

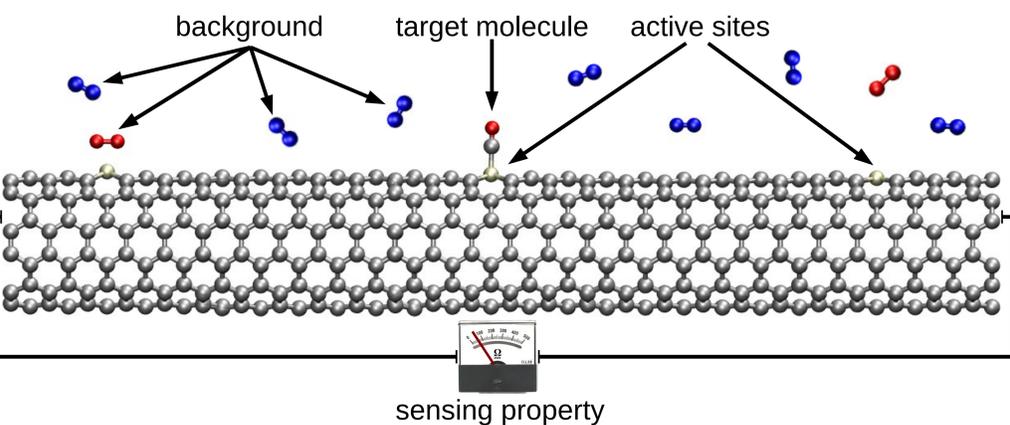
## Introduction

Nanostructures such as carbon nanotubes (CNTs) are well suited as sensor materials because of their large surface to volume ratio, making them highly sensitive to the adsorption of individual gas molecules. However, pristine CNTs are rather inert, making functionalization necessary to control both their activity and sensitivity [1]. This may be accomplished by e.g. decorating the CNT side walls or through substitutional doping.

## Background

Any nanosensing system consists of the following four main components:

- (1) "target molecule" to be detected (CO, NH<sub>3</sub>, H<sub>2</sub>S)
- (2) "active site" where the target molecule may adsorb on the sensor ((6,6) CNT doped by 3d transition metal atoms)
- (3) "sensing property" which changes upon adsorption of the target molecule (resistance)
- (4) "background" of adsorbing molecules forming the background signal (atmospheric air)

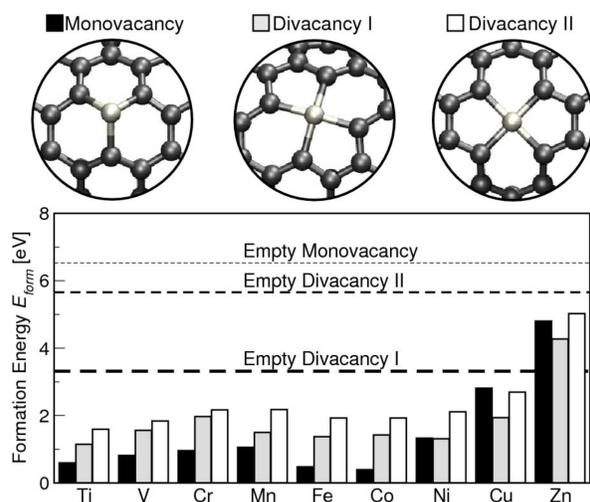


## Methodology

All total energy calculations and structure optimizations have been performed with the real-space DFT code GPAW [2], which is based on the projector augmented wave method. We use a grid spacing of 0.2 Å for representing the density and wave functions, and the PBE exchange correlation functional [3]. Transport calculations for the optimized structures have been performed using the non-equilibrium Green's function (NEGF) method [4] with an electronic Hamiltonian obtained from the SIESTA code [5] in a double zeta polarized (DZP) basis set. Spin polarization has been taken into account in all calculations.

## Stability

We functionalize our CNTs by doping the three types of CNT vacancies with 3d transition metals. Except for Cu and Zn, we find the energy gained by inserting a 3d transition metal atom into a CNT vacancy is significant. Energies for C are relative to the pristine CNT, while transition metal energies are relative to metal atoms physisorbed on a CNT.



