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ARTICLE TYPE

# Self-localization of Polyacrylic Acid molecules on polar ZnO(0001)-Zn surfaces

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## Supporting Information

### Alkaline etching treatment of ZnO(0001)-Zn oriented surfaces

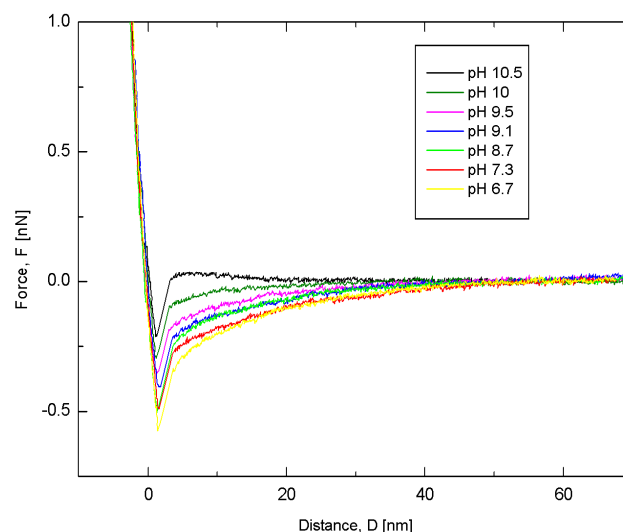
ZnO(0001)-Zn crystals were etched in 3 M NaOH as described in the experimental section. Typical AFM topographies obtained for ZnO(0001) surfaces after etching times of 30 to 60 minutes are depicted in figure 2. In-situ AFM studies of etching in alkaline media showed that ZnO(0001)-Zn surfaces immediately form a flat and single crystalline surface structure, with low-energy step edge terminations.<sup>1</sup> In this work we have extended the studies to longer etching times to archive higher step features in the range of several nanometers which offer enough space for adsorption of ad-molecules. Etching pits as occurred after etching times of about 15 minutes on the ZnO(0001)-Zn surface, with a diameter of about 2  $\mu\text{m}$ , which grew in size with longer etching time. The steps on alkaline etched ZnO(0001)-Zn surfaces were well defined with a typical height of 2 nm to 10 nm. After longer etching times (more than 60 minutes) the hexagonal pits merged to bigger structures. All edges were oriented towards each other by multiples of 60° on the surface, which corresponds to the hexagonal structure of ZnO.

### Substrates for force - distance spectroscopy

Electrostatic interactions of electric double layers can be measured using force distance spectroscopy and are typically detected within several ten nanometers distance to the charged surfaces. Parameters like surface roughness play a crucial role and can hardly be accounted for in theoretical models, thus atomically flat terrace-like structures are optimal for these measurements. Consequently, only new ZnO crystals were used to grant perfect surface quality. The crystals were etched shortly before the experiment.

### Modification of cantilevers for force-distance spectroscopy

Gold coated cantilevers of type *Cont GB-G* (Budget Sensors, Bulgaria) were dipped for two minutes in concentrated sulfuric acid to remove contaminations and intensively rinsed with water and ethanol. Without drying the ethanol (to minimize contact with the lab atmosphere) the cantilevers were put into a 1 mM solution of 15-mercaptopentadecanoic acid in ethanol (27.4 mg/100ml) for 24 hours which forms a carboxyl terminated SAM



**Fig. 1** Force-distance curves of the PZC experiment on the ZnO(10-10) surface at different pH values. The shown curves are approach curves which show long distance interactions of the electric double layers.

on the gold coating via covalent Au-S bonds. Afterwards the cantilevers were extensively rinsed with ethanol and directly used for the AFM experiments.

