Exploring Novel Vanadium Dioxide Tunable Optical Structures

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1 Introduction

Optics is perhaps the one area of physics that is truly everywhere; our world revolves around light and is powered, ultimately, by the light from the sun. It is therefore important that we study how light is and can be affected in new ways, and this essay will explain one such way, in Vanadium Dioxide layered structures. The growing need for many and more reliable optical components comes from almost all industries, from research microscopes to medical equipment, even our smartphones make use of last generation optical lenses. It would be of great value to optical systems if those sought after properties could be turned on and off, preferably in a somehow easy way, and if those components did not add much in terms of bulk. It is exactly that that vanadium dioxide structures try to do. In this essay I try to explain some of the background theory, as well as the research project I conducted for six weeks, which included simulations and modelling of the optical surfaces mentioned. I then expose the results that it provided, which included two potentially relevant structures. In the end I propose some future directions for research as well as possible applications for the findings detailed here.

2 Theory

2.1 Vanadium Dioxide

Vanadium Dioxide (VO_2) is an inorganic compound that has a reversible phase transition at the relatively low temperature of around 68^{o} C; this transition consists of both a structural phase transition (SPT) and a metal-insulator transition (MIT), meaning that it changes its molecular structure and from a metal to an insulator, with it changing many of its material properties [1]. Since its discovery in 1959 vanadium dioxide has been extensively studied due to the changes in electrical conductivity, optical absorption and permittivity that occur due to its transition. Unlike other materials that have a similar transition, vanadium dioxide has a few upsides: the phase and metal-insulator transition seem to be tied together and never occur one at a time, the transition takes place at a very accessible temperature[1], and it can also be induced through strain, pressure, chemical doping, and electrostatic fields [1]. Above the critical phase transition temperature (Tc), vanadium dioxide has a rutile structure (R) (Figure 1a), while below Tc it has a tetragonal monoclinic structure (M1 and M2) (Figure 1b) [1], all this to say that the change in properties comes from a change in the way that the atoms are arranged in the structure of the VO_2.

[1]Most other materials that have such a useful transition do so at incredibly high temperatures, making them unfeasible for most applications outside of experimental labs

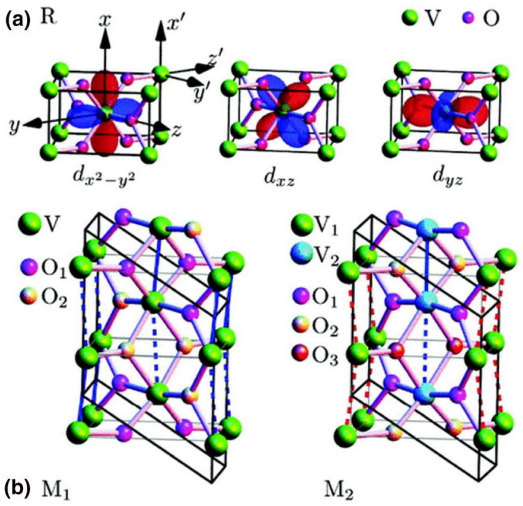


Figure 1: Two different atomic structures of vanadium dioxide, taken from [1]

In the past, vanadium dioxide has been used in metasurfaces[2] and in tunable, meaning their properties can be changed or turned on and off, materials, such as smart windows that could be dimmed [2], various methods of cooling that use less energy than the current standard, and the construction of smart surfaces for aircraft and spaceships [3].

The main interest that vanadium dioxide has for this project, as is for most applications involving optics, is that the two phases have vastly different permittivity [3], reflectance, and absorption [4]. Below Tc, vanadium dioxide has a low reflectance and absorption, being mostly transparent, a dielectric (also known as an insulator). However above Tc, the absorption and reflectance increase making it metallic, increasing its reflectivity and conductivity. It is that change, and it being so easily achievable, that made vanadium dioxide the perfect candidate for this idea of finding a tunable material with valuable properties[4].

[2]Thinner than wavelength (around the hundreds of nanometers) sheets of one or more materials made to have very specific properties not found in nature elsewhere

[3]Here named only permittivity, ϵ (epsilon) is a complex value that refers to the relative permittivity of a material, the ratio of its absolute permittivity and the permittivity of the vacuum, and it varies depending on the relevant wavelength. The permittivity of something is a measure of its electric polarizability, or how well the material reacts to an applied electric field, getting polarized (for example a magnet has is magnetically polarized and has a magnetic moment). Permittivity relates to the refractive index of a material (n) and to its extinction coefficient (k) by the formula $\epsilon = n^2 - k^2$

[4]The transition is explained better in [5], however as of today there is no consensus as to how the metal-insulator transition takes effect. The change in conductivity can be attributed to a different electron density, and the MIT probably originates from small impurities in the pre-transition material.

