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Quick and reliable colorimetric reflectometry for the thickness determination of low-dimensional GaS and GaSe exfoliated layers by optical microscopy

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Abstract: Interest in gallium chalcogenides, i.e., gallium sulfide (GaS) and gallium selenide (GaSe), is growing rapidly due to its layered structure compatible with the fabrication of very thin layers by mechanical exfoliation and its wide band gap desirable for the design and fabrication of visible-UV optoelectronic devices. It is well known that the properties of these materials depend on their thickness; therefore, a facile and fast method is needed to infer the thickness of layered GaS and GaSe. Here, we report and validate a colorimetric method based on optical imaging for the quick and reliable quantitative determination of the thickness of exfoliated GaS and GaSe layers although it can be extended to other layered systems. For the validation of the method, the colorimetric computational estimate of the thickness is compared to the value obtained by atomic force microscopy. Further simulation of GaS and GaSe layers on different substrates of interest for different technological applications is provided as a quick guide for the rapid and reliable thickness determination of GaS and GaSe layers on various substrates.

1. Introduction

Due to their thickness-dependent properties III-VI two dimensional (2D) layered semiconductor chalcogenides (MX, M = Ga, In, Tl; X = S, Se, Te) are emerging as promising candidates for the next-generation ultrathin and flexible electronics and optoelectronics.

On the one hand, due to its high energy indirect and direct band gaps of 2.4-2.5 eV and 3.0-3.1 eV respectively [1], gallium sulfide (GaS) has been proposed as a new material for a novel generation of UV photodetectors [2–4]. Other technological applications of GaS include photoelectric devices, electrical sensors, near-blue light emitting devices [2] and field effect transistors (FET) with a mobility of 0.1 cm^2/V. [5] GaS is also investigated for energy storage [6], gas sensing [7], and as hydrogen evolution catalysts [8]. GaSe has been reported to have indirect and direct band gaps of 2.00 eV and 2.15 eV respectively [1], making it appealing for visible light photodetectors with high responsivity [9–11]. Another interesting property of this materials is it strong nonlinear optical response that enables strong second and third harmonic generations [12,13].

Both GaS and GaSe is a layered van der Waals (vdW) semiconductor consisting of a stacking of individual covalently bonded tetralayers consisting of S(Se)-Ga-Ga-S(Se) atomic planes where the successive tetralayers are held together via van der Waals forces. Therefore, as with many layered chalcogenide materials, the weak vdW bonding provides a way to realize two-dimensional layers. Few layers of GaS and GaSe have been successfully isolated through mechanical exfoliation.

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Nevertheless, the main drawback of this technique is that the resulting layered GaS and GaSe samples result in flakes of different number of layers and, therefore, variable thickness.

Colorimetric approaches based on the optical contrast between the light coming from the substrate and that coming from a neighboring region of a few material layers [14–16] are of interest for a quantitative deterministic identification of the number of layers and thickness of 2D materials on substrates. These colorimetric approaches are favorably sustained by the evolution of integrated microscopy systems with cameras that provide images with a better and more reproducible color specification.

In this work, we provide guidelines for the accurate and systematic colorimetric assessment of the thickness determination of low dimensional GaS and GaSe on several substrate that are often used for different technological applications. Our method is based on the simulation of the spectral reflectance of 2D GaS and GaSe layers of different thicknesses on various substrates using the transfer matrix method and its transformation to color coordinates using color matching functions. The simulated color for each thickness is validated by the comparison with the real color observed by an optical microscope of GaS and GaSe flakes whose thickness is determined by atomic force microscopy (AFM). Calculations can provide sets of color bars to work out thickness values up to 300 nm for GaS and GaSe on various substrates. They constitute a tool to quickly infer thickness and number of layers. Noteworthy, the proposed method, tested herein with GaS and GaSe, can be extended to other layered materials.

