https://prism.ucalgary.ca

The Vault

Open Theses and Dissertations

2019-05-13

# Nanoporous Microcantilevers with Plasmonic Absorbers for Photothermal Infrared Spectroscopy

Simin, Nicholas

Simin, N. (2019). Nanoporous Microcantilevers with Plasmonic Absorbers for Photothermal Infrared Spectroscopy (Master's thesis, University of Calgary, Calgary, Canada). Retrieved from https://prism.ucalgary.c http://hdl.handle.net/1880/110343 Downloaded from PRISM Repository, University of Calgary

## UNIVERSITY OF CALGARY

Nanoporous Microcantilevers with Plasmonic Absorbers for Photothermal Infrared Spectroscopy

by

Nicholas Simin

## A THESIS

# SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

### DEGREE OF MASTER OF SCIENCE

## GRADUATE PROGRAM IN MECHANICAL ENGINEERING

## CALGARY, ALBERTA

MAY, 2019

© Nicholas Simin 2019

#### Abstract

A nanoporous anodic aluminum oxide (AAO) bimetallic cantilever enhanced by a gold coating on the nanopores creates a plasmonic crystal structure. The fabricated sensor is used for photothermal cantilever deflection spectroscopy (PCDS). Explosive compounds tested, showed spectra identifying explosive compounds by their characteristic wavelengths. Through a two-step anodization process, photolithography, and bimetallic and plasmonic coatings, a sensitive photothermal microcantilever was fabricated. The bimetallic layer thickness was optimized through analytical calculations. The ideal plasmonic layer thickness was found through experimentation. Molecules adsorbed onto the cantilever surface had their mass quantified through a measured change in 2nd mode resonant frequency. Simultaneously, the molecules were identified by high power infrared (IR) spectroscopy. For standoff spectroscopy, a plasmonic enhanced AAO cantilever was shown to improve characteristic peak depth 10-fold and 7-fold compared to silicon and AAO bimetallic cantilevers, respectively. The limit of detection (LOD) of the plasmonic AAO cantilever was determined to be 63.42 ng/cm<sup>2</sup>.

*Keywords:* nanoporous, AAO, plasmonic, PCDS, explosives, standoff spectroscopy

## Preface

This thesis is original, unpublished, independent work by the author, N. Simin.

#### Acknowledgements

During my master's degree I have had the support from many people inside and outside of the University of Calgary. With their expert help, given every step of the way, I could not have done this work without them. For this I would like to give thanks.

I would like to acknowledge the help of my supervisor Seonghwan (Sam) Kim. He was the one who introduced me to this area of research and shared with me his experience to get me started. Along with the guidance, he provided me with the independence that allowed my curiosities to conduct my research. This includes the once in a lifetime opportunity to participate in a research exchange at Sogang University in Seoul, South Korea.

I would like to thank my colleagues in the Nano/Micro-Sensors and Sensing Systems (NMSSS) lab. All of whom were always willing to give a helping hand and be there to bounce ideas off. With the variety of perspectives and constant encouragement, they made my MSc experience fuller.

During my trip to Seoul, South Korea I had the chance to work with Dr. Jungchul Lee and his research group. I would like to show gratitude to them for welcoming me into their lab and helping me explore new venues for my research. I also got to meet Dr. Dongkyu Lee who shared his valuable experience on my research topic; getting me over key hurdles in my fabrication process. All of this provided me with an important and enjoyable experience in academia.

Abstract	ii
Preface	iii
Acknowledgements	iv
Table of Contents	v
List of Tables	vii
List of Illustrations, Figures, & Graphics	viii
List of Symbols, Abbreviations and Nomenclature	xi
Chapter 1. Introduction	1
11 Counter Tomoniam	1
1.1 Counter Terrorisin	
1.2 Chemical Sensors	J
1.2.1 Conductivity sensors	4
1.2.2 Optical sensors	
1.2.3 Piezoelectric sensors	
1.2.4 Microcantilever sensors	0
1.3 Vibrational Spectroscopy	9
1.3.1 Fourier transform infrared spectroscopy	10
1.3.2 Non-dispersive infrared spectroscopy	11
1.3.3 Raman spectroscopy	12
1.3.4 Photoacoustic spectroscopy	12
<b>1.3.5</b> Photothermal cantilever deflection spectroscopy	13
Chapter 2: Nanoporous enhanced PCDS	17
2.1 Microcantilever	19
2.1.1 Thermal time constant	19
2.1.2 Adsorbed mass	21
2.1.3 Porosity	
2.1.4 Bimetallic optimization	23
2.2 PCDS	
2.2.1 Pulses	
2.2.2 Quantum cascade laser	
2.2.3 Position sensitive detector	
2.2.4 Plasmonic enhancement	
2.2.4.1 Optimization of plasmonic layer	33
2.2.5 Quartz crystal microbalance	
Chapter 3: Fabrication and Experimental Setup	36
3.1 Materials and Equipment for AAO Microcantilever Fabrication	36
3.1.1 Self-ordering anodization	
3.1.2 Pore widening	
3.1.3 Patterning cantilevers	40
3.1.4 Cantilever releasing	41
3.2 PCDS Setup	46
Chapter 4: Results and Discussion	53

## **Table of Contents**

Chapter 5: Conclusions and Future Work	
References	69
Appendix	77

## List of Tables

Table 1.1: Spectroscopy method comparison table.	14
Table 2.1: Material properties of materials considered for microcantilever fabrication.	18

# List of Illustrations, Figures, & Graphics

Figure 1.1: Number of terrorist incidents by year as tabulated by the Global Terrorism Database as of 2018. Shows an increase in terrorist activity and a peak in 2014. From [1]
Figure 1.2: Optical lever technique used to determine cantilever deflection. A laser is incident on the tip of the cantilever. The laser is reflected at an angle dependent on the deflection of the cantilever. The angle of reflection is picked up by a PSD
Figure 2.1: Cantilever deflection over time as a response to modulating incident IR light at a frequency of 20 Hz
Figure 2.2: Consecutive baseline spectra for one hour taken at 20 Hz (red) and 5 Hz (black) modulation frequency. Increased amplitude and noise at 5 Hz are shown
Figure 2.3: Natural frequency of a porous microcantilever taken by a laser doppler vibrometer. Shows 1 <sup>st</sup> and 2 <sup>nd</sup> mode frequency at 3.97 kHz and 23.5 kHz respectively 22
Figure 2.4: Deflection to power ratio with respect to gold bimetallic layer thickness when varying only one value. Left and right show an increase in peak amplitude as cantilever thickness decreases and length increases, respectively
Figure 2.5: Deflection to power ratio with respect to gold bimetallic layer thickness when varying only one value. Left and right show an increase in peak amplitude as cantilever material thermal conductivity and thermal expansion decreases, respectively
Figure 2.6: Deflection to power ratio with respect to gold bimetallic layer thickness. Left shows the effect Young's modulus has on the deflection to power ratio. Decreasing Young's modulus increases peak amplitude. Right, plots the lowest and highest AAO and TiO <sub>2</sub> values from Table 2.1 to give a range of cantilever thermomechanical sensitivities. AAO and TiO <sub>2</sub> have comparable sensitivity ranges
Figure 2.7: QCL power with respect to wavenumber
Figure 2.8: Schematic of a 2-D linear PSD
Figure 2.9: AAO nanowells being coated with gold resulting in a variety of aggregated particle sizes. Image from [62]
Figure 3.1: Procedure for fabricating AAO cantilevers from bulk aluminum substrate
Figure 3.2: AAO nanowells at various stages of pore widening. Top left, top right, bottom left, and bottom right show 30, 45, 50, and 75 nm pore diameter respectively
Figure 3.3: Released cantilevers with width of 90 $\mu$ m, overhang of 100 $\mu$ m, thickness of 2 $\mu$ m, and lengths ranging from 200 – 550 $\mu$ m. Overhang is the distance from where the

cantilever shape meets the AAO chip to the dark line where the underneath aluminum is in contact with the AAO chip
Figure 3.4: Deflection to power ratio of fabricated AAO cantilever with respect to gold bimetallic layer thickness
Figure 3.5: Optical lever setup showing geometry, reflected angle, and change in reflected angle when deflected. These values were used to determine a deflection value
Figure 3.6: Schematic of point sensing PCDS setup. Readouts display frequency response function showing resonant frequency of the cantilever and the nanomechanical IR spectrum.
Figure 3.7: Photograph of point sensing PCDS setup. Optical lever technique and QCL laser paths are drawn in
Figure 3.8: Schematic of standoff sensing PCDS setup. Readout displays IR spectrum of cantilever and QCM reads out frequency shifts that correlates to deposited mass concentration
Figure 3.9: Photograph of standoff sensing PCDS setup. Optical lever technique and QCL laser paths are drawn in
Figure 4.1: Shows differential absorption spectrum of PETN, RDX, and TNT from a bimetallic AAO cantilever
Figure 4.2: Baseline spectrum of bimetallic AAO cantilever with increasing plasmonic layer thickness. Plasmonic enhancement occurs over the wavenumber range of 1710 – 1930 cm <sup>-1</sup> with the optimum thickness being 17 nm
Figure 4.3: Baseline spectra of bimetallic AAO cantilever with increasing plasmonic layer thickness and added bimetallic layer thickness. An increase in amplitude from 33 nm to 50 nm plasmonic layer was seen. This also shows that the 67 nm plasmonic layer cantilever was benefitted by increasing its bimetallic layer thickness to 125 nm
Figure 4.4: Baseline spectra when varying the incident angle, the IR light made with the cantilever surface. A decrease in amplitude was seen. The spectrum shape and peak position were unaffected
Figure 4.5: Differential PETN mass normalized absorption spectra (left) and recorded peak intensity at 1275 cm <sup>-1</sup> (right). As plasmonic layer is added, mass normalized peak intensity decreased but always remained positive
Figure 4.6: Differential transmission spectra of PETN (top left), RDX (top right), and TNT (bottom left and right) from a silicon cantilever, a bimetallic AAO, and an AAO cantilever with a 17 nm plasmonic layer. It is seen that the bimetallic AAO cantilever has the deepest peaks outside of the 1710 – 1930 cm <sup>-1</sup> range. On TNT between 1750 –

1930 cm <sup>-1</sup> (bottom right) an improvement factor on peak intensity of 10 and 7 from the silicon and bimetallic AAO cantilevers, respectively, were seen	61
Figure 4.7: Baseline compared to TNT spectrum for bimetallic AAO (left) and the 17 nm plasmonic AAO (right). This shows the amplitude increased from 90 mV to 180 mV (a factor of two) by adding the plasmonic layer.	62
Figure 4.8: Differential transmission spectra of TNT from an AAO cantilever with 17 nm plasmonic layer at various surface concentrations. As the surface concentration increased, the spectrum peak intensities increased.	63
Figure 4.9: TNT spectra of plasmonic AAO cantilever at varying surface concentrations using drop casting (left). Transmission peak amplitude vs. surface concentration data that allows calculation of LOD (right). Noise equals 1.484 mV and LOD is 66.77 ng/cm <sup>2</sup> .	64
Figure 4.10: TNT transmission peak amplitude vs surface concentration using a vapor generator to coat the QCM. Noise equals 1.846 mV and LOD was calculated to be 63.42 ng/cm <sup>2</sup> .	65

## List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
AAO	Anodic aluminum oxide
PCDS	Photothermal cantilever deflection spectroscopy
IR	Infrared
NMSSS	Nano/micro-sensors and sensing systems
IED	Improvised explosive device
MEMS	Micro-electro-mechanical systems
LOD	Limit of detection
TMA	Trimethylamine
ZnO	Zinc oxide
PSD	Position sensitive detector
NDIR	Non-dispersive infrared
FTIR	Fourier transform infrared
PAS	Photo acoustic spectroscopy
CO <sub>2</sub>	Carbon dioxide
VOC	Volatile organic compound
QCL	Quantum cascade laser
SPP	Surface plasmon polariton
IFFAEM	Instrumentation facility for analytical electron
	microscopy
DI	Deionized
TL	Transfer layer

FFT	Fast Fourier transform
QCM	Quartz crystal microbalance
PETN	Pentaerythritol tetranitrate
TNT	1:1:1 of trinitrotoluene
RDX	Cyclotrimethylene trinitramine
DAQ	Data acquisition
ppb	Parts per billion
SNR	Signal to noise ratio
AC	Alternating current
EM	Electromagnetic radiation
ТАТР	Triacetone triperoxide
TiO <sub>2</sub>	Titanium dioxide
RAIRS	Reflection absorption infrared spectroscopy
МСТ	Mercury cadmium telluride
ND:YAG	Neodymium-doped yttrium aluminum garnet
μ	Micro
°C	Degree Celsius
λ	Thermal conductivity
α	Linear thermal expansion
$\beta_n$	N <sup>th</sup> mode eigenvalue
$\Delta \mathbf{x}$	Change in "x" quantity
ρ	Density

#### **Chapter 1: Introduction**

This section discusses a brief introduction to the topics in this thesis. It will include information that is relevant to understanding the background and reason for this research. As well as explaining reasons for pursuing the chosen field of research.

#### **1.1 Counter Terrorism**

Counter Terrorism via improvised explosive devices (IEDs) have gradually become a larger concern of governments and the public. This is partially due to information on creating such devices being easier to obtain over the internet. Terrorism hit a high in 2014 resulting in 44,490 deaths and \$105.6 billion in economic cost, Figure 1.1 [1]. The ability to detect such IEDs is only becoming more sought after as incentives continue to accumulate [2] [3]. Explosive compounds are difficult to detect because of relatively low vapor pressures. This results in the molecules readily sticking to surfaces instead of staying suspended in the air. A problem is created for currently used methods such as sniffer dogs that rely on the explosives being present in vapor state. Another commonly used explosive detection technology is the "swab test". A clean wipe is swiped on a surface to pick up any explosive residues and analyzed using an ion mobility spectrometer (IMS). This technique works well on low vapor pressure compounds, showing the ability to detect explosives at 30 picogram [4]. However, a drawback is that it requires contact. The objective of this research is to design a sensor capable of identifying low vapor pressure explosive compounds without requiring contact to the inspected surface.

A reliable method of detection would be required to be both selective and sensitive. With such a measurement tool, it could greatly reduce the chance of undetected explosives getting into airports, parliament buildings, or crowded stadiums. However, with so many areas of interest, the sensor

would also be required to be inexpensive to produce. In utilizing the mass production capability of micro-electro-mechanical systems (MEMS), this could be achieved.





Explosives detection is usually performed one of two ways. By collecting a sample that has trace amounts of explosives and testing the molecules within the sensor setup. This is known as point sensing. Or, explosives may be sensed by standoff detection. This is identifying residue on a target surface at some distance from the sensing setup. Both circumstances were tested using the sensor designed and fabricated within this research.

Sensing explosives in either a point sensing or standoff sensing regime, requires recognition of the explosive makeup. This is done in two main ways. A sensor can either directly interact with the explosive's molecular structure to collect the chemical information. Or, photons can be made to

interact with the explosive then the sensor detects the photons. Both sensor types will be discussed in the following sections.

