

Supplementary Information:

Photothermal Electrical Resonance Spectroscopy of Physisorbed Molecules on a Nanowire Resonator

Kovur Prashanthi*, Arindam Phani, and Thomas Thundat*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton Canada.

*E-mail: kovur@ualberta.ca and thundat@ualberta.ca

1 (a) Equivalent circuit model for the nanowire resonator

The device behaves as a typical electrical series RLC circuit as shown in Scheme 1a where its typical component values drive it to a resonance frequency of the order of tens of MHz. R_s , C_s & L_s are representations of equivalent components as measurable through the impedance analyzer. The nanowire suspends freely in air at a height of 100 nm from the substrate surface and hence the air capacitance C_{air} , as seen by the two electrodes, does not show a dominant effect in determining the resonance frequency of the equivalent circuitry. Also typical value of the substrate capacitance $C_{substrate}$ along with the contact resistances $R_c/2$ at the electrodes, exhibits a resonance frequency in the order of few KHz only, with no nanowire drawn between the electrodes. This ensures that our device response at the MHz frequency regime is that of the nanowire and not dominated by changes on the substrate or the changes in medium around it. The effective dominant dissipation change used in our study can be explained in terms of the ratio of the lost to stored energy through its frequency dependant effective complex impedance parameters. The response of the nanowire resonator recalls to mind the response of a non-ideal capacitive element following Scheme 1b where, it is well known that at SRF, the capacitive and

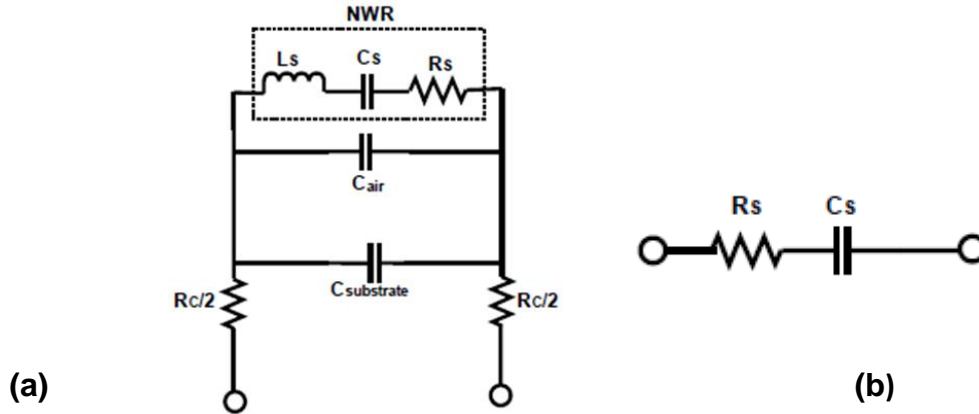
inductive reactance values become equal $\left(X_C = \frac{1}{\omega C_s} = X_L = \omega L_s \right)$ and the device becomes predominately resistive (R_s), ω being the self-resonating frequency (SRF). The inductance L_s variation, in one of the employed fabricated nanowire resonator, as a function of frequency (Figure S1a) is negligible as is evident from its response curve, conclusively implying that the reactance change of the resonator circuit tends to be dominantly capacitive. Following the same argument, the capacitance response of the nanowire resonator (Figure S1b), indeed also exhibits maximum variation at SRF justifying the series equivalent model (Scheme S1b). Evidently, in such a non-ideal capacitive element at SRF, the storage of energy per cycle is through its capacitive reactance X_C while the dissipation is through its effective frequency dependent series resistance component R_s .