2. Color calculation model

The calculation model is based on sequencing two different procedures:

(i) First the spectral reflectance R(λ) of GaS flakes on different substrates (i.e., glass and SiO_2/Si) was calculated using the Transfer Matrix Method (TMM) [17]. TMM allows to calculate the reflectance spectrum of an arbitrary system of homogeneous and non-magnetic multilayers by establishing conditions for the electric field along the boundary of two consecutive media. In the case of a GaS layer on a semi-infinite reflective substrate (that, in turn, can be covered by another layer, e.g. GaS on SiO_2/Si substrates) the reflectance at normal incidence can be expressed as follows,

$$R = |r|^2 = \left| \frac{r_{01} + r_{123} e^{2i\delta_1}}{1 + r_{01} r_{123} e^{2i\delta_1}} \right|^2 \tag{1}$$

where $r_{01} = \frac{m_0 - m_1}{m_0 + m_1}$ is the Fresnel coefficient at the first interface (i.e., air-GaS). m_0 and m_1 are the complex refractive indices of air and GaS respectively. r_{123} is the effective reflection coefficient of the combined second and third interface. It can be expressed as follows,

$$r_{123} = \frac{r_{12} + r_{23} e^{2i\delta_2}}{1 + r_{12} \cdot r_{23} e^{2i\delta_2}} \tag{2}$$

where r_{ij} is the reflection coefficient at the interface between the i^{th} and j^{th} layer, and where $\delta_1 = {}^{2\pi}/_{\lambda} m_1 d_1$ and $\delta_2 = {}^{2\pi}/_{\lambda} m_2 d_2$ with m_1, d_1 and m_2, d_2 being the complex refractive indices and thicknesses of GaS and the substrate overlayer (e.g. SiO_2). λ refers to the incident wavelength. This expression can be easily reduced for the case of GaS directly supported on semi-infinite reflective substrates such as Si or glass.

Therefore, the input for this calculation requires the thickness of the GaS layer and the dielectric functions ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of both the substrate, including the overlayer, and GaS. Such dielectric functions had been previously measured by spectroscopic ellipsometry. Because we want our calculation to be compared with observations under the microscope, we have to sum all the reflected light that arrives to the objective lens. It is angularly modelled with a normal distribution of mean 0 and standard deviation $\theta = sin^{-1}(\mathrm{NA})$ where NA is the numerical aperture (NA) of the

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microscope objective [14,18]. For each case, two reflectance spectra were calculated separately for both polarizations, s- and p-polarizations in order to consider incident unpolarized light.

(*ii*) The determined spectral reflectances are used for the calculation of the CIELAB colors, which represent the colors perceived by the human eye. Specifically, the resulting color depends on the spectral illuminant, spectra reflectivity, and observer. All the color simulations within this work assume standard D65 illuminant, which allow us to better mimic the illumination of the microscope, and a CIE standard observer. CIE standard observer represents mean human spectral sensitivity to visible spectrum range. For comparison with the experimental images, CIELAB coordinates were converted in sRGB values [19].

3. Model validation

In order to validate the color calculated using the aforedescribed method, the thickness was determined by atomic force microcopy (AutoProbe CP, ThermoMicroscope). Height profiles on mechanically exfoliated GaS layers on (300 nm) SiO_2/Si substrates were used to establish a direct correlation. The color of the flakes in sRGB coordinates was obtained from optical microscopy images taken on a Nikon microscope mounted on a HR-LabRam Horiba Raman spectrometer. The objective of the microscope has a NA = 0.25. The same microscopy hardware and software settings were used for all the images considered in this work.

The experimental extracted color was compared with the calculated color looking for the theoretical thickness that minimizes the color difference ΔE between the calculated and experimental color. For this minimization process, CIELAB color coordinates were used, being the color differences (distance in the color space) determined by

$$\Delta E = \sqrt{(L_t - L_e)^2 + (a_t - a_e)^2 + (b_t - b_e)^2} \tag{3}$$

where the subindices *t* and *e* correspond to the theoretical and experimental data respectively. Finally, the thickness that minimizes ΔE is compared with the experimental one to evaluate the goodness of the model.

A flow diagram containing the different steps of the previously described experimental/numerical procedure is summarized in Fig. 1.