2.2 Epsilon Near Zero

What are those properties, then? The project started with the goal of finding a tunable metasurface that would achieve a wide epsilon near zero band which could be turned off and on: in modern optics, epsilon near zero (ENZ) surfaces solve many of the problems that modern optics face and introduce properties not seen elsewhere. Gaining traction in the last twenty years, ENZ refers to materials for which the real part of their permittivity is zero, or gets close as possible, while the imaginary part remains positive. They are extremely interesting for optics as, among other things, these types of materials can approach the wavelength of light towards infinity, decoupling of spatial and temporal field variations, minimize losses, bend, focus, and trap light, and even achieve nonlinear optics [6, 7]; sadly, I do not have the space nor the knowledge to explain each of these in detail but suffice to say they have very useful and sought after properties. ENZ materials have been made in many different ways, including using metals, doped semiconductors and even metamaterials; more over, metals almost always meet the ENZ condition naturally, as through the wavelength spectrum metals will variate between positive and negative real epsilon, having to cross zero at some point. It is still a goal, however, to find of materials that have a relatively wide wavelength range for ENZ properties, and even more one that can be turned on and off as easily as increasing the temperature a bit.

3 Methods

Due to the time and resources that it takes to deposit layer after layer of VO_2 on different materials and to the number of structures it would be nice to test with, the project was conducted in a fully computational manner. I was given originally two algorithms, a Transfer Matrix Method (TMM) one and a Retrieval one: the TMM, explained better below, takes the different materials that make the desired structure, and returns absorption, reflection, and transmission indexes for each wavelength of light, while the retrieval algorithm takes those values and returns the permittivity values for a theoretical material that matches the ones from the structure. Since the layer widths (around the tens of nanometers) are much smaller than the wavelengths (hundreds or thousands of nanometers), some interactions of light can be ignored and lead to a simpler and more efficient model. There will be of course inaccuracies and situations in which the TMM fails, however for a first measurement of such structures it was a good choice.

The transfer matrix method is a process used in optics to calculate the reflection and transmission characteristics of one or more slabs of linear materials [8]. If one

thinks about it, on a system with multiple layers of reflecting and transmitting material, the light reflected by one layer and then reflected back could either interfere constructively with the incoming light, adding onto it, or destructively, diminishing its intensity, and the calculations would get very complicated very quickly. There would be, in fact, an infinite number of reflections as the light would bounce back and forth between layers, getting less and less intense each time. TMM, on the other hand, takes each bilayer (plane where two layers meet), considers the incident plane wave, and models a 4 by 4 matrix for each layer forming the bilayer. It then uses the electric field phasors (complex number that represents a sinusoidal) for the incident wave and relates that to the ones from the reflected and the transmitted wave, making use of the 4 by 4 matrices. For a more thorough (and much better) explanation of TMM see [8]. More than the mathematical method behind it, what is interesting is understanding the importance of the amplitude of those phasors of the electric as opposed to calculating each reflected and transmitted wave, as well as the notion that each layer in a bilayer can be expressed optically as a 4 by 4 matrix. The TMM code then outputs the absorption, transmittance, and reflectance indexes for each wavelength. The retrieval code makes use of the fact that the layers are so thin compared to light that they can be "averaged" out and using a process similar to the TMM but reversed, outputs epsilon indexes for the total structure, as if it was made of a single material.

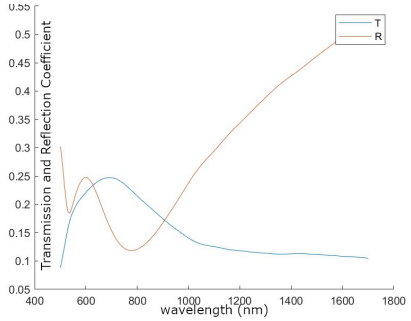
It is easier to understand what the code did with some images (Figure 2), as it is simple to see the overall process as a whole without necessarily needing to understand each individual part. Figure 2a displays the material data that works as input, for each wavelength there are corresponding real and imaginary parts of their permittivity; this data was obtained from [9]. Figure 2b represents the variable inputs inside the code itself: number of repetitions of the bilayer, width of the layers, and the materials the structure is made of. Figure 2c shows the outputs of the TMM code: transmittance, and reflectance values. Figure 2d shows the final retrieval output, both real and imaginary epsilon values. All of the computations were done in MATLAB, and I believe one of the things that took the longest in the project was learning enough MATLAB to read the source codes and manage to implement them both in my code, making sure the units matched and the outputs made sense. Initially there was a normalizing function that expected different outputs to the ones given by the TMM, so the whole thing did not work. It was after realizing this that the program started giving coherent results.

