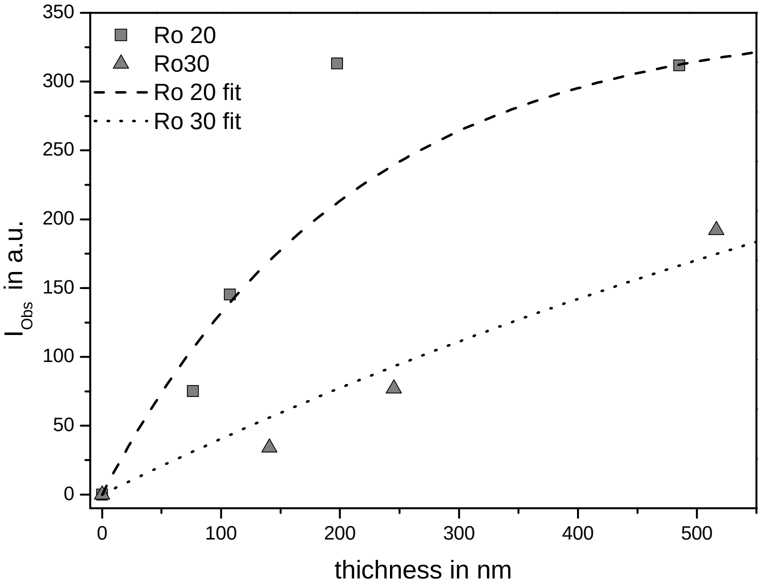

Fig. 3c:

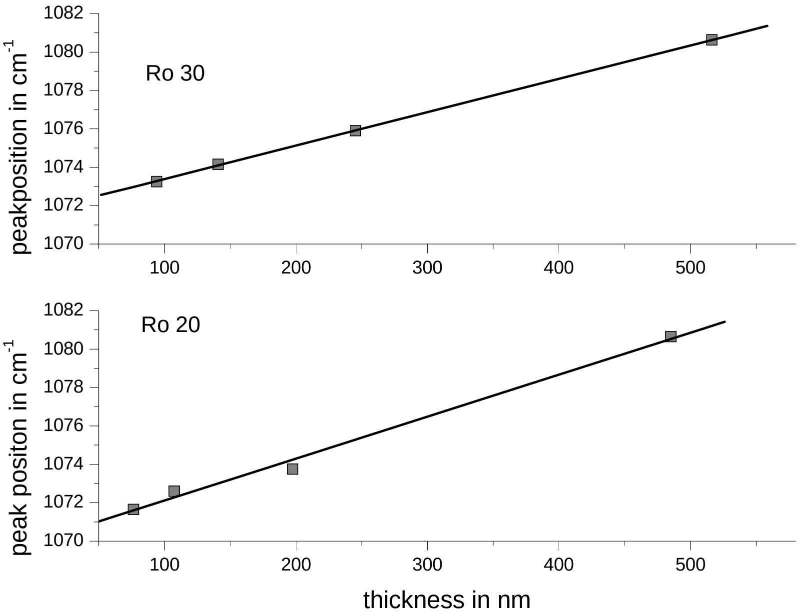

Fig. 4 Peak shift of the TO mode for different thicknesses in Ro = 30 and Ro = 20