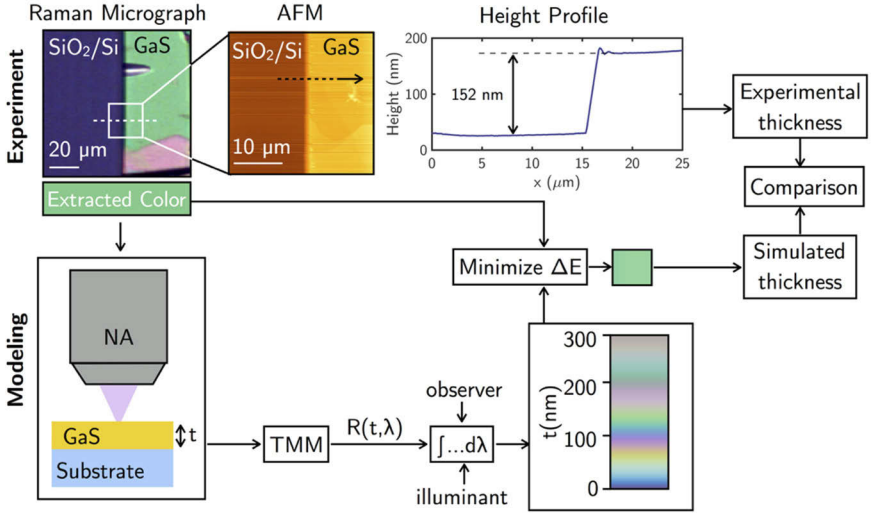

Fig. 1. Flow diagram of the proposed model evaluation.

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4. Results

Figure 2 shows the characteristics of centimeter-scale mechanically exfoliated GaS and GaSe samples on 285 nm SiO_2/Si and Corning glass substrates (Fig. 2(c),(d)). As shown in Fig. 2(a),(b), GaS and GaSe has a layered structure consisting of a stacking of individual tetra-covalently bonded S(Se)-Ga-Ga-S(Se) atomic planes. The tetravalent layers are held together via van der Waals forces. This weak interlayer van der Waals forces allows the easy mechanical exfoliation of GaS crystals. The layered structure of GaS is shown by the scanning electron microscopy (SEM) images in Fig. 2(g); the zoom of the border allows to clearly see the various layers piled-up. Optical micrograph images of the samples also reveal the layered structure of the material, with overlapping flakes, and each color corresponding to a different thickness, i.e., number of layers of GaS (see Fig. 2(h)). Edges, steps and wrinkles characteristic of exfoliated layered materials are also visible in Fig. 4(g). The Raman spectra, as shown in Fig. 2(e),(f), presenting the three GaS prominent peaks at 185, 291 and 357 cm^{-1} assigned to the A^1_{1g}, E^1_{2g} and A^2_{1g} Raman modes, and

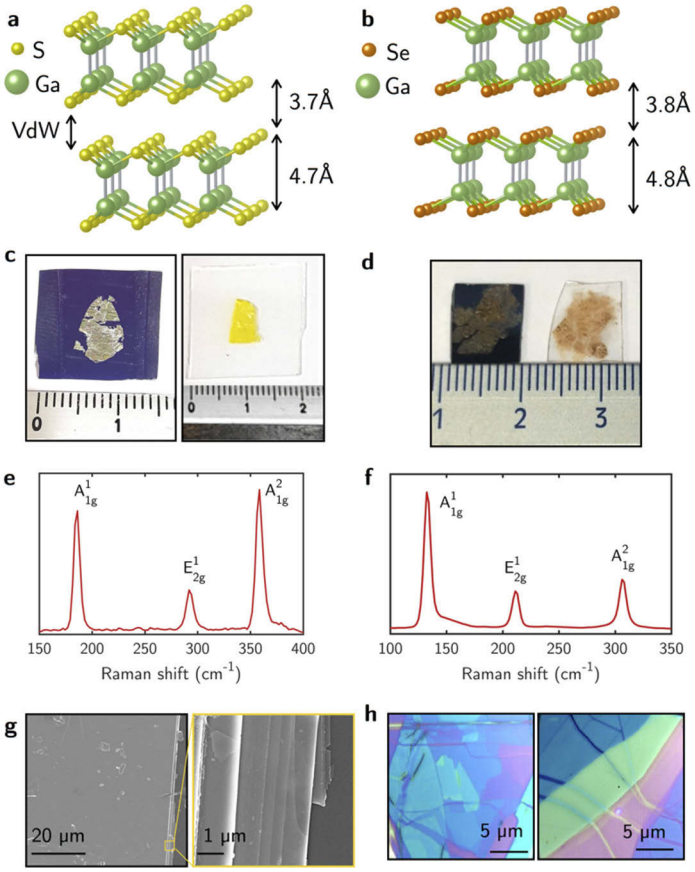

Fig. 2. Crystalline structure of (a) GaS and (b) GaSe. The intralayer and interlayer distance were taken from Ref. [20,21]. Centimeter scale mechanically exfoliated (c) GaS and (d) GaSe on SiO_2/Si and on glass substrates. Raman spectrum of the exfoliated (e) GaS and (f) GaSeflakes on glass. (g) Scanning electron microscopy of the samples showing the layered structure of the materials. (h) Optical micrograph images of the morphology of the GaS sample on glass as in (g); characteristic edges, steps and wrinkles can also be seen. For GaSe similar morphology has been observed.

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GaSe prominent peaks at 133, 212 and 307 cm^{-1} assigned to the A^1_{1g}, E^1_{2g} and A^2_{1g} Raman modes, corroborates the GaS and GaSe crystalline quality.

For the validation of the model we considered GaS flakes ranging from monolayer up to around 250 layers exfoliated on 285 nm SiO_2/Si substrates. The number of layers was cross checked with SEM tilted images, and the thickness values obtained for each flake (that showed different colors under the optical microscope) were measured by AFM. Figure 3 shows the results of the proposed colorimetric model. The thickness, as measured with AFM, ranged from 1.1-1.2 nm (monolayer) to 220 nm. By: (i) sampling and extracting the color of these regions in four different points from the micrograph images and (ii) running a ΔE minimization process with respect to the simulated colors, we obtained a predicted value of thickness. As seen in Fig. 3, there is a very good agreement between the colorimetric prediction and the experimental AFM thickness.

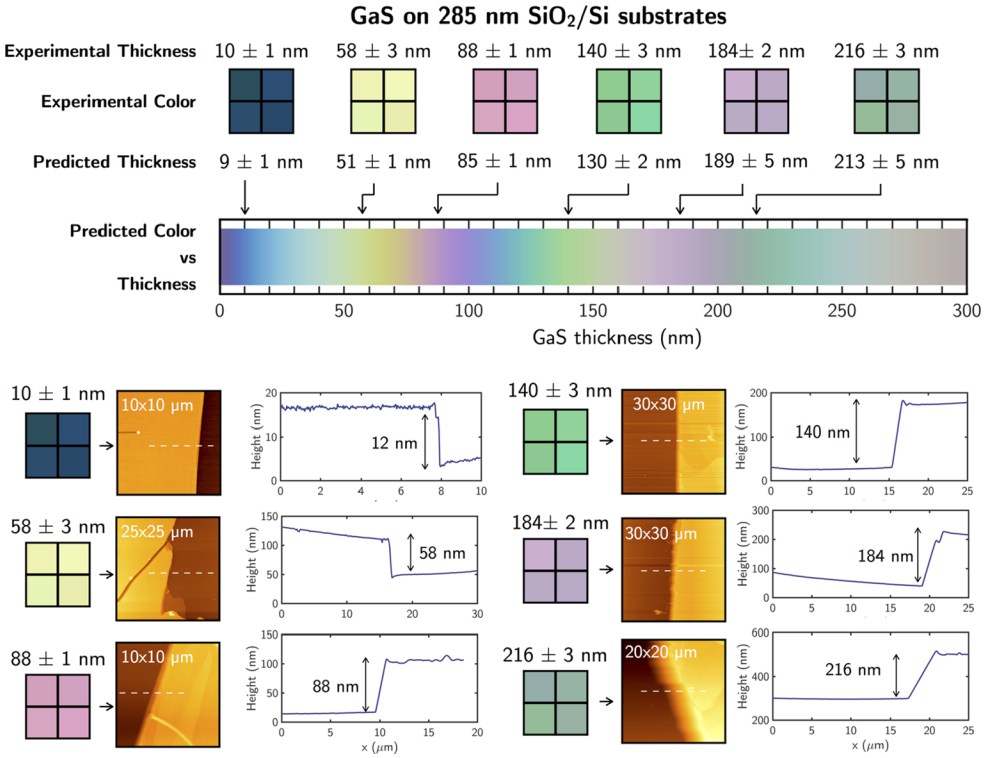

Fig. 3. Evaluation of the proposed model using GaS flakes exfoliated on 285 nm SiO2/Si substrates. The experimental thickness is measured with AFM for GaS flakes. These show the experimental colors sampled in the squared mosaic (optical micrographs). The predicted thickness, obtained by running the ΔE minimization process, follows in the third row, together with its location in the bottom bar, i.e. the predicted color evolution of GaS on 285 nm SiO2/Si substrates as function of the GaS thickness.

The errors in the thickness determination using colors can originate from the following aspects:

- The optical properties of GaS used in the modelization are those of bulk material, which may differ for ultrathin layers.
- The matching of the luminosity in the microscope and simulation might not be perfect.
- The modeling of the light source intensity angular distribution might deviate from a Gaussian distribution assumed in the model.

