AFRL-AFOSR-JP-TR-2019-0024

Graphene oxide: A new functional material for optical waveguide devices

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03/27/2019
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
Air Force Office of Scientific Research
Asian Office of Aerospace Research and Development
Unit 45002, APO AP 96338-5002

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
27-03-2019

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
28 Sep 2016 to 27 Sep 2018

4. TITLE AND SUBTITLE
Graphene oxide: A new functional material for optical waveguide devices

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA2386-16-1-4016

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
Wu Yi Chong

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Malaya
Photonics Research Centre
Kuala Lumpur, 50603 MY

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD
UNIT 45002
APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR IOA

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-JP-TR-2019-0024

12. DISTRIBUTION/AVAILABILITY STATEMENT
A DISTRIBUTION UNLIMITED: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
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15. SUBJECT TERMS
optical polarimeter, fiber-waveguide, integrated photonics, graphene oxide

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
Unclassified	Unclassified	Unclassified	SAR	

19a. NAME OF RESPONSIBLE PERSON
KIM, TONY

19b. TELEPHONE NUMBER *(Include area code)*
315-227-7008

Graphene Oxide: A new functional material for optical waveguide devices

Submission date: 26th December 2018

Points of interest:

- *Light propagation in GO-coated planarised silica waveguide studied.*
- *Polarisation selection characteristics changes with GO-coating thickness.*
- *Maximum TM-pass polarisation extinction ratio measured is 34.5 dB.*
- *Maximum TE-pass polarisation extinction ratio measured is 46.0 dB.*
- *FEM analysis used to obtain the complex refractive index of GO layer.*
- *Refractive index for TM- and TE-polarisation states are 1.61+0.001i and 1.66+0.07i, respectively.*

1.0 Abstract

Light propagation in graphene oxide (GO) coated silica-on-silicon planarised stripe optical waveguides has been studied. GO film with sub-micron thickness has been coated on the planarised waveguide surface using drop-casting technique. This technique allows control of GO coating thickness in steps of ~0.1 μm. The optical characteristics of the GO-coated waveguide have been investigated for coating thicknesses between 0.1 μm and 1.0 μm. The single mode GO-coated waveguide shows a polarisation-dependent transmission characteristic that switches from TM-pass to TE-pass when the GO coating thickness is increased beyond 0.45 μm. The highest extinction ratio measured for a TM-pass polarizer was 34.9 dB, using a coating length and thickness of 1.0 mm and 0.34 μm respectively, while the highest extinction ratio for a TE-pass polarizer was 46.0 dB using a coating length and thickness of 1.0 mm and 0.71 μm respectively. This result was measured across a wavelength range of 1520 nm to 1620 nm, with a PDL variation of less than 3.0 dB. The coating thickness dependent polarisation characteristics of the GO-coated waveguide provide an avenue for tailoring of the polarisation selection by controlling the coating thickness, while the broadband response enables it to be used in multi-wavelength applications.

Subject terms: Graphene oxide, silica waveguide, planarised waveguide.

2.0 Research objective

This project aims to study the propagation characteristics of light in a planarised optical waveguide structure coated with a GO overlay. Planarized stripe waveguides with 3% index contrast have been realised using modified fabrication processes. The fabricated waveguides exhibit low insertion losses in the 1550 nm wavelength band. The width of the waveguide was chosen to support only the fundamental mode, in order to simplify analysis. A low loss TM-pass waveguide polariser was demonstrated with a polarisation extinction ratio of 34.9 dB, measured at the wavelength of 1550 nm. By analysing the change in polarisation behaviour of the GO coated waveguide with different GO coating thicknesses, the complex refractive index of the GO coating has been determined with greater precision.

3.0 Experimental Method

3.1 High index contrast silica waveguide fabrication

The fabrication steps for the planarised high index contrast (HIC) silica waveguide are shown in Fig. 1. The substrate used was a 100 mm diameter silicon wafer with a thickness of 525 μm and 7 μm of thermal oxide (TOx) layer. The TOx layer had a refractive index of 1.444 measured at 1550 nm using a prism coupler (Sairon Technology SPA-4000) and acted as the undercladding of the eventual optical waveguide, thereby alleviating the need for an undercladding deposition process.

Flame hydrolysis deposition (FHD) was used for the HIC silica layer deposition, with silicon tetrachloride ($SiCl_4$) used as precursor. To increase the refractive index of the silica (waveguide core*)* layer, germanium tetrachloride ($GeCl_4$) was introduced during the deposition process, with the addition of boron trichloride (BCl_3) as conditioner. These precursors were then hydrolysed in an oxyhydrogen flame to produce their corresponding oxides. Liquid source $SiCl_4$ and $GeCl_4$ were transported as vapour to the FHD chamber using helium gas, while BCl_3 was vaporised at elevated temperatures and introduced into the flame directly. The flow rates of $SiCl_4$, $GeCl_4$ and BCl_3 were 20 sccm, 80 sccm and 15 sccm, respectively. Four passes were made by the torch over the substrate during the FHD process. The as-deposited silica layer was then thermally annealed at 1300 ^{o}C for 2 hours to produce an optical quality HIC silica layer. The refractive index and thickness of the HIC silica layer were 1.486 and 3.0 μm, respectively, measured at 1550 nm. The propagation loss of the layer was also measured using a prism coupling and oil immersion technique - and was found to be less than 0.2 $dB.cm^{-1}$ at 1550 nm.

