Fabrication of Distributed Bragg Reflectors (DBR) by spin-coating for the development of a novel optical ultrasound sensor

The Laidlaw Research and Leadership Programme

Aug 2022

Rachel Wan, Dr Thomas Allen
Biomedical Optics Research Laboratory (BORL), Photoacoustics Imaging Group
UCL Medical Physics and Biomedical Engineering, University College London

MEDICAL PHYSICS & BIOMEDICAL ENGINEERING

LAIDLAW FOUNDATION

Foreword

Over the course of a six- week period between June 2022 to July 2022, I had the amazing opportunity to conduct research with Dr. Thomas Allen of the Department of Medical Physics and Biomedical Engineering at University College London, operating under the generous funding by the Laidlaw Foundation. I maximized this opportunity by exploring around this fascinating research topic, as well as laying the foundations of this project. This report outlines the details of my project this summer, highlighting the present and future potential of this technology.

Abstract

The utilization of optical ultrasound sensors have increased in medical diagnosis and photoacoustic imaging due to their high bandwidth and sensitivity (1). Herein, we investigate a new method of fabricating Distributed Bragg Reflector (DBR) via spin-coating for the design of a novel optical ultrasound sensor.

Introduction

Photoacoustic imaging is a relatively novel biomedical imaging technique, which is based on laser generated ultrasound. It offers the possibility of acquiring high-quality 3D images of the internal structure of soft biological tissues such as blood vessels. Ultrasound detection plays a crucial role in photoacoustic imaging. High performance ultrasound sensors are needed, especially in the field of intravascular and endoscopic photoacoustic imaging, where probes require not only a high bandwidth and sensitivity but also a small footprint (2).

Currently, photoacoustic imaging relies on piezoelectric ultrasound sensors. However, piezoelectric ultrasound sensors require a large sensing area to achieve high sensitivity, their frequency tends to be narrow, preventing the accurate measurement of the incident acoustic wave. These problems will all lead to a degradation in image quality. We propose to overcome these limitations by developing an entirely new optical ultrasound sensor. The novel ultrasound sensor, as shown in Figure 1, is in essence a laser composed of two Distributed Bragg Reflectors (DBR) which forms an optical cavity, an active medium and a pump source. As an ultrasound wave compresses the sensor, the distance between the two mirrors is modulated resulting in a change of the wavelength emitted by the laser. The ultrasound wave is then recorded by monitoring this change in wavelength. The novel optical ultrasound sensor will provide high bandwidth and sensitivity as well as a small element size, all required to achieve a high quality photoacoustic image.

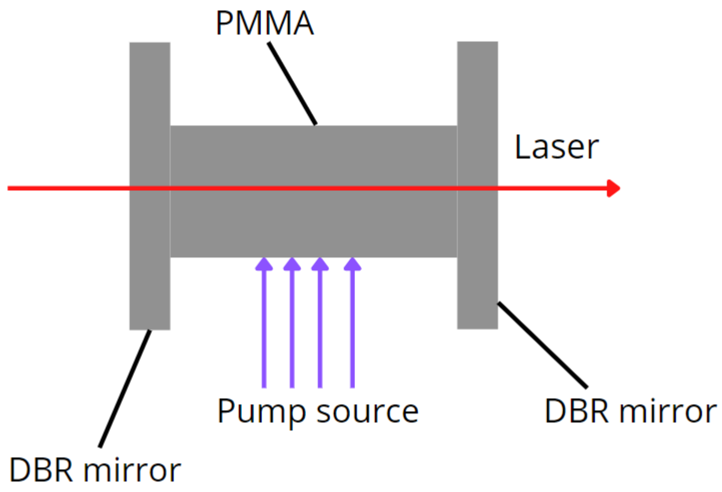

Figure 1: *Prototype of a novel optical ultrasound sensor*

The work presented in this report focuses on designing and building a DBR using spin-coating, a cost-effective fabrication method. The method developed will ultimately be used, to create DBRs for the novel optical ultrasound sensor being developed at UCL.

Distributed Bragg Reflectors (DBR)

A DBR consists of a multi-layer stack of high refractive and low refractive index films (see Figure 2), with each layer being one quarter wavelength thick. λ is the centre wavelength of the Bragg mirror. On every point between the 2 layers, a part of the incident beam is reflected. The phase difference of all the reflected beams are either zero or a multiple of 360°(6), where constructive interference occurs. Through travelling the stack of the Bragg mirror, the reflected light increases while the intensity of the incident light decreases.

