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ESRF

Experiment Report Form

ESRF	**Experiment title:** Tuning the band-gap of semiconductor crystals by introducing internal lattice distortions via the incorporation of biologically originated molecules.	**Experiment number**: MA- 1692
Beamline: Id31	**Date of experiment**: from: 14.11.2012 to: 19.11.2012	**Date of report**: 20.02.2013
Shifts: 12	**Local contact(s)**: Christina Drathen	*Received at ESRF:*

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Report:

During our work in ESRF beam ID31, we measured XRD diffractions of ZnO powders modified with different biologically originated molecules.
Twenty one biomolecules (amino acids) with several concentrations each, were added during the crystallization process of ZnO in order to the examine their effect on the micro and nano structure of the crystal.
Our goal was to determine lattice parameter changes via measuring the peak positions and using Rietveld analysis method. Furthermore, our goal was to prove that incorporation of biomolecules within the crystal structure can be used for technological application such as band gap engineering.

Analysing the data we received during out stay in the ESRF we found that biomolecules in ZnO, indeed, have a strong effect on lattice parameters caused by intra-crystalline strain. This result can be seen from figure 1a, presenting the most intense peak ($\theta = 11.05°$) of four ZnO samples (pure ZnO, ZnO with 3mg/ml glutamic acid, 3mg/ml lysine and 3mg/ml serine added to solution during the crystallization process). A clear shift of the peak center position can be noticed. A low intensity of serine peak (pink colour) was caused by the existence of an addition phase of $Zn(OH)_2$. This phase formed due to inhibition of ZnO growth induced by the presence of serine in the solution during the crystallization process. The coexistence of both phases influenced peak intensity but had no effect on peak position. Figure 1b, presents the same XRD peak after heating the samples to 300^0C for 90 min. It can be seen from the figure that all the peaks returned to the original position (indicated by the pure ZnO sample) due to strain release caused by amino acid destruction. The $Zn(OH)_2$ phase of serine disappeared due to water evaporation.
Figure 2a shows that there is a strong correlation between amino acid concentration and the resulting peak shift for glutamic acid in different concentrations in solution (0.5mg/ml, 1mg/ml, 3mg/ml, 6mg/ml). The same correlation was noticed for many others samples. We can conclude that increasing amino acid concentration in the solution leads to stronger XRD peak shift and therefore an increase in lattice parameters.

Figure 2b presents the same XRD peak for two glutamic acid concentrations (3mg/ml, 6mg/ml) after heating the samples to 300^0C for 90 min. The figure shows that both peaks returned to the original position and overlap with the pure ZnO sample. In addition, it can be seen from figure 2a that the peak for ZnO grown with 6mg/ml glutamic acid is split up. The reason for this is anisotropic interaction between the amino acid and the bulk material. The incorporation of the amino acid crystal took place in some of the crystals whereas some of them remained pure. After the thermal heating, the peak returned to its original position and form (fig2b).

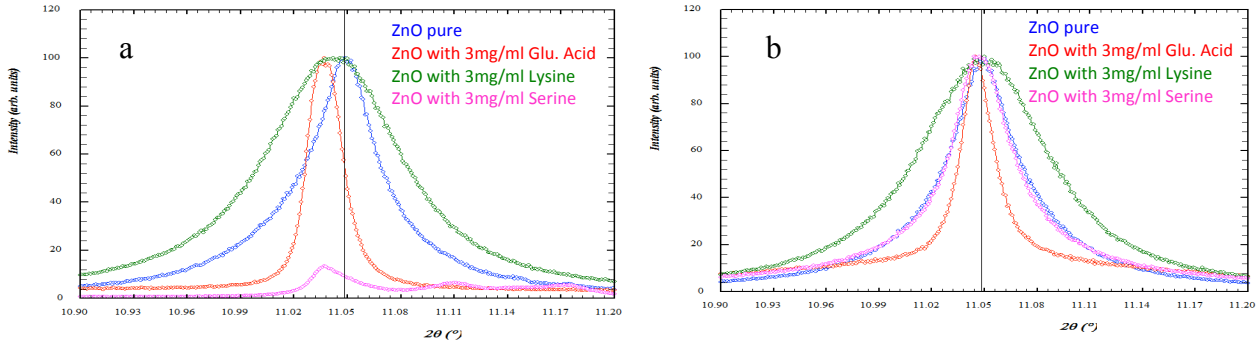

Figure 1: Main XRD peak position of pure ZnO (blue) and ZnO crystallized in the presence of 3mg/ml of glutamic acid (red), lysine (green) and serine (pink). a) As received after crystallization, b) After thermal treatment at 300°C for 90 min.

