

# Towards an electronic nose based on nano-structured transition metal oxides activated by a tuneable UV light source

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**Abstract**—Traditional gas sensors involve heating the sensor material for gas selectivity. New gas approaches require activation by a broadband UV light source. We propose to employ a tuneable UV source in which this source is tuned for its many wavelengths via a grating and associated optics and transducers. The theory of UV activated gas sensing is presented and the first calculated sensitivity spectrum is discussed in term of the energy balance among the many channels of energy loss when the light interacts with the sensing nano-structure's surface. Experiments to validate the calculations are on-going and some preliminary results are presented.

**Keywords:** UV activation, nanowire, sensor spectrometer

## *Introduction*

Gas sensors become more efficient in sensitivity and selectivity as the sensing materials are reduced in their dimensions down to the nano-scale [1-7]. The sensitivity of a sensor material to a particular gas is defined as  $S = (\chi - \chi_0) / \chi_0$  or simply  $S = \chi / \chi_0$  where  $\chi$  and  $\chi_0$  are resistances or conductances in the presence and absence, respectively, of the test gas (when the sensor material is biased as a two terminal device) or are trans-conductance and/or gain when the materials is biased as a transistor.

The selectivity of the sensor is traditionally accomplished through heating the sensor material and determining the sensitivity as a function of temperature. The sensor material responds differently to different gases at different temperature. A plot of sensitivity versus temperature normally gives out what we could call a selectivity spectrum in temperature. Powering of sensors by thermal means can be expensive as it involves heating up the sensing materials to have the sensor running [8-20]. Applying electrical contacts to such small

structures has been a global challenge in the micro-electronics world [5], let alone the complex electronic behavior of such structures at the nano-scale [21-26]. Literature on nano-wire-based sensors suggests that very few reports exist on single nanostructure sensors [5, 27-30].

UV activation has been proposed as the cheaper route to running gas sensors. Currently, most reported work on UV activated sensors involve a wide band of wavelengths impinging on an ensemble of nano-structured or thin films of sensor material. However, the many individual lines of wavelengths in a typical UV source such as a tungsten lamp could be isolated to interact with an individual nano-wire sensor.

We first show theoretically how gas sensing by a material activated by photons can be accomplished via the Hamiltonian of the sensor-gas-photon system and the ensuing solutions to the Schrodinger equation to obtain the energy levels that the conduction electrons are allowed to take in this system. The drift velocities of the electrons in the sensor material are affected by the presence or absence of the sensed gas.

## I. THEORY OF GAS SENSING BY A SINGLE NANOWIRE

### A. *Scattering of Electrons in a One-Dimension Channel and the Current-Voltage Characteristics*

Grabert [31] has considered transport of non-interacting electrons in a one-dimensional channel which are also scattered by some defects on their trajectories. This description can be applied to electrons in a single nanowire gas sensing device in which electron motion is modulated by the presence or absence of gas molecules on the nanowire surface. Understanding of the interactions through *ab initio*

calculations on sensors is hampered by the many inevitable approximations since full solutions lead to unsolvable Schrodinger differential equation as we show.

### B. Electron Motion in $MO_x$ Under Photon Excitation and in Presence of a Gas Molecule

An electron in a hydrogenic atom or ion can occupy any of the  $|nlsjm\rangle$  eigen states of the Hamiltonian of the atom or ion. In ions or atoms with more than one electron, the solutions of the time independent Schrödinger equations become complicated because the electrons interact not only with the positively charged nucleus, but also with each other. Particles with half-integer spin angular momentum, such as electrons, must also satisfy Pauli's exclusion principle, which forbids two such particles to occupy the same quantum state. Furthermore, the electrons in the multi-electron ion or atom are indistinguishable from one another. During the interaction of the excitation light photons with the sensor material whose atoms have  $n$  electrons in absence of the sensed gas molecules, a photon of wavelength  $\lambda$  interacts differently with each electron. Each interaction yields a Hamiltonian  $H_{atom}$  on the  $i^{\text{th}}$  electron of a wavefunction  $\psi_i$ . On a single  $n$ -electron atom, one can then write the Hamiltonian as [32]

$$H_{atom} = \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right] + \sum_{i,j=1}^N \frac{e^2}{r_{ij}} \quad (3)$$

