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# Assessment and modeling of $NH_3$-$SnO_2$ interactions using individual nanowire sensors

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**Abstract:**

In this work, DFT (density functional theory) calculations were applied to study the interaction between $NH_3$ and the $SnO_2$ surface. To that end, two types of scenarios were selected; (i) the clean stoichiometric $SnO_2$ (110) surface and (ii) a $SnO_2$ (110) surface with pre-adsorbed $O_{ads}$. The $NH_3$ adsorption mechanism and charge transfer to the metal oxide after the adsorption and dissociation steps of the molecule were simulated to gain a deeper insight into the $NH_3$ sensing mechanism of this metal oxide. Making use of the intrinsic advantages of nanoscale prototypes, the analysis of the nanowires' resistance modulation upon exposure to $NH_3$ and their dynamic response, as function of temperature and gas concentration, allowed validating some of the theoretical results.

**Key words:** $NH_3$, $SnO_2$, Nanowire, Model

## Introduction

$SnO_2$ as sensing material has been widely used in solid state metal oxide gas sensors due to the low cost and good sensitivity [1,2]. When used as a sensor, the resistance of $SnO_2$ usually decreases in response to reducing gases, and in general, the gas response has been considered to be the result of charge transfers either directly between adsorbed molecules and the surface or indirectly between the surface and the products of surface reactions involving the pre-adsorbed oxygen species [3, 4]. This second mechanism is believed to be the origin of $NH_3$ detection with $SnO_2$. Nevertheless, it remains not fully understood from a theoretical and experimental point of view.

Different from more studied gases such as $O_2$[5], $H_2O$[6] and CO[7] , our knowledge about the behavior of $NH_3$ onto the $SnO_2$ surface is still limited. Temperature Programmed Desorption (TPD) experiments performed by Abee and Cox [8] concluded that $NH_3$ adsorbs on the 5-coordinated Sn site on the stoichiometric surface with the desorption temperature at around 250K. On the other hand, the Sn4c is a stronger adsorption site when there are bridging oxygen vacancies available. The desorption peak for the Sn4c is at around 470K. UPS experiment reported by the same author validated the charge transfer from the $NH_3$ molecule to the metal oxide surface.

On the side of theoretical simulation, the interaction of $NH_3$ with the MOX surface and metal decorated MOX is highly interesting for heterogeneous catalysis [9-11]. Nevertheless, no literature about the adsorption of this molecule and further reactions onto $SnO_2$ has been pulbished to the best of our knowledge. Only similar DFT calculations have been reported for $NH_3$ adsorption on $TiO_2$[12], ZnO[13] and RuO[11].

In parallel, the adsorption of oxygen (O) on $SnO_2$ surface has been demonstrated by many different TPD works, and the ionic charge states has been proved by Electron Spin Resonance (ERS) experiments. However, the existence of atomic charged $O^-$ on $SnO_2$ has been questioned by A. Gurlo [14] due to the lack of direct spectroscopic evidence. Oxygen adsorption and dissociation have been intensively studied [16, 17] by using ab-initio methods, and the common results from these

works are: (i) molecular oxygen ($O_2$) only adsorbs to the reduced $SnO_2$ (110) surface and (ii) atomic O adsorbent can be produced on top of $Sn_{5c}$ sites following the dissociation step at the $O_b$ vacancy. In more recent DFT studies [5], calculated adsorption energy was successfully correlated with previous experimental evidences for the different charged oxygen species including atomic $O^-$.

In this work, we studied the adsorption of $NH_3$ onto (i) the clean stoichiometric $SnO_2$ (110) surface and (ii) $SnO_2$ surface with $O_{ads}$ pre-adsorbed after healing an oxygen vacancy. Charge density difference analyses were performed for several critical steps and interactions to study the electronic property changes associated with the $NH_3$-$SnO_2$ activity.

**Computational and experimental methods and details**

DFT calculations were performed with the Vienna ab initio simulation Package (VASP) [18, 19] using the generalized gradient approximation [20] (GGA). The core electrons were represented by projector-augmented wave [21] (PAW) potentials. Revised-Perdew-Burke-Ernzerhof [22] (r-PBE) functional was employed to treat the exchange correlation potentials. Plane wave cut off energy of 400eV was applied throughout the work. The surface slab containing 5 $SnO_2$ (110) layers and having a (2×1) periodicity of surface unit cell was applied. A 10Å vacuum layer was placed between the slabs to eliminate the interaction between them. K-point sampling was set to 4×4×1 for the surface slab and 1×1×1 for the molecules in vacuum adopting the Monkhorst-Pack grids (*Fig.1*). Geometry relaxation was performed until the energy change of electronic step goes under $1\times10^{-5}$eV and ionic step below $1\times10^{-4}$eV. The top three layers of atoms were allowed to move in the relaxation. The accuracy of current model has been verified in previous works [23]. Spin polarization was enabled when free electrons were present.