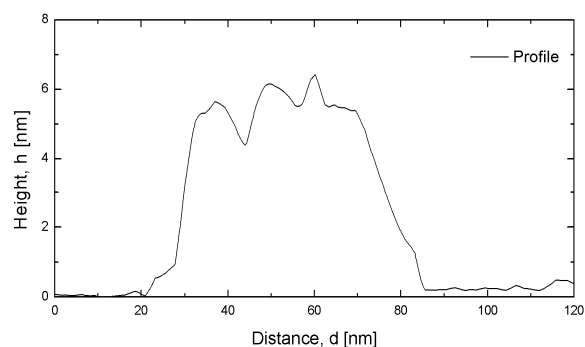
### Determination of the PZC of the ZnO(10-10) surface

As determined from the etching studies, the crystallographic orientation of the step faces used for the adsorption experiments is most certainly (10-10). In order to discriminate the influence of the electric double layer properties of the ZnO(0001)-Zn surface and the Zn(10-10) surface the PZC of the respective orientations was determined. For this purpose we used a chemically modified cantilever to probe the surface-charge as a function of the pH value. Using this method the PZC can be determined with an accuracy of about  $\pm 0.2$  pH values by multiple repetition of the experiment which is comparable to e.g. zeta-potential measurements. At the PZC the force curves change from attractive to repulsive in the non-contact regime, which is caused by the electrostatic interactions by the negatively charged tip and the change of the electrostatic double layer from negatively to positively charged. From figure 1 shown above, the point of zero charge of the ZnO(10-10) surface can be estimated to be  $\text{pH}_{\text{PZC}} =$

10.2 ± 0.2 which is considerably higher than the PZC of the ZnO(0001)-Zn surface which was previously measured to be 8.7.<sup>3</sup> The impact of these results on the adsorption behavior will be discussed in the main article.

### Adsorption of PAAc at ZnO(0001)-Zn surfaces at 50 mM concentration of the background electrolyte

The adsorption was performed analogue the procedure as described in the main article. To achieve consistent results the solution used for the light scattering experiments was diluted with a 50 mM NaClO<sub>4</sub>/NaOH solution to a concentration of PAAc of 0.1 mg/l. The adsorption was performed on a freshly prepared ZnO(0001)-Zn crystal in a PTFE beaker for 5 minutes followed by rinsing the crystal with ultrapure water und drying with nitrogen. As shown in Fig. 2 no preferential adsorption of the molecules at step edges is visible. The size of the observed polymers was about 60 nm in diameter. This value is in good agreement with the results of the light scattering experiments although the observed structures hint to agglomerated polymer coils which is potentially caused by the increased concentration of background electrolyte. Additionally the shrinkage of the molecules during drying has to be considered when discussing the observed PAAc coils, as all AFM imaging was performed ex situ after drying the surfaces. Anyhow it has to be kept in mind that the investigation of only few molecules in an AFM experiment does not lead to statistically significant data compared to the bulk method of light scattering. The cross section shows vertically compressed structures with a height of several nanometers.

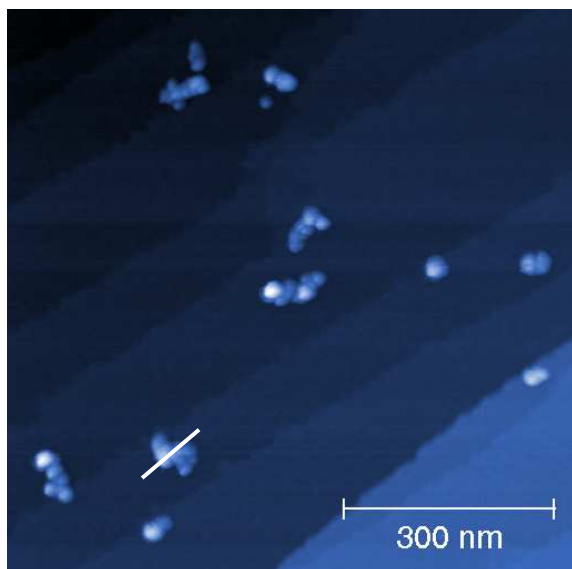


**Fig. 2** The size of the polymer coils observed after adsorption with a concentration of the background electrolyte of 50 mM is in good agreement with the values found in the light scattering experiments. Nevertheless the structure of the observed polymers hints to agglomerated coils, thus the values found for  $R_g$  cannot be directly transferred to the coil structures discussed in the main work.

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## References

- 1 M. Valtiner, X. Torrelles, A. Pareek, S. Borodin, H. Gies and G. Grundmeier, *J. Phys. Chem. C*, 2010, **114**, 15440-15447.