The DBR will be fabricated by alternatively spin-coating polymers of high and low refractive index. The polymers used for the fabrication of the Bragg mirrors stacks are CA (cellulose acetate) and PVK (polyvinylcarbazole), where CA has a refractive index of 1.469 (4) and PVK has a refractive index of 1.675 (5). The thickness of the different layers will be precisely controlled by fine tuning the rotation speed and duration of the spin-coating process (3).

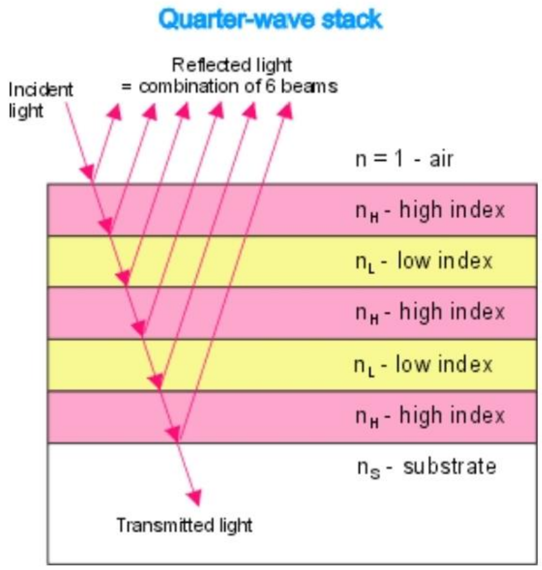

Figure 2: The construction of a Bragg mirror with alternative layers of high and low refractive index films(6)

Experimental details

Materials and fabrication

Glass microscope slides around 1mm thick and 26 x 76mm (VWR 50 Super Premium Microscope Slides, Catalogue Number: 631-0117) were used. The glass slides were cleaned using lens paper with acetone.

To fabricate high-refractive index and low refractive index layers of DBR mirrors, PVK (polyvinylcarbazole) along with its solvent toluene and CA (cellulose acetate) along with its solvent diacetone alcohol were used. An Ossila spin-coater was used for spin-coating all the glass slides.

Fabricating CA glass slides:

Firstly, CA was dissolved into diacetone alcohol at a concentration of 28.6mg/mL (7). 572mg of cellulose acetate was weighed and dissolved with 20mL of diacetone alcohol. The mixture was then placed on a hot plate to undergo vigorous magnetic stirring for around 2 hours. After syringe filtering the solution to remove the remaining particles, 50μL of the resultant solution was spin-coated onto the glass slides at different speeds (1000RPM, 2000RPM, 3000RPM, 4000RPM, 5000 RPM) for 2 minutes. The spin-coated film glass slides were then cured in a 130°C oven for 5 minutes, so the material deposited on the slide would dry at a quicker rate.

Fabricating PVK glass slides:

PVK was dissolved into toluene at a concentration of 22.2mg/mL(7). 444mg of polyvinylcarbazole was weighed and dissolved with 20mL of toluene. The mixture was then placed on a hot plate to undergo vigorous magnetic stirring for around one and a half-hour, same as what was done with CA. After syringe filtering the solution to remove the remaining particles, 50μL of the resultant solution was spin-coated onto the glass slides, at different speeds (1000RPM, 2000RPM, 3000RPM, 4000RPM, 5000 RPM) for 2 minutes. The spin-coated film glass slides were then cured in a 130°C oven for 5 minutes.

PMMA (Poly(methyl methacrylate)) was spin-coated to be sandwiched between the DBR mirrors (PVK and CA layers), acting as a gain medium for the laser.

Fabricating PMMA glass slides:

PMMA was dissolved into toluene at a concentration of 20g/dL. 2g of PMMA was weighed and dissolved with 10mL of toluene. The solution was then submerged into an ultrasonic bath for 10 hours to ensure the solid particles are fully dissolved. It was further diluted to 5g/dL. After undergoing syringe filtering, 100μL of the resultant solution was deposited in the center of the glass then spin-coated at different speeds (100RPM, 400RPM, 1000RPM, 5000RPM). The slide was spin-coated for 5 minutes accelerating at 100RPM, unlike the others that were spin-coated at

400RPM, 1000RPM and 5000RPM, where they were spin-coated for 45s. The spin-coated film glass slides were then cured in a 60°C oven for 2 minutes (8).