For oxides such as  $MO_x$ , each molecule has two types of atoms, hence the Hamiltonian changes to  $H_{molecule} = H_{oxygen} + H_{metal}$ . In the presence of the sensed gas molecules, then the total Hamiltonian include the interactions between the sensor molecule and the sensed gas molecule. In the case of the sensing of the presence of the  $GO_x$  gas molecule, for instance, one can write:  $H_{sensor} = H_{molecule} + H_{gas} + H_{metal-gas}$ . The typical Hamiltonian is then used as an operator on the electron's wave function within the sensor material. The energy level structure as a function of the excitation photon wavelength of the photon can be thought of as the "conductivity spectrum" or photoconductivity. At the laboratory scale, one has to consider an energy balance at the time a photon interacts with the surface of the sensor material in the presence of absence of the test gas.

### C. Energy Balance Equation During UV Excitation on a Single Nanowire in the Absence of a Gas

The conservation of energy during the irradiation of a nano-wire for its gas sensing excitation, initially in the absence of the test gas, demands that the incident photon intensity be absorbed partially but the rest is spent in four major pathways as illustrated in Figure 1, viz.: the elastic Rayleigh scattering and other inelastic processes such as photoluminescence, Raman scattering and lasing, with varying probabilities for each process. We write the energy balance equation thus

$$I_i(\lambda) = I_{abs}(\lambda) + I_{Rayleigh}(\lambda) + I_{PL}(\lambda) + I_{Raman}(\lambda) + I_{laser}(\lambda) \quad (4)$$

Only one in every  $\sim 10^7$  photons are Raman scattered and the numbers for most materials are much less for photons that can

be involved in a lasing process. Thermal effects in the nano-wire are taken as negligible for the UV region in bulk materials, however, at the nano-scale materials, UV irradiation becomes important and it causes both thermal and photochemical effects. We assume that  $I_{Rayleigh}(\lambda)$  and  $I_{PL}(\lambda)$  take the form of Gaussians. The  $I_{Rayleigh}$  has its peak at a wavelength the same as the source wavelengths whereas the  $I_{PL}$  peak is centered at a characteristic wavelength intrinsic in the sensor material.  $I_{Raman}(\lambda)$  can take the form of the Richter equation for optical phonon confinement in nanostructures which was modified for one-dimensional (nano-wire, nano-rod *etc*) type of structures[24]. The PL intensity can be given converted to wavelength domain from the Planck's blackbody emission,  $I_{PL} = \int (8\pi n^2 v^2 \alpha(\nu)) / (c^2 [\exp(h\nu/k_B T) - 1]) d\nu$  as modified by Sarace et al in 1965 and reproduced by Shionoya 1998 [33].

### D. Energy Balance Equation During UV Excitation on a Single Nanowire in the Presence of a Test Gas

The intensity of photons absorbed  $I_{abs}$  is further modulated by the presence of the test gas. One can then write the equation for the useful photons used for the nano-wire excitation as follows:

$$I_{abs}(\lambda) = I_i(\lambda) - I_{Rayleigh}(\lambda) - I_{PL}(\lambda) - I_{Raman}(\lambda) - I_{test\_gas}(\lambda) \quad (5)$$

The photon-electron process is used to explain the mechanism of such modulation in the presence or absence of the test gas. A practical application of this interaction is the phenomenon called photo-chromism, a change of color of materials due to varying intensity of illumination, which  $WO_3$  is a candidate.