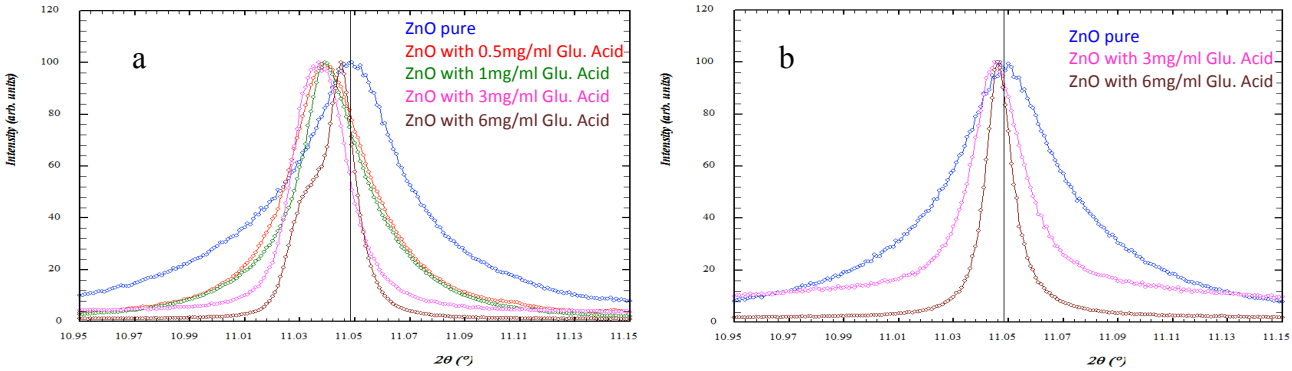

Figure 2: a) Main XRD peak position of pure ZnO (blue) and ZnO crystallized in the presence of 0.5mg/ml of glutamic acid (red), 1mg/ml of glutamic acid (green), 3mg/ml of glutamic acid (pink) and 6mg/ml of glutamic acid (maroon). b) The same peak for 3mg/ml of glutamic acid (pink) and 6mg/ml of glutamic acid (maroon) after thermal treatment at 300°C for 90 min.

In order to prove that the peak position shifts is caused by the presence of intra-crystalline amino acids, we performed EDS analysis for a ZnO sample grown in the presence of 0.5 mg/ml in the crystallization solution. This sample showed a strong shift in peak position. We chose cysteine due to the presence of Sulphur atoms in the molecule structure, which can be easily noticed by EDS. The analysis showed that there is at least 1atomic% of cysteine inside the crystal (fig 3).

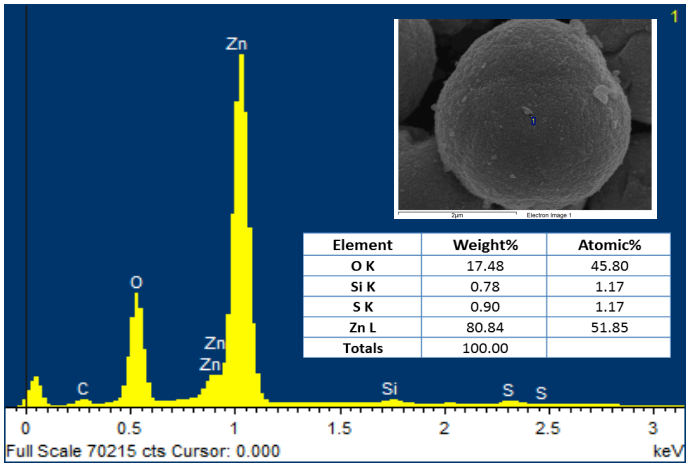

Figure 3: EDS results for ZnO crystal grown in the presence of 0.5mg/ml amino acids.

To determine the value of inrta-crystalline strain, we performed Rietveld analysis (using EXPGUI program) for all the measured samples. Lattice parameters were received and the strain calculated as the change in lattice parameter for each direction of the Wurtzite structure (table 1). The quality of the estimation is presented by chi^2 parameter. From table 1, it can be noticed that a significant strain value (more than 0. 1%) was received for ZnO crystals incorporated with Glutamic acid 3 and 6 mg/ml, Histidine 3mg/ml, Lysine 4mg/ml, Serine 6 and 3 mg/ml, Cysteine 0.5 and 0.3 mg/ml and Seleno-cysteine 0.5mg/ml. For all samples, except cysteine and seleno-cysteine, the strain released after thermal treatment of 300°C for 90 min. For cysteine and seleno-cysteine, the presence of sulphur and selenium atoms in the molecule caused a strong chemical interaction, which could not be released by a simple low temperature thermal treatment.

Band gap energy was measured using a Cary 5000 spectrophotometer with the addition of an integrated spear. The band gap energy was estimated from reflectance spectra in diffusion mode. A clear shift of band gap energy is noticed in figure 4, for the ZnO sample crystallized with 3mg/ml of serine in solution (red). Moreover, the band gap moved toward the pure ZnO value (3.3eV) after heating to 300°C for 90 min and coincides with pure ZnO band gap after additional heating to 500°C for 90 min. Inset in figure 4 is a zoom-in on the band gap area.