$NH_3$ adsorption profiles were calculated on the clean and O pre-adsorbed stoichiometric surface with one O atom binding to the $Sn_{5c}$ site. The atomic O in the latter case is assumed to be generated by the $O_2$ dissociation which heals the $O_{2c}$ vacancy at the same time. These two surfaces properly simulate the non-perfect $SnO_2$ surface existing in real conditions.

The adsorption energy is given by equation:

$$E_{ads} = E_{tot} - E_{sur} - E_{ad}, \text{ (i)}$$

where $E_{tot}$ is the ground state energy of surface with adsorbed molecule, $E_{sur}$ is the energy of the initial surface and $E_{ad}$ is that for a gas molecule in vacuum. Therefore, a negative value of $E_{ads}$ indicates the adsorption at 0K.

To analyze the influence of $NH_3$ adsorption and dissociation to the electronic property of $SnO_2$, charge density difference was calculated applying following equation:

$$\Delta\rho = \rho_{sub+ads} - \rho_{sub} - \rho_{ads} \text{ (ii)}$$

where $\rho_{sub+ads}$ represents the charge density of the complete surface system and $\rho_{sub}$ $\rho_{ads}$ the charge density of the substrate and the adsorbate, respectively. $\rho_{sub}$ , $\rho_{ads}$ were obtained from the same atomic structures and space coordinates as those in the relaxed molecule on surface system.

$SnO_2$ nanowires grown by CVD were used to fabricate the tested prototypes. Individual nanowires were electrically contacted by direct Focused-Ion-Beam (FIB) platinum deposition, using a FEI Dual-Beam Strata 235 instrument combined with a metallorganic injector to deposit platinum. Electrical measurements were performed using a Keithley 2400 Source Meter Unit (SMU). For gas sensing experiments, the devices were placed in a Linkam chamber with an integrated heater; the gas flow (≥ 99.999% purity) was regulated by mass flow controllers.

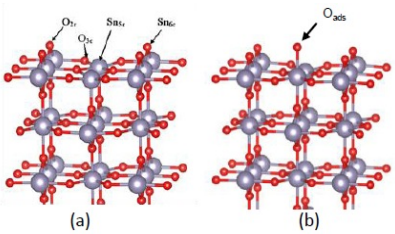


*Figure.1. (a) Clean stoichiometric surface of $SnO_2$ (110), (b) $SnO_2$ (110) surface with $O_{ads}$*

**Results**

$SnO_2$ (110) has four kinds of surface atoms: $Sn_{5c}$, $Sn_{6c}$, bridging $O_{2c}$ and in-plane $O_{3c}$ (*Fig.1*). The $Sn_{5c}$ is considered to be a Lewis acid site which is able to withdraw electrons from an electron rich atom, e.g. N, in the case of $NH_3$. In addition, DFT calculations of $NH_3$ adsorption on other MOX have shown that bonding happens between the unsaturated metal and the N atom of $NH_3$. Our searching for adsorption profile of ammonia onto tin oxide confirms this point: the adsorption occurs onto the $Sn_{5c}$ site, with Sn-N bond perpendicular to the surface plane, as shown in *Fig.2(a)*. The adsorption energy was found to be -1.14eV. The other considered adsorption geometries included the N binding to the $O_{3c}$ and the H binding to $O_{3c}$. Adding a

second $NH_3$ on the other $Sn_{5c}$ site to imitate the 100% coverage reduced the average $E_{ads}$ to -0.73eV. The lateral interaction between the adsorbed molecules was concluded from such decrease.

On the other hand, the $E_{ads}$ of a $NH_3$ molecule onto the remaining $Sn_{5c}$ of the surface with pre-adsorbed $O_{ads}$ was found to be -1.58eV. This value is 0.44eV larger than on the clean stoichiometric surface. The $O_{ads}$ had its bond with $Sn_{5c}$ 5.3° tilted from the surface normal and the distance from the $O_{ads}$ to the closest H of $NH_3$ was found to be 1.98 Å, indicating the presence of hydrogen bonding.