Characterization of DBR mirrors and gain medium

The thickness of PVK, CA and PMMA layers were measured by a contact profilometer (Mitutoyo SJ-400). By analysing the data the surface roughness tester produced, the thickness for each material was obtained (see Figure 3, 4, 5). Using the data, the desired speed is obtained for PVK and CA, which entails that the stack of mirrors can be created. 100 μL of PVK solution was deposited at the centre of the glass first due to having a higher refractive index compared to CA. PVK was spin-coated for 2 minutes at a speed of 2040 RPM, and the slide was placed in the oven at 130°C oven for 5 minutes afterwards. The slide was then left out to cool for another 5 minutes, then another layer was placed on top, in this case, CA, also with a volume of 100 μL. CA was spin-coated for 2 minutes at a speed of 4160RPM. The process was repeated until 14.5 layers were created, and a Bragg mirror is designed.

Results

The data collected for CA, PVK, and PMMA is measured by a contact profilometer. One of the examples are shown below for PMMA spin-coated at 400RPM (see Figure 3). The blue line illustrates the original data collected, the orange line is a line extended based on 2 points on the original data graph, creating a straight line using the equation $y = mx+c$. Finally, the grey line highlights the thickness of the material, in this case for PMMA at 400RPM, the thickness is 0.758 μm (see red dot in Figure 3). Data was collected and graphs were analysed for the rest of the speeds and materials.