The observed electrical resonance response of the employed nanowire resonator, promptly recalls the characteristics of a non-ideal capacitive element with an effective inductance in series. At the self-resonating frequency (SRF), $\omega = 2\pi f_{res}$, the capacitive reactance (X_C) and inductive reactance (X_L) exactly compensate each other $\left(X_C = \frac{1}{\omega C_s} = X_L = \omega L_s \right)$ making the device predominately resistive or dissipative. In effect, the storage of energy in such a non-ideal capacitive element at SRF is through X_C , per alternating cycle, while the dissipation is through its effective frequency dependent series resistive component R_s . R_s and X_C are representations in terms of the impedance parameters obtained from the impedance analyzer used in our study. Essentially, the ratio of the energy lost to that stored per cycle becomes a critical and sensitive

measure of the quality of resonance. This ratio, commonly referred as the dissipation or D-factor (dimensionless) is given by

$$D = \frac{R_s}{X_C} = \frac{R_s}{1/\omega C_s} = \omega R_s C_s$$

The variations of resonance characteristics of the nanowire resonator are sensitively reflected by D-factor responses when subjected to external parameter variations, in turn reflecting changes in its internal dissipation. It should be noted, that for high enough temperature changes, R_s change can be significant in metal nanowire resonator as well reflecting similar dissipation trend.



Scheme 1: Equivalent RLC circuit model for nanowire resonator (with typical RLC values; $R \sim \Omega$, $L \sim 10^{-7} H$ and $C \sim nF$)

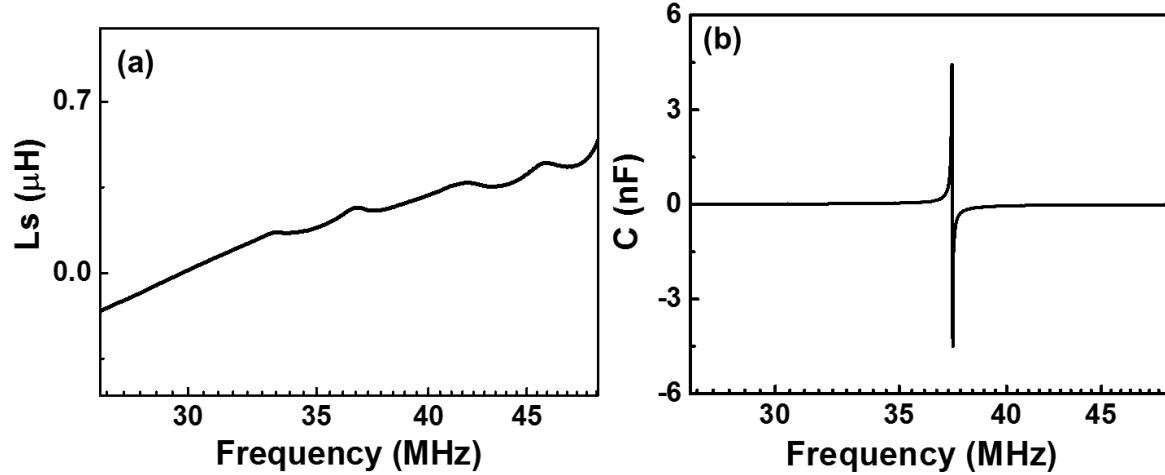


Figure S1 Variation of electrical series inductance (a) and series capacitance (b) of the nanowire resonator as a function of frequency. Variation in inductance is insignificant at resonance whereas, a clear capacitance variation is seen at resonance.

1 (b) Electrical resonance of nanowire resonators

Electrical resonance measurements have been performed on nanowire resonators in a wide range of frequencies (ranging from 20-50 MHz). The resonances for different nanowire designs measured at room temperature are presented in Figure S2a. The resonance frequencies of nanowire resonators exhibit a decreasing trend as a function of increasing nanowire length (electrode spacing) whereas the dissipation response is just the reverse. The variation of electrical resonance frequency and dissipation of nanowire resonators as a function of the nanowire length is presented in Figure S2b. The observed variations can be attributed to the increasing capacitance (decreasing capacitive reactance (X_C)) as a function of decreasing electrode spacing which effectively is the length of the nanowire. In essence it is the predominant variation of electrical length at the nanoscale that governs the operational SRF.