#### **1.2 Chemical Sensors**

The premise of a chemical sensor is to take chemical information and convert it into a readable signal [5]. This can be generalized into a receptor transducer pairing. The receptor collects the data and the transducer transmutes the chemical information to a readout [6] [7]. Receptors can be designed to detect a specific chemical and combined into an array for robust sensing [8]. Unspecialized receptors have the advantage of not requiring an array, however they may adsorb undesired compounds. For unspecialized receptors, a photon-based intermediator step must be included for specific compound identification. Here, the photon's interaction with the compound picks up the chemical data and then transfers that data to a photon sensitive detector. Whichever transducer is used, the readouts may also vary between electrical, optical, dynamic, or static. In the following sections I will discuss some of these receptor/transducer pairings.

In the practice of analyzing sensors, there are specific characteristics that measure performance. Limit of detection (LOD) refers to the lowest amount of compound, vapor or solid, that can be sensed. It is based on a statistically significant change in signal compared to the background noise. A signal to noise ratio (SNR) of three is commonly used as the detection limit. Values of this may be denoted in mass, surface concentration, or parts per sample size, ie. parts per billion (ppb). Another characteristic, sensitivity, refers to the amount of change in a signal compared to the change in the amount of the target substance [9]. This is commonly seen in values specifying signal amplitude over analyte amount (V/ng, V/ppb, etc.). Selectivity is the sensors ability to identify between which compounds are being sensed [10]. Limit of recognition is the minimum ratio of target molecules to others present molecules that can still be reliably identified [11]. Stability is the sensor's performance over time. Characteristics like sensitivity and selectivity should not significantly change over time for a reliable sensor [6]. Other performance parameters such as resolution, response time, portability, and regeneration can also be important in characterizing sensors.

#### **1.2.1 Conductivity sensors**

Conductivity sensors utilize a shift in conductivity brought on by target vapor analytes [12]. Polymer based conductivity sensors utilize a conductive polymer that changes volume when vapors are absorbed. The increased volume of the polymer severs electrical connections raising the resistance [13]. An advantage of this type of sensor is that choosing different conducting polymers selects which vapors the sensor will interact with. More advantages are how easy electrical readouts are to work with and the low-cost of polymers. Polymers can be set into an array for multiple compound sensing. However, not all compounds absorb well into polymers. For example, organic compounds like trimethylamine (TMA) are not absorbed well [14]. Also, polymers' inherent instability due to degradation causes an issue for building a reliable sensor.

The main reason for not choosing a conductivity sensor for this research is in the limitations in identifying a variety of compounds. A conductivity sensor is designed to sense a single compound or group of similar compounds. The sensor's ability to detect a target molecule is based on the increased affinity that molecule has to the sensor. It does not become easy to build a conductivity-based setup that can sense a variety of explosive species.

#### **1.2.2 Optical sensors**

Optical sensors have the benefit of a compact size and relatively fast response time, less than 10 seconds. However, the complexity of the color quantification software required for quantitative analysis leads to high operation costs. Also, high fabrication cost mixed with short lifetime due to easy saturation make marketing such sensors difficult. Nonetheless, research has been done to use fluorescent dye that changes color on contact with target molecules. Optical sensors tend to have a short lifetime due to photochemical quenching of the dye. However, the dye may be coated onto optical fibers and surrounded by polymer matrix to increase lifetime [15]. The principle is that the incident vapor molecules change the polarity of the dye leading to optical property changes [16]. Such properties include intensity, spectrum, and wavelength. These changes are quantified by optical software and converted into a target molecule concentration measurement. Alumina has been combined with optical sensors by coating them onto the fluorescent polymer matrix to increase adsorption of the target compounds to increase sensitivity [17]. However, metal oxides like alumina have the disadvantage of being vulnerable to ethanol and sulphuric compounds, limiting their application [18].

Similar to the reason for not choosing a conductivity sensor, optical sensor's ability to identify varieties of compounds is limited. Optical sensors also require the compounds being sensed to come into direct contact with the sensor. The objective of this research is to build a sensor that is capable of sensing at a distance. An important ability when dealing with dangerous explosives.

#### **1.2.3 Piezoelectric sensors**

Piezoelectric sensors measure adsorbed molecules on their surface through a shift in their resonant frequency [12]. By driving the piezoelectric with an alternating current (AC) voltage, the resonant

frequency can be found [18]. Adding mass to a vibrating body lowers its resonant frequency [12]. Actuating the device as you subject the surface to analytes, you can calculate the amount of added mass by the resonant frequency drop. A quartz crystal microbalance (QCM) is used as the standoff target in this research. It has explosives deposited onto the surface and accurately measures surface concentrations down to tens of nanograms per centimeter squared. The main disadvantage to this technology is that the frequency will shift indistinct of which molecule lands on the surface. Much research is being done to functionalize the surface by adding a layer of selective molecules to increase the selectivity of this method. Also, this method has a low response time (less than 10 seconds) [19]. However, in ambient conditions this still makes detecting a variety of molecules selectively, difficult. To improve a piezoelectric sensor's ability to collect chemical information for identification, one was designed to also be a photon detector. A. Ahmed et al utilized a piezoelectric membrane that was designed to react sensitively to photons [20]. Photons collected the chemical data and transferred it to a piezoelectric membrane that was the readout. The result was a sensor that could selectively identify chemical species.

The combination of mechanisms by A. Ahmed et al is a technique used in this thesis. However, a piezoelectric membrane was not chosen due to the rigidity of the membrane geometry. Having vibrational constraints on every side as opposed to a microcantilever's single side clamped region, the microcantilever is inherently more flexible. Instead of a membrane, the following chapters discuss a microcantilever that is made to be photosensitive to collect chemical data.

#### **1.2.4 Microcantilever sensors**

Microcantilever sensors can either use a shift in resonant frequency to determine added mass [21] [22] [23], or measure static deflection through surface stress calculations to determine adsorbed

molecules [24]. Either method uses the easily approximated cantilever stiffness through controlled dimensions and cantilever material. Fabricated cantilever stiffness is approximated in Chapter 3 using the Sader method. Microcantilevers benefit from compact size, room temperature operation, reproducibility, ability to work in vapors or fluids, rapid response time, and detection sensitivity down to atto-gram mass changes [25] [26] [27] [28]. To readout the deflection of the cantilever either statically or dynamically, four main methods are employed. Figure 1.2 shows an optical readout. This method uses a red laser incident on the cantilever surface that changes the reflected angle as the cantilever deflects [29]. It is notable, a cantilever when subject to a red laser used for the optical lever technique, was measured at approximately 20°C above ambient temperature due to laser heating [30]. The red laser's reflected angle is measured using a position sensitive detector (PSD) [31]. Using basic optical and geometric tricks, the small deflection can be amplified onto the PSD giving high deflection sensitivity. Secondly, using changing capacitance to readout cantilever deflection requires a fixed electrode. Measuring the capacitance between the deflecting cantilever and the fixed electrode can work if it is not in a conductive fluid environment [24]. The piezoelectric readout requires a material such as zinc oxide (ZnO) to be coated on the surface. The piezoelectric properties of the ZnO will create a charge from the mechanical bending of the cantilever [32]. This enables a reading to be taken. Finally, a piezoresistive readout can be used. A semiconducting or metallic circuit must be built into the cantilever. The resistance of the circuit must be carefully monitored using a dc-biased Wheatstone bridge. This amplifies any slight changes in the resistance into a readable signal. Due to the resistance change of a material as it is stressed, the stress applied as the cantilever deflects is measurable [33]. This method has been proven suitable for static mode, however lacks much success with dynamic mode cantilever

deflection. Future work into the piezoresistive readout could help in miniaturizing such a system. Miniaturization is a main facet in commercializing microcantilever sensors.



Figure 0.2: Optical lever technique used to determine cantilever deflection. A laser is incident on the tip of the cantilever. The laser is reflected at an angle dependent on the deflection of the cantilever. The angle of reflection is picked up by a PSD.

Microcantilevers also have the advantage of being able to be functionalized. A cantilever may be designed to have an affinity to specific compounds. Polymers can be coated onto a cantilever surface that increases the cantilever's ability to interact with a target analyte. A. Loui et al coated

7 different polymers onto a multi array of piezoresistive microcantilevers allowing selective detection of 10 different volatile organic compounds (VOCs) [25]. Sensitivity may also be increased using functionalization. T. Thundat et al coated gelatin onto a silicon nitride microcantilever increasing its affinity to water molecules for humidity testing. A sensitivity of 55 Hz shift per relative humidity percent compared to 5 Hz per relative humidity percent when uncoated [34].

Cantilevers can be used for a wide variety of applications using a variety of techniques to enhance selectivity, sensitivity, and other important sensor qualities. Therefore, a microcantilever was chosen for the purposes of this research. The specific technique that utilizes the microcantilever in this research is spectroscopy. The spectroscopic technique collects chemical data via photons. This makes it inherently selective and capable of detecting at a distance. Paired with the sensitivity of a microcantilever, a selective and sensitive sensing setup can be created. Section 1.3 is an outline of the mechanism that make spectroscopic techniques selective in nature.

#### **1.3 Vibrational Spectroscopy**

Vibrational Spectroscopy is a category of spectroscopy that involves identifying target molecules by the vibrational modes of their molecular bonds. Chemical bonds get excited in predictable ways allowing for a chemical makeup to be determined by looking at the vibrational energy levels. The most popular way to excite the bonds for identification is electromagnetic (EM) radiation. A specific compound when excited by EM waves, will absorb certain wavelengths based on the chemical bonds in the compound. The same chemical bond may be excited in multiple modes, absorbing multiple wavelengths. A chemical "fingerprint" can be predicted for which wavelengths will be absorbed based on the chemical makeup. The selectivity limit of this technique may be set by the wavelength range of the light source used. A broadband light source enables more selective detection. In the literature, the term "molecular fingerprint region" has become known for encompassing a variety of molecular vibrational modes. This makes sensing in this range efficient at selective identification. The region is denoted by the wavelength range between 2.5  $\mu$ m and 20  $\mu$ m. Pentaerythritol tetranitrate (PETN), 1:1:1 of trinitrotoluene (TNT), and cyclotrimethylene trinitramine (RDX), ammonia nitrate, and triacetone troperoxide (TATP) are five commonly discussed materials in IED research [35]. All five have significant peaks within the molecular fingerprint region.

Vibrational spectroscopy contrasts with IMS, as used in the swab test. IMS has its own mechanism but is not discussed as it requires in situ sensing. Utilizing EM radiation in vibrational spectroscopy is key to enabling standoff detection. EM radiation based vibrational spectroscopy encompasses multiple methods. Each with their own advantages and disadvantages. For example, Non-Dispersive Infrared (NDIR) spectroscopy is designed to detect gaseous target molecules, while Raman spectroscopy can detect any state but has difficulty increasing signal amplitude.

#### **1.3.1 Fourier transform infrared spectroscopy**

Fourier Transform Infrared (FTIR) spectroscopy uses a broadband light source, a set of carefully controlled mirrors, and an infrared (IR) detector to collect data that must be analyzed by the mathematical Fourier transform method to produce a spectrum. The broadband light source is chosen to contain the range of wavelengths used to excite the target molecule's chemical bonds (700 nm to 1 mm). This light source is incident on a beam splitter that divides the light towards one stationary mirror and one carefully controlled mirror. The moving mirror changes the distance that half of the beam travels when the beams are recombined at the beam splitter. During the

recombination, there is constructive and destructive interference that produces a predictable spectrum [36]. This new beam with missing wavelengths of light is shone on the gaseous, liquid, or solid sample. Whether the light is transmitted or reflected, it is collected by a detector. Moving the mirror allows for the detector to collect data on different spectrum incident on the target. After collecting the various data, it is processed by Fourier Transform, allowing for a resultant spectrum to be plotted. This spectrum matches the broadband light source except for the wavelengths that got absorbed as vibrational energy by the target molecules. Utilizing these techniques with a reflection/absorption infrared spectroscopy (RAIRS) setup, O. Primera-Pedrozo et al. reported quantifying TNT at 160 ng/cm<sup>2</sup> [37].

#### **1.3.2** Non-dispersive infrared spectroscopy

NDIR is a simpler method than FTIR and is used solely for gaseous target molecules [38]. This involves an IR light source, a gas chamber (sometimes two for a reference spectrum), and a photon detector. The IR light travels through a gas chamber and is absorbed depending on the molecules present. If there is a refence chamber, it is filled with a non-absorptive gas such as nitrogen. Once collected by the detector, the spectrum will be missing vibrationally absorbed wavelengths. The reference spectrum allows removal of external factors allowing a spectrum that is only affected by the target molecules. J. Hildenbrand et al. showed using a quantum cascade laser (QCL) IR source and mercury cadmium telluride (MCT) detector, the explosive TATP was detected in laboratory conditions with a standoff detection limit of 5 ppm\*m [39].

#### **1.3.3 Raman spectroscopy**

Raman spectroscopy was developed around the "Raman Effect". The Raman Effect occurs when a photon incident on a molecule interacts with the electron cloud and atomic bond. This interaction results in the electron briefly taking on a higher energy virtual state. Virtual states are inherently unstable so the electron jumps "inelastically" down to a new stable state. Due to the process being inelastic, the energy of the incident photon does not equal the energy of the scattered photon. This energy change manifests itself in a frequency shift. The direction and amplitude of the shift is predictable by the polarizability of the electric dipoles involved in the interaction. This predictability allows for identification of the molecular makeup. Raman spectroscopy lends itself well to delicate samples in that the sample prep is one of the simplest. The downside is that Raman scattering occurs for one in approximately 10<sup>7</sup> photons incident on a sample [40]. Signal amplitude can become a problem. Moreover, water, carbon dioxide (CO<sub>2</sub>), and some minerals scatter photons especially weakly [41] [42] [43] [44] [45]. Despite these challenges, J. Carter et al. reported detection of explosives in concentrations of as low as 250 ppm at a standoff distance of 27 m in ambient conditions [46].

#### **1.3.4 Photoacoustic spectroscopy**

Photoacoustic (PA) spectroscopy utilizes the creation of sound waves from molecular vibrations to identify chemical compounds [47]. Photons modulated at certain frequencies can cause sound waves to form. This principle is used on discs, tuning forks, microcantilevers, and other sensors to detect nearby molecules. In a vapor phase, an acoustic chamber filled with target molecules will absorb certain wavelengths of photons more effectively than others. The absorbed photons will heat and cool the molecules at the modulation frequency creating acoustic waves. The acoustic

waves may then be recorded by a pressure sensor or other transducer [48] [49]. Conventional PA spectroscopy requires tedious sample preparation and calibration to attain quantitative results. However, to improve on this, newer methods utilizing adsorbed molecules and specifically designed cantilevers allow for multi-modal quantitative analysis [50]. Such research was done by C. W. Van Neste et al, who reported identification of explosive compounds at 0.5 to 20 meters with a LOD of 100 ng/cm<sup>2</sup> [51].