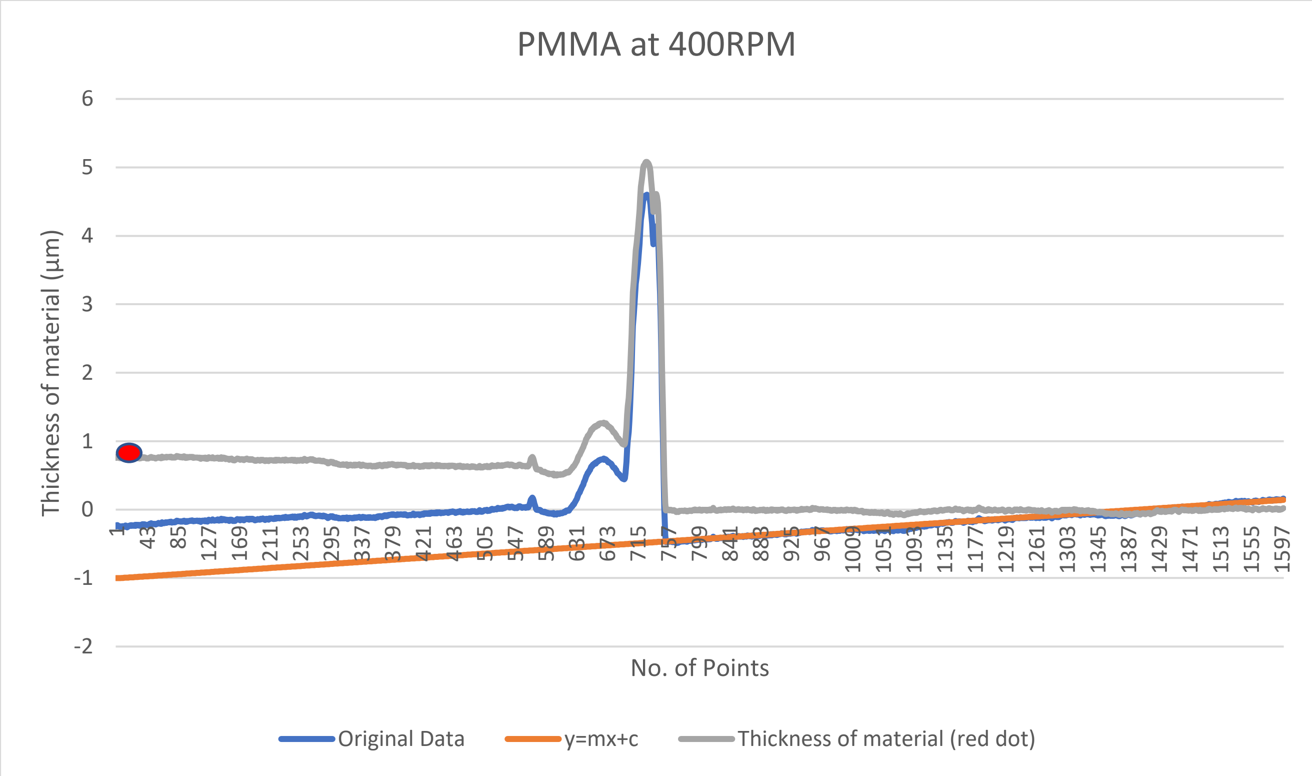

Figure 3: PMMA's thickness at 400RPM

After the thickness of PVK, CA and PMMA were obtained for all the independent speeds, graphs were plotted for thickness (nm) against speed (RPM). This is to prove the existing theory that the faster the spin-coating speed is, the thinner the material deposited on the glass microscope slide is (8). Figure 4, 5, 6 shows a graph plot of the materials' film thicknesses as a function of spin -coating speed. As shown, they show a similar trend of demonstrating an inverse relationship.