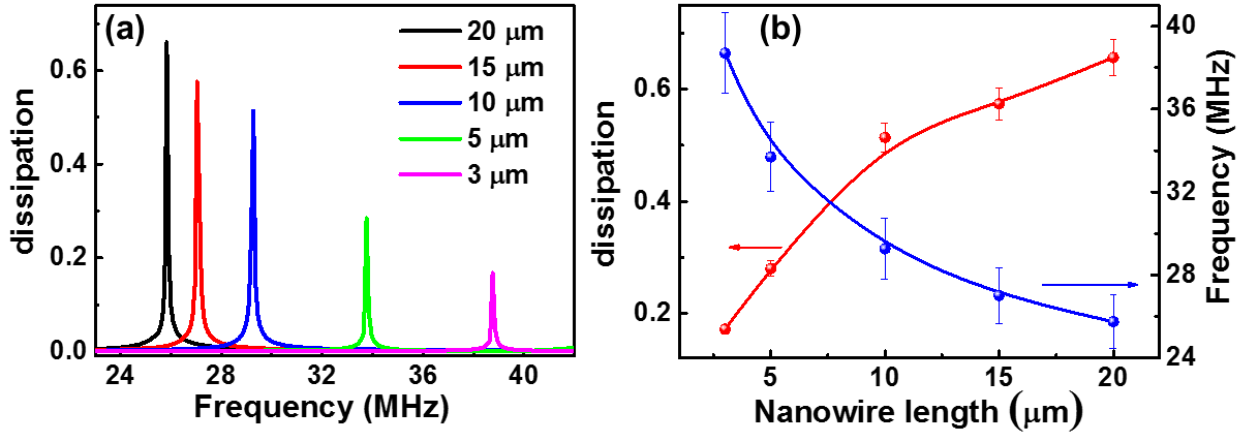


Figure S2 (a) Electrical resonance response of nanowire resonators with various lengths of nanowires. (b) Dissipation and resonance frequency response of nanowire resonators obtained for various nanowire lengths.

2. Dissipation response due to the adsorption of molecules

As discussed earlier, the effective dissipation (D) is the ratio of dissipated to stored energy per cycle

$$D = \frac{R_s}{X_c} = \frac{R_s}{T/C_s} = \frac{R_s C_s}{T} \quad (i)$$

$$T \left[T = \frac{1}{\omega} \right], \text{ being the time period of a cycle.}$$

$$\Rightarrow D_i = R_{S_i} C_{S_i} \omega_i \quad \Rightarrow \Delta C = C_{S_i} \left[\frac{D_2 \omega_1}{D_1 \omega_2} - 1 \right]$$

A quick analysis of the obtained data (Figure S3) shows an increase in effective capacitance on adsorption of RDX molecules by a factor of 1.038 following equation (i). Increase in capacitance

corresponds to an effective decrease in capacitive reactance which leads to reduced storage of energy per cycle of response thus leading to a higher dissipation at its SRF as also clear from equation (i) above. The shift in SRF on adsorption may be attributed to the effective complex variation in resonator elements (dominant real part variation of complex permittivity), This observed response agrees to an earlier report where it was envisaged that the dissipation variations can be a useful indicator of the change in dipole-dipole interactions caused by the adsorption of a volatile chemical onto the polymer film employed in the study^{S1}. They related the higher dissipation at the device's SRF to the maximum efficient transfer of energy at the natural resonance frequency of molecules binding to the polymer. Such efficient energy transfer was conclusively associated to lower energy storage at SRF in their developed sensor system.