#### **1.3.5** Photothermal cantilever deflection spectroscopy

Photothermal Cantilever Deflection Spectroscopy (PCDS) takes the spectrum signal from the deflection of a cantilever that is excited by photons. Photons incident on the cantilever heat it up. By having a bimetallic cantilever, in which the coefficients of thermal expansion are different, heating of the cantilever causes deflection. When heated, one layer will expand more than the other, imposing surface stresses. These stresses bend the cantilever. The heat will dissipate both through conduction to the cantilever chip and convection to the environment. As it cools, the reverse happens. By modulating the incident photons at a modulation frequency, the cantilever will vibrate proportional to the amount of energy transferred from the photons. This deflection is then monitored by either the optical lever technique (Figure 1.2), a capacitor, a piezoelectric, or a piezoresistive circuit. Each readout allows a spectrum to be plotted [52]. Cantilevers are popular for their sensitivity, in some cases detecting picowatt energy levels [21] [53]. S. Kim et al show a 350  $\mu$ m long and 35  $\mu$ m wide bimetallic silicon cantilever identified adsorbed explosives at a LOR of <32:1 and LOD as low as 28 pg (22.86 ng/cm<sup>2</sup> cantilever surface concentration) [54].

In the same way as other IR spectroscopic techniques, target molecules absorb certain characteristic wavelengths. In point sensing, cantilevers adsorb target molecules onto their surface

where the molecules vibrational energy will be transferred to the cantilever as heat. When such a spectrum is plotted, there are positive peaks at the characteristic wavelengths. Otherwise, in standoff sensing, cantilevers can be used to detect gases or deposited chemicals at a distance by measuring the light transmitted or reflected from the target. Here, a spectrum can be plotted revealing missing wavelengths. This type of spectrum, called a negative spectrum, identifies a compound by negative peaks at the characteristic wavelengths.

A comparative table was constructed to provide an understanding of published results from a variety of techniques. This table was used to determine which technique would be used in this research.

Method	Excitation	LOD	Sensing	Detector Type
	Source		Distance	
IMS [4]	Electric field	30 pg	N/A	Ionized molecules
RAIRS [37]	Spectrometer	$160 \text{ ng/cm}^2$	Point sensed	MCT detector
	laser			
NDIR [39]	QCL	430 ppb or 5 ppm*m	~1 m	MCT detector
Raman	Nd:YAG laser	250 ppm	27 – 50 m	Telescope
spectroscopy [46]				
PAS [51]	QCL	100 ng/cm <sup>2</sup>	0.5 – 20 m	Quartz tuning fork
PCDS [54]	QCL or	28 pg or	Point sensed	Silicon bimetallic
	monochromator	22.86 ng/cm <sup>2</sup>		cantilever

Table 0.1: Spectroscopy method comparison table.

It is difficult to compare spectroscopic methods directly as there are numerous variables to consider. With so many variables changing between each test, directly comparing LOD has varied value. However, considering the tests as a whole, can bring certain insight. As one of the objectives of this research is to develop a standoff sensing setup, IMS is not pursued in this research. IMS requires target molecules to be sensed within the machine. NDIR only does sensing on vapor state samples. While many explosive compounds have a low vapor pressure, such molecules are more readily available in solid state. Raman spectroscopy is shown in Table 1.1 as the method with the longest standoff distance. However, its neodymium-doped yttrium aluminum garnet (Nd:YAG) laser produces high power (532 nm) light. The Rama paper states, "while Raman signal levels were found to increase linearly with increasing laser energy", TNT showed degradation at higher laser power densities [46]. This limits the usable laser power. The lower power, IR based, RAIRS, PAS, and PCDS examples do not have such degradation problems. The RAIRS example uses an MCT detector. In that paper, a cooling system was used to decrease MCT noise. Noise in MCT detectors increase exponentially as a function of temperature [55]. This makes expensive and difficult to handle cryogenic cooling systems required to achieve high SNR. The RAIRS and PCDS examples both are tested using point sensing and the LOD values have the same units of ng/cm<sup>2</sup>. Due to this, a direct LOD comparison holds more valid. LOD values of 160 vs 22.86 ng/cm<sup>2</sup> for RAIRS and PCDS respectively, supports the idea that cantilevers are exceedingly sensitive detectors. A specific LOD value is not aimed at, however lower values do indicate a more sensitive experimentation setup. Decreasing LOD is an indicator of overall increased detection efficiency. Due to this, RAIRS is not the topic of this research. PAS and PCDS can be quite similar. PAS has been done before using a cantilever [50]. However, PAS is limited to operating at the acoustic resonant frequency of the oscillator. As molecules adsorb onto the oscillator's surface, the resonant frequency will change. Having to make the IR pulse frequency follow the changing acoustic resonant frequency poses a challenge. PCDS however, can be operated at a range of frequencies limited by the cantilever's thermal heating and cooling rate. Since the thermal time constant of a microcantilever does not change significantly with added mass, the modulation frequency may be constant. Choosing a tuning fork as the oscillator in PAS would reduce the acoustic resonant shifting as it is less mass sensitive than a microcantilever. However, this would also reduce photon sensitivity as the mechanical response to photons would be less just as the mechanical response to added mass. For these reasons, PCDS was chosen as the sensing mechanism for this work. All the techniques that rely on an IR light source, have a positive relationship between IR power and readable signal. S. Kim et al showed an order of magnitude increase in detection sensitivity when upgrading the monochromator IR source to the more powerful QCL [54]. For this, a QCL was chosen as the IR source used in this research. Standoff explosive detection has many challenges. These include noise caused by ambient light, diffuse surfaces not reflecting IR well, standoff distance limitations based on attenuation, and the high cost of IR sources. While cantilevers cost on the scale of tens of dollars, the QCL used, encompasses much of the setup budget costing approximately \$25,000. Developments in photon detector technology would help with all these problems. That is including reducing the necessity of high power / high cost IR sources. Improvements in this sense would manifest as increased baseline amplitude. The following sections will outline the development and testing of a microcantilever designed to have enhanced photosensitive properties.

#### **Chapter 2: Nanoporous enhanced PCDS**

The use of a microcantilever with high surface area has two advantages when used for PCDS. The increased surface area enhances adsorption by target molecules and absorption by photons. Both aspects increase sensitivity. Two high surface area materials that have been used to fabricate microcantilevers for PCDS are titanium dioxide (TiO<sub>2</sub>) and anodic aluminum oxide (AAO). First, when TiO<sub>2</sub> is fabricated by a two-step anodization process, it creates a nanoporous structure. D. Lee et al showed a TiO<sub>2</sub> cantilever had a surface area increase of 2 orders of magnitude to a plain cantilever. The LOD for RDX and TNT using a UV photodegradation enhanced PCDS was determined to be 300 parts-per-quadrillion (ppq) [26]. Similarly, a two-step anodization process can be done on aluminum to create a nanoporous AAO structure. D. Lee used an AAO microcantilever to detect explosive compounds at a LOD of 70 ng/cm<sup>2</sup> [50]. Such a cantilever will be used and modified in this research to enhance its response to photons.

Porosity enhances sensitivity by reducing effective parameters such as stiffness and thermal expansion. Porosity increases surface area and allows for fabrication of a plasmonic structure to increase IR absorption. A top coating of a conductor onto the nanopores creates a dielectric/conductor interface that enables plasmonic resonance when excited by IR. This plasmonic response enhances absorption.

Choices of materials and fabrication methods have a large impact on the sensitivity of PCDS systems. The stiffness of the bimetallic materials, magnitude of difference in coefficient of thermal expansions, dimensions, surface area, and ability to absorb IR light all can alter a cantilever's spectroscopic performance. A nanoporous material was chosen as the main cantilever material to have a low effective thermal expansion and be a template for a plasmonic structure. AAO and TiO<sub>2</sub> are the two materials that were considered for this research. Table 2.1 indicates important material

properties of the considered cantilever and bimetallic layer materials. Before directly comparing the material choices, the mechanism that influence sensitivity will be discussed.

Material	Thermal	Thermal	Young's
	Expansion (x10-	Conductivity	Modulus (GPa)
	6 K-1)	(W/mK)	
AAO [56]	4.5-10.9	10-38.5	215-413
TiO <sub>2</sub> [57]	8.4-11.8	4.8-11.8	230-288
Gold [58]	14.4	301	77.2
Aluminum [59]	23.5	238	68.3

Table 0.1: Material properties of materials considered for microcantilever fabrication.

Gold and aluminum were considered as the bimetallic layer material as they both have high reflectance (~90%) to the red laser used for the optical lever technique [60]. They have relatively high thermal expansion coefficients compared to the porous cantilever materials and can create the plasmonic dielectric/conductor interface. Aluminum has the higher thermal expansion compared to gold, which would increase the thermal expansion coefficient gap. Aluminum also has a lower Young's modulus making the cantilever more flexible. However, aluminum would be subject to oxidation. Gold being a noble metal greatly increases its lifetime capability as a sensing material as no oxidation will occur. For this reason, gold was chosen as the bimetallic material.

#### 2.1 Microcantilever

Bimetallic nanoporous cantilevers require fine tuning to analytically design them for spectroscopic sensing purposes. The incident IR is pulsed to create the heating and cooling that causes deflection of the microcantilever. The pulsing frequency can be modulated to determine the ideal response [61]. The porosity of the cantilever can be increased to reduce stiffness, thermal expansion, increase surface area, and IR absorption [62]. However, there is a practical limit to the porosity for structural purposes. The thickness of the bimetallic layer also must be designed to maximize the deflection to input power ratio.

#### **2.1.1 Thermal time constant**

The thermal time constant of the cantilever refers to how quickly the cantilever can be heated and cooled to (near) full deflection. When pulsed with IR light, the cantilever responds with a deflection as illustrated in Figure 2.1. Once heated (or cooled) to a point, maximum deflection is approached, and signal amplitude can be determined. Extending the heating or cooling time will have little effect on amplitude measured but will increase noise. The thermal time constant of the cantilever chip is based on the heating from radiation, and cooling from convection and conduction.



Figure 0.1: Cantilever deflection over time as a response to modulating incident IR light at a frequency of 20 Hz.

Figure 2.1 shows the deflection response of a modulation frequency of 20 Hz. This modulation frequency is used in this thesis as it produced (near) maximum amplitude while keeping noise low. Figure 2.2 shows consecutive baseline measurements taken for one hour on a bimetallic cantilever. From the baseline spectra, measurements of noise when modulating IR at 5 Hz and 20 Hz produce standard deviations of 13.8 and 0.641 mV respectively.



Figure 0.2: Consecutive baseline spectra for one hour taken at 20 Hz (red) and 5 Hz (black) modulation frequency. Increased amplitude and noise at 5 Hz are shown.

#### 2.1.2 Adsorbed mass

To produce quantitative results, the amount of measured target molecules must be determined. To do this, the shift in resonant frequency due to added mass is analyzed. Porous microcantilevers have relatively low resonant frequencies (Figure 2.3: 3.97 kHz) due to their low stiffness. Due to that, the second mode resonant frequency (Figure 2.3: 23.5 kHz) was used to enhance mass detection sensitivity. Equation 2.1 shows that higher resonant frequencies, produce greater frequency shifts for the same adsorbed mass.



Figure 0.3: Natural frequency of a porous microcantilever taken by a laser doppler vibrometer. Shows 1<sup>st</sup> and 2<sup>nd</sup> mode frequency at 3.97 kHz and 23.5 kHz respectively.

Assuming mass is uniformly deposited, and the stiffness of the cantilever is constant, change in mass ( $\Delta m$ ) can be approximated [63].

$$\Delta m \approx -2m_c \frac{\Delta f_n}{f_n} \tag{0.1}$$

Where  $m_c$  is the mass of the microcantilever,  $\Delta f_n$  is the n<sup>th</sup> mode frequency shift, and  $f_n$  is the n<sup>th</sup> mode resonant frequency. The cantilever mass can be determined by its density, dimensions, and porosity.

#### 2.1.3 Porosity

Porosity plays a part in the adsorption of mass. The porosity also affects the calculation of added mass by changing  $m_c$  and  $f_i$ . As porosity increases, both  $m_c$  and  $f_n$  decrease, counter acting each other's effect on added mass in Equation 2.1. However, the change to surface area as caused by the change in porosity is the dominating factor in the adsorption of target molecules. The surface area is greatly increased as the porosity increases [26]. The increase in surface area results in an increase in the amount of space target molecules may adsorb to. Therefore, more mass adsorbs

onto the surface, shifting the resonant frequency more. That, in combination with the cantilever's stiffness reduction caused by the porosity, leads to larger deflection due to adsorbed mass than similar nonporous microcantilevers.

As the porosity is due to cylindrical nanowells, the porosity (P) may be found using the well radius (r) and well-to-well distance (d) [63].

$$P = \frac{2\pi}{\sqrt{3}} \left(\frac{r}{d}\right)^2 \tag{0.2}$$

From this analysis, the larger the pore, the better sensitivity of the cantilever. However, practicality dictates there is a limit to the maximum pore size determined by the cantilever's well-to-well distance. Making the pore size too big for the set well-to-well distance, the pores would collapse into a congregated mesh structure. This structure would be significantly less rigid, causing problems when fabricating it into a cantilever structure. The practical limit set on a maximum pore size is discussed in Chapter 3.

#### **2.1.4 Bimetallic optimization**

To illicit a deflection response from thermal pulses, a second layer with a differing thermal expansion coefficient must be added to the microcantilever. In this case gold was chosen due to its high reflectance for the optical lever readout, relatively high thermal expansion coefficient compared to AAO and TiO<sub>2</sub>, and immunity to oxidation. The design of the microcantilever and bimetallic layer has a large effect on the thermomechanical sensitivity. Equation 2.3 was formulated to detail the behavior of a bi-material rectangular beam that experiences stress based on the difference in thermal expansion between the materials. The deflection (*z*) is driven by a temperature difference along the length of the cantilever (*T*-*T*<sub>0</sub>) [64].
24

$$\frac{d^2z}{dx^2} = 6(\alpha_2 - \alpha_1) \frac{t_1 + t_2}{t_2^2 K} (T - T_0) x$$
(0.3)

Where  $\alpha_i$ ,  $t_i$ , and  $E_i$  are thermal expansion coefficient, thickness, and Young's modulus of the respective layers. Subscript 1 and 2 indicate the two cantilever materials. A relation between temperature variation along the length of the cantilever can be made to incident power (*P*). That relationship was used to relate deflection to power as in Equation 2.4. It is ideal to have the largest deflection (*z*) to input power (*P*) ratio. To analytically design the nanoporous/gold microcantilever for these experiments, the bilayer microcantilever deflection equations may be used as [63]:

$$z = -\frac{3}{4} (\alpha_1 - \alpha_2) \frac{t_1 + t_2}{t_2^2 K} \frac{l^3}{(\lambda_1 t_1 + \lambda_2 t_2) w} P$$
 (0.4)

$$K = 4 + 6\left(\frac{t_1}{t_2}\right) + 4\left(\frac{t_1}{t_2}\right)^2 + \frac{E_1}{E_2}\left(\frac{t_1}{t_2}\right)^3 + \frac{E_2}{E_1}\left(\frac{t_2}{t_1}\right)$$
(0.5)

Where  $\lambda_i$  is thermal conductivity and subscript 1 and 2 indicate the gold and nanoporous layers respectively. Equation 2.4 and 2.5 assume the two layers are perfectly bonded. The nanoporous parameters are approximated as effective parameters derived from bulk parameters and porosity. Effective parameters such as  $\alpha$ ,  $\lambda$ , and  $\rho$  are calculated from the following equation

$$X_{eff} = X(1 - P)$$
 (0.6)

Where  $X_{eff}$  is the effective value, X is the value of the bulk parameter, and P is porosity. The Young's modulus used in Equation 2.5 is the effective Young's modulus but is calculated instead from the following equation.

$$f_n = \beta_n \frac{1}{2\pi\sqrt{12}} \frac{t}{l^2} \sqrt{\frac{E}{\rho}}$$
 (0.7)

Where  $f_n$  and  $\beta_n$  are the n<sup>th</sup> mode resonant frequency and eigenvalue ( $\beta_2 = 4.694$ ), and *E* and  $\rho$  are the effective Young's modulus and effective density, respectively. The n<sup>th</sup> mode resonant frequency is taken by a laser doppler vibrometer as in Figure 2.3.