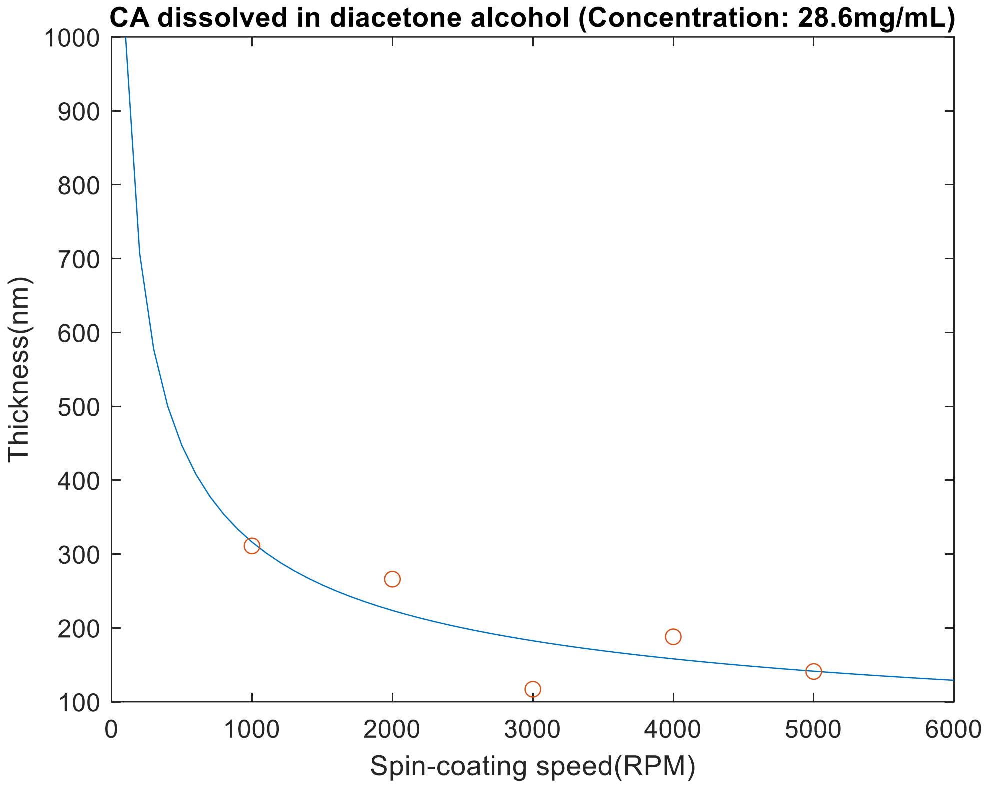

Figure 4: CA material thickness as a function of spin-coating speed

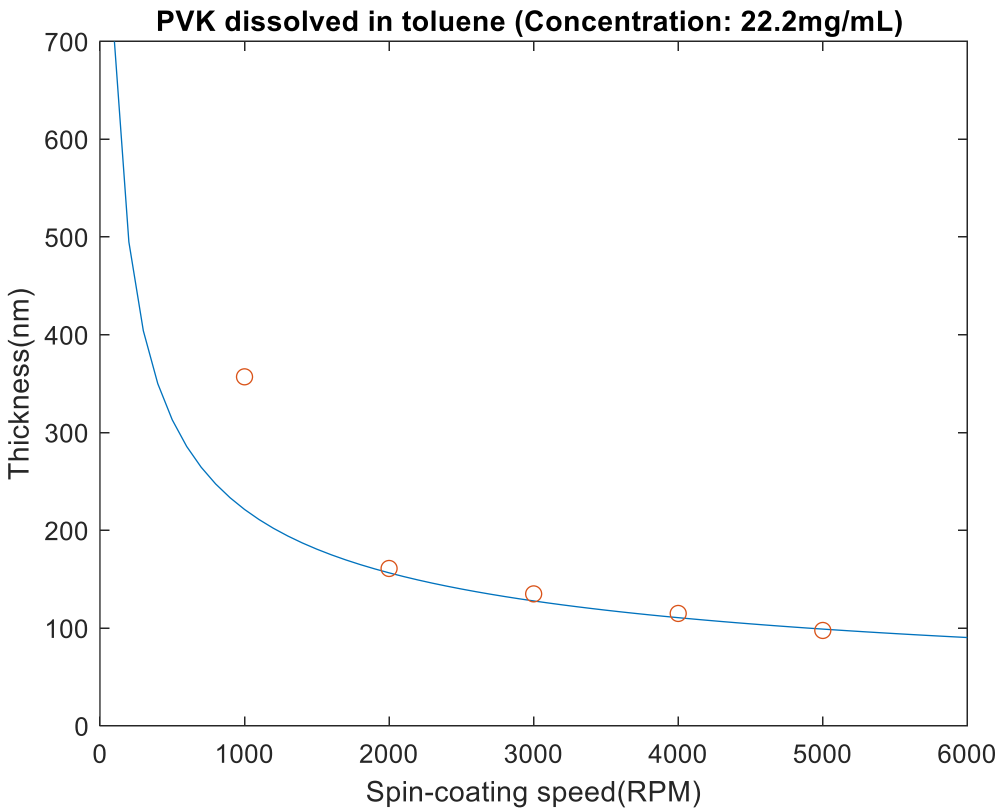

Figure 5: PVK material thickness as a function of spin-coating speed

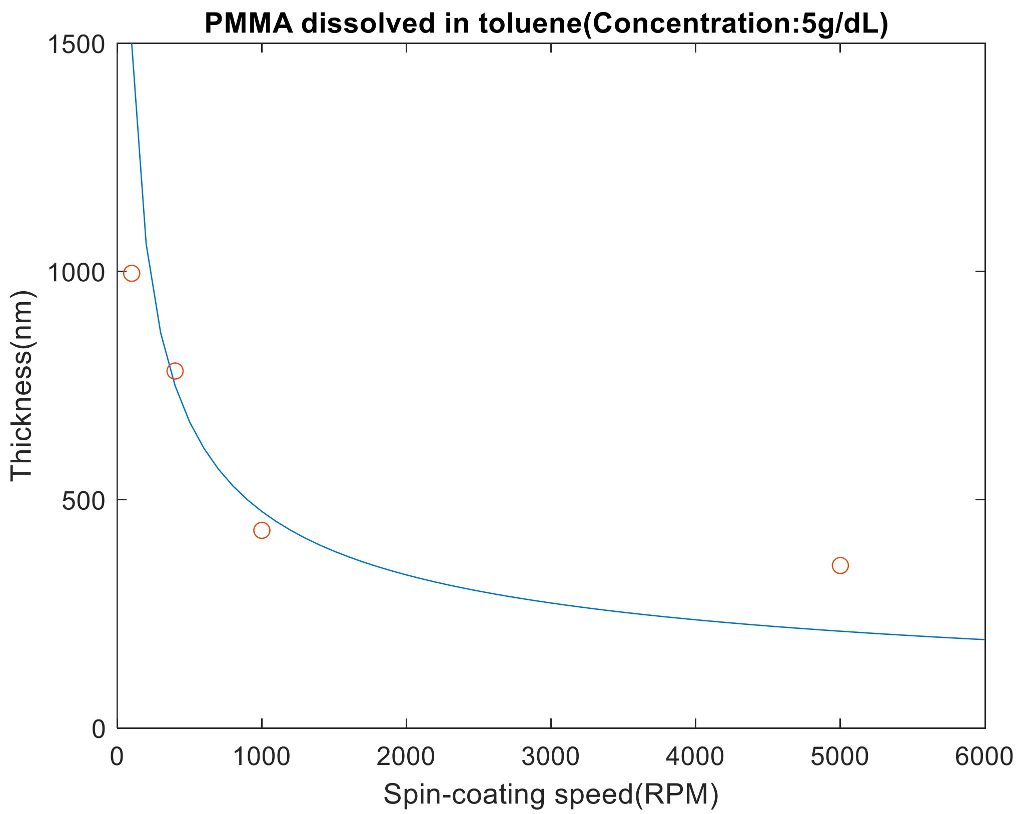

Figure 6: PMMA material thickness as a function of spin-coating speed

The central wavelength (620nm) was chosen to be midway of the region of interest (see Figure 7). To design a DBR mirror, each optical layer thickness corresponds to one-quarter of the wavelength for which the mirror is designed (9). Calculation for the desired thickness of the material is shown below:

$$620 \cdot \frac{1}{4} = 155nm$$

According to the graphs (Figure 4 & 5), for CA, at a thickness of 155nm, the spin-coating speed is 4160 RPM. For PVK, at a thickness of 155nm, the spin-coating speed is 2040 RPM. Using the decided speeds, a stack of DBR mirrors compromising of PVK and CA layers were created (see Figure 8).