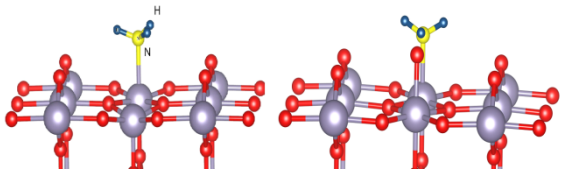


*Fig.2. (a) Adsorption geometries of a $NH_3$ molecule onto a clean stoichiometric surface and (b) onto a surface with pre-adsorbed $O_{ads}$*

Charge density difference was calculated for several critical structures to evaluate the charge redistribution on the surface region induced by molecule adsorption and dissociation. As shown in *Fig.3.(a)* , the cyan color indicates the decrease of charge density in the bottom of the N atom and on top of $Sn_{5c}$ while the yellow color indicates the increase of charge density between the N and $Sn_{5c}$ and at the upper part of the N. This kind of charge distribution is the typical character of covalent bond. Also, charge polarization was found on the in-plane $O_{3c}$.

On the clean stoichiometric surface, charge transfer between $O_{2c}$ and two underneath $Sn_{6c}$ atoms was able to see. Charge is drawn from the $Sn_{6c}$ to the $O_{2c}$. When $H_2O_{2c}$ is formed, less amount of charge transfer was indicated by the smaller iso-surface value. It is a similar situation with the $O_{ads}$ on the $Sn_{5c}$; charge density difference figure showed the ionic character of the bonding and charge transfer from the surface to $O_{ads}$. When $H_2O_{ads}$ was formed, the smaller volume inside the iso-surface on $Sn_{5c}$ atom suggested less amount of charges are transferred.

Over all, drawing of charges from surface happened with the adsorption of $NH_3$, O ion and oxidation of an $O_{2c}$ vacancy. Nevertheless, $NH_3$ was not a charge donator to the surface and adsorption of $NH_3$ itself on surface did not generate the sensing effect we experimentally measured. Forming $H_2O$ and the later desorption from the surface returned the electrical charges to surface and reduced the resistance of the material.

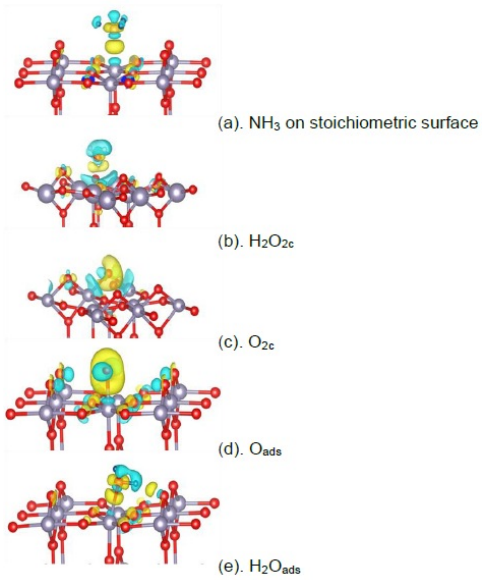


*Fig.3. charge density difference plot, iso-surface: (a),(c),(d),(e):0.005e/Br$^3$, (b): 0.002e/Br$^3$*

Confronting experimental data (*Fig.4*) with ab-initial DFT simulations, the main $NH_3$-$SnO_2$ sensing characteristics were validated. This analysis will be presented in this contribution.

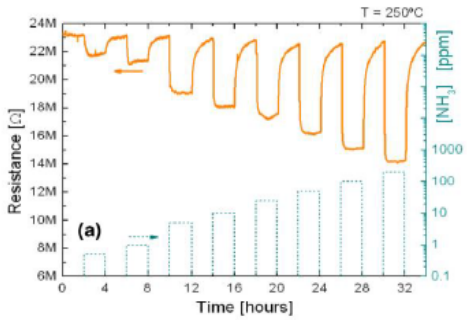


*Fig.4. Nanowire response towards sequential pulses of ammonia (500 ppb to 200 ppm) in synthetic air at a temperature of 250 °C*

## Conclusion

In summary, the adsorption sites of $NH_3$ on clean $SnO_2$ stoichiometric surface and a surface with pre-adsorbed oxygen $O_{ads}$ have been successfully identified. The adsorption energy was found to be larger with the $O_{ads}$ presence. The charge density difference analysis showed that $NH_3$ is not a charge donor to the surface. The sensing effect of $SnO_2$ towards $NH_3$ could be induced by the $H_2O$ formation and desorption either with the $O_{2c}$ or the $O_{ads}$ as all these processes reduce the amount of charges drawn from surface.