wavelength	e1	e2
190.77	-0.17571	2.2374
191.36	-0.17842	2.25216
191.95	-0.18114	2.266968
192.55	-0.18165	2.279772
193.15	-0.18438	2.29467
193.75	-0.1849	2.307552

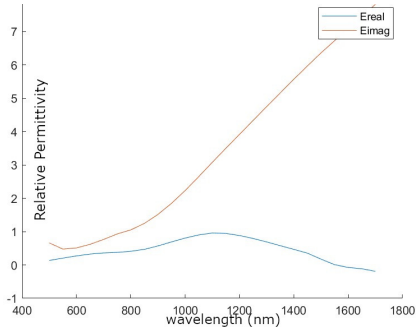
(a) Example of the data inputted to the TMM code, first column displays the wavelength of light, second column the real permittivity coefficient and the third the imaginery. Data from silver shown.

```
matFiles = dir(fullfile(join([pwd, '\MaterialData'], ""), '*.csv'));
multilayer=[1, 3, 5]; %number of repetitions of mat|van layers
orders=[true, false];
layers=[5, 10, 15, 20]; % thicknesses of material layers
vo2layers=[67]; % thickness of vanadium layers
Van=["VanRT", "Van90"];
```

(b) Snippet of the code showing the parameters to be set by the user, notably the layer width (layers) and the number of repetitions of each vanadium-material layer (multilayer)



(c) Example graph of transmission and reflection data outputted by the TMM section of the code, where the x axis indicated wavelength and the y axis a coeficient between 1 and 0. Data from 3 layers of silver at 5 nanometers shown.



(d) Example graph of real and imaginary permittivity data outputted by the retrieval section of the code, where the x axis indicated wavelength and the y axis epsilon values. Data from 3 layers of silver at 5 nanometers shown.

Figure 2: Example graphs to display the formatting of future plots and some features of the data and the code.

4 Results

After constructing the program and running a few test runs to make sure both the TMM and the retrieval algorithms worked, it was time to focus on what the entire project began as a search for: a layered structure that could switch between epsilon near zero and significantly big epsilon; turn it "on and off" if you will. I started off computing singly bilayered structures (where the bilayer of VO_2 and another material is only present once) using a selection of 14 materials containing a mix of metals and dielectrics, chosen mainly based on the ease of deposition of VO_2 on them[5].

The code ran each of the combinations and stored absorption, reflection, transmission, and both epsilon coefficients for some of the materials, considering both VO_2 at room temperature and at 90 Celsius. After some runs, I increased the wavelength to go up to 1700 nm as there were some interesting features missing, added materials to make the full 14, added 3 and 5 multilayer options and started saving all the data as .fig files for ease of use later on[6]. The project turned into a cycle of: set parameters for simulation, run simulation, check graphs for interesting features, adjust parameters, repeat. The metals turned out to be too reflective so the original spread of layers every 5 nanometers (5, 10, 15...) did not work as the structure was reflecting most of the incident light, so they were reduced. Some of the dielectrics behaved oddly and absorbed way too much light so they were discarded as possible candidates. I increased the spread of possible bilayers to also include 2 and 4. While doing this, I was also in the process of making the code more and more automated, so I would have to change less things from run to run and do less repetitive work. I started cataloguing the results into folders and subfolders, I divided the materials into groups each of which would have a different set of parameters to try with, and the naming system for the files was changed three or four times. However, in the end of this process the ideal structure with a big epsilon shift still eluded me, and I was forced to accept that maybe it would not be this easy. Maybe the structure could only do what we wanted in the case where it absorbed 98% of the light. The search for the initial property was abandoned for the time being, and instead, after multiple meetings with my supervisor, we decided to focus on two other things we had found in the process.

The first one was that there were a few structures that had a reasonably wide ENZ region (Figure 3), close to the visible light spectrum as well, which was something worth pursuing, and it did not have such a poor transmission as the previous structures that tried to implement a big epsilon shift as well. Using Aluminum, Silver and

[5]A list of the materials used as well as the VO_2 data provided by my supervisor can be found in Appendix A.

[6]More of the intermediate and final results can be found in Appendix B

gold, layer widths of around 3 nanometers, and 3 or 5 repetitions of the bilayer, the material achieved a 400-500 nm wide ENZ region just below the 1000 nm wavelength for the VO_2 at 90 Celsius, while retaining a 10-20% transmission. It could be turned off by cooling the vanadium, however the shift in epsilon is not as big as I initially had hoped for. Nonetheless, it would still be a useful structure just because it has a wider ENZ region than most available technology.