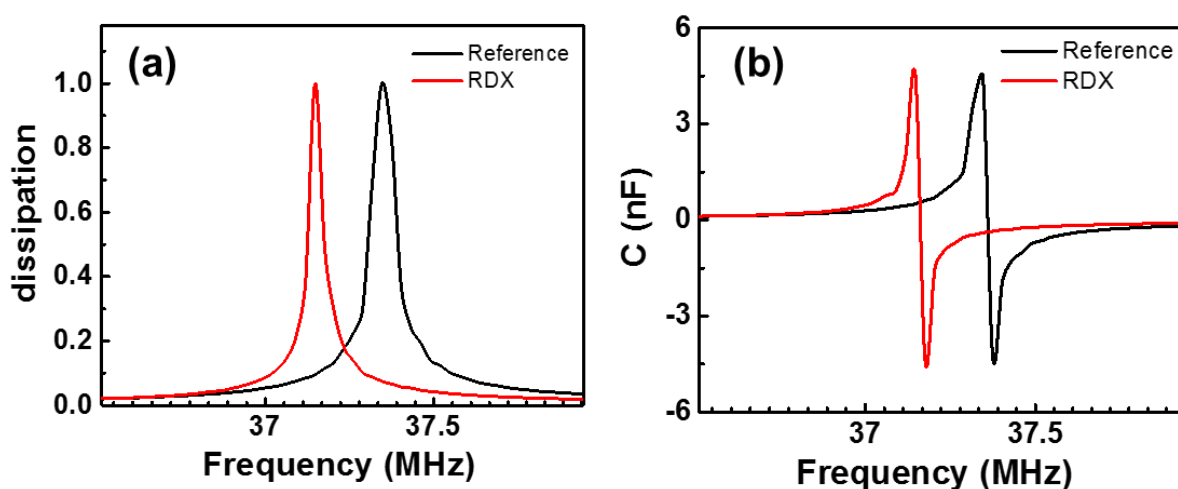


Figure S3: Variation in dissipation (a) & capacitance (b) obtained for the nanowire resonator without and with RDX molecules. The order of shift is in KHz to even minute quantities of adsorbates of the order of fg .

3. Adsorbed RDX mass calculation

a) From electrical resonance of the nanowire resonator

From the dynamic impedance parameter variations using equation (i),

$$\Delta C = 0.038 \times 4.48 nF$$

$$\Delta Q = \Delta C \times V = 8.512 \times 10^{-12} C$$

Now charge of an electron is $e^- = 1.602 \times 10^{-19} C$

Therefore, Number of electrons $N_e = \frac{\Delta Q}{e^-} = 5.3134 \times 10^7$

Now charge contribution per atom from individual sites of H₁ H₂ and N₂ in RDX = $0.84e^-$.

There are 3 such sites in a RDX molecule^{S2}.

Hence the number of atoms taking part in charge change

$$N_{atoms,RDX} = \frac{N_e}{3 \times 0.84} = 2.1085 \times 10^7$$

Therefore, weight of RDX can be calculated as

$$\begin{aligned} W_{RDX} &= \frac{N_{atoms,RDX}}{AvogNo.} \times MW_{RDX} \\ &= \frac{1.23 \times 10^9}{6.023 \times 10^{23}} \text{ moles} \times 222.12 \text{ gm / mole} \\ &= 7.78 \times 10^{-15} \text{ gm} \cong 10 \text{ fg} \end{aligned}$$

b) From surface coverage

Typically, in monolayer coverage, it is considered that the total number of atoms in 1 cm² is about 10¹⁵ atoms/cm². However, for adsorbed mass calculations, authors consider that only fraction of RDX droplet is exposed to effectively half the nanowire surface. Therefore, the fraction of half the surface area of nanowire to the total area covered by 0.4 μ l droplet on the substrate surface (as measured from the droplet stain) multiplied with concentration of RDX molecules in the solution used gives the estimated mass of adsorbed molecules.