Plugging in the effective parameters and solving for deflection over power  $\left(\frac{z}{p}\right)$  in Equation 2.4, produces a curve with respect to bimetallic gold layer thickness  $(t_i)$ . Prior to cantilever fabrication, this analysis provided insight into the ideal cantilever dimensions for thermomechanical sensitivity. When keeping all values except one the same, an idea of cantilever length and thickness that will maximize thermomechanical sensitivity is found, Figure 2.4. Representative values taken from a nanoporous and gold bimetallic cantilever (Table 2.1). This was used to determine the target dimensions of cantilevers to fabricate.



Figure 0.4: Deflection to power ratio with respect to gold bimetallic layer thickness when varying only one value. Left and right show an increase in peak amplitude as cantilever thickness decreases and length increases, respectively.

Figure 2.4 displays the effect cantilever thickness and length have on thermomechanical sensitivity. As thickness decreases and length increases, sensitivity increases. This is expected as

the flexibility of the cantilever increases with decreasing thickness and increasing length. From this, the thinnest and longest cantilever are expected to produce the highest deflection per incident power. However, flexibility will be limited by the practicality of fabricating the thinnest and longest cantilever possible.

A similar analysis varying the two thermal property values was done to determine their effect on the deflection to power ratio. Again, using the representative values, thermal conductivity was varied. The thermal expansion coefficient was then varied and plotted in Figure 2.5.



Figure 0.5: Deflection to power ratio with respect to gold bimetallic layer thickness when varying only one value. Left and right show an increase in peak amplitude as cantilever material thermal conductivity and thermal expansion decreases, respectively.

It is seen in Figure 2.5, a low thermal expansion coefficient and thermal conductivity for the nanoporous material enhance thermomechanical sensitivity. This information was then used in deciding between AAO and  $TiO_2$  as the nanoporous cantilever material.

From Table 2.1, AAO has a lower thermal expansion coefficient which increases the gap between thermal expansion coefficients of itself and the bimetallic material. The increase in this gap will

result in higher deflection stresses. Due to this, the sensitivity of the cantilever is increased with a lower thermal expansion coefficient.  $TiO_2$  has a lower thermal conductivity. From Figure 2.5,  $TiO_2$ 's lower thermal conductivity gives it an advantage to thermomechanical sensitivity. The effect Young's modulus has on increasing deflection under the same thermal loading is plotted using a similar analysis. Finally, a thermomechanical sensitivity analysis between AAO and  $TiO_2$  was done by plotting the lowest and highest values from Table 2.1. The range of thermomechanical sensitivity for AAO and  $TiO_2$  bimetallic cantilevers was used to determine the material to be used for PCDS explosive testing.



Figure 0.6: Deflection to power ratio with respect to gold bimetallic layer thickness. Left shows the effect Young's modulus has on the deflection to power ratio. Decreasing Young's modulus increases peak amplitude. Right, plots the lowest and highest AAO and TiO<sub>2</sub> values from Table 2.1 to give a range of cantilever thermomechanical sensitivities. AAO and TiO<sub>2</sub> have comparable sensitivity ranges.

Figure 2.6 shows the benefit a low Young's modulus has on the deflection to power ratio. Figure 2.6 also shows that the range of thermomechanical sensitivity for AAO and TiO<sub>2</sub> cantilevers are comparable. From this analysis, a clear identification of the more sensitive nanoporous cantilever material cannot be determined. TiO<sub>2</sub> has an advantage of being a photocatalyst [26]. Photocatalyst being a material that enhances the photodegradation process when excited with powerful rays. However, in this research, this property will not be utilized as the light source used will be IR for spectroscopy and a red laser for the optical lever technique. These light sources are not powerful enough to cause significant photodegradation of the explosive compounds. AAO fabrication is a slightly more established protocol in previous PCDS studies [50] [61] [65] [66] [67] [68]. For this reason, AAO was chosen as the nanoporous material as it shows comparable analytically calculated thermomechanical sensitivity. Future work could be done on comparing TiO<sub>2</sub> to AAO cantilevers experimentally. However, the scope of this research is limited to AAO/gold bimetallic cantilevers.

# **2.2 PCDS**

PCDS puts together the sensitivity of thermally responsive bimetallic cantilevers and the selectivity of spectroscopy. This technique has been used for VOC vapor sensing [61], moisture sensing [67], and explosive compound sensing [50]. All of which use the mechanical response of the cantilever to the adsorption of molecules onto its surface. The cantilever can then both quantify the number of adsorbates through a resonant frequency shift as well as characterize the chemistry of the adsorbent through spectroscopy.

#### 2.2.1 Pulses

PCDS can be done statically or dynamically. The static mode requires continuous shining of the IR source onto the cantilever. The cantilever will deflect due to the heat transferred from the IR.

I. Chae measured a 1.021 µm/K thermal deflection on a bimetallic AAO cantilever like the ones used in this research. For comparison, a bimetallic silicon cantilever of the same dimensions was measured to have a lower thermal sensitivity at 0.2687 µm/K [61]. Due to the similarity between the bimetallic AAO cantilever tested by Chae compared to the ones tested in Chapter 4, a thermal deflection sensitivity of the same order of magnitude is assumed. By measuring the static deflection, the amount of absorption for the incident wavelength may be obtained. Each wavelength will result in a different amplitude of deflection based on the vibration of the target molecules and subsequent heating of the cantilever. Scanning through the wavelengths with and without the target molecules, allows for baseline and differential spectra to be plotted. Considering dynamic PCDS, the IR light is pulsed at the cantilever. The pulsing rate is related to the thermal time constant of the cantilever. The IR is left on and off long enough to approach maximum and minimum deflection. A lock-in amplifier is then used to filter out all frequencies except the reference signal which is set by a function generator as the pulse rate. This is done by the lock-in amplifier using a phase lock loop to produce an internal reference signal that matches the external reference in phase and frequency. The reference and input signals get put through a mixer, that, when separated, allow the identification of the amount of oscillation in the input signal at the reference signal's frequency. The amplitude of oscillation within the input signal at the reference frequency is the output of the lock-in amplifier. In measuring the amplitude of vibration at the pulse rate, a wavenumber amplitude may be plotted like in static PCDS. However, dynamic mode measures the maximum and minimum deflection of numerous oscillations consecutively. Due to this, dynamic mode is much more common as it does not experience much of the noise inherent in static sensing.

### 2.2.2 Quantum cascade laser

This method requires some source of spectroscopy light. The light is most commonly chosen as mid-IR as that encompasses many molecule's vibrational modes in the "molecular fingerprint region". IR source selection is determined by two main factors. The power and the wavelength range of the laser. A QCL was chosen due to its broad range that spans part of the fingerprint region, from 5.18 µm to 10.8 µm. QCLs also have higher power than IR monochromators [53].



Figure 0.7: QCL power with respect to wavenumber.

Figure 2.7 was the measured power spectrum of the QCL used in this research. The power measurement was taken using a S401C thermal power head and PM100USB power and energy meter interface (Thorlabs Inc, Newton, NJ, USA). Utilizing this power source alongside an anodic aluminum oxide cantilever, the resultant baseline would expect to be a superposition of this power spectrum with aluminum oxide mid-IR peaks. In this wavenumber range, aluminum oxide nanoparticles were shown to have one absorption peak at 1020 cm<sup>-1</sup> and one at 1630 cm<sup>-1</sup> [69]. The expected result would be a combination of these two peaks added to the QCL power

spectrum. The baseline spectra in Chapter 4 show peak intensities to vary from the expected. However, the experimental and expected spectra share the same peak positions and overall shape.

# 2.2.3 Position sensitive detector

PSDs are used to monitor the position of the laser used in the optical lever technique. The position gives a measurement of the deflection of the cantilevers. This deflection is used to plot the spectroscopic data. PSDs contain two or four separate sensors that can give reading of position in 1-D or 2-D respectively. Using the photoelectric effect, light incident on the sensor produces a current. The amount and direction of current flow is measured by the sensors. This current flow determines the laser's position.



Figure 0.8: Schematic of a 2-D linear PSD.

Figure 2.8 shows a schematic of a 2-D linear PSD like the one used in this research. When doing PCDS, the red laser reflects off the cantilever tip which vibrates in a torsional mode, Y-axis bending mode, and X-axis bending mode. By designing the cantilever with a large width to height ratio and using proper alignment, the Y-axis bending can be made dominant. In this case, the error in monitoring only the Y-axis of vibration is reduced. A secondary method to pick up the multi axis bending and to account for misalignment can be employed by the following formula.

$$I = \sqrt{(I_2 - I_1)^2 + (I_4 - I_3)^2}$$
(0.8)

Where I is the multi axis vibration signal and  $I_i$  are the individual current signals as denoted in Figure 2.8. This model follows the vibrating light incident onto the PSD as a vector with its origin at the center. If vibration occurs in the X-axis and Y-axis, the magnitude of the vector is monitored.

# 2.2.4 Plasmonic enhancement

Plasmonic enhancement is attained using the mechanism of surface plasmon polaritons (SPPs). By coating a layer of gold onto the AAO nanowells, it creates a conductor dielectric interface that acts as a plasmonic crystal structure. SPPs are the EM excitations that occur at this interface [70]. The incident IR wave couples with surface electrons to form an electron dense collective oscillation that strongly amplifies the electric field [71]. The SPPs are subject to nonradiative decay, which leads to their confinement proximal to the interface. Other disciplines often try to reduce this decay, however in photon detectors, it is beneficial as it enhances thermal absorption [72] [73]. This mechanism directly enhances heating of a bimetallic cantilever during IR spectroscopy [68].

In the case of an AAO/gold bimetallic cantilever, coating the plasmonic layer onto the nanopores, may come at the sacrifice of the bimetallic deflection response. The bending stresses applied to the bottom side of the AAO due to the bimetallic gold layer happen similarly on the plasmonic side. These counteracting forces reduce the deflection to power ratio. D. Lee et al shows at some plasmonic layer thicknesses, the IR sensitivity of the cantilever is enhanced. This is due to increasing the absorbed power enough to overcome the effect of the deflection to power ratio dampening. At other plasmonic thicknesses, IR sensitivity is reduced [68].

### 2.2.4.1 Optimization of plasmonic layer

The design of the plasmonic crystal structure has an impact on the SPP resonant frequency [20]. A gold structure with diverse geometry would enable broadband SPPs. By coating gold onto the AAO nanopores, nanoparticles aggregate faster near the surface, creating a gradient of nanoparticle sizes down into the nanowells (Figure 2.9). L. Zhou et al showed how a variety of particle sizes enhanced SPP excitation at a broad range of wavelengths [62].



Figure 0.9: AAO nanowells being coated with gold resulting in a variety of aggregated particle sizes. Image from [62].

The use of this plasmonic structure to enhance AAO microcantilever IR spectroscopy has been shown over a wavenumber range of 1565 cm<sup>-1</sup> to 1762 cm<sup>-1</sup> [68]. D. Lee et al found the optimum thickness of the plasmonic layer by consecutively coating layers and measuring the amplitude of the IR baseline spectrum. In their case, the optimum plasmonic thickness was found to be 40 nm. Similarly, in this research, to determine the plasmonic thicknesses that enhanced the cantilever as a sensor, the plasmonic layer was coated in steps. At each step the baseline amplitude would be measured. The ideal plasmonic layer thickness was the thickness that produced the largest baseline amplitude. Such thermomechanical sensitivity tests are discussed in Chapter 4.

### 2.2.5 Quartz crystal microbalance

A QCM is a device that allows for quantification of the mass of a substance deposited. The QCM has a quartz crystal that resonates at a frequency with respect to the amount of mass deposited on

the surface. Using the Sauebrey equation, the frequency shift due to deposited molecules can be used to calculate the deposited mass. See Sauebrey equation below [74],

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m \tag{0.9}$$

Where  $\Delta f$ ,  $f_0$ , A,  $\rho_q$ ,  $\mu_q$ , and  $\Delta m$  are change in frequency (Hz), resonant frequency (Hz), active piezoelectric crystal area (cm<sup>2</sup>), quartz density (2.648 g/cm<sup>3</sup>), quartz shear modulus for AT-cut crystal (2.947E11 g\*cm<sup>-1\*</sup>s<sup>-2</sup>), and added mass, respectively. The QCM used, had a resonant frequency of 5038157 Hz. A frequency shift of negative 2 Hz indicated a deposited surface concentration of 35 ng/cm<sup>2</sup>.

#### **Chapter 3: Fabrication and Experimental Setup**

In this section, the details of the AAO cantilever fabrication as well as the PCDS experimental setup are laid out. The materials and equipment used in the self-ordering anodization process used to create the nanopores, as well as the photolithography techniques to pattern the cantilever shapes are discussed. Pore widening to optimize cantilever flexibility and plasmonic pore size along with the process to release the cantilever from the bulk substrate are explained. Finally, the process to focus the IR source, utilize the optical lever technique, align the PSD, and setup the equipment to process the data will be discussed.

# 3.1 Materials and Equipment for AAO Microcantilever Fabrication

A high purity aluminum sample (99.998%) and 99.5% Chromium Oxide (VI) were purchased from Alfa Aesar. 60% Perchloric acid, 99.5% oxalic acid, and 99% ethanol were purchased from VWR. 70% Nitric acid, 99.7% acetic acid, and 85% phosphoric acid were purchased from Avantor. A carbon electrode was purchased from GSC International. A Laurell Precision Spinner, MA6 Mask Aligner, Photoresist HPR504, 354 developer, and a Kurt J. Lesker CMS-18 Sputterer were used in the University of Calgary Microsystems Hub cleanroom for photolithography and sputtering. Refrigerated bath circulators from Fisher Scientific was used for heating and cooling during the AAO fabrication process. The scanning electron microscope images of the AAO were taken at the University of Calgary's Instrumentation Facility for Analytical Electron Microscopy (IFFAEM).

# **3.1.1 Self-ordering anodization**



Figure 0.1: Procedure for fabricating AAO cantilevers from bulk aluminum substrate.