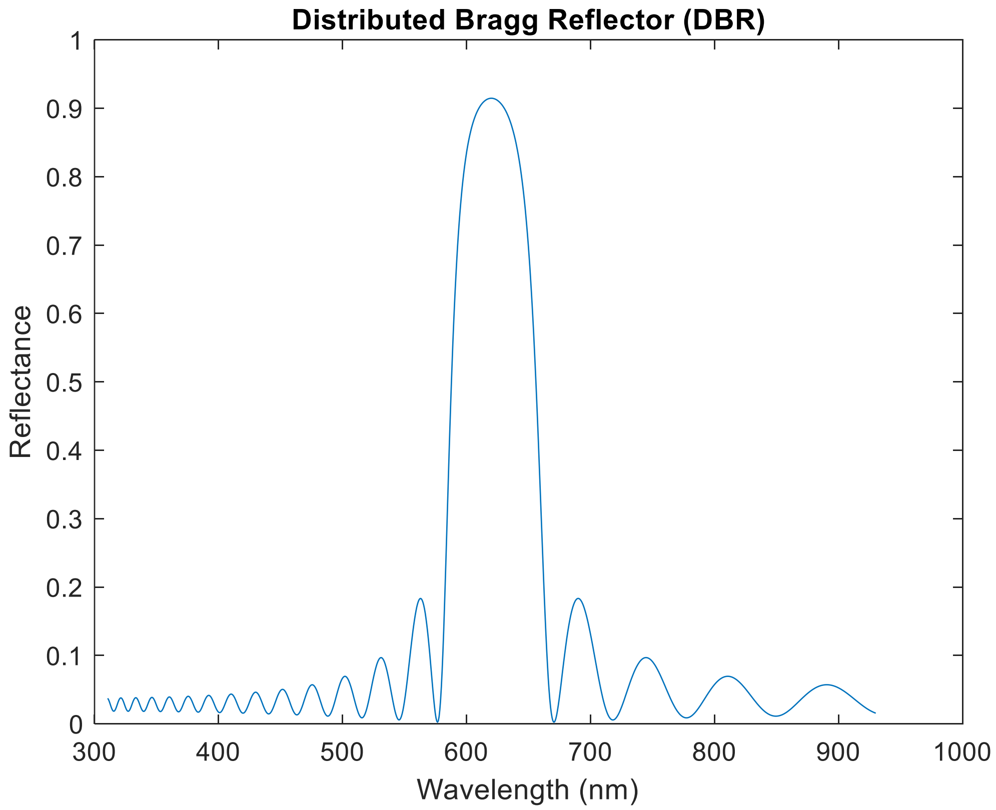

Figure 7: Distributed Bragg reflector of reflectance as a function of wavelength

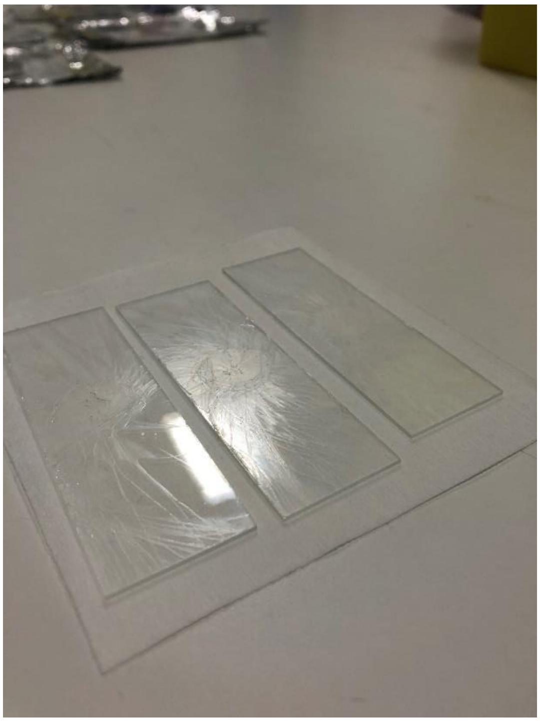

Figure 8: Photo of the DBR mirrors showing reflectivity

Discussion & Conclusion

The multi-layer distributed Bragg reflector mirrors were fabricated by a simple procedure, alternating the spin-coating of 2 different solutions, PVK and CA. Predictive models have been generated for the thickness of films of the materials CA, PVK and PMMA, proving that the thickness varies with the function of spin-coating speed at the determined concentrations.

Measuring the thickness of the PVK, CA and PMMA layers using a contact profilometer was not ideal. The use of a microscope and an interferometer had been explored prior to using the contact profilometer, however the smallest the devices could measure were 6-15 μm, which was not feasible due to majority of our samples being in nm range. Whilst the contact profilometer has a large measuring range, the device itself was extremely sensitive to surroundings which made it difficult to take consistent readings. Moreover, the stylus probe may be contaminated with the surface of the sample, generating inaccurate data (10). A contact profilometer is slower than non-contact techniques, which may influence measurements.

Since the layer of the material is so thin, the cleanliness of the glass microscope slides itself is extremely crucial. All the spin-coating was either done in the fume cupboard or the cleaning room to ensure no dust was deposited on the glass slide, on top of that acetone was used to clean the slides.

Future Directions

The development of this novel optical ultrasound sensor by using a fabrication technique has a broad premise and can be applied to medical diagnosis and therapy. This sensor not only provides structural information, but also functional information through different methods such as spectroscopy, flow measurements or thermometry(11). Potential applications include detection of breast cancer, skin pathologies or cardiovascular diseases.

The laser will pass through the DBR mirrors, testing if it detects ultrasound. In the future, a scanning ellipsometer should be considered instead of a contact profilometer as it is non-contact, non-destructive and it allows the user to determine several film thicknesses simultaneously. This increases the efficiency and productivity of measuring the sample(12).

UV spectra transmission will be measured using a photospectrometer, where a plot of transmission of a 14.5-layer mirror versus wavelength will be displayed. For characterization of laser properties, a Q-switched laser will be used as a pump source(7). The laser will pass through the DBR mirrors, testing if it detects ultrasound. The prototype is as shown above (see Figure 1).

The prototype is established by sandwiching the gain medium (PMMA) between 2 DBR mirrors with alternating layers of PVK and CA. PMMA was in between due to its high solubility, and its ability to provide strong adhesion(7).

In the future, other solvents will be considered. For example, PVK was dissolved in toluene in this research project. However, dissolving it in toluene created a cloudy effect on the layer of the glass slide (see Figure 9), leading to a great reflectance as shown on the photospectrometer as most of the light passed through.

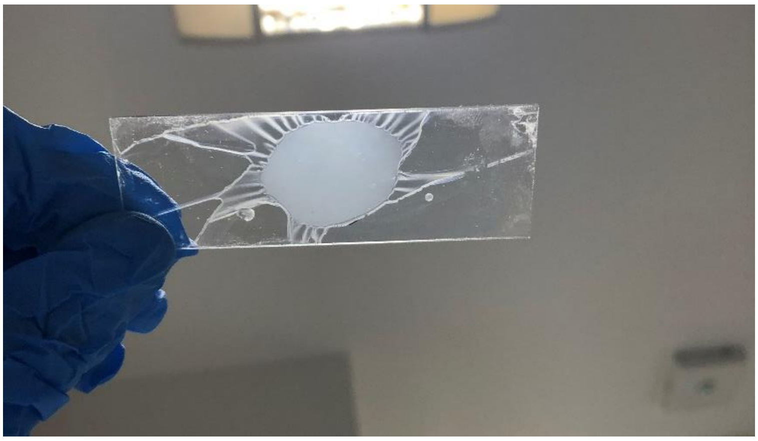

Figure 9: Photo of a glass slide with a layer of PVK & toluene deposited, in which a cloudy effect was created

Prior to using toluene, other solvents had been explored for usage such as chlorobenzene. However, chlorobenzene is flammable and toxic. Being hazardous, it would had been dangerous to use. In the near future, under a safely contained process, chlorobenzene would be dissolved in PVK to test if the cloudy effect is still observed.