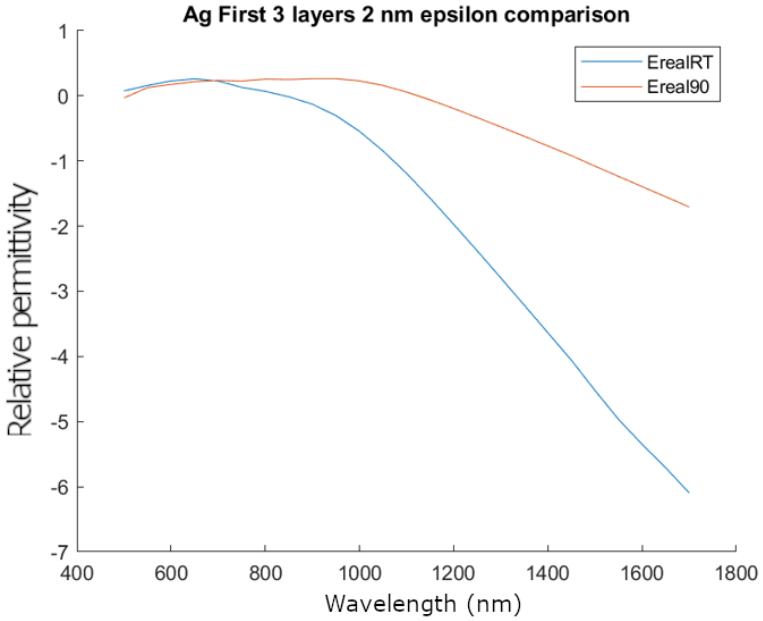


Figure 3: Plot of real epsilon coefficients, blue indicating vanadium at room temperature and orange at 90 Celsius. Structure formed by three repetitions of vanadium and silver at 2 nm thickness and vanadium at 67 nm. First indicates that the structure is of the form Ag—VO_2—Ag—VO_2—Ag—VO_2 as opposed to starting with VO_2. A wide ENz region can be seen between 600 and 1200 nm in the orange line.

With Al_2O_3, SiO_2, Ta_2O_5 and TiO_2, there were also promising results again in the form of wide ENZ regions for the room temperature vanadium (Figure 4), with an even better transmission than with the metals previously mentioned. These regions, however, seemed to be less favorable than the ones from Al, Ag and Au as there are some fluctuations. They also had the interesting feature of returning to ENZ after a peak, at around 1500 nm.

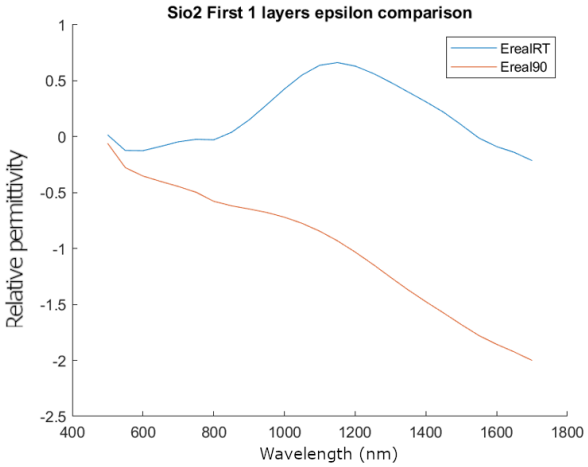
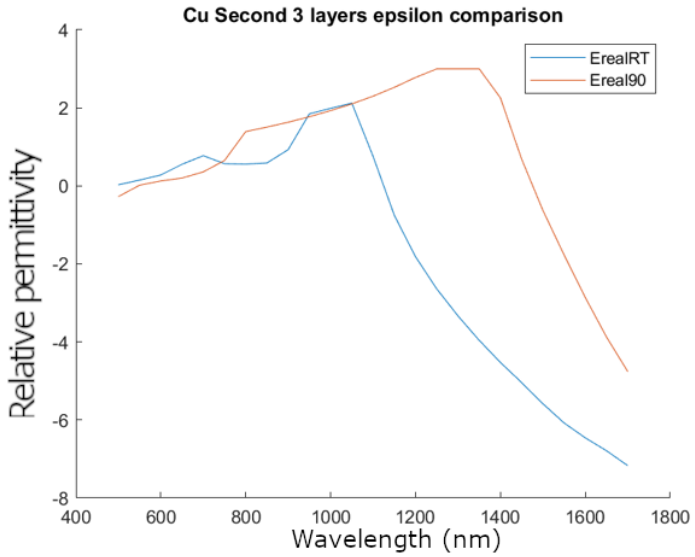


Figure 4: Plot of real epsilon coefficients, blue indicating vanadium at room temperature and orange at 90 celsius. Structure formed by one repetition of vanadium and silica at 10 nm thickness and vanadium at 67 nm. Wide ENZ at room temperature this time, between 600 and 1000 nm, that comes back to near zero after the peak, around 1600 nm.