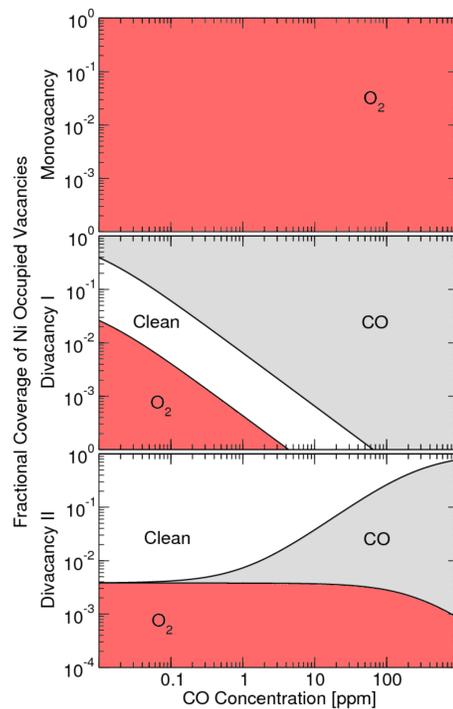
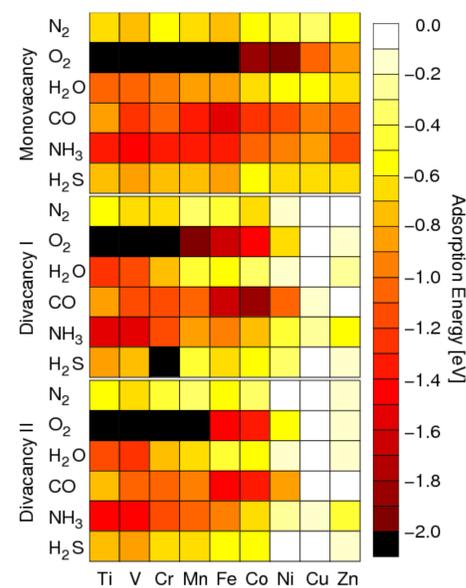
## References

- [1] J. M. García Lastra, D. J. Mowbray, K. S. Thygesen, A. Rubio, and K. W. Jacobsen, arXiv:1001.2539 [cond-mat.mes-hall] (submitted 2010).
- [2] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Phys. Rev. B **71**, 035109 (2005).
- [3] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [4] M. Strange, I. S. Kristensen, K. S. Thygesen, and K. W. Jacobsen, J. Chem. Phys. **128**, 114714 (2008).
- [5] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

## Adsorption & Coverage

We find that Ti, V, Cr, Mn, and Fe occupied vacancies bind O<sub>2</sub> so well that they would be completely oxidized in air. On the other hand, Cu and Zn occupied vacancies are too unstable to be of practical interest. However, Ni occupied divacancy I and divacancy II sites tend to bind CO stronger than O<sub>2</sub>.

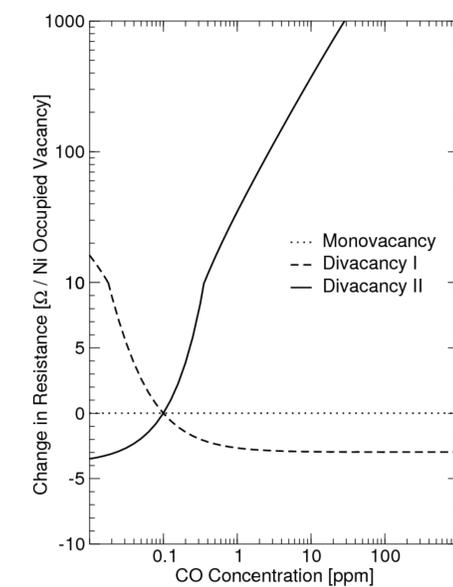
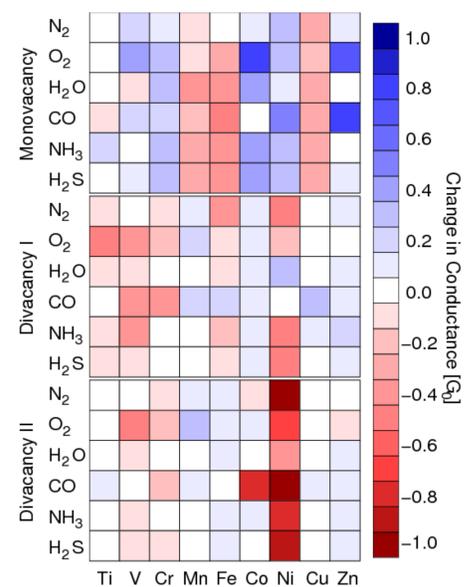
Using adsorption energies in thermodynamic equilibrium, we obtain the CO coverage of Ni occupied vacancies in air versus CO concentration. We find the CO coverage changes dramatically at toxic concentrations (10 ppm) for divacancy I.



## Resistance

Employing the NEGF methodology, we calculate the change in conductance of a single metal doped vacancy upon adsorption of either target or background molecules. We find strongly adsorbed molecules substantially change conductivity.

Combining the calculated CO coverage of Ni occupied vacancies with their conductivity, we estimate their resistance as a function of CO concentration. The resistance changes significantly for Ni occupied divacancies at toxic concentrations (10 ppm).



## Conclusions

We have presented a general model of nanostructured chemical sensors which takes the adsorption energies of the relevant chemical species and their individual scattering resistances as the only input. On the basis of this model we have performed a computational screening of transition metal doped CNTs, and found that Ni doping is the most promising candidate for detecting CO in a background of air at room temperature and pressure. Further, this model may also be applicable for other nanostructures, functionalization, and backgrounds than CNTs, metal doping, and air, respectively.