To create the well-ordered nanowells of AAO, a two-step anodization process was used (Figure 3.1). The high purity aluminum sample was first cleaned by sonicating in acetone and rinsing in deionized (DI) water. The cleaned sample was then smoothed through an electropolishing process at 20 V for 5 minutes in a 1:4 perchloric acid and ethanol solution in a cooled bath at 5°C. All solution processes were stirred using a magnetic stirrer unless stated otherwise. The 1<sup>st</sup> anodization process was then done at 40 V in a 15°C, 0.3 M oxalic acid solution for 8 hours. This anodization process created a non-ordered oxide layer that, when etched, left a

dimple shape structure on the substrate. The oxide etching solution was prepared by dissolving 9 grams of chromium oxide into 500 ml of DI water, then adding 21 ml phosphoric acid. The process was done in the fume hood at 65°C for 6 hours. When anodizing for a second time, the oxide layer was built on top of the dimple structure creating well-ordered nanowells. The thickness of the oxide nanowells was determined by the anodization time under identical conditions as the 1<sup>st</sup> anodization. 10, 15, and 20 minutes resulted in 1, 1.5, and 2 µm thicknesses respectively [61]. As discussed in Chapter 2, the thinner the cantilever, the higher the thermomechanical sensitivity. 2 µm thick cantilevers were used in this research as thinner cantilevers would break during the fabrication process. Four cantilever chips of 1 µm and four of 1.5 µm thickness were attempted to be fabricated but broke during fabrication. 2 µm thick cantilevers were the thinnest cantilevers to increase flexibility that would have the robustness to not break during fabrication. Anodization voltage of 40 V resulted in a pore to pore distance of 100 nm. Higher voltage anodization process increases the pore-to-pore distance [75]. The anodization voltage of 40 V, creating 100 nm pore to pore distances, was chosen as it is an established protocol that has been done in PCDS AAO cantilever studies before [50] [61] [65] [66] [67] [68].

#### 3.1.2 Pore widening

After 2<sup>nd</sup> anodization, the nanowells were fabricated. Tuning of the nanowell diameter was done through a pore widening process using a 0.1 M phosphoric acid solution at room temperature. This solution etched the AAO at a slower rate than the previous AAO etching process. This slower etch rate allowed for more controlled etching. This process was designed to etch the walls of the nanowells rather than removing the bulk AAO structure. Pores started at approximately 35 nm and were widened to 40, 50, and 75 nm in 30, 50, and 95 minute intervals respectively (Figure 3.2).



Figure 0.2: AAO nanowells at various stages of pore widening. Top left, top right, bottom left, and bottom right show 30, 45, 50, and 75 nm pore diameter respectively.

Pore widening enhances the cantilever's sensitivity due to increasing flexibility and surface area. However, there is a limit that is determined by the pore-to-pore distance. At 100 nm pore to pore distance, widening pores past 75 nm at this pore-to-pore condition impacted the cantilever's structural integrity. Eight cantilevers were tested with pore widening times of 100 and 105 minutes. These times were expected to create pore widths of approximately 80 and 85 nm respectively. All eight had their cantilevers broken during the fabrication process. It was believed that at 100 nm pore to pore distance, 75 nm pore diameter is approximately the highest porosity while maintaining the structural integrity to form a cantilever shape. The widest pore diameter of 75 nm was used in this research to maximize flexibility. Higher porosity has also been shown to increase the plasmonic enhancement effect. At a pore to pore distance of 450 nm, L. Zhou et al showed over 50% absorption increase in the range of 930-1930 cm<sup>-1</sup> when increasing plasmonic coated AAO pore diameter from 300 to 365 nm [62].

### **3.1.3 Patterning cantilevers**

Once the AAO structure was created on the bulk aluminum substrate, the cantilever shape was patterned. To do this, a temporary 500 nm aluminum transfer layer (TL) was sputtered using a Kurt J. Lesker CMS-18 Sputterer onto the pores to create an even surface for photolithography. A photomask was designed and fabricated using chrome on a glass substrate. The shadow mask design was fabricated by University of Alberta's Nanofab. The cantilever width was set to 90 µm as it matched previously studied cantilever widths [61] [68]. The cantilever length ranged from 200 to 550 µm. A variety of lengths were chosen as increasing cantilever length was shown to increase thermomechanical sensitivity (Figure 2.4). However, at too great a length, it was expected the cantilever would not be able to support itself and would break. Five cantilever chips were fabricated. Four of these chips had their 550 µm long cantilever broken during the fabrication process. The next longest cantilever, 500 µm long, was used in testing as it possessed the highest thermomechanical sensitivity while also being robust enough to support itself.

Photoresist (PR) HPR504 was spin coated using a WS-650-23 spinner from Laurell Technologies Corp. The PR was dropped onto the aluminum TL and spun at 3000 rpm spread speed then baked at 110°C for 90 seconds. HPR504 was used as the PR as it is an industry standard positive PR that has relatively insensitive processing characteristics. Meaning, if development steps are done slightly off their target values, it will have little effect on the quality of the finished product. The PR then got patterned by a Karl Suss MA/BA6 mask aligner. The mark aligner shined 365 and 405 nm collimated UV radiation for 4 seconds with a mask gap of 20 µm. There is a mask gap to protect the mask from being contaminated with PR, which increases the life of the mask and decreases manufacturing cost. HPR504 being a "positive" PR means UV radiation destroys the cross links formed during the baking process. This allows the exposed area to be washed away by the PR developer. Once the PR was patterned into the cantilever shape, the uncoated aluminum TL was etched away by a phosphoric acid, nitric acid, acetic acid, and DI water solution in a ratio of 10:1:1:2 at room temperature. This exposed the AAO that was not part of the cantilever chip. This AAO was then etched using a 0.5 M phosphoric acid solution at room temperature.

# **3.1.4 Cantilever releasing**

The AAO cantilevers still coated in aluminum TL and PR were then released in an electropolishing process using the same conditions as the initial smoothing process for one hour. This solution was not stirred as the released cantilevers were fragile and the circulating fluid may have broken them. This etched underneath the cantilevers allowing them to release from the aluminum substrate and hang freely. The bulk aluminum behind the released cantilevers was removed to coat the bimetallic gold layer. To do this, the cantilever chip was repositioned so that the cantilevers were submerged by the chip was not. This selectively etched the backside substrate but no longer etched the chip. This was to ensure the overhang was minimized. Overhang refers to the distance between the start of the cantilever shape and where the AAO meets the supporting aluminum substrate (Figure 3.3).

Manual manipulation was required to remove remaining bulk aluminum beneath the cantilevers that would block the coating of the bimetallic layer. This aluminum layer was bent away from the cantilevers using tweezers. The final steps were to dip the cantilever chip in acetone to remove the remaining PR, and etch the TL using the same aluminum etchant as described above. These processes are not stirred to ensure the cantilevers are not broken. Five such cantilever chips were successfully released.



Figure 0.3: Released cantilevers with width of 90  $\mu$ m, overhang of 100  $\mu$ m, thickness of 2  $\mu$ m, and lengths ranging from 200 – 550  $\mu$ m. Overhang is the distance from where the cantilever shape meets the AAO chip to the dark line where the underneath aluminum is in contact with the AAO chip.

Figure 3.3 shows one of the five successfully fabricated cantilever chips. The other four had the longest cantilever (550  $\mu$ m) broken during fabrication. The 500  $\mu$ m long cantilever was taken as the cantilever to have the highest thermomechanical sensitivity while also being rigid enough to

be practical to fabricate. Therefore, the cantilever tested in Chapter 4 is the second from the right (500  $\mu$ m long). Between cantilever chips, the lengths and widths had dimension variations within the measurement error of the SEM (2% error). The overhang was the critical dimension to control. This dimension ranged from 80 – 120  $\mu$ m. D. Lee et al studied an AAO cantilever array with an overhang of 1.2 mm [50]. There, the overhang was sufficiently large to become a resonator itself. In this research, the <120  $\mu$ m overhang was assumed to be small enough to be approximated as rigid. Where only the cantilever vibrated.

The cantilevers were then ready for bimetallic and plasmonic gold deposition which both used the Lesker sputterer at a gold deposition rate of 50 nm/min. Measuring the second resonant frequency (Figure 2.3: 23 kHz) of the released AAO cantilever allowed the calculation for the effective Young's modulus. The maximum length, maximum pore diameter, and minimum thickness that were able to be fabricated were used. These being 500  $\mu$ m, 75 nm, and 2  $\mu$ m, respectively. The effective thermal conductivity (11 Wm/K) and thermal expansion (5x10<sup>-6</sup> K<sup>-1</sup>) were found from their bulk values. These values were used in the bimetallic equation (Eq. 2.4) to determine an optimum bimetallic layer thickness, Figure 3.4.



Figure 0.4: Deflection to power ratio of fabricated AAO cantilever with respect to gold bimetallic layer thickness.

The curve showed a thermomechanical sensitivity peak at a bimetallic gold layer thickness of 75 nm. This is the bimetallic gold layer thickness used going forward. The plasmonic layer was analyzed experimentally. Chapter 4 outlines testing the plasmonic layer at different thicknesses to determine the plasmonic thickness that resulted in the highest thermomechanical sensitivity.

Once the first successful chip out of the five were fabricated, the four subsequent chips were made consecutively without failure. From this, the fabrication process appeared be reproducible. However, a sample size of five is not sufficient to statistically determine the reproducibility. Further research through mass production of these sensors is recommended as future work to determine yield percent.

The final bimetallic cantilever was tested to estimate its stiffness value. The Sader method was used to do this [76].

$$k_{sader} = A * Q * f_R^{-1.3}$$
 (3.1)

Where  $k_{Sader}$  is the Sader method estimated cantilever stiffness, *A* is a coefficient for a particular cantilever geometry,  $f_R$  is the measured cantilever resonant frequency, and *Q* is the resonant frequency's quality factor. This method calculated a stiffness for the AAO bimetallic cantilever of 7.3 mN/m. A silicon cantilever sold by Micromotive Mikrotechnik that is used for comparative testing in Chapter 4 had a reported stiffness of 23 mN/m.

Once the bimetallic AAO cantilever was fabricated, the optical lever technique was calibrated. In Figure 3.5, the height of the laser spot (*h*) on the PSD and distance between the cantilever and PSD (*d*), was used to calculate a reflected angle ( $\theta_r$ ).



Figure 0.5: Optical lever setup showing geometry, reflected angle, and change in reflected angle when deflected. These values were used to determine a deflection value.

The reflected angle was found at ambient conditions and while being deflected by QCL

excitation. To calculate the angle difference between reflected angle when cantilever is deflected

and when cantilever is undeflected ( $\Delta \theta$ ), the following equation was used.

$$\Delta\theta = \tan\frac{h_{deflected}}{d} - \tan\frac{h_{ambient}}{d}$$
(3.2)

Where  $h_{deflected}$  and  $h_{ambient}$  are the height of the laser spot when the cantilever is being excited by the QCL and under ambient conditions, respectively. Using trigonometry, the angle difference between the undeflected and deflected cantilever ( $\Delta \theta$ ) allowed a deflection value to be approximated using Equation 3.3.

$$\partial = L * \sin(\Delta \theta) \tag{3.3}$$

Where  $\delta$  is deflection of the cantilever at the tip and *L* is the length of the cantilever. Deflection was found under two QCL power levels. Figure 2.7 shows QCL power levels of 3.1 mW at 1785 cm<sup>-1</sup> and 2 mW at 1850 cm<sup>-1</sup>. These power levels produced cantilever tip deflections of 1.1 µm and 0.73 µm, respectively. Using Equation 3.4, a theoretical point force applied at the tip of the cantilever was calculated [77].

$$\partial = \frac{F}{k_{Sader}} \tag{3.4}$$

Where *F* is the point force. Force values of 8.03 nN and 5.33 nN were approximated. By dividing deflection by QCL power, deflection to power ratios of  $3.5 \times 10^{-4}$  m/W and  $3.6 \times 10^{-4}$  m/W were compared to Figure 3.4. Figure 3.4 shows the deflection to power ratio calculated using the bimetallic equation, Equation 2.4. The 0.01 m/W value is two orders of magnitude larger than the values found by optical lever calibration.

## **3.2 PCDS Setup**

The bimetallic cantilevers are ready for testing and placed in a stage that is electronically controlled in the X and Y directions. This stage was used along with a red laser and a plano-convex lens to focus the laser beam onto the cantilever tip. The reflected laser was then aimed at the center of a PSD to enable an optical lever readout. The signal from the PSD was sent to an amplifier circuit that outputs the X-sum, Y-sum, X-diff, and Y-diff signals. X and Y sum refer to the PSD's signal that takes the sum of opposite end signals. While the "diff" signal refers to the difference between opposing signals. The signal Y-diff was tested as well as the multi axis vibration signal as calculated in Equation 2.8. Using the multi axis vibration equation produced similar data with increased noise. Due to this, the uniaxial Y-axis signal was used for this research. An investigation into the reason for the increased noise when using the multi axis method could be done as future work. However, the scope of this research is limited to utilizing the uniaxial signal.

To obtain the resonant frequency, the Y-diff signal was normalized by the Y-sum signal. This was to reduce the impact external light sources would have on the noise. The normalized signal was input into a Labview program that used a fast Fourier transform (FFT). This converted the voltage vs. time signal to an amplitude vs. frequency plot. The identified second resonant frequency was used in the adsorbed mass calculations, Equation 2.1.

For IR spectroscopy, a LaserTune QCL was focused onto the cantilever using an off-axis gold coated parabolic mirror. Gold was used on the off-axis mirror and other optics as it is a highly reflective coating (~90% [60]). Each wavenumber incident on the cantilever elicits a vibrational amplitude. The response of the cantilever by the IR source was picked up by the PSD. Here, the PSD's Y-diff signal was used. Normalizing by Y-sum was tested but produced a less consistent signal. The amplitude of vibration when excited by the QCL made the probing laser vibrate slightly past the borders of the PSD. This would make the Y-sum change depend on the deflection of the cantilever. It was believed the inconsistency of the normalized signal was due to the changing Y-sum value. Therefore, the unnormalize Y-diff signal was input into a SR850 lock-in amplifier. The lock-in tracked and amplified the modulation frequency component of the PSD signal. The lock-in amplifier used was calibrated at purchase by the manufacturer. A function generator

controlled the modulation frequency by sending pulse information to the QCL. The function generator signal included 20 Hz modulated packets of 183 kHz pulses with 5% duty cycle. The QCL manufacturer specified that if the laser was turned on constantly, the components would overheat. 183 kHz with 5% duty cycle pulses were used to make up the 20 Hz modulation packets as to not burn out the QCL. The 183 kHz laser frequency did not influence the PSD signal. This was due to the cantilever's thermal time constant being too slow (~20 Hz) to respond thermally to the 183 kHz frequency. The result was a 20 Hz heating and cooling cycle of the microcantilever. The lock-in amplifier filtered all other frequencies in the PSD signal, monitoring the amplitude of the 20 Hz modulation of the Y-diff signal. The lock-in signal was collected by a data acquisition (DAQ) module and sent to a Labview program that triggered the QCL. The QCL was triggered to sweep the desired wavelength range. The modulation amplitudes at each wavelength were collected and plotted as a spectrum. This setup allowed for multi-modal analysis that provided quantitative measurements of adsorbed mass and wavenumber vibration amplitude. Mass normalized spectra were formulated from this. Figures 3.6 and 3.7 include a schematic and a photograph of the point sensing setup.



Figure 0.6: Schematic of point sensing PCDS setup. Readouts display frequency response function showing resonant frequency of the cantilever and the nanomechanical IR spectrum.



Figure 0.7: Photograph of point sensing PCDS setup. Optical lever technique and QCL laser paths are drawn in.

Slight modification was done to the setup for taking standoff spectroscopy readings. Instead of the QCL being focused directly onto the cantilever, the IR light was focused on an SRS 200 QCM which acted as a target. The QCM's frequency shifted as a function of deposited explosive concentration allowing quantification of the target mass. The QCM used was coated with gold making it suitable as a reflector for the IR light to either be absorbed by the target molecules or be reflected off with few losses. The IR light reflected off the QCM hit another off-axis gold coated parabolic mirror that focused the light onto the cantilever. The target was placed at a standoff measurement distance of 15 cm. Figures 3.8 and 3.9 are a schematic and photograph of the standoff spectroscopy setup.



Figure 0.8: Schematic of standoff sensing PCDS setup. Readout displays IR spectrum of cantilever and QCM reads out frequency shifts that correlates to deposited mass concentration.



Figure 0.9: Photograph of standoff sensing PCDS setup. Optical lever technique and QCL laser paths are drawn in.

Both setups were tested in dark but otherwise ambient conditions. The setup was enclosed in a dark box removing external light sources. Inside the dark box, the cantilever was not protected from settling dust. Deposited dust may have influenced the spectra or deposited mass measurements outlined in Chapter 4. The temperature, humidity, and pressure were not tracked but were assumed relatively constant at indoor conditions as the experiment took place in a laboratory setting. Future work is recommended on testing this sensor's response to sunlight, artificial light, temperature changes, humidity changes, and pressure changes. A vacuum cell may enhance standoff sensor performance as it would limit contaminants and reduce air caused vibrational damping.

Considering the commercialization of this sensor, a cost analysis was done. The glassware, temperature controllers, and other upfront costs for cantilever fabrication came to approximately

\$800. The consumed cantilever materials, use of cleanroom facilities, and utilization of MEMS batch processing ability resulted in a cost per cantilever of \$13.47. The majority of the cost came from the experimental setup and processing equipment. The QCL IR source costs \$25,000. The optical lever technique components also had a high cost. Due to this, research on a cheaper readout system such as a piezoresistive readout would be recommended for miniaturization and cost reduction. The lock-in amplifier, function generator, and computer could be specifically designed to product specifications to save space and cost. As stated before, the largest cost associated with commercializing such a technology is the IR source. For a reference, IMS spectrometers used in the "swab test" cost \$10,000. Commercialization is far off, however increasing the spectroscopic ability of the implemented IR sensor would expedite the progress. Advancement in the photosensitive properties of an AAO microcantilever would maximize the utility of the chosen IR source. The ability of the designed plasmonic AAO microcantilever for standoff sensing to achieve this objective, is outlined in Chapter 4.

#### **Chapter 4: Results and Discussion**

Prior to testing for optimum plasmonic thickness, differential spectra of three commonly measured explosives were taken on bimetallic AAO cantilevers. PETN, TNT, and RDX spectra were taken with measured cantilever resonant frequency shifts of 286, 393, and 438 Hz respectively. These frequency shifts denoted respective adsorbed masses of 3.88, 5.18, and 6.48 pg. The measured spectra peaks have comparable absorption peaks to FTIR spectra, Figure 4.1. Spectroscopic absorption peaks appear for PETN at approximately 1270 and 1650 cm<sup>-1</sup>. RDX peaks are at 1325 and 1580 cm<sup>-1</sup>. TNT peaks match at approximately 1350 and 1530 cm<sup>-1</sup>. It is notable that the absorption peaks measured by the bimetallic AAO cantilever are consistently shifted to a slightly higher wavenumber than in the FTIR spectrum. This could be calibration related, either from the QCL or FTIR setup. Nonetheless, this shows proof of concept that the AAO cantilevers fabricated produce correct spectrum peaks from known compounds. Each of the five cantilever chips were successfully tested on one of the three explosive compounds and compared against the FTIR spectra. They each produced a spectrum that matched the FTIR peaks. This calibration was done before the cantilevers were used in any novel tests.



Figure 0.1: Shows differential absorption spectrum of PETN, RDX, and TNT from a bimetallic AAO cantilever.

Every spectrum taken, began by scanning the baseline three times. Baseline tests were done with no explosive molecules. Baseline spectrum amplitude were used to analyze plasmonic absorption and cantilever thermomechanical sensitivity. To do explosive testing, the target molecules were deposited onto the cantilever for point sensing and onto the QCM for standoff sensing. After deposition, three more spectra were taken. Each one of the three baseline spectra got subtracted from each of the three target spectra. This resulted in three differential spectra with the same deposited mass. The three differential spectra allowed for plotting of an average differential spectrum, as plotted in graphs. They were also used to quantify peak intensity at a wavenumber and calculate a standard deviation to plot error bars. The deposition method for point sensing was done by dropping a solution with dissolved explosive compounds onto the cantilever surface and letting the solvent evaporate. Depositing onto the QCM used the same technique but was also tested using a vapor generator. From the noise test in Chapter 2, each modulation frequency was tested by taking consecutive baseline scans for one hour. This serves as an indicator for drift. A modulation frequency of 20 Hz produced no significant drift over one hour. Since every spectroscopic test is done with a consecutive baseline, drift over a timeframe of longer than one hour is not crucial to taking differential spectra.

The ideal plasmonic thickness was then investigated. To do this, the baseline spectra were taken with no plasmonic layer then 17, 33, 50, and 67 nm plasmonic thickness. The baseline signal intensities were compared. In the range of  $930 - 1710 \text{ cm}^{-1}$  the amplitude decreased with added plasmonic layer (Figure 4.2). This is believed to be due to the plasmonic layer counteracting the bimetallic effect. The exception for this being an increase in amplitude going from 33 to 50 nm plasmonic thickness (Figure 4.3). The increase in amplitude is believed to be a point of optimum plasmonic absorption. It increased overall amplitude, despite the bimetallic cancelation effect. Three cantilever chips were tested with varying plasmonic thicknesses. The same relationship between baseline amplitude and plasmonic thickness was observed to be consistent for each of the three chips.



Figure 0.2: Baseline spectrum of bimetallic AAO cantilever with increasing plasmonic layer thickness. Plasmonic enhancement occurs over the wavenumber range of  $1710 - 1930 \text{ cm}^{-1}$  with the optimum thickness being 17 nm.



Figure 0.3: Baseline spectra of bimetallic AAO cantilever with increasing plasmonic layer thickness and added bimetallic layer thickness. An increase in amplitude from 33 nm to 50 nm plasmonic layer was seen. This also shows that the 67 nm plasmonic layer cantilever was benefitted by increasing its bimetallic layer thickness to 125 nm.

The concept of the plasmonic layer hindering the bimetallic effect is shown in Figure 4.3 between the 67 nm (purple) line and the 125 nm bimetallic (brown) line. Both lines have 67 nm plasmonic thickness, but the 125 nm bimetallic line was the spectrum taken after adding 50 nm of gold to the bimetallic layer. By adding more bimetallic layer, the plasmonic hinderance of the bimetallic effect was reduced while keeping the enhancement from the plasmonic effect. However, most importantly, the 17 nm plasmonic cantilever showed an increase in the range of  $1710 - 1930 \text{ cm}^{-1}$ . The peak in the 17 nm curve was a 3.7 times increase in signal at 1815 cm<sup>-1</sup> from the bimetallic baseline.

To further investigate the plasmonic absorption of the 17 nm plasmonic AAO cantilever, an angle dependency test was done. Figure 4.4 shows the effect IR incident angle has on the baseline spectra.



Figure 0.4: Baseline spectra when varying the incident angle, the IR light made with the cantilever surface. A decrease in amplitude was seen. The spectrum shape and peak position were unaffected.

Figure 4.4 showed that the spectrum shape and peak position had little relation to the incident angle. However, the amplitude decreased with increasing incident angle.

Along with taking baseline spectra at each plasmonic thickness, differential spectra using PETN were collected (Figure 4.5). PETN as well as other commonly measured explosive compounds RDX and TNT have low vapor pressures resulting in them adsorbing readily onto the cantilever surface. For AAO cantilevers without plasmonic layers, these compounds showed positive spectra. Meaning, the adsorbed molecules absorb their characteristic IR wavelengths into vibrational energy and transfer it to the cantilever as heat more efficiently than the cantilever transforms the light into heat. The result of this difference in energy conversion efficiency is higher spectroscopic amplitudes at the molecule's characteristic wavelengths compared to the baseline. A novel experiment was conducted by taking PETN spectra at various plasmonic thicknesses to illuminate the relationship between the two light-to-heat conversion efficiencies. The efficiency of the target chemicals to absorb and transform IR light into vibrational energy and subsequently cantilever heat.



Figure 0.5: Differential PETN mass normalized absorption spectra (left) and recorded peak intensity at 1275 cm<sup>-1</sup> (right). As plasmonic layer is added, mass normalized peak intensity decreased but always remained positive.

This test was done three times on the same cantilever allowing plotting of the error bars. Adsorbed mass in this point sensing test was calculated using the shift in resonant frequency of the cantilever. The cantilever started at a 2<sup>nd</sup> mode resonant frequency of 23.488 kHz. For the 67 nm plasmonic coating test in Figure 4.5, a frequency shift to 23.016 kHz was observed. A deposited mass of 7.234 pg was calculated using Equation 2.1. Figure 4.5 shows the mass normalized peak intensity at 1275 cm<sup>-1</sup> decreased with increased plasmonic thickness. This agrees with the principle that plasmonic absorption enhances IR absorption by the cantilever. The enhancement in absorption brings the two light-to-heat efficiencies closer together. However, the fact that the peak sign always stayed positive implies that the efficiency of the plasmonic absorption never exceeded the efficiency of the molecule's ability to transfer energy to the cantilever. The plasmonic effect works contrary to detection of molecules adsorbed onto the cantilever surface. Due to this, the plasmonic AAO cantilever was utilized for standoff detection.
For standoff detection, the target molecules on the QCM absorb their characteristic wavelengths, removing those wavelengths from the light that is reflected towards the cantilever. This produces negative spectrum peaks. The enhanced absorption of the plasmonic layer enables deepening of the negative spectrum peaks, enhancing sensitivity [68]. For these tests I used the explosive compound TNT because it has a characteristic peak in the plasmonic enhanced range at 1830 cm<sup>-1</sup>. Standoff TNT spectra were taken with a bimetallic silicon cantilever, a bimetallic AAO cantilever before coating a plasmonic layer, and then again on the same cantilever after coating 17 nm of plasmonic layer. The silicon cantilever was purchased from Micro Motive with dimensions 1 µm thickness, 90 µm width, 500 µm length. Using the same bimetallic equation (Eqn 2.4), an thermomechanical efficient gold thickness of 300 nm was coated onto the bottom of the silicon cantilevers. Silicon cantilevers are commonly used as a benchmark for cantilever comparison tests [50]. These cantilevers were also tested outside the plasmonic enhanced range on wavenumbers 930 – 1710 cm<sup>-1</sup>. These tests included PETN, RDX, and TNT (Figure 4.6). These tests further showed that the plasmonic AAO cantilever only enhanced sensitivity in the small range of 1710 – 1930 cm<sup>-1</sup>. Outside of this range, the bimetallic AAO cantilever had the greatest spectroscopic response. Both AAO cantilevers consistently had higher baseline and peak amplitudes that the silicon cantilever. This is believed to be due to the bimetallic silicon cantilever having lower flexibility (23 mN/m) as compared to the bimetallic AAO cantilever (7.3 mN/m). All cantilevers are compared under the same QCM surface concentration (PETN =  $14.2 \ \mu g/cm^2$ , RDX = 8.61 $\mu g/cm^2$ , and TNT = 11.8  $\mu g/cm^2$ ). Each cantilever spectrum was tested three times and averaged to plot the curve on the graph.



Figure 0.6: Differential transmission spectra of PETN (top left), RDX (top right), and TNT (bottom left and right) from a silicon cantilever, a bimetallic AAO, and an AAO cantilever with a 17 nm plasmonic layer. It is seen that the bimetallic AAO cantilever has the deepest peaks outside of the  $1710 - 1930 \text{ cm}^{-1}$  range. On TNT between  $1750 - 1930 \text{ cm}^{-1}$  (bottom right) an improvement factor on peak intensity of 10 and 7 from the silicon and bimetallic AAO cantilevers, respectively, were seen.

Comparing the TNT peak intensity in the range of  $1710 - 1930 \text{ cm}^{-1}$ , the 17 nm plasmonic AAO cantilever shows peak depth increases of 10 and 7 compared to the silicon and bimetallic AAO

cantilevers respectively (Figure 4.6, bottom right). Figure 4.7 shows the baseline and TNT spectra used to create the Figure 4.6 bottom right graph. It shows an amplification of baseline and TNT spectra amplitudes of approximately two times (~90 mV to ~180 mV) by adding the plasmonic layer to the bimetallic AAO cantilever.



Figure 0.7: Baseline compared to TNT spectrum for bimetallic AAO (left) and the 17 nm plasmonic AAO (right). This shows the amplitude increased from 90 mV to 180 mV (a factor of two) by adding the plasmonic layer.

Testing TNT at varying concentrations shows a predictable increase in the depth of the characteristic peaks. Figure 4.8 shows the differential spectrum from four TNT tests with varying QCM surface concentrations. Resonant frequency shifts of the QCM that referred to  $1.52 \,\mu\text{g/cm}^2$ ,  $2.77 \,\mu\text{g/cm}^2$ ,  $3.52 \,\mu\text{g/cm}^2$ , and  $4.10 \,\mu\text{g/cm}^2$  were 86 Hz, 157 Hz, 199 Hz, and 232 Hz, respectively.



Figure 0.8: Differential transmission spectra of TNT from an AAO cantilever with 17 nm plasmonic layer at various surface concentrations. As the surface concentration increased, the spectrum peak intensities increased.

This relationship between surface concentration and peak intensity solidifies the idea that deposited compounds on the QCM absorb their characteristic wavelengths on the target, not allowing them to reach the cantilever. These TNT tests were done by one cantilever three times at each surface concentration and averaged together.

LOD measurements were done on the plasmonic AAO cantilever within the enhanced range of  $1750 - 1930 \text{ cm}^{-1}$  (Figure 4.9). The LOD was calculated assuming a minimum SNR of three. Tests were done by drop casting TNT onto the QCM surface. Resonant frequency shifts of the QCM that referred to 12 µg/cm<sup>2</sup>, 16 µg/cm<sup>2</sup>, 21 µg/cm<sup>2</sup>, and 26 µg/cm<sup>2</sup> were 679 Hz, 906 Hz, 1189 Hz, and 1472 Hz, respectively. This is done by placing a drop of TNT dissolved in acetonitrile and letting the solvent evaporate. Using this protocol, the noise was found to be 1.484 mV with a LOD of 66.77 ng/cm<sup>2</sup>. The TNT spectra that produced the LOD data is included in Figure 4.9.