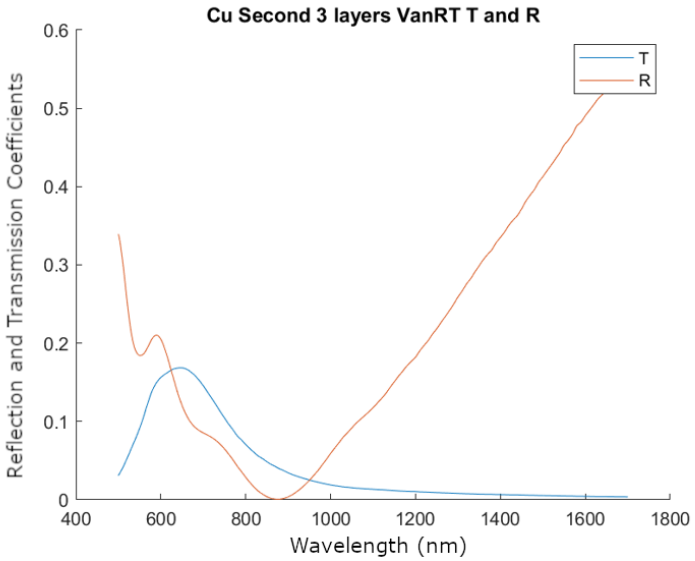
The second thing that was revealed in the graphs, however, was not something I had been expecting. When observing the copper graphs, I found it strange that the graph looked less smooth than usual (Figure 5a) and, when looking at the reflection plot (Figure 5b), there was a zero in reflection at around 800 nanometers. My supervisor mentioned that it might be a resonant cavity: in a nutshell, the widths of the layers were such that the light was bouncing back and forth without actually reflecting back, and when it left on the other side it had been phase shifted[7]. From the transmission and reflection data calculated by the TMM I wrote some code that would produce phase shift[8] graphs for each structure and, observing them, it turned out to really be a resonance. After some optimization done by hand (testing many structures and slowly fine tuning the parameters) I was able to reach a phase shifter for nickel, copper and chromium, each of them with a shift of as closely as possible to pi.

[7]This is one of the times where the TMM approach did not work so well, because the light was behaving in ways that the method was not design to account for, so the results were not what really would happen in the physical world but rather some mathematical curiosity.

[8]Here phase shift is used to describe the phase difference between the light that is reflected by one such structure at room temperature and the light that is transmitted through the same structure at 90 C. There would be a phase shift if in one case the light was travelling a different distance, so the light waves would arrive "out of sync", and the bouncing between layers explained that different distance.



(a) Graph of real epsilon values for copper at three layers, 10 nm. Here was can see some strange features on both epsilon values around the 800 nm mark, indicating that the model is struggling, in this case later revealed to be the resonant cavity.



(b) Reflection and transmission graph for the same structure as (a), the reflection dips to zero at around 800 nm, indicating that the light is getting trapped inside the structure, a resonance.

Figure 5: Graphs of copper showing interesting features.

If we imagine optical circuits as very similar to electronic circuits but using light rays, materials that can change the relative phase of light are very important: if the original light meets the light phase shifted by pi they interfere destructively, cancelling each other out. The structures modelled here, however, have the added benefit that they are tunable. The phase shift can be turned from close to pi to 0 depending on the temperature the vanadium is at (Figure 6).

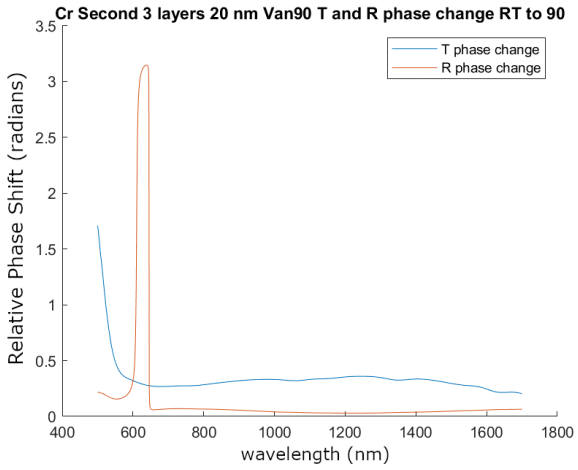


Figure 6: Plot of relative phase shift for chromium between different phased vanadium dioxide, blue indicating transmission and orange reflection. The peak at 800 nm indicated the resonance frequency and is the phase shift we are after.