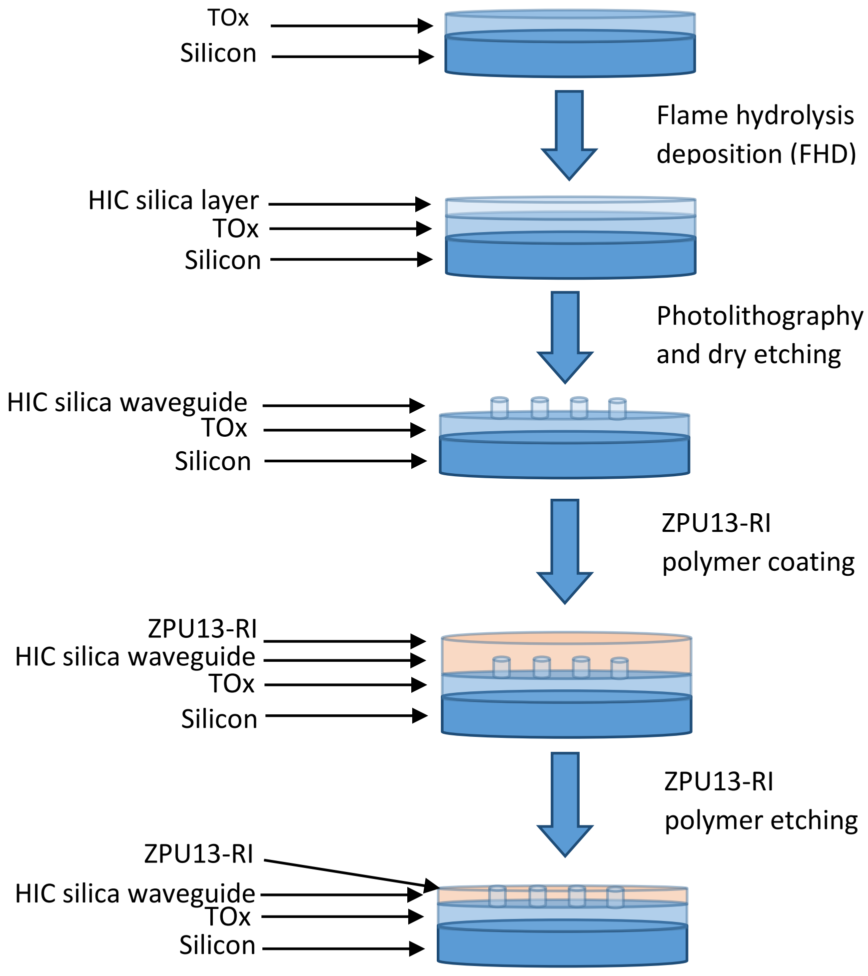
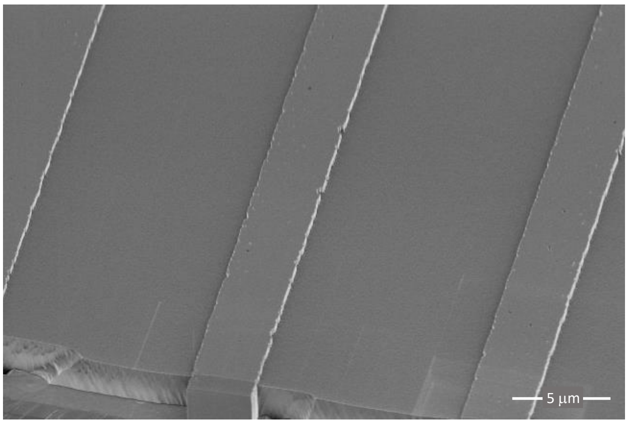
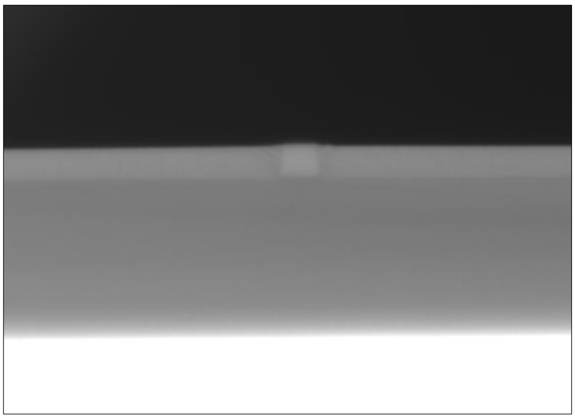


Fig. 1: Fabrication process steps for planarised HIC silica waveguide (Not to scale).

Straight stripe waveguides were then produced from the HIC silica layer via photolithography and a plasma-etching process. Positive photoresist (MicroChemicals AZ MIR 701) was used as an etch mask in the plasma-etching process. ZPU13-RI polymer (with a refractive index of 1.44 measured at 1550 nm) was then spin-coated on to the straight waveguides as an overcladding, before being etched down to the top surface of the waveguide again - using oxygen plasma etching to produce a planarised stripe waveguide structure.

A scanning electron microscope (SEM) image of the planarised HIC silica stripe waveguide is shown in Fig. 2(a). It can be seen that the ZPU13-RI polymer side cladding is slightly over-etched, while the surface quality for both the HIC silica stripe waveguides and the ZPU13-RI polymer side cladding is very good, after the plasma dry etching process has been carried out. The over-etching of the ZPU13-RI polymer cladding means that the waveguide has not been perfectly planarised, but instead has a slightly protruding waveguide core. The protruding waveguide core height has been measured using surface profiling (Veeco DEKTAK D150) and the height of the protrusion was found to be in the range from 0.5 μm to 0.9 μm. The microscope image of the waveguide in Fig. 2(b) shows a distinct "embedded" waveguide structure where the top surface of the waveguide is exposed. This provides a suitable structure for GO multi-layer functionalisation of the waveguide.





(a) (b)

Fig. 2: (a) SEM image of planarised HIC silica waveguide with ZPU13-RI polymer as side-cladding and (b) microscope image of the cleaved cross-section of a planarised HIC silica waveguide.

3.2 Graphene oxide coating

Graphene oxide (GO) was produced using an improved version of Hummer's method. The GO solution concentration was 12.0 μg/μL. De-ionised (DI) water with unequal volumes was added to the GO solution for dilution into the solution, with several different lower concentrations of 1.6 μg/μL, 2.0 μg/μL 3.0 μg/μL and 4.0 μg/μL. Using a micropipette, 0.5 μL of GO solution was drop-cast onto the planarised HIC silica waveguides. The GO solution droplet was then allowed to dry under ambient conditions. The GO solution concentration and the number of solution drops applied were varied, in order to obtain GO coating with different thicknesses. For the latter case, each GO solution droplet was allowed to dry before the next drop of GO solution was applied to the dried GO coating - and these steps were repeated for the desired number of drop applications. The diameter and thickness of the GO coating regions were measured using surface profiling.

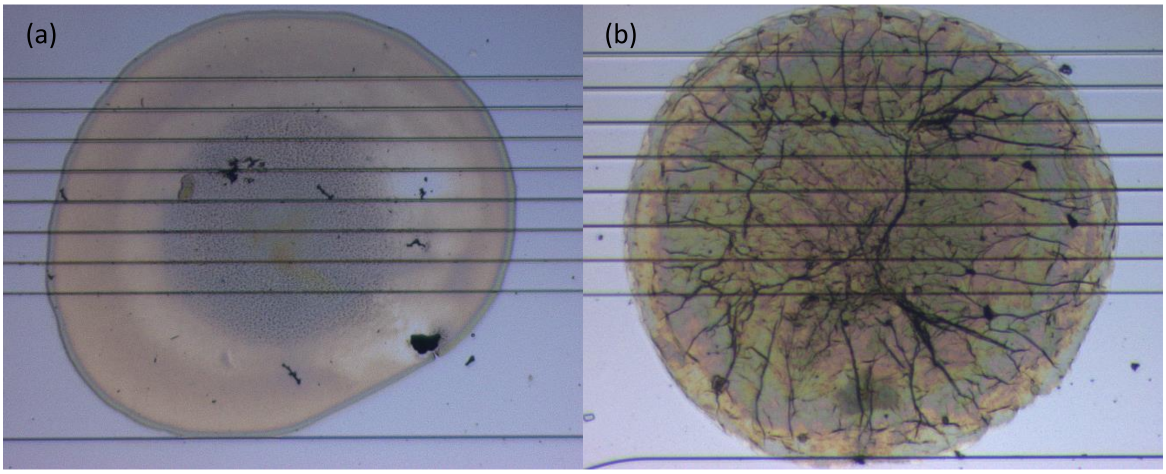
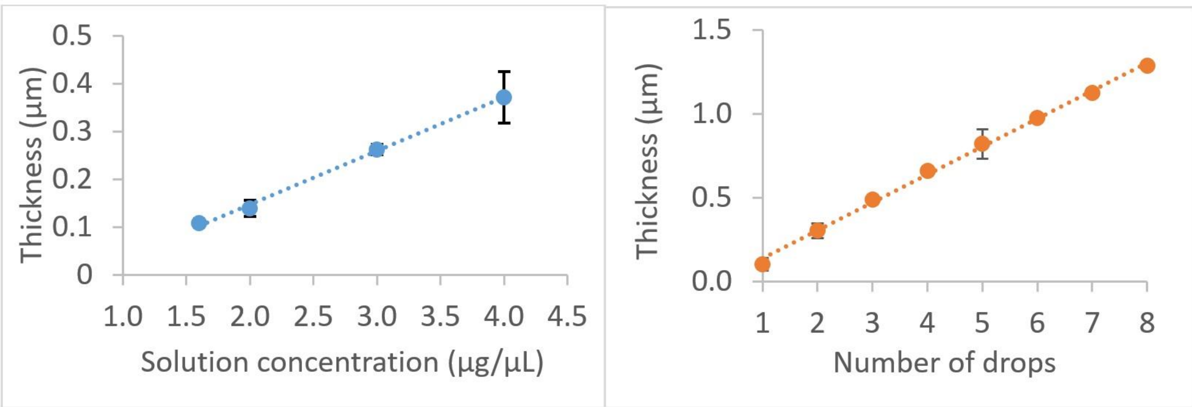


Fig. 3: Top view of the GO coatings formed using GO solution concentrations of (a) 1.6 μg/μL and (b) 4.0 μg/μL on straight waveguides. The average thicknesses and diameters of the GO coatings are (a) 0.11 μm and 1.44 mm and (b) 0.37 μm and 1.39 mm respectively.

Figures 3(a) and 3(b) are optical micrographs of GO coatings formed using GO solution concentrations of 1.6 μg/μL and 4.0 μg/μL, respectively. There were distinct differences between the two coatings. GO coatings formed with a lower GO concentration were typically slightly larger in diameter, i.e. approximately 1.44 mm, c.f. 1.39 mm. Furthermore, GO coatings formed with a GO solution concentration of 4.0 μg/μL were close to circular, while coatings formed with a GO solution concentration of 1.6 μg/μL showed some deviation from the circular symmetry profile - possibly due to their lower viscosity and hence weaker surface tension in the coating formation process. The thickness of the coating formed with 1.6 μg/μL of GO solution was measured to be 0.11 μm, as compared with the thickness of 0.37 μm formed using GO solutions with a 4.0 μg/μL concentration. Perhaps the biggest difference between the two GO coating regions was in their appearance. While the coating formed using

4.0 μg/μL GO solution showed macro-wrinkling on its surface, with no observable "coffee-ring", the coating formed using 1.6 μg/μL GO solution did not show any wrinkling, but did exhibit a profound "coffee-ring" effect. Suppression of the coffee-ring effect in drop-cast GO coating was attributed to the asymmetrical shapes of the GO flakes suspended in DI water. However, it appears that this suppression effect is no longer significant for GO coatings with a solution concentration lower than 2.0 μg/μL. The onset of coffee-ring formation in GO coatings is determined by the relationship between the GO flake size and the drying process. On the other hand, the suppression of macro-wrinkles is accompanied by the formation of a "coffee-ring". One possible cause for macro-wrinkling is the larger contact angle of 45^o for a 4.0 μg/μL drop of GO solution, as compared with the contact angle of 26^o for a 1.6 μg/μL GO solution drop. The large mismatch between the initial surface area of the droplet and the base area may result in macro-folding of the GO film formed after the drying process. The details of the processes that underlie the use of the drop-casting technique for GO coating merit a more detailed study.



(a) (b)

Fig. 4: (a) Thickness of GO coating formed with different GO solution concentrations. (b) Thickness of GO coating formed by multiple drop coating using 0.5 μL of GO solution with concentration of 1.6 μg/μL.

The thickness of GO coating formed using different GO solution concentrations and the number of solution drops applied are shown in Fig. 4. The solution volume applied for each coating was 0.5 μL. The GO coating thickness increases linearly from 0.11 μm to 0.37 μm for GO solution concentrations of 1.6 μg/μL and 4.0 μg/μL, respectively, as shown in Fig. 4(a). The greater uncertainty in the GO coating thickness formed using a solution concentration of 4.0 μg/μL is due to the larger surface roughness that results from macro-wrinkling, as shown in Fig. 3(b). Fig. 4(b) shows a linear increase of GO coating thickness with the number of GO solution drops applied. The GO solution volume and solution concentration used were 0.5 μL and 1.6 μg/μL, respectively. The GO coating thickness for a single drop coating process was 0.11 μm. The number of subsequent drops increased the GO coating thickness by about 0.16 μm per drop, up to a thickness of 1.29 μm for a coating formed by 8 drops of GO solution. Fig. 5 shows field-emission scanning electron-microscope (FESEM) images of GO-coated waveguides produced using a solution concentration of 1.6 μg/μL. The GO coating forms a sheet layer on the waveguide surface. A FESEM image with higher magnification is shown in Fig. 5(b). An air gap has formed between the side of the protruded waveguide core and the GO sheet, in a similar manner to that observed in previous work.

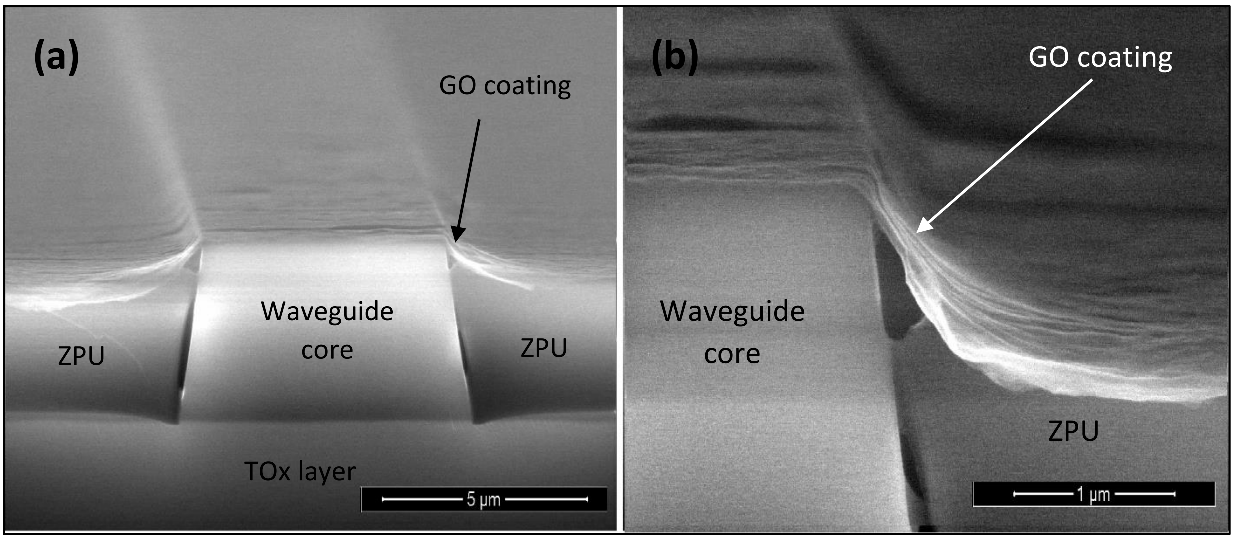


Fig. 5: (a) FESEM image of cleaved cross-section of GO-coated waveguide with a solution concentration of 1.6 μg/μL where waveguide core protruded with a height of approximately 0.5 μm. (b) Air gap is observed between the GO coating, the protruded section of the waveguide core and the ZPU side-cladding. GO coating thickness is 0.11 μm.

3.3 Optical characterization of the waveguide

The optical waveguide characterisation set-ups are shown in Fig. 6. The set-up shown in Fig. 6(a) was used for both input fibre-waveguide alignment and mode profiling. The light sources used were a 650 nm semiconductor laser for initial input alignment and ease in tracing the output beam - and a 1550 nm tunable laser source for mode profiling. High numerical aperture (NA) fibres (Nufern UHNA-3) were used both for their larger NA and better mode matching with the planarised HIC silica stripe waveguides. The UHNA fibres were spliced to standard single mode fibres (SMF-28) using customised splicing parameters to reduce the splicing loss. The input fibre was butt-coupled to the waveguide input and a microscope objective lens (40x magnification, NA = 0.45) was used to focus the waveguide output beam into an infrared (IR) camera (ElectroPhysics MicronViewer 7290A) for mode profiling - or into a polarimeter (Thorlabs PAN5710IR3) for polarisation state measurement. The objective lens and IR camera combination was then replaced by an output fibre, as shown in Fig. 6(b). The output fibre was connected to an optical power meter (OPM; Thorlabs S144C) for insertion loss and polarisation dependent loss measurement. The transmission spectrum of the waveguide was measured using an optical spectrum analyser (OSA; Yokogawa AQ6317C). A fibre polarisation controller (FPC) was placed between the laser source and the input fiber, in order to control the polarisation state of the light coupled into the GO-coated waveguide.

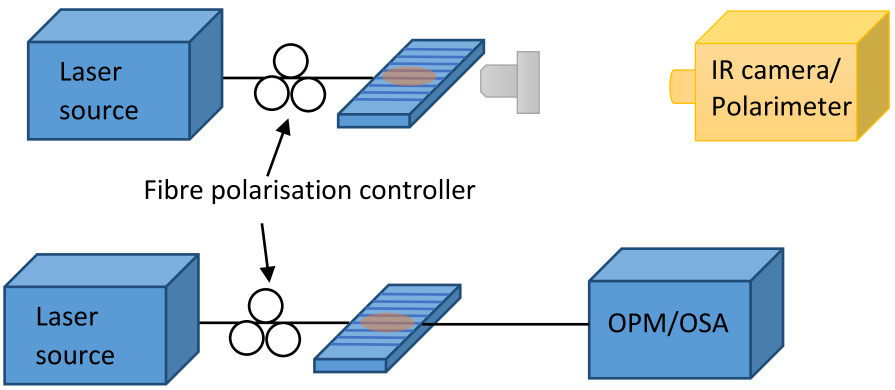


Fig. 6: (a) Set-up for input fibre-waveguide alignment and mode profiling and (b) set-up for optical waveguide characterisation.

The output mode profiles of the planarised HIC silica waveguides with different widths are shown in Fig. 7. The wavelength of the incident light was set at 1550 nm. For waveguide widths of 1 μm and 2 μm, only the fundamental mode was supported by the waveguides. However, for wider waveguides, higher order modes could be excited by changing the input coupling conditions (i.e. through lateral misalignment between the input fibre and the waveguide).

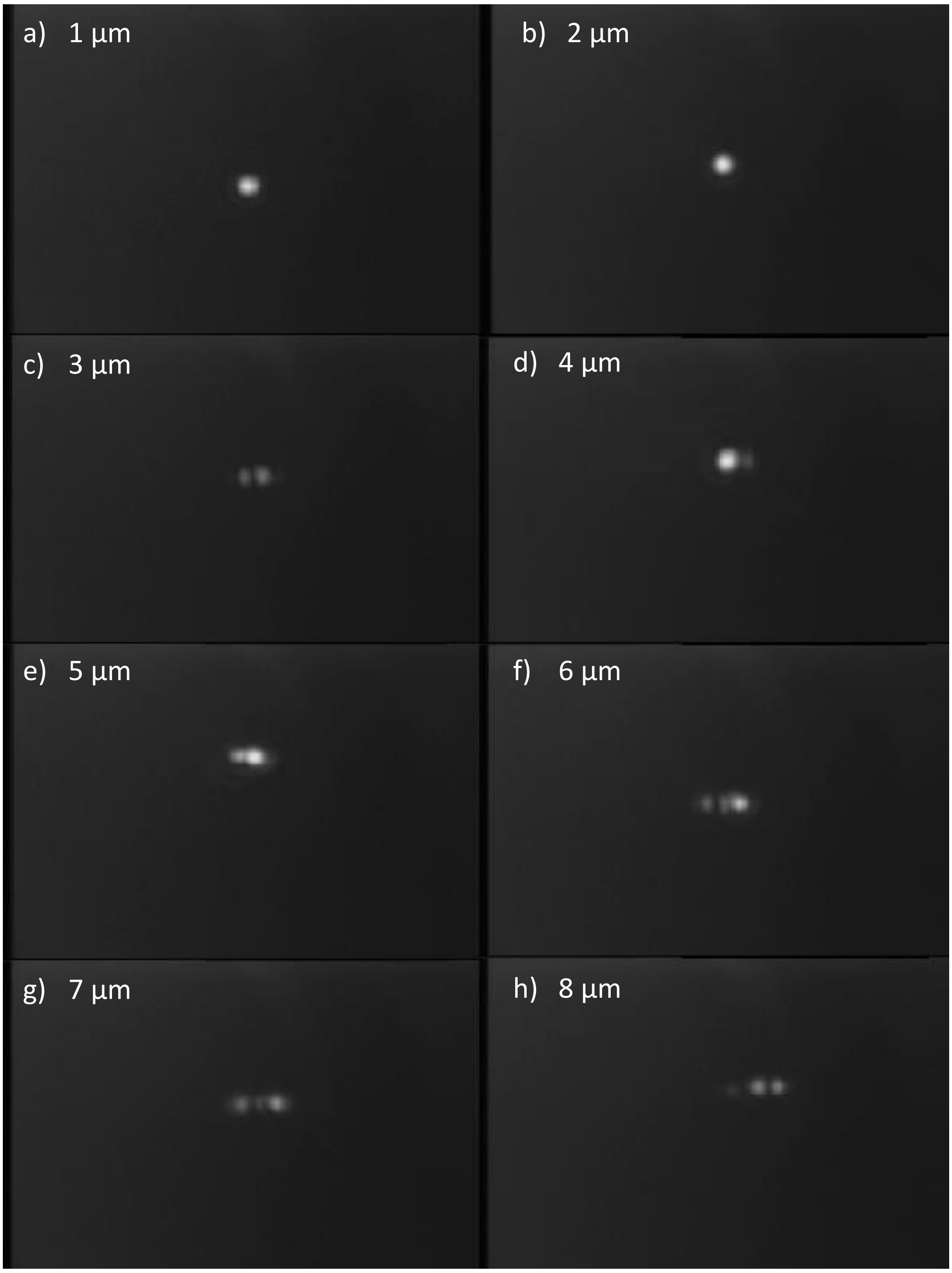


Fig. 7: Mode distribution of 1550 nm light at the output of planarised HIC silica waveguides with waveguide width of (a) 1 μm, (b) 2 μm, (c) 3 μm, (d) 4 μm, (e) 5 μm, (f) 6 μm, (g) 7 μm and (h) 8 μm.

The fibre-to-fibre insertion losses of the waveguides with 1 μm and 2 μm widths were measured to be 7.9 dB and 4.4 dB, respectively. The lower insertion loss of the 2 μm wide waveguide can be attributed to the lower coupling losses resulting from smaller modal field mismatch between the coupling fibres and the waveguides. The coupling loss could be improved further by applying index matching material between the fibres and the waveguides normally used in the standard waveguide bonding process. For the purpose of studying the light propagation characteristics of GO-coated planarised HIC silica waveguides, only the output from the planarised HIC silica waveguides with a width of 2 μm was analysed.

4.0 Results and discussion

Fig. 8(a) and (b) show the propagation loss and the corresponding extinction coefficient of both TM- and TE-polarized light propagating through the planarised HIC silica waveguide – as coated with different GO-coating thicknesses. For GO coating thicknesses less than 0.34 μm, the TM-mode propagation loss increases progressively with increasing GO coating thickness - from 1.57 dB/mm to 9.70 dB/mm over the GO thickness range up to ~ 0.4 µm, while the loss for TE-mode propagation increases more strongly with GO layer thickness - from about 2.48 dB/mm to 44.60 dB/mm over the GO thickness range up to ~ 0.4 µm. The GO-coated waveguide therefore behaves like a TM-pass waveguide polariser - with a highest polarisation extinction ratio (PER) of 34.9 dB measured for the waveguide with GO coating length and thickness of 1.0 mm and 0.34 µm respectively. When the GO coating thickness is increased above 0.34 µm, the propagation loss of TE-polarised light begins to decrease to about 14.2 dB/mm with GO coating thickness of 0.71 μm, before increasing to between 20 and 35 dB/mm with GO thickness range above 0.8 μm. On the other hand, the propagation loss for TM-polarised light increases significantly - to more than 60 dB/mm - when the GO coating thickness is more than 0.7 µm. In this case, the GO-coated waveguide behaves like a TE-pass waveguide polariser with the highest PER of 46.0 dB measured for waveguides with a GO coating length and thickness of 1.0 mm and 0.71 µm respectively. It should be noted that, for a GO coating of thickness greater than 0.7 µm, the transmitted power for TM-polarised light is close to, or lower than, the detection sensitivity of the optical power meter used - and therefore the propagation loss of TM-polarised light in waveguides with a GO coating thicker than 0.7 µm may be even higher. The wavelength dependence of light propagation through the GO-coated waveguides has been evaluated over the wavelength range from 1520 nm to 1620 nm - and the variation in PER across the measured wavelength range was found to be less than 3.0 dB.

The optical propagation behaviour of the GO-coated waveguides with different GO coating thicknesses can be explained by the modal field distributions of the light in the waveguides. In addition, the distinct TE- and TM-polarised light extinction coefficient profiles can be used to obtain a more accurate value of the complex refractive index of the GO coating, using modal analysis based on the finite element method (FEM).

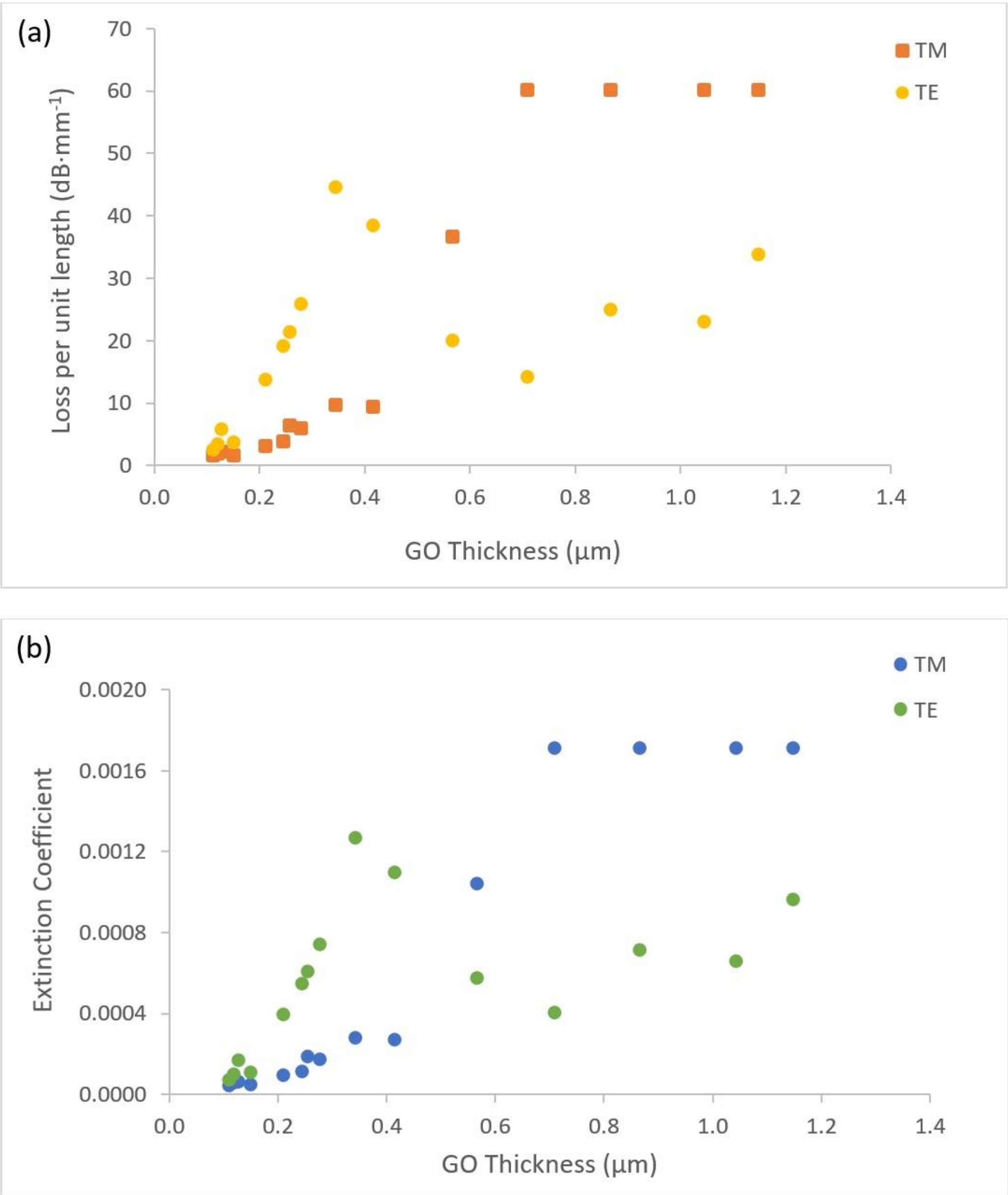


Fig. 8: (a) loss and (b) extinction coefficient of TM- and TE-polarized light at different GO-coating thicknesses.

Fig. 9 is a schematic of the GO-coated waveguide cross-section used for finite element method (FEM) analysis, which was carried out using COMSOL Multiphysics software. The GO-coated waveguide height and width are set at 3 μm and 2 μm, respectively. The protrusion of the waveguide core above the side cladding was measured, using surface profiling, to be 0.8 μm – and this value was used in the analysis. Air gaps between the GO coating and side-cladding, with a spacing of 1.0 μm at the base have also been considered in the analysis. The wavelength used in the simulation was 1550 nm. The variables in this analysis were the GO thickness and its complex refractive index. The GO thickness was varied over the range between 0.1 and 1.0 μm. The complex refractive index of the GO coating was first measured using spectroscopic ellipsometry (J. A. Wollam M-2000) to be 1.655 + 0.02*i*. Using this value as reference in the analysis, the real part of the refractive index of GO was varied between n = 1.50 and n = 1.70, while the extinction coefficient κ (i.e. the imaginary part of the refractive index) was varied between κ = 0.001 and κ = 0.1.

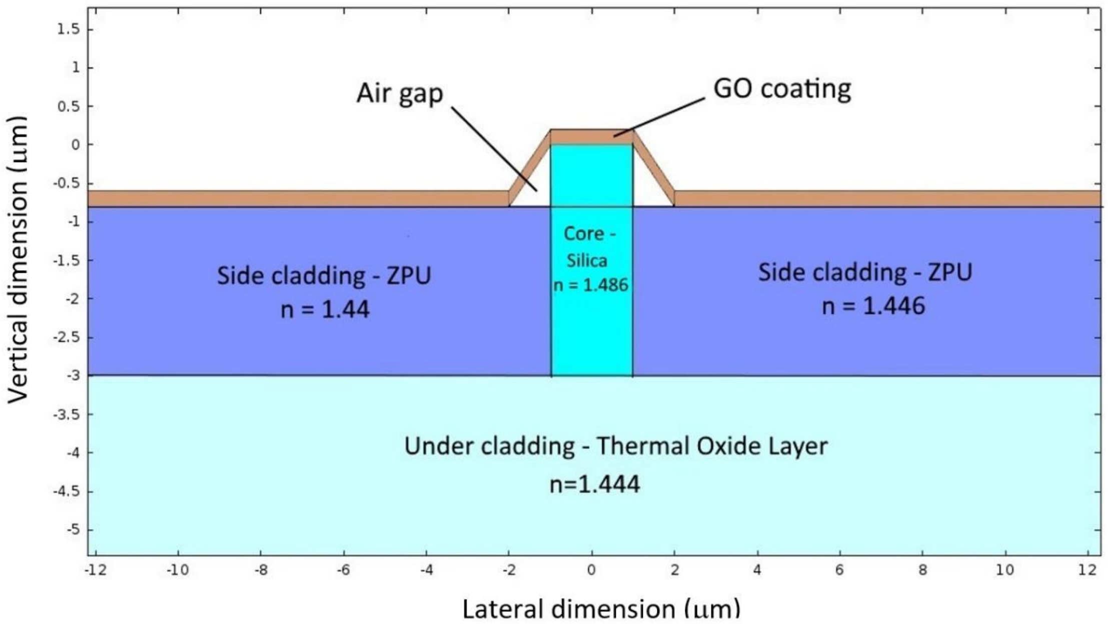
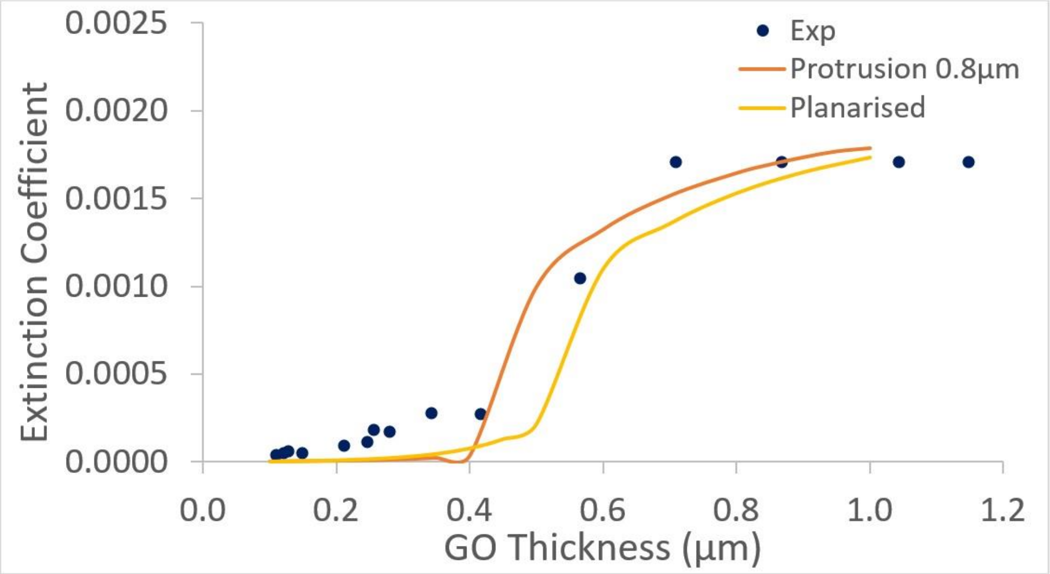


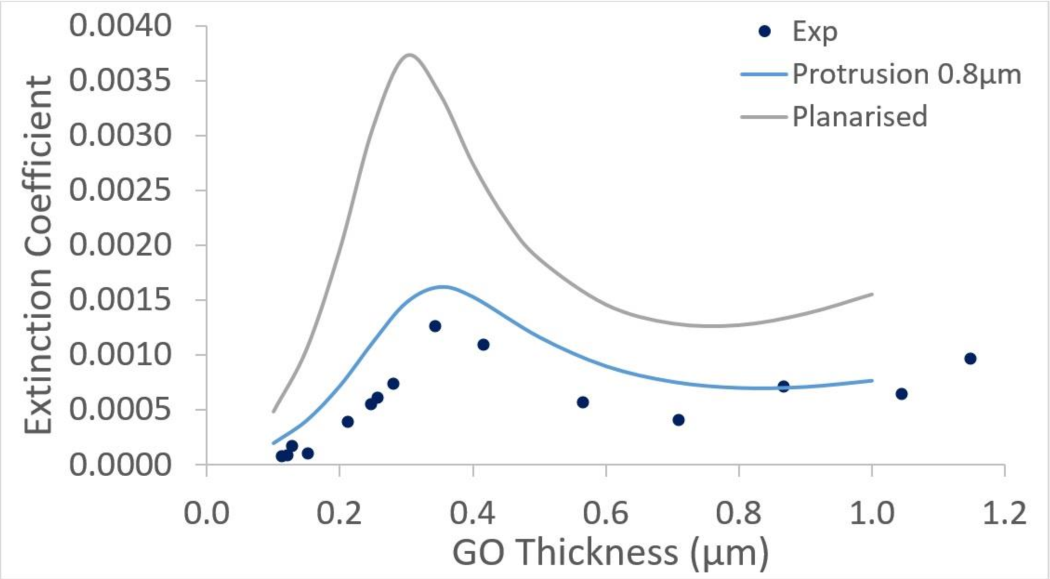
Fig. 9: Cross section of the 2 μm wide waveguide with GO-coating thickness set at 0.2 μm for finite element analysis. (Note that the horizontal and vertical scales are different).

Fig. 10 shows the extinction coefficients for GO-coated waveguides obtained from both experimental measurements and the results of FEM analysis that give the best fit to the experimental results, for both TE- and TM-polarised light. Good agreement between the experimental and FEM analysis results is obtained with a complex refractive index for GO of

1.61+0.001*i* (TM-mode) and 1.66+0.07*i* (TE-mode). The uncertainties of these values, defined as the values for which the FEM analysis results give an acceptable fit with the experimental results, are ±0.02 and ±0.01 for TM- and TE-polarised light, respectively, for the real part of the refractive index. The uncertainties for the imaginary parts of the refractive index are ±0.0001 and ±0.01 for TM- and TE-polarised light, respectively.



(a)



(b)

Fig. 10: Comparison of extinction coefficients obtained from both simulation and experiment for (a) TM-polarised light and (b) TE-polarised light.

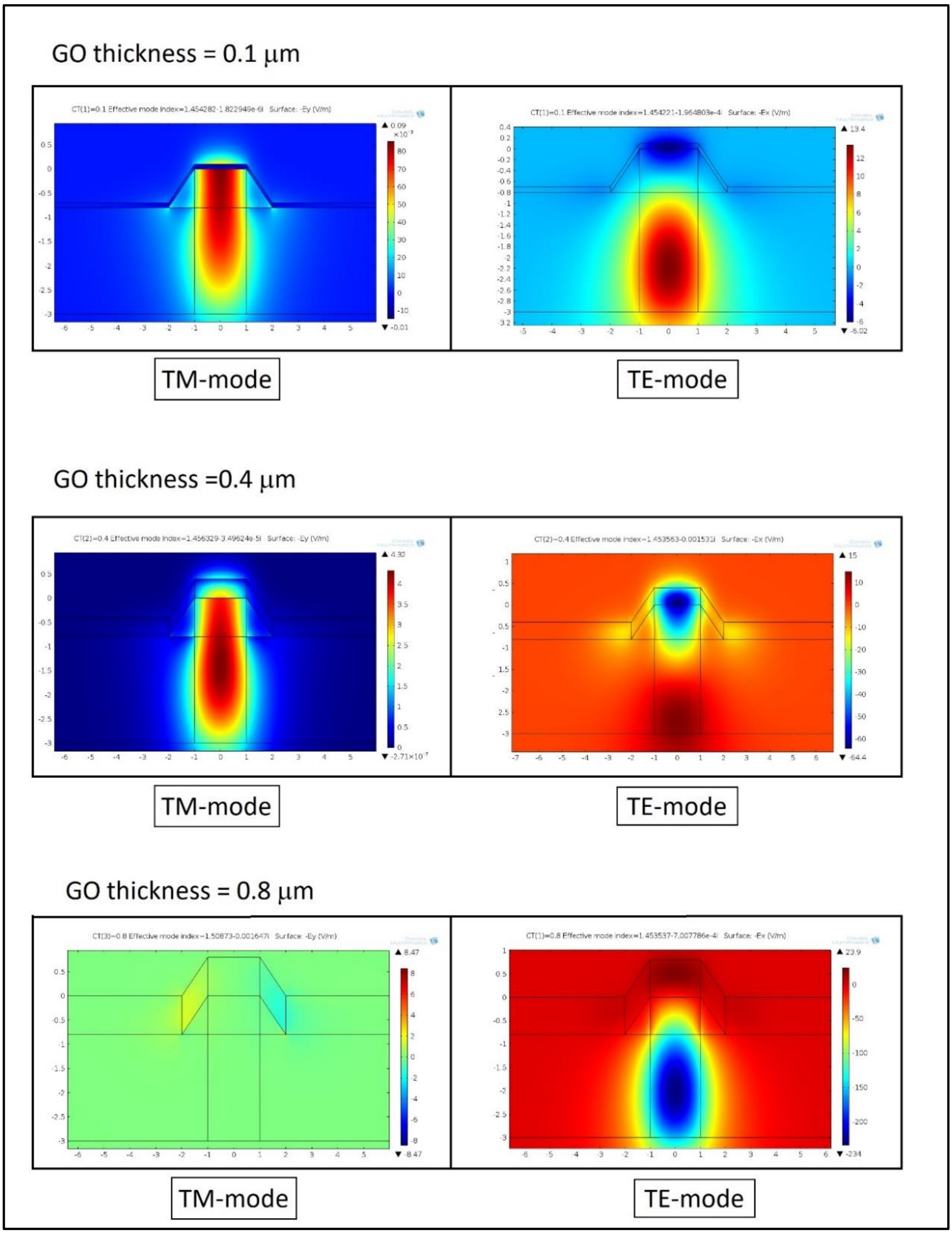


Fig. 11: Simulated mode distributions for TM-polarised light in waveguide coated with GO-layer at thicknesses (a) 0.1 µm (b) 0.4 µm and (c) 0.8 µm

The abrupt increase in extinction coefficient, and hence propagation losses, for TM-polarised light when the thickness of the GO layer is increased beyond 0.4 µm, can be explained by the power distribution of the optical mode in the GO-coated waveguide, as shown in Fig. 11. For

TE-polarised light, the modal power is distributed over both the waveguide core and the GO-coating, forming modes in the waveguide core and GO coating as a result of the optical coupling process. For TM-polarised light, the interaction is only between the evanescent field in the waveguide core and the GO-layer for a GO coating thickness up to 0.4 µm, as shown in Fig. 11(a) and (b). When the GO coating thickness is greater than 0.4 µm, TM-polarised light becomes leaky, as shown in Fig. 11(c). This leakiness results in very high propagation losses, in agreement with the experimental results.

Since the ultimate objective is to produce GO coatings on a perfectly planarized waveguide, FEM analysis of this waveguide structure using the parameters and values above was performed and the results are shown in Fig. 10. In can be seen that the extinction coefficient profile for different GO coating thicknesses remains the same, but the magnitude of the extinction coefficient for TE-polarised light increases for perfectly planarised waveguides, as shown in Fig. 10(b). TM-polarised light experienced a smaller change when the protrusion height of the waveguide core was eliminated, as shown in Fig. 10(a). Our view is that it is likely that a perfectly planarised waveguide will produce a waveguide polariser with superior performance.

5.0 Summary

It is observed that the TM-light propagation loss is low for GO coating thickness up to 0.4 µm. When the GO coating thickness is increased above 0.4 µm, TM-light becomes unguided in the waveguide, resulting in an abrupt increase in propagation loss to more than 60 dB/mm. On the other hand, the propagation loss of TE-polarised light increases to 44.6 dB/mm in GO-coated waveguides with a 0.34 µm GO coating - before decreasing to 14.2 dB/mm in GO-coated waveguides with a GO coating thickness of 0.71 µm. With the extinction coefficient profile of TM- and TE-polarised light of GO-coated waveguides with different GO thicknesses, the complex refractive index of GO coating is obtained using FEM analysis. The complex refractive index of our GO coating, with TE- and TM-polarised light, are 1.66+0.07*i* and 1.61+0.001*i*, respectively. The uncertainties of these values are smaller by an order of magnitude when compared to values measured using the conventional method of spectroscopic ellipsometry.

In addition to a previously published research article in IEEE Photonics Journal. A new manuscript based on the content of this report has been prepared and submitted to IEEE Journal of Lightwave Technology in November 2018 and is currently under review.

6.0 Suggestion for future studies

Apart from the understanding of light propagation in GO-coated optical waveguide, the current analysis method can be used to determine the complex refractive index of other thin film materials. In addition, light propagation characteristics in reduced-graphene oxide (rGO) at different reduction levels can be next studied. The information of optical characteristics between the two coatings can then be utilised to fabricate optical switches and modulators.