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**References**

[1] J. Huang, Q. Wan, Gas Sensors Based on Semiconducting Metal Oxide One-Dimensional Nanostructures, sensors, 9 (2009) 9903–9924.

[2] S.K. Pandey, K.-H. Kim, K.-T. Tang, A review of sensor-based methods for monitoring hydrogen sulfide, TrAC Trends in Analytical Chemistry, 32 (2012) 87-99.

[3] N. Barsan, U. Weimar, Conduction model of metal oxide gas sensors, J. Electroceram. , 7 (2001) 143-167.

[4] M. Batzill, U. Diebold, The surface and materials science of tin oxide, Prog. Surf. Sci. , 79 (2005) 47−154.

[5] M. Habgood, N. Harrison, An ab initio study of oxygen adsorption on tin dioxide, Surface science, (2008) 1072−1079.

[6] D. Koziej, N. Barsan, U. Weimar, J. Szuber, e. al., Water- oxygen interplay on tin dioxide surface: implication on gas sensing, Chemical Physics Letters, (2005) 321-323.

[7] N. Bârsan, U. Weimar, Understanding the fundamental principles of metal oxide based gas sensors; the example of CO sensing with $SnO_2$ sensors in the presence of humidity J. Phys.: Condens. Matter 15 (2003) R813.

[8] M.W. Abee, D.F. Cox, $NH_3$ chemisorption on stoichiometric and oxygen-deficient $SnO_2$(110) surfaces, surface science, (2002) 65−77.

[9] R.M. Yuan, G. Fu, X. Xu, H.L. Wan, Mechanisms for Selective Catalytic Oxidation of Ammonia over Vanadium Oxides, Journal of Physical Chemistry C, (2011) 21218−21229.

[10] D.J. Cheng, J.H. Lan, D.P. Cao, W.C. Wang, Adsorption and dissociation of ammonia on clean and metal-covered $TiO_2$ rutile (110) surface: A comparative DFT study, Applied Catalysis B: Environmental, (2011) 510−519.

[11] J. Perez-Ramirez, N. Lopez, E.V. Kondratenko, Pressure and materials effects on the selectivity of $RuO_2$ in $NH_3$ oxidation, J. Phys. Chem. C, 114 (2010) 16660.

[12] I. Onal, S. Soyer, S. Senkan, Adsorption of water and ammonia on $TiO_2$-anatase cluster models, Surf. Sci., (2006) 2457−2469.

[13] Q.Z. Yuan, Y.P. Zhao, L.M. Li, T.H. Wang, Ab Initio Study of $ZnO_2$ Based Gas Sensing Mechanisms: Surface Reconstruction and Charge Transfer, J. Phys. Chem. C, (2009) 6107−6113.

[14] A. Gurlo, Interplay between $O_2$ and $SnO_2$: Oxygen Ionosorption and Spectroscoic Evidence for Adsorbed Oxygen, CHemPhysChem, 7 (2006) 2041− 2052.

[15] T. Sahm, A. Gurlo, N. Barsan, U. Weimar, Basics of oxygen and $SnO_2$ interaction: work function change and conductivity measurements, Sens. Actuators: B, 118 (2006).

[16] J. Oviedo, M.J. Gillan, First-principles study of the interaction of oxygen with the $SnO_2$ (110) surface, Surf. Sci., (2001) 221−236.

[17] W. Wei, Y. Dai, B.B. Huang, Role of Cu Doping in $SnO_2$ Sensing Properties Toward $H_2S$, J. Phys. Chem. C, 115 (2011) 18597−18602.

[18] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Physics review B, 47 (1993) 558.

[19] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review B, 54 (1996) 11169-11186.

[20] J.A. White, D.M. Bird, Implementation of gradient-corrected exchange-correlation potentials in Car-Parrinello total-energy calculations, Physical Review B, 50 (1994) 4954-4957.

[21] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Physical Review B, 59 (1999) 1758-1775.

[22] B. Hammer, L.B. Hansen, J.K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, Physical Review B, 59 (1999) 7413-7421.

[23] N. Lopez, J.D. Prades, F.H. Ramirez, J.R. Morante, S. Mathur, Bidimentional versus tridimentional oxygen vacancy diffusion in $SnO_{2-x}$ under different gas environments, Phys. Chem. Chem. Phys., 12 (2010) 2401.