5 The Way Ahead

As the structures could not be produced in the time span of my Laidlaw project, I will not be able to experiment with them and check if the properties found by the TMM hold in the experimental world. However, the university has a partner lab in Canada that frequently produces the metasurfaces that cannot be produced here, and my supervisor has been in close contact with them, with the intention of manufacturing the structures I designed with the model. When they are ready, experimental tests will be conducted to confirm (or deny) what I have found. The most promising ones will probably be the ones that are easiest to deposit. The layering of vanadium dioxide highly depends on the base material, so if aluminum makes the process easier it will surely be more feasible in the long run.

As far as more modelling is concerned, one thing I would like to have done but was impossible due to time constraints was applying an optimization algorithm to the code. With one it would be easier to find the best possible parameters, from

number of bilayers to layer width, considering the epsilon shift, the ENZ regions, and the transmission of the structure. Running more tests and using different materials and/or geometry (for example using fins instead of regular layers, found in many metasurfaces) with the principles used in this project might as well yield curious results. For the applications of the structures found here if they turn out to be functional and a good option, ENZs have a plethora of different uses and new ones are being developed, while for optical switches there is a growing market and research into optical circuits.

6 Conclusion

In conclusion, this project started with me reading over existing literature and, after a lot of back and forth with the code, managed to get some interesting results. I loved learning about vanadium dioxide and its transition phase, as well as discovering epsilon near zero surfaces for the first time, and I believe the structures designed here could indicate some research space in multilayered vanadium dioxide-based materials. We did not find the initially sought after wide ENZ big epsilon shift structure, however wide ENZ regions on their own can prove to be useful, as can tunable optical switches. If I were to conduct the project again, I would run more tests and start with a wider range of things to look after, but for the most part I am satisfied. It is strange how one can go looking for something and find something entirely different yet equally interesting. It is clear to me that optics as a field has been thoroughly researched, however there are new ideas and new theories arising all the time, which leads to a fascinating subject and a home for innovation.

7 Acknowledgements

I would like to thank my supervisor, Dr. Sebastian Schulz for the guidance, help, and support he provided throughout my research. I would also like to thank Lord Laidlaw and the Laidlaw Foundation for providing the financial and institutional support for me to conduct this project through the Laidlaw Scholarship Programme for Leadership and Research. Finally I would like to thank the University of St Andrews Laidlaw team, as well as the physics building staff for the continuous support.

8 References

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[9] "Refractiveindex.Info." RefractiveIndex.INFO - Refractive Index Database, `refractiveindex.info/`. Accessed 24 Aug. 2023.

9 Appendix A

The 14 materials used (their refractive index and epsilon data gathered from [9]) were:

1. Silver (Ag)
2. Aluminium (Al)
3. Aluminium oxide (Al_2O_3)
4. Gold (Au)
5. Chromium (Cr)
6. Copper (Cu)
7. Germanium (Ge)
8. Niquel (Ni)
9. Silica (SiO_2)
10. Tantalum Pentoxide (Ta_2O_5)
11. Titanium (Ti)
12. Titanium Dioxide (TiO_2)
13. Zinc (Zn)
14. Zinc oxide (ZnO)

Database for Vanadium Dioxide data

10 Appendix B

Some of the other interesting results that were not shown in the essay:

10.1 Wide ENZ - Metals

The three metals that worked for getting a wide ENZ region were Silver and Gold. For Silver and Gold I show the comparison between layer widths adn multilayers, the nomenclature following first number = number of multilayers, second number = width of the material layer. All the vanadium layers were 67 nm thick as that was how the original data was measured. Van90 refers to post MIT van, above 90 celsius. VanRT refers to room temperature vanadium.