Figure 0.9: TNT spectra of plasmonic AAO cantilever at varying surface concentrations using drop casting (left). Transmission peak amplitude vs. surface concentration data that allows calculation of LOD (right). Noise equals 1.484 mV and LOD is 66.77 ng/cm<sup>2</sup>.

Drop casting resulted in uneven distribution of the TNT onto the QCM surface. This could be seen visibly, as a residue deposited in evaporation rings. The QCM equation (Eqn 2.9) used to calculate deposited mass, assumes an even coating of molecules onto the surface. Drop casting TNT resulted in an uneven coating, putting into question the accuracy of the deposited surface concentration values. A second method of depositing molecules onto the QCM surface was used to increase accuracy of the surface concentration reading. A vapor generator that contained quartz wool was heated to 80°C and the TNT solution was deposited onto the wool. The QCM was put over the top opening of the vapor generator and dry air was blown past the quartz wool and past the QCM surface. The heated explosive molecules were assumed to be picked up by the dry air and blown past the QCM. Since the explosives have low vapor pressure, as they cool down when exiting the vapor generator, the explosive compounds were expected to adsorb to the QCM surface. The resulting QCM coating was visibly more even than when drop cast. This

method of coating was then used to plot a similar peak intensity vs surface concentration graph to compare the two methods (Figure 4.10).



Figure 0.10: TNT transmission peak amplitude vs surface concentration using a vapor generator to coat the QCM. Noise equals 1.846 mV and LOD was calculated to be 63.42 ng/cm<sup>2</sup>.

Figure 4.10 shows a noise level of 1.846 mV and LOD of 63.42 ng/cm<sup>2</sup>. The LOD was comparable to the LOD of the drop cast method (66.77 ng/cm<sup>2</sup>). However, the surface concentration values drastically changed. Resonant frequency shifts of the QCM that referred to  $0.28 \ \mu g/cm^2$ ,  $0.46 \ \mu g/cm^2$ ,  $0.53 \ \mu g/cm^2$ , and  $0.64 \ \mu g/cm^2$  were 16 Hz, 26 Hz, 30 Hz, and 36 Hz, respectively. During testing the vapor generator deposition method, a uniform coating was visible. This method was believed to be superior for determining surface concentration and therefore LOD for standoff PCDS sensing.

#### **Chapter 5: Conclusions and Future Work**

It was concluded that the AAO cantilevers fabricated without a plasmonic layer match with known FTIR spectra. It has been shown that adding a plasmonic layer enhanced the PCDS amplitude in a range from 1710 - 1930 cm<sup>-1</sup>. Outside of that, in the range of 930 - 1710 cm<sup>-1</sup>, the signal decreases. This was believed to be due to the bimetallic thickness equations being calculated for only two layers. By adding a third plasmonic layer, the bimetallic effect was dampened due to the layer deviating from the bimetallic equation assumptions. The exception for this was seen when going from 33 – 50 nm plasmonic layer. An increase in amplitude over the entire scanned range (930 – 1930 cm<sup>-1</sup>) was observed. This was evidence that plasmonic absorption got stronger at 50 nm. However, the 50 nm plasmonic cantilever still preformed worse than the bimetallic AAO and 17 nm plasmonic AAO due to the bimetallic effect dampening. A novel investigation into the competing light-to-heat efficiencies of the adsorbed molecules and plasmonic absorption was conducted. Testing PETN spectra at various plasmonic thicknesses revealed that the plasmonic effect was not strong enough to make the differential spectra have negative peaks. This implied that the plasmonic absorption efficiency never surpassed the efficiency of the adsorbed molecules to transfer EM energy into cantilever heat.

The objective to design a standoff spectroscopy sensor with enhanced photosensitive properties was achieved. Standoff spectroscopy tests showed the bimetallic cantilever had the largest baseline amplitude over the range of 930 - 1710 cm<sup>-1</sup>. However, the 17 nm plasmonic AAO cantilever had the highest baseline signal in the range of 1710 - 1930 cm<sup>-1</sup>. The improved baseline resulted in an improvement of 7 and 10-fold on the characteristic peak depth in the plasmonic enhanced range when comparing the 17 nm plasmonic layer to the bimetallic AAO and silicon cantilevers, respectively. This was seen, in part through the increase from 90 mV to 180 mV in baseline

amplitude when comparing bimetallic AAO to a 17 nm plasmonic thickness AAO cantilever. It was also shown that as target surface concentration measured by the QCM increased, the TNT spectrum's characteristic peaks become more negative for both drop casting and vapor depositing methods. The vapor depositing method appeared to provide a more reliable QCM surface concentration reading as the residue was visibly more evenly coated as compared to the drop casting residue. The LOD of the plasmonic cantilever sensor in the enhanced range was found to be 63.42 ng/cm<sup>2</sup> when measured using the vapor deposition method. This limit of detection was comparable to the values in Table 1.1 (22.86 ng/cm<sup>2</sup>, 100 ng/cm<sup>2</sup>, and 160 ng/cm<sup>2</sup>). However, since the tests were done at a low standoff distance (15 cm) and in a dark environment, more work is required. The goal that was achieved here, was to show that an advancement on the photosensitive properties of bimetallic AAO cantilevers used for standoff spectroscopy can be made by coating a plasmonic layer onto the nanopores.

Preliminary work on this research was combined with D. Lee's work and presented as a poster presentation in NMC 2019 in Seoul, South Korea. A presentation in summary of this work was presented at the University of Calgary Graduate Student Conference in April 2019. The results were presented in a poster presentation at the Alberta Nanotechnology Research Symposium in May 2019. A manuscript is currently being written to publish the plasmonic AAO cantilever standoff spectroscopy results.

Recommended future work would involve finding out analytically and experimentally the optimum bimetallic layer in combination with the optimum plasmonic layer. A trimetallic equation could be used to determine the optimum bimetallic layer given a known optimum plasmonic thickness. This could be compared to the experimental findings from coating various bimetallic thicknesses onto an AAO cantilever that has the optimum plasmonic thickness coated.

More recommended future work could be done on AAO cantilevers with a larger pore-to-pore distance. Larger inter-pore distances would allow for larger nanowell diameters. This may, when coated with gold, have further enhanced plasmonic effects. Increased standoff measurement distance, lower explosive concentration, mixed explosive tests, specular vs diffuse reflection tests, and ambient condition tests are all recommended. Testing the manufacturability of plasmonic AAO cantilevers could be done. Mass producing AAO cantilevers could statistically determine yield percent.

#### References

- M. Roser, M. Nagdy, and H. Ritchie (2019) "Terrorism". Published online at OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/terrorism' [Online Resource]
- S. F. Hallowell, "Screening people for illicit substances: A survey of current portal technology," *Talanta*, vol. 54, no. 3, pp. 447–458, 2001.
- [3] L. Senesac and T. G. Thundat, "Nanosensors for trace explosive detection," *Mater. today*, vol. 11, no. 3, pp. 28–36, 2008.
- [4] R. Ewing, "A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds," *Talanta.*, vol. 54, no. 3, pp. 515–529, 2001.
- [5] A. Hulanicki, S. Glab, and F. Ingman, "Chemical sensors: definitions and classification," *Pure Appl. Chem.*, vol. 63, no. 9, pp. 1247–1250, 1991.
- [6] V. E. Bochenkov and G. B. Sergeev, "Sensitivity, selectivity, and stability of gas-sensitive metal-oxide nanostructures," *Met. oxide nanostructures their Appl.*, vol. 3, pp. 31–52, 2010.
- [7] A. J. Bandodkar and J. Wang, "Non-invasive wearable electrochemical sensors: a review," *Trends Biotechnol.*, vol. 32, no. 7, pp. 363–371, 2014.
- [8] M. Viberg and B. Ottersten, "Sensor array processing based on subspace fitting," *IEEE Trans. signal Process.*, vol. 39, no. 5, pp. 1110–1121, 1991.
- B. Friedlander, "A sensitivity analysis of the MUSIC algorithm," *IEEE Trans. Acoust.*, vol. 38, no. 10, pp. 1740–1751, 1990.
- [10] R. Vargas-Bernal, "Techniques to optimize the selectivity of a gas sensor," in *Electronics*, *Robotics and Automotive Mechanics Conference (CERMA 2007)*, 2007, pp. 579–584.

- [11] E. T. Zellers, J. Park, T. Hsu, and W. A. Groves, "Establishing a limit of recognition for a vapor sensor array," *Anal. Chem.*, vol. 70, no. 19, pp. 4191–4201, 1998.
- [12] K. J. Albert *et al.*, "Cross-reactive chemical sensor arrays," *Chem. Rev.*, vol. 100, no. 7, pp. 2595–2626, 2000.
- [13] B. C. Munoz, G. Steinthal, and S. Sunshine, "Conductive polymer-carbon black composites-based sensor arrays for use in an electronic nose," *Sens. Rev.*, vol. 19, no. 4, pp. 300–305, 1999.
- [14] K. Arshak, E. Moore, G. M. Lyons, J. Harris, and S. Clifford, "A review of gas sensors employed in electronic nose applications," *Sens. Rev.*, vol. 24, no. 2, pp. 181–198, 2004.
- [15] H. T. Nagle, R. Gutierrez-Osuna, and S. S. Schiffman, "The how and why of electronic noses," *IEEE Spectr.*, vol. 35, no. 9, pp. 22–31, 1998.
- [16] T. C. Pearce, S. S. Schiffman, and H. T. Nagle, *Handbook of Machine Olfaction: Electronic Nose Technology*. 2002.
- [17] D. R. Walt *et al.*, "Optical sensor arrays for odor recognition," *Biosens. Bioelectron.*, vol. 13, no. 6, pp. 697–699, Sep. 1998.
- [18] E. Schaller, J. O. Bosset, and F. Escher, "Electronic Noses' and Their Application to Food," *LWT - Food Sci. Technol.*, vol. 31, no. 4, pp. 305–316, Apr. 1998.
- [19] W. P. Carey and B. R. Kowalski, "Chemical piezoelectric sensor and sensor array characterization," *Anal. Chem.*, vol. 58, no. 14, pp. 3077–3084, 1986.
- [20] A. Ahmed, "Enhancing the sensitivity of NDIR spectroscopy using plasmonic crystal structures," 2016.
- [21] P. I. O. T. Thundat and R. J. Warmack, "MICROCANTILEVER SENSORS," *Microscale Thermophys. Eng.*, vol. 1, no. 3, pp. 185–199, Jul. 1997.

- [22] C. Papadopoulos, D. Vlachos, and J. Avaritsiotis, "Comparative study of various metal-oxide-based gas-sensor architectures," *Sensors Actuators B Chem.*, vol. 32, no. 1, pp. 61–69, Apr. 1996.
- [23] R. Datar *et al.*, "Cantilever Sensors: Nanomechanical Tools for Diagnostics," *MRS Bull.* (previously 'Materials Res. Soc. Newsletter'), vol. 34, no. 6, pp. 449–454, 2009.
- [24] M. Chaudhary and A. Gupta, "Microcantilever-based Sensors," *Def. Sci. journal.*, vol. 59, no. 6, pp. 634–641, 2009.
- [25] A. Loui *et al.*, "Chemical vapor discrimination using a compact and low-power array of piezoresistive microcantilevers," *Analyst*, no. 133, pp. 608–615, 2008.
- [26] D. Lee, S. Kim, S. Jeon, and T. Thundat, "Direct Detection and Speciation of Trace Explosives Using a Nanoporous Multifunctional Microcantilever," *Anal. Chem.*, vol. 86, no. 10, pp. 5077–5082, 2014.
- [27] A. R. Krause, C. Van Neste, L. Senesac, T. Thundat, and E. Finot, "Trace explosive detection using photothermal deflection spectroscopy," *J. Appl. physics.*, vol. 103, no. 9, 2008.
- [28] S. Olcum *et al.*, "Weighing nanoparticles in solution at the attogram scale.," *Proc. Natl. Acad. Sci. United States Am.*, vol. 111, no. 4, pp. 1310–1315.
- [29] N. V Lavrik, M. J. Sepaniak, and P. G. Datskos, "Cantilever transducers as a platform for chemical and biological sensors," *Rev. Sci. instruments online.*, vol. 75, no. 7, pp. 2229– 2253, 2004.
- [30] G. S. Shekhawat *et al.*, "Micromachined Chip Scale Thermal Sensor for Thermal Imaging," *ACS nano.*, vol. 12, no. 2, pp. 1760–1767, 2018.
- [31] G. Meyer and N. M. Amer, "Novel optical approach to atomic force microscopy," Appl.

Phys. Lett., vol. 53, no. 12, pp. 1045–1047, 1988.

- [32] L. Sekaric, D. W. Carr, S. Evoy, J. M. Parpia, and H. G. Craighead, "Nanomechanical resonant structures in silicon nitride: fabrication, operation and dissipation issues," *Sensors and actuators.*, vol. 101, no. 1–2, pp. 215–219, 2002.
- [33] S. J. Patil, N. Duragkar, and V. R. Rao, "An ultra-sensitive piezoresistive polymer nanocomposite microcantilever sensor electronic nose platform for explosive vapor detection," *Sensors and actuators.*, vol. 192, pp. 444–451, 2014.
- [34] T. Thundat, G. Y. Chen, R. J. Warmack, D. P. Allison, and E. A. Wachter, "Vapor Detection Using Resonating Microcantilevers," *Anal. Chem.*, vol. 67, no. 3, pp. 519–521, 1995.
- [35] W. Zhang *et al.*, "Recent Developments in Spectroscopic Techniques for the Detection of Explosives," *Materials.*, vol. 11, no. 8, 2018.
- [36] C. Berthomieu and R. Hienerwadel, "Fourier transform infrared (FTIR) spectroscopy," *Photosynth. Res.*, vol. 101, no. 2–3, pp. 157–170, 2009.
- [37] O. M. Primera-Pedrozo, Y. M. Soto-Feliciano, L. C. Pacheco-Londoño, and S. P. Hernández-Rivera, "Detection of High Explosives Using Reflection Absorption Infrared Spectroscopy with Fiber Coupled Grazing Angle Probe/FTIR," *Sens. imaging.*, vol. 10, no. 1–2, pp. 1–13, 2009.
- [38] J. Zosel, W. Oelßner, M. Decker, G. Gerlach, and U. Guth, "The measurement of dissolved and gaseous carbon dioxide concentration," *Meas. Sci. Technol.*, vol. 22, no. 7, 2011.
- [39] J. Hildenbrand, J. Herbst, J. Wöllenstein, and A. Lambrecht, "Explosive detection using infrared laser spectroscopy," in *Proc.SPIE*, 2009, vol. 7222.