### E. Derivation of the Sensitivity and Selectivity Spectra

A fraction  $\alpha$  of the photons absorbed by the nano-wire are used in the electron conduction process or photoconductivity and the rest i.e.  $(1-\alpha)$  are spent on interaction with phonons. By assuming thermal conduction and convection components are negligible at the nano-scale, the latter fraction is dissipated as heat predominantly through thermal emission thus

$$(1-\alpha)I_{abs} = \epsilon \sigma_{SB} (T^4 - T_0^4) \quad (6)$$

where  $\epsilon$  is the emissivity of the nano-wire,  $\sigma_{SB}$  is the Stefan – Boltzmann's constant and  $T_0$  is the temperature of the

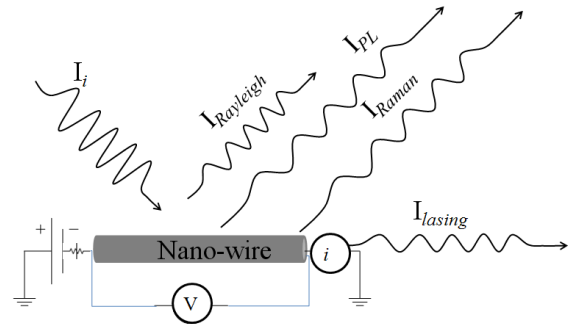


Figure 1. Schematic of energy conservation during the UV excitation of a nanowire in circuit

surrounding before the nano-wire excitation. Since the nano-wire is made of semiconducting oxides, its resistance  $R$  in the absence of the test gas is given by  $R = R_0 \exp(-E_a/k_B T)$  where  $E_a$  is the activation energy and  $R_0$  is the resistance of the nano-wire at ambient temperature. In the presence of the test gas the equation changes to:  $R_{\text{gas}} = R_0^{\text{gas}} \exp(-E_a^{\text{gas}}/k_B T)$ . The sensitivity then becomes

$$S(T) = \frac{R_0^{\text{gas}}}{R_0} \exp\left(\frac{E_a - E_0^{\text{gas}}}{k_B T}\right) \quad (7)$$

By substituting Eq. 6 into Eq. 5 one can transform the  $S(T)$  into  $S(\lambda)$  as follows:

$$S(\lambda) = \frac{R_0^{\text{gas}}}{R_0} \exp\left(\frac{E_a - E_0^{\text{gas}}}{k_B \left[ (\epsilon \sigma_{SB})^{-1} (1 - \alpha) I_{\text{abs}}(\lambda) + T_0^4 \right]^{1/4}}\right) \quad (8)$$

$I_{\text{abs}}(\lambda)$  (refer to Eq. 5) has  $I_i$  and  $I_{\text{Rayleigh}}$  terms common to all sensor and test gas materials but  $I_{\text{PL}}$  and  $I_{\text{Raman}}$  vary from sensor material to another and also  $I_{\text{test-gas}}$  varies from test gas to another. The plot of  $S(\lambda)$  therefore is expected to be unique to each sensor material as well as each test gas and therefore should be able to mimic the experimental data.

## II. EXPERIMENTAL

The calculated spectrum of Eq. 8 was undertaken in Mathematica software. The parameters used to obtain the spectrum are as follows:  $\lambda_{\text{source}} = 300$  nm,  $\lambda_{\text{gas1}} = 320$  nm,  $\lambda_{\text{gas2}} = 350$  nm,  $\lambda_{\text{PL}} = 380$  nm,  $\lambda_{\text{Raman1}} = 12500$  nm and  $\lambda_{\text{Raman2}} = 14300$  nm. Each peak or trough has a standard deviation of 10 nm.

### A. Electrical Contacts to a Single Nanowire by FIB-SEM Technique

An aliquot of  $\text{WO}_3$  nanowire powder was suspended in 5 ml of isopropanol and agitated under ultrasound waves for 5 min. A drop of such a suspension was placed on a clean Corning glass substrate. Morphology studies as well as evaporation of Pt contacts to the ends of one isolated nanowire were conducted in a Carl Zeiss FIB-SEM.

### B. Temporal Resistance and Current-Voltage Characteristics Under UV Excitation

The two terminal device was placed under UV illumination in air to test if the contacts were reliably existent. A Keithley semiconductor characterization system (SCS) loaded with KITE software was employed in the measurement of resistance in time as well in current-voltage sweep setting.