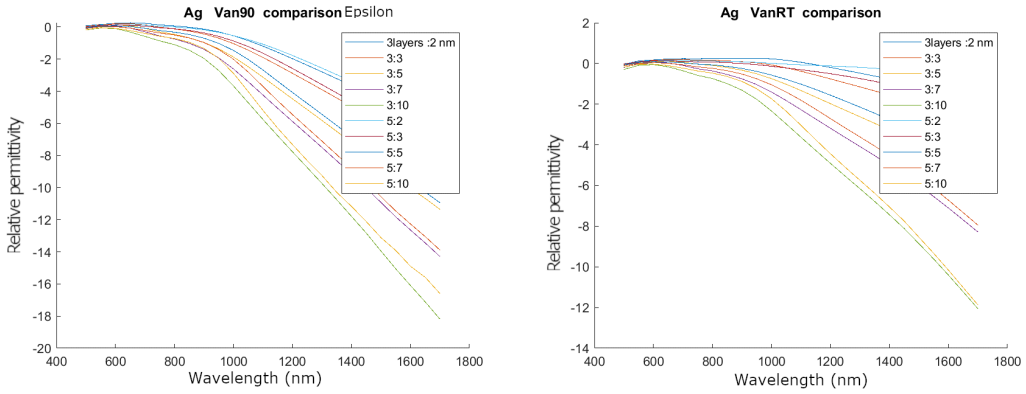

Figure 7: Graphs for silver

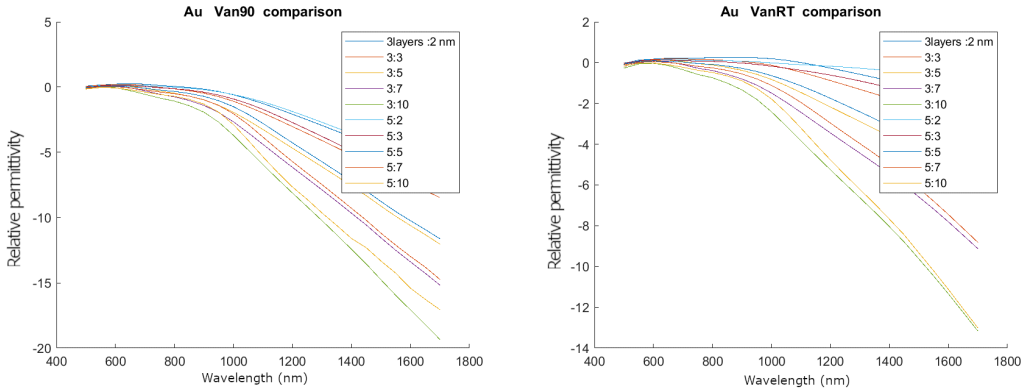

Figure 8: Graphs for gold

It can be seen that for a multitude of different structure there is a wide ENZ region, and it is also possible to see which ones work best. Now an example of a specific structure, the 3:2, showing that the transmission is pretty good around the ENZ region.

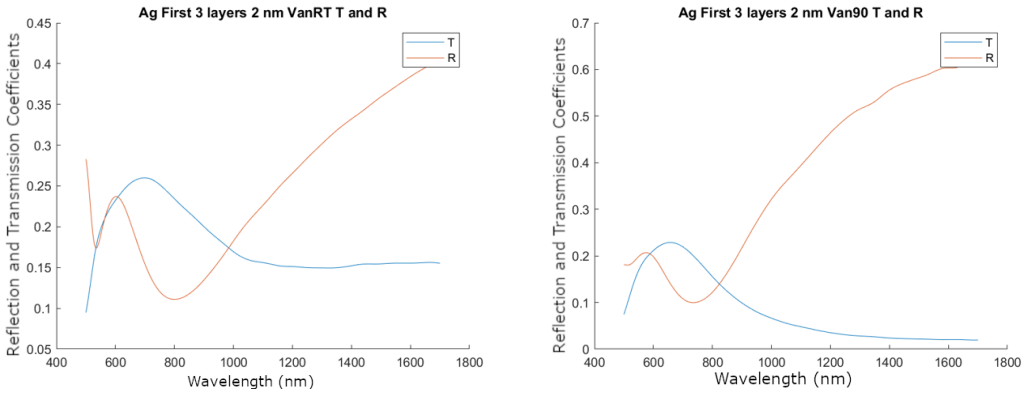

Figure 9: Graphs for silver 3:2

10.2 Wide ENZ - Insulators

For the dielectrics, the ENZ region is at room temperature as oposed to the 90 celsius of the metals. As an example let us look at Al_2O_3. It has a good ENZ region which comes back after a peak, as well as having very good transmission.