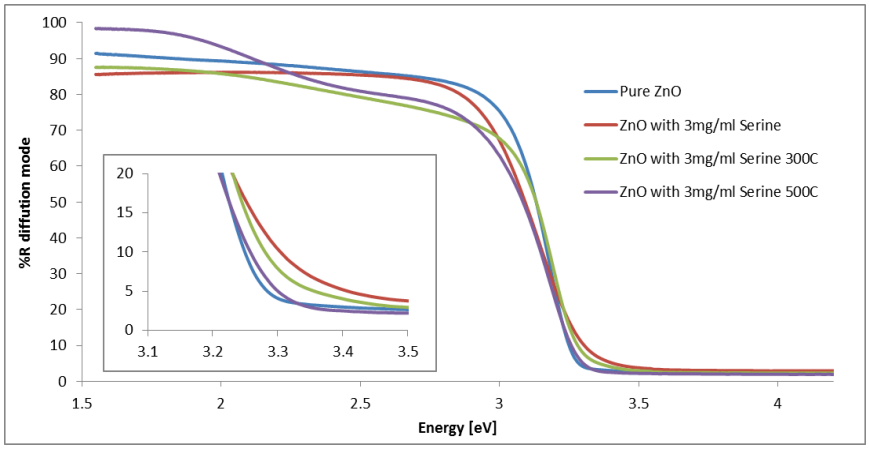

Figure 4: Cary 5000 spectroscope reflectance (using integrated spear) for pure ZnO (blue) and ZnO crystallized in the presence of 3mg/ml of serine at different temperatures. At room temperature (red), after thermal treatment at 300°C for 90 min (green) and after additional thermal treatment at 500°C for 90 min (purple). Inset, zoom of the band gap energy area.

For a better understanding of the incorporation of amino acids within the crystal structure, an accurate concentration measurement of intra-crystalline amino acids is required. To achieve this the samples have been sent to Aminolab laboratory Rehovot, Israel, for chemical analysis, but the results have not yet been received.

Table 1: Measured absolute strain values achieved by Rietveld analysis for each sample at a,b and c direction of the Wurtzite structure of ZnO. The strain values after thermal treatment of 300°C for 90 min presented in red.

Amino acid	Amino acid concentration in solution	% Starin a,b	% strain c	χ2
Pure ZnO	-	0.000	0.000	5.684
Aspartic acid	0.3 mg/ml	0.084	0.097	1.635
	0.3 mg/ml Thermal treatment	0.001	0.000	1.308
	0.5 mg/ml	0.053	0.042	4.230
	1 mg/ml	0.037	0.030	4.391
Glutamic acid	0.5 mg/ml	0.063	0.066	2.665
	1 mg/ml	0.065	0.062	2.369
	3 mg/ml	0.112	0.070	2.889
	3 mg/ml Thermal treatment	0.019	0.013	1.439
	6 mg/ml	0.104	0.085	6.347
	6 mg/ml Thermal treatment	0.013	0.001	8.503
Arginine	3 mg/ml	0.015	0.062	2.169
	4 mg/ml	0.066	0.051	1.42
	6 mg/ml	0.005	0.027	3.867
Histidine	3 mg/ml	0.121	0.107	1.957
	1 mg/ml	0.056	0.012	4.667
Lysine	4 mg/ml	0.120	0.108	3.457
	4 mg/ml Thermal treatment	0.009	0.014	4.437
	3 mg/ml	0.050	0.055	1.707
Serine	6 mg/ml	0.192	0.135	1.876
	6 mg/ml Thermal treatment	0.002	0.007	1.006
	4 mg/ml	0.052	0.047	1.585
	3 mg/ml	0.104	0.031	4.099
	3 mg/ml Thermal treatment	0.007	0.001	5.043
	1 mg/ml	0.036	0.035	2.458
	1 mg/ml Thermal treatment	0.004	0.022	2.184
Threonine	1 mg/ml	0.005	0.011	4.091
Asparagine	1 mg/ml	0.001	0.002	3.043
Glutamine	1 mg/ml	0.008	0.050	4.878
Cysteine	0.5 mg/ml	0.202	0.203	1.764
	0.5 mg/ml Thermal treatment	0.243	0.233	1.635
	0.3 mg/ml	0.234	0.161	1.787
Seleno-Cysteine	0.5 mg/ml	0.161	0.161	1.631
	0.5 mg/ml Thermal treatment	0.099	0.208	1.573
Glycine	4 mg/ml	0.014	0.011	3.206
	1 mg/ml	0.044	0.055	1.745
	1 mg/ml Thermal treatment	0.007	0.008	1.606
Proline	3 mg/ml	0.022	0.005	3.731
Alanine	3 mg/ml	0.013	0.013	3.36
Valine	3 mg/ml	0.003	0.042	4.574
Isoleucine	3 mg/ml	0.015	0.025	4.035
Leucine	1 mg/ml	0.001	0.014	3.482
Methionine	3 mg/ml	0.061	0.074	1.650
Phenylalanine	3 mg/ml	0.007	0.016	3.824
Tyrosine	0.5 mg/ml	0.088	0.102	2.304
	0.5 mg/ml Thermal treatment	0.012	0.008	1.324
Tryptophane	1 mg/ml	0.072	0.094	1.935
	1 mg/ml Thermal treatment	0.004	0.004	1.26