- [40] S. Wallin, A. Pettersson, H. Östmark, and A. Hobro, "Laser-based standoff detection of explosives: a critical review," *Anal. Bioanal. Chem.*, vol. 395, no. 2, pp. 259–274, 2009.
- [41] M. Moskovits, "Surface-enhanced Raman spectroscopy: a brief retrospective," J. Raman Spectrosc., vol. 36, no. 6-7, pp. 485–496, 2005.
- [42] K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, and M. S. Feld, "Ultrasensitive Chemical Analysis by Raman Spectroscopy," *Chem. Rev.*, vol. 99, no. 10, pp. 2957–2976, 1999.
- [43] O. Katz, A. Natan, Y. Silberberg, and S. Rosenwaks, "Standoff detection of trace amounts of solids by nonlinear Raman spectroscopy using shaped femtosecond pulses," *Appl. Phys. Lett.*, vol. 92, no. 17, 2008.
- [44] S. Botti, L. Cantarini, and A. Palucci, "Surface-enhanced Raman spectroscopy for tracelevel detection of explosives," *J. Raman Spectrosc. JRS.*, vol. 41, no. 8, pp. 866–869, 2010.
- [45] X. Fang and S. R. Ahmad, "Detection of explosive vapour using surface-enhanced Raman spectroscopy," *Appl. Phys. B*, vol. 97, no. 723, 2009.
- [46] J. C. Carter, S. M. Angel, M. Lawrence-Snyder, J. Scaffidi, R. E. Whipple, and J. G. Reynolds, "Standoff Detection of High Explosive Materials at 50 Meters in Ambient Light Conditions Using a Small Raman Instrument," *Appl. Spectrosc.*, vol. 59, no. 6, pp. 769–775, Jun. 2005.
- [47] Y. H. Pao, *Optoacoustic spectroscopy and detection*. 2012.
- [48] A. Rosencwaig, *Photoacoustics and photoacoustic spectroscopy*. 1980.
- [49] M. W. Sigrist, *Air monitoring by spectroscopic techniques*. 1994.
- [50] D. Lee, S. Kim, C. W. Van Neste, M. Lee, S. Jeon, and T. Thundat, "Photoacoustic spectroscopy of surface adsorbed molecules using a nanostructured coupled resonator

array," Nanotechnology, vol. 25, no. 3, 2014.

- [51] C. W. Van Neste, L. R. Senesac, and T. Thundat, "Standoff photoacoustic spectroscopy," *Appl. Phys. Lett.*, vol. 92, no. 23, 2008.
- [52] B. H. Mahalik, N. P.; Iyuke, S. E.; Ahn, *Micromanufacturing and Nanotechnology*. 2006.
- [53] S. Kim, D. Lee, and T. Thundat, "Photothermal cantilever deflection spectroscopy," *EPJ Tech. Instrum.*, vol. 1, no. 1, p. 7, 2014.
- [54] S. Kim, D. Lee, X. Liu, C. Van Neste, S. Jeon, and T. Thundat, "Molecular recognition using receptor-free nanomechanical infrared spectroscopy based on a quantum cascade laser," *Sci. Rep.*, vol. 3, p. 1111, Jan. 2013.
- [55] P. K. Day, H. G. LeDuc, B. A. Mazin, A. Vayonakis, and J. Zmuidzinas, "A broadband superconducting detector suitable for use in large arrays," *Nature.*, vol. 425, no. 6960, pp. 817–821, 2003.
- [56] AZoM, "Alumina aluminum oxide a refractory ceramic oxide," AZO Materials, 2001. .
- [57] AZoM, "Titanium dioxide titania," AZO Materials, 2002. .
- [58] AZoM, "Gold (Au) properties, applications," AZO Materials, 2013. .
- [59] Aalco, "Aluminum specifications, properties, classifications, and classes," AZO Materials, 2005. .
- [60] E. Fearon, T. Sato, D. Wellburn, K. G. Watkins, and G. Dearden, "Thermal effects of substrate materials used in the laser curing of particulate silver inks," *Rapid Prototyp. Manuf.*, pp. 379–390, 2007.
- [61] I. Chae, "Development of an electronic nose for detection of volatile organic compounds based on nanoporous microcantilevers by using photothermal spectroscopy," 2015.
- [62] L. Zhou et al., "Self-assembly of highly efficient, broadband plasmonic absorbers for solar

steam generation," Sci. Adv., vol. 2, no. 4, 2016.

- [63] I. Chae, D. Lee, S. Kim, and T. Thundat, "Electronic Nose for Recognition of Volatile Vapor Mixtures Using a Nanopore-Enhanced Opto-Calorimetric Spectroscopy," *Anal. Chem.*, vol. 87, no. 14, pp. 7125–7132, 2015.
- [64] J. R. Barnes *et al.*, "A femtojoule calorimeter using micromechanical sensors," *Rev. Sci. instruments online.*, vol. 65, no. 12, pp. 3793–3798, 1994.
- [65] P.-S. Lee *et al.*, "Microcantilevers with Nanochannels," *Adv. Mater.*, vol. 20, no. 9, pp. 1732–1737, 2008.
- [66] M. Lee, D. Lee, N. Jung, M. Yun, C. Yim, and S. Jeon, "Evaporation of water droplets from hydrophobic and hydrophilic nanoporous microcantilevers," *Appl. Phys. Lett.*, vol. 98, no. 1, 2011.
- [67] D. Lee, N. Shin, K.-H. Lee, and S. Jeon, "Microcantilevers with nanowells as moisture sensors," *Sensors and actuators.*, vol. 137, no. 2, pp. 561–565, 2009.
- [68] D. Lee *et al.*, "Plasmonic absorbers with optical cavity for the enhancement of photothermal/opto-calorimetric infrared spectroscopy," *Appl. Phys. Lett.*, vol. 110, no. 1, 2017.
- [69] I. of Chemistry, "Database of ATR-FT-IR spectra of various materials," *University of Tartu, Estonia*, 2005. .
- [70] S. A. Maier, *Plasmonics: fundamentals and applications*. 2007.
- [71] P. Berini, "Surface plasmon photodetectors and their applications," *Laser photonics Rev.*, vol. 8, no. 2, pp. 197–220, 2014.
- [72] W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature.*, vol. 424, no. 6950, pp. 824–830, 2003.

- [73] J. A. Dionne *et al.*, "Localized fields, global impact: Industrial applications of resonant plasmonic materials," *MRS Bull. (previously 'Materials Res. Soc. Newsletter')*, vol. 40, no. 12, pp. 1138–1145, 2015.
- [74] G. Z. Sauerbrey, "Use of quartz crystal units for weighing thin films and microweighing," *Magazine of Physics*, 1959.
- [75] W. Lee, R. Ji, U. Gösele, and K. Nielsch, "Fast fabrication of long-range ordered porous alumina membranes by hard anodization," *Nat. Mater.*, vol. 5, no. 9, pp. 741–747, 2006.
- [76] J. E. Sader *et al.*, "Spring constant calibration of atomic force microscope cantilevers of arbitrary shape," *Rev. Sci. instruments online.*, vol. 83, no. 10, 2012.
- [77] T. Beléndez, C. Neipp, and A. Beléndez, "Large and small deflections of a cantilever beam," *Eur. J. physics.*, vol. 23, no. 3, pp. 371–379, 2002.

#### Appendix

### **PERMISSION REQUEST - SCI ADVANCES - THESIS**

Nicholas Simin Mon 2019-04-01 8:57 AM

(No message text)

You forwarded this message on Mon 2019-04-01 8:57 AM

permissions <permissions@aaas.org>

Fri 2019-03-29 11:05 AM

Dear Nicholas:

Thank you very much for your request and interest in the figure. Please feel free to include the figure in your thesis:

The following should be done when reproducing the figure per the CC BY-NC license terms:

1. Credit the author and credit the original Science Advances article.

Appropriate credit lines follow this format: "From/modified from [INSERT Science Advances REFERENCE CITATION]. © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) <u>http://creativecommons.org/licenses/by-nc/4.0/</u>"

2. If any modifications are made to the material, those changes must be identified.

3. Use of the material must not imply any endorsement by the authors or by AAAS and Science Advances.

4. No legal terms or technological measures may be applied to the reproduced material that conflicts with CC BY-NC license terms.

Please note: Portions, images, or figures appearing in the original Science Advances article that are attributed to other publishers or individuals are not subject to the article's Creative

Commons license. Permission from the credited party should be sought prior to reproduction of such material.

If you have any questions about please let me know.

Kind regards,

Liz

\*\*\*

Elizabeth Sandler

Rights & Permissions

Science/AAAS

1200 New York Ave. NW

Washington, DC 20005

Tel: + 1-202-326-6765

From: Nicholas Simin <nsimin@ucalgary.ca>

Sent: Friday, March 29, 2019 12:56 PM

To: permissions

Subject: Image Use

Hi,

I am a master's student at the University of Calgary writing my thesis. I am hoping to use an image (below) from a paper published in the Science Advances journal [L. Zhou, Y. Tan, D. Ji, B. Zhu, P. Zhang, J. Xu, Q. Gan, Z. Yu, J. Zhu, Self-assembly of highly efficient, broadband plasmonic absorbers for solar steam generation. Sci. Adv. 2, e1501227 (2016)]. Could you please advise me on if and how I may obtain permission?

## Regards

Nicholas Simin



## Citation

Our articles and data visualizations rely on work from many different people and organizations. When citing this entry, please also cite the underlying data sources. This entry can be cited as:

Max Roser, Mohamed Nagdy and Hannah Ritchie (2019) - "Terrorism". *Published online at OurWorldInData.org.* Retrieved from: 'https://ourworldindata.org/terrorism' [Online Resource]



# How to use Our World in Data

- 1. How to use Our World in Data
- 2. How is our work copyrighted?
- 3. How can you reproduce or cite our work in your publication?
- 4.• If I link to Our World in Data will the link break?
- 5. How to make static visualizations for your text or presentation?
- 6. How to embed interactive charts in your article?

# How to use Our World in Data in your presentations, in your writing, and your web articles and blog.

How is our work copyrighted?

**Visualizations and text:** All our charts, maps, and text is licensed under a very permissive 'Creative Commons' (CC) license: The <u>CC-BY license</u>. The BY stands for *'by attribution'* and this means you are free to take whatever is useful for your work. You just need to provide credit to Our World in Data and our underlying sources (<u>see below</u>).

Note: In early 2019 we changed our Creative Commons license from "By Attribution-Share Alike" (CC-BY-SA) to "By Attribution" (CC-BY). Some of our static charts still have the CC-BY-SA mark in the bottom right corner. You can disregard this, and consider all our work as licensed under CC-BY.

**Software:** We develop our own data visualization and database tool: The <u>Our</u> <u>World in Data-Grapher</u>. This tool is completely open source – <u>here on</u> <u>GitHub</u> – and is free to use on any other web publication. The code is licensed under the *MIT License*.

How can you reproduce or cite our work in your publication?

All our work is licensed under a very permissive 'Creative Commons' license. This means you are free to take whatever is useful for your work from <u>www.OurWorldInData.org</u>.

This applies to all work done by us, all text and all visualizations with our logo on them.

[At times we reproduce graphics from other sources, it is clearly stated when it is the case, and in those cases the copyright remains with the original authors and we can't give any permissions for reproduction.]

We do ask however that whenever you use our work for a publication, you stick to the following guidelines:

1.

1. Cite the corresponding entry from Our World in Data where the original content is located. For example: Max Roser and Esteban Ortiz-Ospina (2019) - "Global Rise of Education". Published online at OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/global-rise-of-education' [Online Resource]

- 2. **Make sure you add links and cite underlying data sources.** For example, if you are redrawing a chart from Our World in Data for which we cite an external data source, then you should cite both Our World in Data and this underlying source.
- 3. If you can, send us a quick note telling us where you used our work. It is encouraging to hear our work is helpful and we can learn from seeing how you used it.
- 4. In online publications embed interactive charts when possible. We encourage online publications to embed our interactive charts. This is easy to do and you can trust us that the embedded chart won't break all our links are stable.

If I link to Our World in Data will the link break?

We know that dead links are a major issue on the Internet. From day on we made it a priority that links to our pages and charts will not break. You can rely on us. If you link to us or if you embed a chart from us you can be assured that this link won't break ever.

How to make static visualizations for your text or presentation?

The normal case – save as an image: It is straightforward to make static versions of Our World In Data visualizations in web articles, text documents or presentations. Just click on 'PNG' below the chart and the static version of the chart is shown in a new tab of your browser. You can then right-click on the chart and chose 'Save image as' to save it on your computer. Try it out on the map below.

**In case you need to edit the chart further:** Click on SVG and the chart will open as a Scalable Vector Graphic (.svg) file in a new tab in your browser. You can then save it in your browser – through "save page as" – and you will have a vector graphic of the chart that you can then edit in Inkscape (<u>free</u>), Adobe Illustrator or similar software.

For a step-by-step explanation with examples, see here.

How to embed interactive charts in your article?

You can use any of the interactive visualizations from Our World In Data in your articles.

Here are three recent examples of articles that embed OWID visualizations:

- Politifact using OurWorldInData in fact checking claims about global poverty.

<u>The Brazilian website</u> o futuro das coisas in an article about the future of global education.

 Vox.com in an article on the decline of global malaria deaths on World Malaria Day.

An example:

For example let's assume you want to write about fertility and on the <u>fertility</u> page you find this map that you want to embed in your own article:

Children per woman, 2015

Shown is the 'total fertility rate' (TFR). The TFR is the number of children that would be born to a woman if she were to

live to the end of her childbearing years and bear children in accordance with age-specific fertility rates of the specified

year. **No data0123456789** <u>CC BY</u> Source: UN Population Division (2017 Revision) 1950 2015

> 1...CHART 2...MAP 3...DATA 4...SOURCES 5... 6... 7... 8...

All you have to do to embed it in your article:

At the bottom of the chart you click on the little share symbol (one dot that connects to two dots) and then you can chose the **</>Embed** option and you will see a box popping up (try it!) with the following bit of text:

<iframe src="https://ourworldindata.org/grapher/children-per-woman-UN" width="100%" height="600px"></iframe>

Now you just take this bit of html code and place it in the text of your own article.

An iframe is used to display a website within another website (*w3schools* has <u>more info on iframes</u>.) Similar to when you embed a YouTube video in your article, your article now embeds an Our World In Data visualization.

## Change the map focus or change the year:

We try to make the embed tool as useful as possible: For example, you can focus on Africa instead of World in the map above; and you can move the time slider to 2015 (you will get <u>this</u>). Now when you click on **</> Embed** you get the following bit of code:

<iframe src="https://ourworldindata.org/grapher/children-per-woman-UN?region=Africa&year=2015" width="100%" height="600px"></iframe>

If you copy-paste this code your article will embed the map with a focus on Africa and the fertility rate for 2015.

And the same works for the chart view. Just switch to Chart in the visualization above and add the countries that you are interested in – like <u>this</u>. When you click on **</> Embed** you can now get the code to embed this line chart. And if you want to select different countries that are shown in your embedded chart then just chose the option '+ Add Country' at the bottom of the chart and will have these countries shown in your chart.