Co-Salen on NaCl(001) and NiO(001): Substrate influence on adsorption geometry and growth

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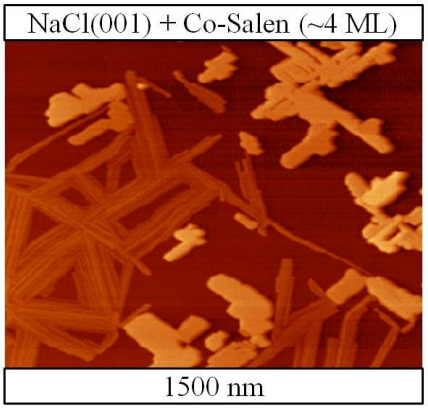
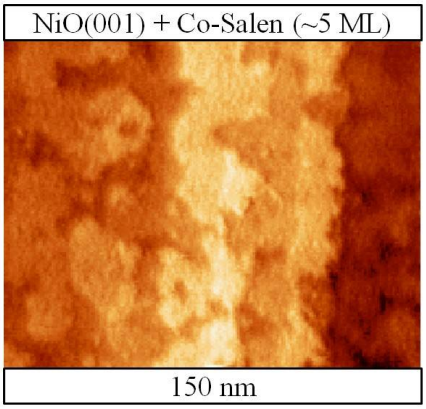
By depositing the same molecule on two chemically different substrates with the same surface structure disparities as well as equalities regarding adsorption geometry and growth are investigated. A previous experimental and theoretical study of Co-Salen on the bulk insulator NaCl(001) at low temperature revealed the exact adsorption site and geometry of the molecule [1]. For comparison we deposited Co-Salen on NiO(001), which also is an ionic insulator with rock salt structure, and performed density function theory (DFT) based calculations for this system as well. Note that they need to be more sophisticated, since the electronic structure of NiO(001) is more complex.
On both surfaces the central cobalt atom adsorbs on top of the anion. However, on NiO(001) only half of the number of orientations can be found. The previously on NaCl(001) observed 8 orientations along the <110>-directions are still present, yet the energetically less favored additional 8 orientations along the <100>-directions are absent. Indeed, DFT confirms that no metastable state exists on NiO(001).
Moreover, tip-induced displacements of individual molecules can be observed on NaCl(001) as well as on NiO(001). Interestingly, the preferred directions of these displacements coincide with the preferred orientations of the molecule axis on the respective substrate. These experimental findings are in agreement with DFT calculations, which include the interaction between tip and Co-Salen and allow to estimate diffusion barriers on the substrate.
Since tip-induced displacements are more frequent on NaCl(001) than on NiO(001), bonding appears to be stronger on the latter, which is again confirmed by the larger adsorption energy calculated for the Co-Salen/NiO(001) system. This result is also reflected by the growth modes observed for higher coverages at room temperature: On NaCl(001) Co-Salen exhibits island growth, which is characteristic for a molecule-molecule interaction that is stronger than the substrate-molecule interaction [2]. The layer-by-layer step flow growth that takes place on NiO(001) indicates a stronger molecule-substrate interaction than on NaCl(001).





References

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[2] S. Fremy et al, Nanotechnology **20**, 405608 (2009).