Diameter of nanowire = 100 nm, Length of nanowire = 3 μ m

Concentration of RDX molecules: 1000 μ g/mL

Volume of droplet (RDX) = $0.4\mu L$

Hence effective mass of analyte in $0.4\mu L = 0.4\mu L \times 1\mu g / \mu L = 0.4\mu g$

Droplet diameter on surface = $2mm$ (*measured*)

Area of droplet on substrate: $\frac{\pi d^2}{4} = \frac{\pi \times (2 \times 10^{-3})^2}{4} = 3.14 \times 10^{-6} m^2$

Area of nanowire: $\pi d_{NW} l = \pi \times 100 \times 10^{-9} \times 3 \times 10^{-6} m^2$

Assuming only top surface of nanowire is covered with droplet, area exposed

$$\frac{\pi d_{NW} l}{2} = \frac{\pi \times 100 \times 10^{-9} \times 3 \times 10^{-6}}{2} = 4.712 \times 10^{-13} m^2$$

Hence the estimated adsorbed mass is $\frac{4.712 \times 10^{-13}}{3.14 \times 10^{-6}} \times 0.4 \times 10^{-6} = 60 fg$

4. The variation in dissipation due to IR absorption by molecules

The overall dissipation rise as a function of IR wavelengths (Figure S4a), on absorption by the adsorbed analyte, predominantly becomes a function of the effective series capacitance change (higher capacitance and lower capacitive reactance – dominant imaginary part variation of complex permittivity reflecting more loss) (Figure S4b). The capacitance variation is due to excited phonon relaxation induced carrier separation amplified by the higher density of surface states.

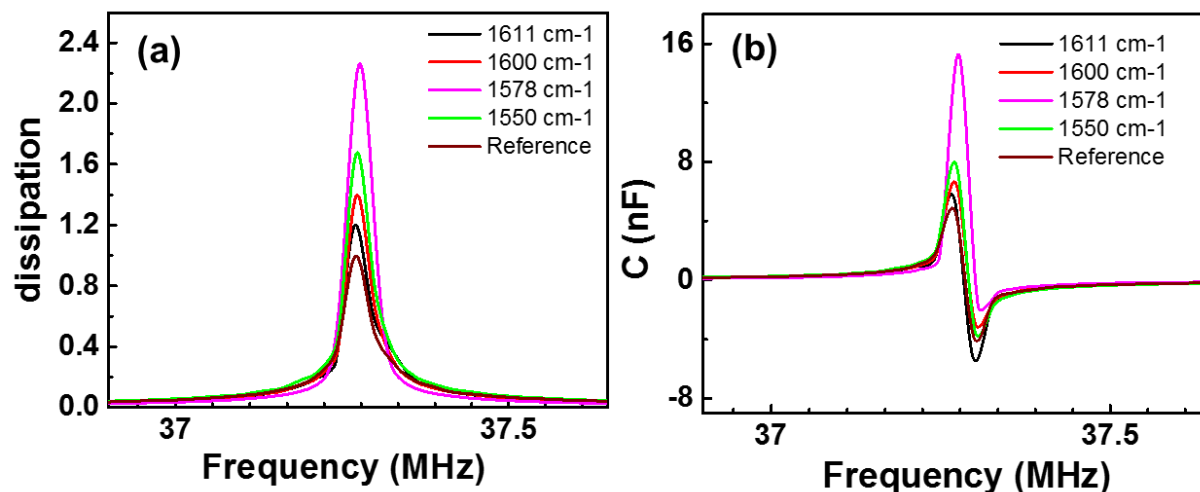


Figure S4: Variation in dissipation (a), series capacitance (b) obtained for the nanowire resonator with RDX irradiated at different IR wavelengths

References

- S1. Amrani, M. E. H., Persaud, K. C. & Payne, P. A. High-frequency measurements of conducting polymers: development of a new technique for sensing volatile chemicals. *Meas. Sci. Technol.* **6**, 1500–1507 (1999).
- S2. Ahuja, B. L., Jain, P., Sahariya, J., Heda, N. L., & Soni, P. Electronic properties of RDX and HMX: Compton scattering experiment and first-principles calculation. *J. Phys. Chem. A* **117** (27), 5685–5692 (2013).