## III. RESULTS AND DISCUSSION

A plot of the calculated sensitivity of the nanowire in the presence of a gas versus the excitation wavelength from the light source [from Equation 8] is given in Figure 2. The calculation shows that the wire becomes less resistive when

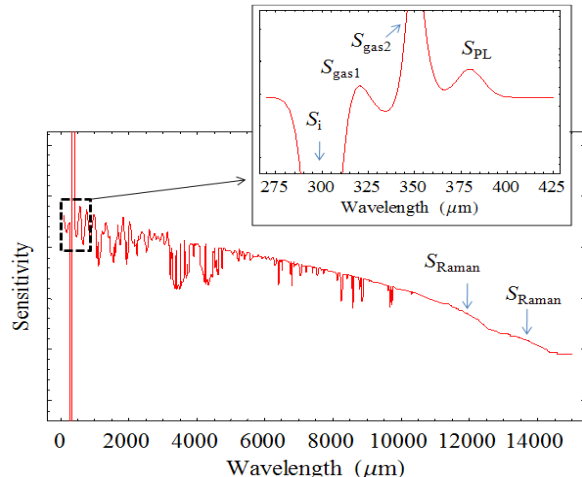


Figure 2. Sensitivity spectrum calculated from Eq. 8 with  $\lambda_{\text{source}} = 300$  nm,  $\lambda_{\text{gas1}} = 320$  nm,  $\lambda_{\text{gas2}} = 350$  nm,  $\lambda_{\text{PL}} = 380$  nm,  $\lambda_{\text{Raman1}} = 12500$  nm and  $\lambda_{\text{Raman2}} = 14300$  nm. Each peak or trough has a standard deviation of 10 nm.

light from the source impinges on it indicated by troughs in the resistance spectrum. Energy losses due to Raman scattering and photoluminescence of the nanowire display humps in the spectrum showing the nanowire becomes more resistive after relaxing itself through light scattering and emission. More importantly, the wire becomes much more resistive when the gas in its ambience not only absorbs part of the radiation but also adsorbs onto the wire surface possibly shunting away more energy from the excited nanowire. This enhanced resistance, by improving the resolution only in the UV region, is illustrated in the inset of Figure 2. We are in the process of assigning the peaks and dimples in the spectrum between 500 nm up to 11000  $\mu\text{m}$ .

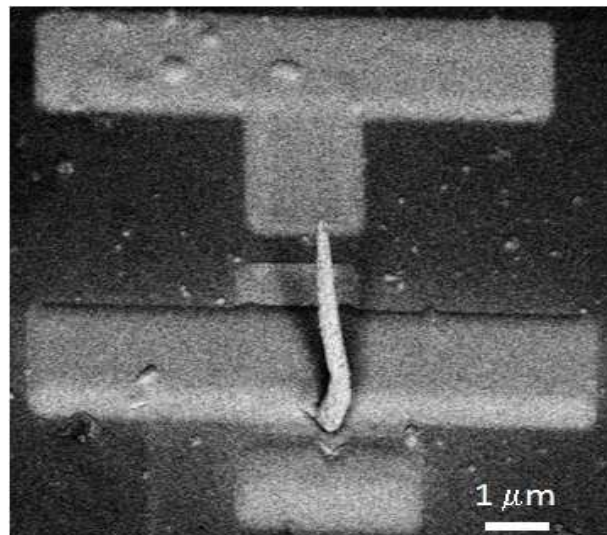


Figure 3. Pt contacts (rectangles) applied to a  $\text{WO}_3$  single nanowire placed on a glass substrate.

Work on establishing electrical (platinum) contacts to single nanowires by employing FIB-SEM has been carried and a typical image is shown in Figure 3.

#### IV. CONCLUSION, ON-GOING STUDIES AND OUTLOOK

We have shown that gas sensors can be selective to different gases by exciting them with light of different wavelengths. The energy balance leading to Eq. 8 has displayed a first sensitivity spectrum showing the possibility to sense several gases with a single sensor. Many feature on the calculated have unknown identities and these will be studied further. Contacts to a single  $\text{WO}_3$  nanowire have been accomplished. Sensitivity tests on the  $\text{WO}_3$  sensor devices to validate their sensitivity spectra in an environment of mixed gases are underway.

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