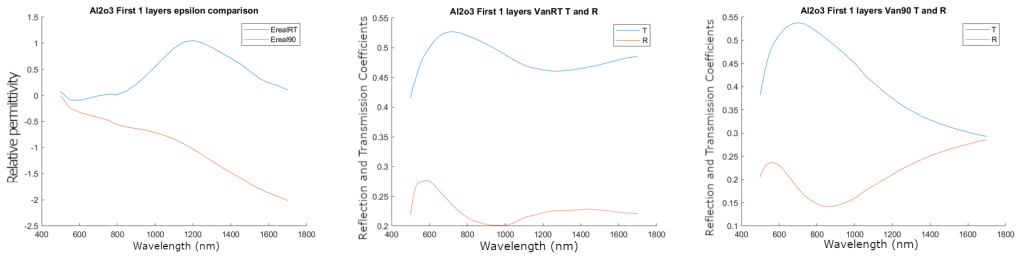

Figure 10: Graphs for Al_2O_3 1:10

10.3 Phase Shifters

The treatment for the phase shifters was similar to the one done with gold and silver. Make a comparison graph with all the structures and, more importantly here, the layer thickness, and see which one approached pi the best. In the figures it can be seen that for Ni, Cu and Cr there is the trend of approaching pi as the thickness increases and once reached the relative phase shift declines again.

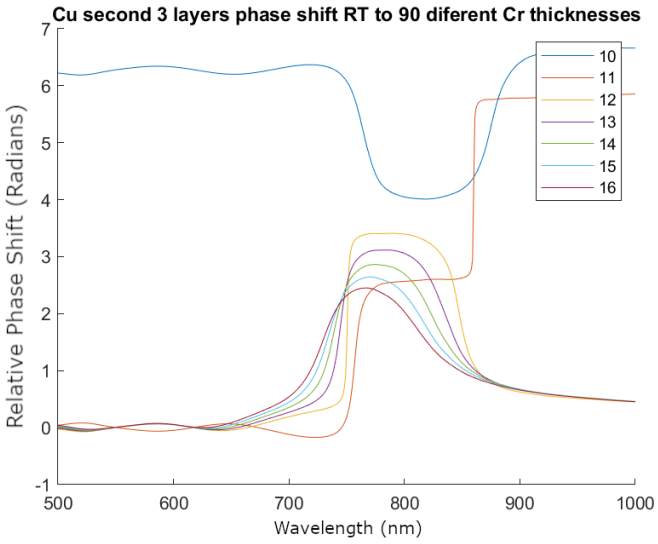

Figure 11: Comparison graph for Cu

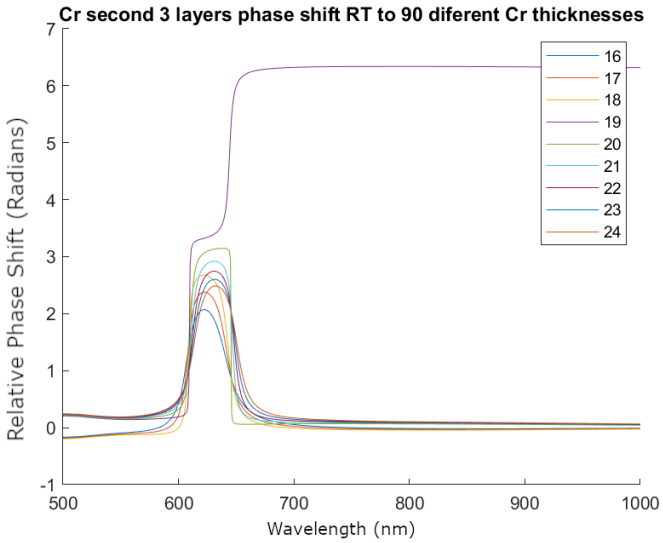

Figure 12: Comparison graph for Cr

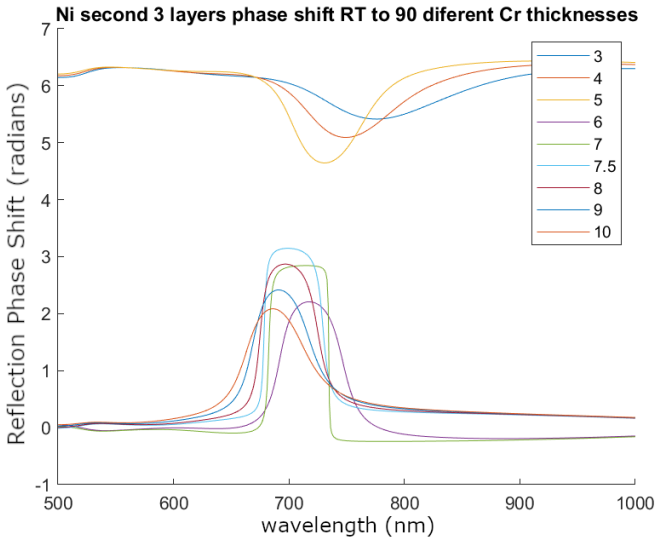

Figure 13: Comparison graph for Ni

The full compilation of results can be found in a presentation form here: