Achieving extremely high optical contrast of atomically-thin MoS$_2$

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Abstract

Extraordinarily high optical contrast is instrumental to research and applications of two-dimensional materials, such as, for rapid identification of thickness, characterisation of optical properties, and quality assessment. With optimal designs of substrate structures and light illumination conditions, unprecedented optical contrast of MoS$_2$ on Au surfaces exceeding 430% for monolayer and over 2600% for bilayer is achieved. This is realised on custom-designed substrates of near-zero reflectance near the normal incidence. In particular, by using an aperture stop to restrict the angle of incidence, high-magnification objectives can be made to achieve extraordinarily high optical contrast in a similar way as the low-magnification objectives, but still retaining the high spatial resolution capability. The technique will allow small flakes of micrometre size to be located easily and identified with great accuracy, which will have significant implications in many applications.

Keywords: optical contrast, 2D materials, near-zero reflectance, transition metal dichalcogenides (TMDCs), molybdenum disulphide (MoS$_2$)

(Some figures may appear in colour only in the online journal)

1. Introduction

Optical contrast spectroscopy is a valuable tool for easy location and identification of the layers of two-dimensional (2D) materials [1–5]. Monolayers of 2D materials are routinely identified through contrast measurements [5–12]. Machine vision has also been applied to allow rapid, automated and reliable identification of a flake’s presence [13]. Large optical contrast is beneficial in many applications. It allows a rapid and accurate identification of the layer number of 2D materials and enables the development of sensors for ultrasensitive label-free molecular sensing [14].

Recently it has been demonstrated that optical contrast of thin films is completely determined by the underlying substrate and the illumination conditions of light [15]. The role of substrate is fully represented by a complex reflectivity $r = r_0 e^{i\varphi}$. Both the amplitude $r_0$ and the phase $\varphi$ are important. By optimising the structure of the substrate and the light illumination conditions such as incident angle and polarisation, extremely high optical contrast can be achieved on any thin film of any thickness [15]. In a previous publication [16], we demonstrated that complex reflectivity can be custom-designed with stratified layers composed of thin Au films and oxidised Si substrates. We demonstrated that the optical contrast of graphene and graphene oxide can be significantly improved with appropriate stratified structures. It will be of significant interest to extend this investigation to transition metal dichalcogenides (TMDCs) 2D materials. TMDCs on Au and other conductive metallic substrates have received significant research attention in a broad range of areas, including memory devices [17], electrochemistry [18], surface enhanced Raman scattering [19], plasmonics [20], molecular sensing [21] and nonlinear optical effects [22].
Here we demonstrate how to achieve extremely high optical contrast on atomically-thin molybdenum disulphide (MoS$_2$), one of the most important TMDC materials. In addition to optimising the design of the structures, we systematically investigate the effects of light illuminating conditions, including the numerical apertures (NA) of objectives and the aperture stops (AS). A range of high contrast substrates composed of stratified multilayers are designed and fabricated. A range of objectives of different magnifications (see Table 1) are used and it is shown that highest peak contrast is achieved with low-magnification objectives, which provides near-zero reflectance for light illumination near the normal incidence. These low magnification contrast measurements are possible due to the very large size of exfoliated flakes on the Au substrate [18]. To achieve both high contrast and high spatial resolution, various sizes of AS are employed in the optical path of the incident beam to restrict the average angle of incidence. By optimising these conditions, unprecedented contrasts exceeding 430% and 2600% are realised on monolayer and bilayer MoS$_2$ films respectively, with a 10× objective. These are orders of magnitude larger than previously reported contrast for monolayer MoS$_2$ on a 90 nm thick SiO$_2$/Si cavity which has been shown to be approximately 30% [23, 24]. The experimental results are in excellent agreement with theoretical simulations.

Table 1. Specifications of the objectives used.

| Lens model | Magnification | NA | $\theta_0$ (°) | Focal spot size ($\mu$m$^2$) |
|------------|---------------|----|---------------|-----------------------------|
| MPLN 5xBD  | 5             | 0.1| 5.7          | 268                         |
| MPLN 10xBD | 10            | 0.25| 14.4       | 67                          |
| MPLN 20xBD | 20            | 0.4 | 23.5        | 17                          |
| MPLN 50xBD | 50            | 0.75| 48.5        | 3                           |

2. Methods

2.1. Fabrication of multilayer heterostructures

Multilayer optical heterostructures were produced by magnetron sputtering in a Lesker physical vapour deposition system (Kurt J Lesker CMS- A DC magnetron sputterer). Oxidised Si wafers (IDB Technologies Ltd Specified as 90 nm thick, with the actual thickness of 93 nm SiO$_2$, as measured by ellipsometry) were cleaned and sputtered with 1 nm Ti, followed by a thin layer of Au film of $t$ nm thickness, as schematically shown in figure 1. Unless stated otherwise, the substrates discussed in this paper all have the same structure as that shown in figure 1, with the varying thickness of Au film.

The Ti layer acts to increase the adhesive forces between the Au layer and SiO$_2$, thus preventing delamination during the exfoliation procedure [25]. MoS$_2$ films were mechanically exfoliated from bulk crystals (purchased from 2D Semiconductors) onto the Au surfaces quickly after the removal of the Au from the vacuum chamber to provide a clean and pristine interface between the 2D material and the Au. This maximises the flake coverage and prevents contamination interfering with the measured optical contrast [17].

2.2. Au film characterisation

The thickness of Au films was characterised using x-ray reflectometry (XRR) and ellipsometry. XRR was carried out using a Bruker D8 discover diffractometer, DIFFRAC measurement centre, and Leptos 7.8 software were used to determine the thickness of Au and Ti films. An ESM-300 ellipsometer (J A Woollam Co, Inc.) was then used to determine the real and imaginary parts of the refractive index ($n$ and $k$) of the Au and Ti films with Complete EASE 5.0 software (J A Woollam Co, Inc.), which were utilised in the theoretical simulations.

2.3. Characterisation of 2D materials

The quality and thickness of exfoliated MoS$_2$ films were characterised with optical contrast spectroscopy, Raman spectroscopy and atomic force microscopy (AFM). Optical images were taken using a BX51 microscope (Olympus Corp) with an Infinity2-2 CCD camera and Infinity Capture 6.2 software (Lumenera Corp). Raman spectra were measured with a 532 nm laser of 1 mW power, focused through a 50× objective to $\sim 3 \mu$m$^2$ spot size. The signals were collected through a back-reflection configuration and measured by a Jobin Yvon HR640 Raman spectrometer operated with an Andor CCD (Andor MCD 2.6 software). AFM measurements were taken on an Asylum research AFM MFP-3D in tapping mode. Pt-coated Si AFM cantilevers were used with a resonance frequency of $\sim 70$ kHz, a spring constant of 0.5–9.5 N m$^{-1}$ and a tip end radius of $\sim 50$ nm. Measurements were taken at a constant set point to maintain similar tapping mode forces for consistent step-height measurements [26].
2.4. Optical contrast measurements

The contrast spectrum \( C(\lambda) \), was determined from the reflectance measurements using the following formula:

\[
C(\lambda) = \frac{R_b(\lambda) - R_m(\lambda)}{R_b(\lambda)}
\]

where \( R_b(\lambda) \) and \( R_m(\lambda) \) are the wavelength-dependent reflectance \( (R = n/2) \) of the bare and the MoS\(_2\)-coated substrates, respectively. The contrast spectra are measured with a range of objectives of various NA as listed in table 1. For an objective of NA, the beam illuminating the sample surface is within a cone with the semi-cone angle of \( \theta_0 \), defined as \( \sin \theta_0 = \text{NA} \). Details of reflection measurement have been described in previous publications [14, 16, 18].

2.5. Optical contrast simulations

Simulations for the optical contrast of few-layer MoS\(_2\) on various substrates were carried out based on the transfer-matrix method [15]. The measured optical constants of Au thin films and Ti adhesion layer were used. The optical properties of monolayer MoS\(_2\) are taken from literature [27] as well as those of the SiO\(_2\) and Si substrate which have been shown in a previous publication [16]. As light focused by an objective contains incident angles ranging from 0 to \( \theta_0 \) [14], the calculated reflectance is averaged by the incident angle and polarisations [15].

3. Results and discussion

Compared to transparent 2D films such as graphene and graphene oxide, monolayer MoS\(_2\) is readily visible on many surfaces [26] due to strong absorption in the visible range. On highly reflective bulk Au (≈100 nm), the peak contrast for a monolayer MoS\(_2\) film is \( \sim13\% \), when measured with the 50× objective (figure 2(a)).

Reflectivity of substrates can be tailored with custom-designed multilayer structures, so the contrast of MoS\(_2\) can be tuned. Figure 2 shows the measured optical contrast spectra of monolayer MoS\(_2\) on substrates with varied Au thickness. It is noted that both the spectral profiles and the magnitudes of the peak contrast evolve significantly with the Au film thickness. The peak contrast increases with decreasing Au film thickness. Figures 2(e) and (f) show respectively how the position and magnitude of the measured contrast maxima/minima, evolve with the Au thickness. The largest peak contrasts are found on the structure coated with a 2.1 nm Au film (figure 2(d)): \(-79\%\) for the negative contrast minimum at 464 nm and \(+42\%\) for the positive contrast maximum at 535 nm. Both are significantly higher than the 13% peak positive contrast on bulk Au (figure 2(a)). Figure 2 seems to suggest that the thinner the Au film, the better the contrast, this however is not always the case. Without the Au film, the peak optical contrast of monolayer MoS\(_2\) deposited on 90 nm SiO\(_2\)/Si is \( \sim30\% \) [23], much less than the surface coated with 2.1 nm of Au. The enhanced contrast on surfaces coated with thin Au films is due to reduced reflectivity of the surface caused by light absorption in the thin gold film.

Apart from substrates, optical contrast also depends on the illumination conditions of incident light [15]. Fundamental optics states that reflection is sensitive to the angle of incidence and the polarisation states of light. To evaluate the effects of incident angle, for the first time, for improving 2D material contrast on these Au coated heterostructures, we characterised the optical contrast of MoS\(_2\) films with objectives of different NAs. Figure 3(a) shows the optical micrographs of MoS\(_2\) films exfoliated on the 4.6 nm Au coated substrate with different objectives (5×, 10×, 20× and 50×, respectively. Details see table 1). The images were taken with a 490±5 nm bandpass filter to enhance the contrast level. It is evident that contrast changes dramatically with different objectives. Of all objectives the low magnification 10× objective provides the best visibility for the films.

Raman spectroscopy is employed to characterise the thickness and quality of the exfoliated MoS\(_2\) films. Figure 3(c) shows the Raman spectra taken on 1–4 layer MoS\(_2\) flakes, showing the typical \( E_{2g} \) modes and the \( A_{1g} \) modes [28]. The intensities of the Raman modes increase
with increasing layer number, in agreement with the literature [29], while in both modes in this work show a blueshift with increasing layer number which is consistent with our previous work [18]. As in our previous work [18] the blueshift measured for the A_{1g} mode with increasing layer number appears larger than expected from previous work on a SiO_{2} substrate [29]. Electron doping has been shown to cause a redshift of the A_{1g} mode of MoS_{2} [30, 31]. Which is expected to be largest for the MoS_{2} layers closest to the Au surface and is consistent with the redshift in thin MoS_{2}. A higher resolution Raman investigation, which is beyond the scope of this work, may reveal further details of this behaviour. The thickness of MoS_{2} film is also characterised by AFM. Figure 3(c) shows the topographic images of the MoS_{2} flakes. A step-height line profile across the 1L and the 2L films is 0.8 ± 0.2 nm, consistent with the thickness difference of one layer (inset, figure 3(c)).

Figure 3(d) shows the measured contrast spectra of monolayer MoS_{2} on 4.6 nm Au with various objectives. The contrast is most pronounced at the negative side. The peak negative contrast increases notably with decreasing magnification, peaking for the 10× objective before decreasing slightly when the 5× objective is used. The 10× objective provides the lowest negative contrast of −320% for a monolayer, about six-fold increase from that measured by the 50× objective (−46%). The bilayer film exhibits much higher contrast (figure 3(e)), on which the peak negative contrast of −1400% is measured with the 10× objective, about a nine-fold increase compared to that of the 50× objective (−150%).

Figure 3(f) shows the measured reflectance spectra of the bare Au film with the different objectives. This elucidates where these enhancements in measured contrast originate from. Here it can be seen that as the magnification decreases so does the reflectance minimum of the substrate. This decreasing value of R_{f}(λ) acts to create larger negative values for the contrast due to its inverse relationship on the measured contrast.

The largest contrast is observed with the 10× objective lens. As seen in figure 3(f), the reflection measured for the 10× objective is larger across most regions of the visible range than that measured with the 5× objective, but almost the same at 500 nm (inset, figure 3(f)). This is because the reflection difference is minimal at this point which is difficult to distinguish due to the limited spectrometer sensitivity. However, with the addition of MoS_{2} films, the reflectance spectra slightly redshift, so the 10× records higher reflectance than the 5× objective, leading to higher negative contrasts based on equation (1).

To understand the mechanisms of the observed contrast spectra, we carried out theoretical simulations of the contrast spectra of monolayer and bilayer MoS_{2} on the 4.6 nm Au-coated substrate, with various objectives. The results are shown in figures 4(a) and (b), respectively, which match the measured spectra (figures 3(e), (f)) very well, displaying...
similar spectral profiles and the evolution trends with the objective magnifications, apart from the absolute magnitudes of contrast, which is due to the deviation of the actual experimental conditions from the ideal conditions adopted in simulations.

Figure 4(c) shows the calculated reflection spectra of various substrates at normal incidence, including 100 nm Au film, bare 90 nm SiO2 coated Si and the one coated with 4.6 nm Au. At \( \lambda = 500 \) nm, the reflectance decreases from 50% on 100 nm Au to 11% on 90 nm SiO2 on Si, and further down to 0.037% on the substrate coated with 4.6 nm Au film (figure 4(c)). Accordingly, the peak contrast drops from 13% to 6% and –0.090%, respectively (figure 4(d)). This indicates that the massively enhanced contrast on the Au-coated substrate is due to the significantly reduced reflectivity of substrate, in agreement with theory [15].

It is established both experimentally and theoretically that high contrast is achieved on these substrates with lenses of low NA, where light is incident at small angles. For MoS2 and this particular type of substrate (it could be different in other cases [15]), the averaged reflectance (averaged for TM and TE polarisations) decreases with reducing incident angles (figure 4(e)). The minimum reflectance occurs at the normal incidence, where the contrast is maximum (figure 4(f)). This implies that, to achieve the extreme contrast, one has to use low-magnification lenses, which however have large focusing and collection spots, thus coming at a price of poor spatial resolution and being limited to large-area samples. In many circumstances, high-NA objectives are desirable, e.g. to characterise micron-sized flakes which are often produced during mechanical exfoliations, and to image samples with high spatial resolution. It is therefore of significant interest to extend the high contrast conditions to high NA objectives and thus harness their high-resolution capability. To this end, we inserted an AS into the illumination optical column to restrict the incident beam to the central part of the objective, so that light is incident on sample within the cone of a spanning angle much smaller than \( \theta_0 \) defined by the NA (\( \sin \theta_0 = N_A \)), as schematically shown in figure 5(a). The AS is out of the collection optical path, without interfering with the collection optics. The size of collection spot is still limited by the NA, due to a confocal arrangement in the collection optics, in which the focal spot of the objective is optically conjugated to the input aperture of the spectrometer. As such, this AS positioning allows an effective reduction of the incident angle without the loss of the high spatial resolution in the collection spot inherent when using lower magnification lenses.
To evaluate the effects of the AS positioning, two different sizes of AS (4.5 and 2.5 mm diameter) are inserted separately in the incident illumination path of the 50× objective (the input aperture diameter of the 50× objective is 6 mm) to measure the contrast of 1-4L MoS₂ on the substrates coated with 4.6 nm Au. The results are shown in figures 5(b) and (c), respectively. It is notably obvious that with the AS the contrast is significantly enhanced (the spectra without AS are also shown in the inset in figure 5(b)). The smaller AS of 2.5 mm increases the contrast more significantly. To make a quantitative comparison, the contrast spectra of monolayers are presented together in figure 5(d). The 4.5 mm AS increases the peak negative contrast of monolayer MoS₂ from −46% to −120%, whereas the 2.5 mm AS increases it to −190%. An enhancement by a factor of three and five times is achieved with the application of the 4.5 mm and 2.5 mm apertures, respectively. Amazingly, the measured monolayer contrast taken by the 50× objective with the 2.5 mm AS is now close to that of the 5× objective (figure 5(d)).

The same technique can also be employed on objectives of low magnifications to further improve the contrast level. Figure 5(e) shows that when a 2.5 mm AS is applied to the 10× objective, which provided the highest optical contrast among all objectives previously, additional enhancement of ~1.4 times is achieved on monolayers, increasing the peak contrast from −300% to −430% (figure 5(e)). When this is applied to a bilayer of MoS₂, the contrast is about twice as large as that without the AS, with a magnitude of −2600% at 504 nm (figure 5(f)).

Extremely high optical contrast is highly beneficial for many applications. This includes applications for 2D materials on metal substrates [17-19] as well as 2D materials on insulating substrates [32], which could be created on a modified optical heterostructure. It allows easy and quick identification of atomically-thin films, saving much time and effort. The accuracy of determining the thickness and assessing the quality of thin films is crucially dependent on the contrast level. The higher the contrast level, the more accurate the results will be. Owing to their extremely large surface-to-volume ratios, 2D materials can adsorb many species of molecules, making them excellent platforms for sensors [14, 33, 34]. Optical contrast spectroscopy is a facile technique for ultrasensitive label-free detection of tiny quantities of molecules [14]. The detection sensitivity critically relies on the contrast level. The higher the contrast level, the better the detection sensitivity. It is interesting if a figure of merit (FOM) for the detection sensitivity of these high contrast systems could be comparable to the FOM of plasmonic sensors [35, 36], which are some of the key technologies widely adopted in molecular sensing. Here we demonstrate the large sensitivity of enhanced contrast for atomically-thin MoS₂ films, which may have the potential to be employed as excellent platforms for ultrasensitive molecular sensing.
4. Conclusion

Here we demonstrate that, by optimising the substrate structure and the conditions of light illumination, extremely high optical contrast can be achieved on atomically-thin MoS2 films, 430% for monolayer and 2600% for bilayer films. Such extreme contrast is achieved on substrates of near-zero reflectance with light incident at small angles near the normal incidence. By inserting an AS into the optical path of the incident beam to restrict the range of incident angles, we achieve extremely high optical contrast with objectives of high NA, without compromising their high spatial resolution. With the significantly enhanced contrast, the sensitivity of the contrast spectrum also improves dramatically. It is of interest whether a FOM for sensing with these extremely high contrast systems could be comparable to that of plasmonic nanoparticles, this may render them excellent platforms for ultra-sensitive molecular sensing. This technique could be extended to a wide variety of other 2D materials, on other near zero reflectance substrates facilitating a broad range of research and applications.

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References

[1] Wu J P, Wang L and Zhang L Y 2017 Rapid and nondestructive layer number identification of two-dimensional layered transition metal dichalcogenides Rare Met. 36 698–703
[2] Hyun Kim D, Kim S-J, Yu J-S and Kim J-H 2015 Measuring the thickness of flakes of hexagonal boron nitride using the change in zero-contrast wavelength of optical contrast J. Opt. Soc. Korea 19 503–7
[3] Li H et al 2013 Rapid and reliable thickness identification of two-dimensional nanosheets using optical microscopy ACS Nano 7 10344–53
[4] Ni Z H et al 2007 Graphene thickness determination using reflection and contrast spectroscopy Nano Lett. 7 2758–63
[5] Gorbachev R V et al 2011 Hunting for monolayer boron nitride: optical and raman signatures Small 7 465–8
[6] Ottaviano L et al 2017 Mechanical exfoliation and layer number identification of MoS2 revisited 2D Mater. 4 045013
[7] Jung I et al 2007 Simple approach for high-contrast optical imaging and characterization of graphene-based sheets Nano Lett. 7 3569–75
[8] Kaplas T, Zolotukhin A and Svirko Y 2011 Thickness determination of graphene on metal substrate by reflection spectroscopy Opt. Express 19 17226
[9] Rubio-Bollinger G et al 2015 Enhanced visibility of MoS2, MoSe2, WS2 and black-phosphorus: making optical identification of 2D semiconductors easier Electronics 4 847–56
[10] Benamer M M, Radisavljevic B and Héron J S 2017 Optical contrast of 2D InSe on SiO2/Si and transparent substrates using bandpass filters Nanotechnology. 28 115706
[11] Gant P et al 2017 Optical contrast and refractive index of natural van der Waals heterostructure nanosheets of franckeite Beilstein J. Nanotechnol. 8 2357–62
[12] Rani R, Kundu A and Hazra K S 2019 Spectral dependent white light reflection mapping of MoS2 flake for improving accuracy of conventional optical thickness profiling Opt. Mater. 90 46–50
[13] Jassen B S et al 2018 Quantitative optical mapping of two-dimensional materials Sci. Rep. 8 6381
[14] Katzen J M et al 2018 Rigorous and accurate contrast spectroscopy for ultimate thickness determination of micrometer-sized graphene on gold and molecular sensing ACS Appl. Mater. Interfaces 10 22520–8
[15] Huang F 2019 Optical contrast of atomically thin films J. Phys. Chem. C 123 7440–6
[16] Veličký M et al 2018 Optimising the visibility of graphene and graphene oxide on gold with multilayer heterostructures Nanotechnology 29 275205
[17] Ge R et al 2018 Atomiristor: nonvolatile resistance switching in atomic sheets of transition metal dichalcogenides Nano Lett. 18 434–41
[18] Veličký M et al 2018 Mechanism of gold-assisted exfoliation of centimeter-sized transition-metal dichalcogenide monolayers ACS Nano 12 37
[19] Xia M 2018 A review on applications of two-dimensional materials in surface-enhanced Raman spectroscopy Int. J. Spectrosc. 2018
[20] Kleemann M E et al 2017 Strong-coupling of WS2 in ultra-compact plasmonic nanocavities at room temperature Nat. Commun. 8
[21] Wei W et al 2017 Graphene-MoS2 hybrid structure enhanced fiber optic surface plasmon resonance sensor Plasmonics 12 1205–12
[22] Zeng J et al 2015 Enhanced second harmonic generation of MoS2 layers on a thin gold film Nanoscale 7 13547–53
[23] Benamer M M et al 2011 Visibility of dichalcogenide nanolayers Nanotechnology 22 125706
[24] Li H et al 2013 Rapid and reliable thickness identification of two-dimensional nanosheets using optical microscopy ACS Nano 7 10344–53
[25] Todeschini M, Bastos Da Silva Fanta A, Jensen F, Wagner J B and Han A 2017 Influence of Ti and Cr adhesion layers on ultrathin Au films ACS Appl. Mater. Interfaces 9 37374–85
[26] Shearer C J, Slattery A D, Stapleton A J, Shapter J G and Gibson C T 2016 Accurate thickness measurement of graphene Nanotechnology 27 125704
[27] Zhang H et al 2015 Measuring the refractive index of highly crystalline monolayer MoS2 with high confidence Sci. Rep. 5 8440
[28] Buscema M, Steele G A, van der Zant H S J and Castellanos-Gomez A 2014 The effect of the substrate on the Raman and photoluminescence emission of single-layer MoS2 Nano Res. 7 1–11
[29] Lee C et al 2010 Anomalous lattice vibrations of single- and few-layer MoS2 ACS Nano 4 2695–700
[30] Chakraborty B *et al* 2012 Symmetry-dependent phonon renormalization in monolayer MoS$_2$ transistor *RAPID Commun. Phys. Rev.* B 85 161403–4

[31] Pimenta M A, Del Corro E, Carvalho B R, Fantini C and Malard L M 2015 Comparative study of Raman spectroscopy in graphene and MoS$_2$-type transition metal dichalcogenides *Acc. Chem. Res.* 48 41–7

[32] Choi W *et al* 2017 Recent development of two-dimensional transition metal dichalcogenides and their applications *Mater. Today* 20 116–30

[33] Anichini C *et al* 2018 Chemical sensing with 2D materials *Chem. Soc. Rev.* 47 4860–908

[34] Donarelli M and Ottaviano L 2018 2D materials for gas sensing applications: a review on graphene oxide, MoS$_2$, WS$_2$ and phosphorene *Sensors* 18 3638

[35] Liao H, Nehl C L and Hafner J H 2006 Biomedical applications of plasmon resonant metal nanoparticles *Nanomedicine* 1 201–8

[36] Lodewijks K, Roy W V, Borghs G, Lagae L and Van Dorpe P 2012 Boosting the figure-of-merit of LSPR-based refractive index sensing by phase-sensitive measurements *Nano Lett.* 12 1655–9