My experience this summer coincides with the values of leadership: all about empowering and inspiring others. By developing this medical technology, this project can be further developed in different directions. Through the possibility of collective discovery, the project will be continued in the future and set up as an eventual clinical application in the field of photoacoustic imaging.

Acknowledgements

I would first like to thank Dr. Thomas Allen, my supervisor, for all his continuous support and guidance towards me throughout this project. His style of mentorship has not only allowed me to conduct advanced research within our lab, the responsibility and trust he granted me has been greatly appreciated. Secondly, the Laidlaw Foundation for their generosity in this summer research project. I am extremely grateful for this opportunity to be able to be a part of this organization, and be connected to like-minded scholars all around the world where we all align with the same values. Lastly, Christopher Cullen, the scholarship coordinator at University College London, for his continuous support throughout my six-week research project.

References

1. Ma J, Ma X, Xu L. Optical ultrasound sensing for biomedical imaging. Measurement [Internet]. 2022 Aug 15 [cited 2022 Aug 5];200:111620. Available from: https://www.sciencedirect.com/science/article/pii/S0263224122008302

2. Liang Y, Jin L, Wang L, Bai X, Cheng L, Guan BO. Fiber-Laser-Based Ultrasound Sensor for Photoacoustic Imaging. Sci Rep [Internet]. 2017 Jan 18 [cited 2022 Aug 5];7(1):40849. Available from: https://www.nature.com/articles/srep40849

3. Fast and simple fabrication of organic Bragg mirrors—application to plastic microchip lasers - IOPscience [Internet]. [cited 2022 Aug 5]. Available from: https://iopscience.iop.org/article/10.1088/1612-2011/10/5/055808

4. Refractive Index of Cellulose for Thin Film Thickness Measurement [Internet]. [cited 2022 Aug 5]. Available from: https://www.filmetrics.com/refractive-index-database/Cellulose

5. Poly(N-vinyl carbazole) PVK - Vinyl - Matmatch [Internet]. [cited 2022 Aug 5]. Available from: https://matmatch.com/materials/mama440012-poly-n-vinyl-carbazole-pvk

6. Bragg reflector [Internet]. [cited 2022 Aug 5]. Available from: https://www.batop.de/information/r_Bragg.html

7. Yang Y, Zhou Y, Liao Z, Yu J, Cui Y, Garcia-Moreno I, et al. Mechanically tunable organic vertical-cavity surface emitting lasers (VCSELs) for highly sensitive stress probing in dual-modes. Opt Express [Internet]. 2015 Feb 23 [cited 2022 Aug 2];23(4):4385–96. Available from: https://opg.optica.org/oe/abstract.cfm?uri=oe-23-4-4385

8. Chapman N, Chapman M, Euler W. Modeling of Poly(methylmethacrylate) Viscous Thin Films by Spin-Coating. Coatings. 2021 Feb 9;11:198.

9. Fig. 6. Schematic of a distributed Bragg reflector consisting of a... [Internet]. ResearchGate. [cited 2022 Aug 6]. Available from: https://www.researchgate.net/figure/Schematic-of-a-distributed-Bragg-reflector-consisting-of-a-quarter-wavelength-thick-of_fig5_312185773

10. Optical Profilometry [Internet]. Nanoscience Instruments. [cited 2022 Aug 6]. Available from: https://www.nanoscience.com/techniques/optical-profilometry/

11. Beard P. Biomedical photoacoustic imaging. Interface Focus [Internet]. 2011 Aug 6 [cited 2022 Aug 6];1(4):602–31. Available from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3262268/

12. Advantages of spectroscopic ellipsometry - HORIBA [Internet]. [cited 2022 Aug 6]. Available from: https://www.horiba.com/pol/scientific/technologies/spectroscopic-ellipsometry/advantages/