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- According to the manufacturer, the substrate SiO_2 thickness of 285 nm has a 10% uncertainty. This local inhomogeneities of the SiO_2 layer thickness can affect reflected color of GaS layers.

Due to the good agreement achieved, we have extended the colorimetric approach to GaS deposited on other substrates of technological interest. Figure 4 shows the colors as a function of the thickness of GaS layers on different substrates of glass, indium tin oxide (ITO) and Si compared to the previous 285 nm SiO_2/Si. These colors palettes can serve as a quick guide to estimate the thickness of GaS layers on the different substrates. The substrates selected here have been chosen according to their importance for applications in different technological fields. Glass and ITO are common substrates in the design of displays containing thin layers of chalcogenide materials [22]. We also considered Si and SiO_2/Si which are usual substrates in the fabrication of FET transistors and photodetectors [4,5,23]. For these calculations, the dielectric functions were taken from different sources in the literature: Si [24] and ITO [25]. For glass and the 285 nm SiO_2/Si substrates, the dielectric function was measured using spectroscopic ellipsometry. Two different numerical apertures have been considered, i.e., NA = 0.25 and 0.90. When changing to larger NA, it is possible to see how the color bar is shifted towards higher GaS thickness values, as expected from an increase in the average optical path. In the same figure, we also show the experimental micrograph images of exfoliated GaS on glass, Si and SiO_2/Si substrates, to put in evidence that the predicted colors are present in the experimental images, further supporting the results of the modelling proposed here. It is worth mentioning that the micrographs shown here, which are highly inhomogeneous, have been specifically chosen with the purpose to show the

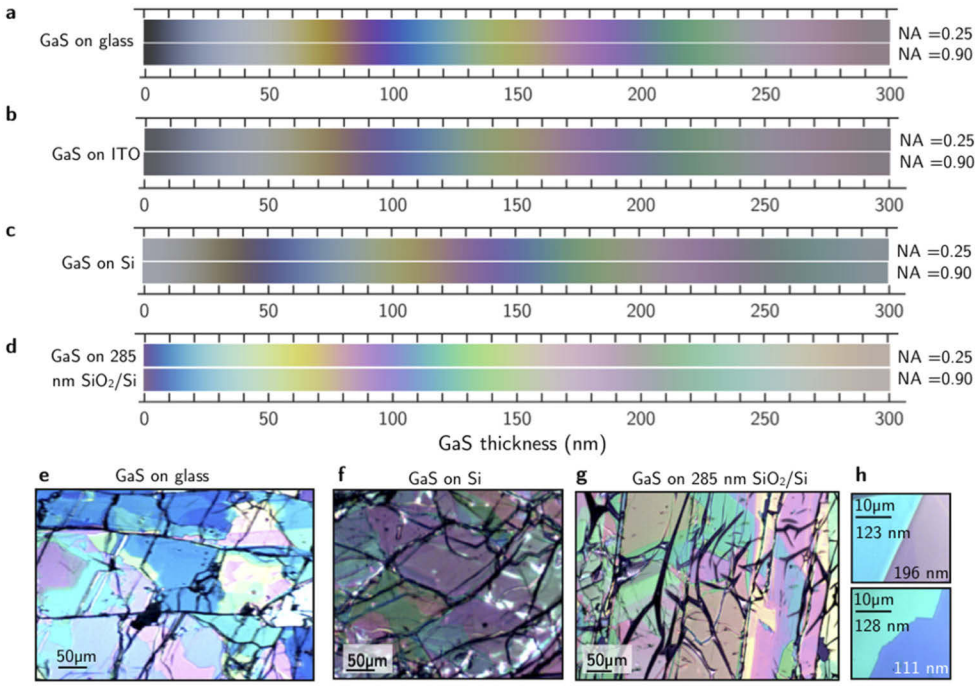

Fig. 4. Color evolution of GaS thin layers of different substrates as a function of their thickness considering a NA = 0.25 and 0.9. The substrates considered are: (a) glass, (b) ITO, (c) Si and (d) 285 nm SiO_2/Si. Micrograph pictures of the GaS surface exfoliated on (e) glass, (f) Si and (g) 285 nm SiO_2/Si. In (h) the smaller micrographs show homogenous regions with their predicted thickness.

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wide gamut of colors that could be seen on mechanically exfoliated samples. More homogenous flakes, with sizes of the order of tens of microns have also been achieved through mechanical exfoliation of GaS (see Fig. 4(h)). For this last case the thickness of each layer, inferred by the developed colors palette and confirmed by AFM, is indicated.

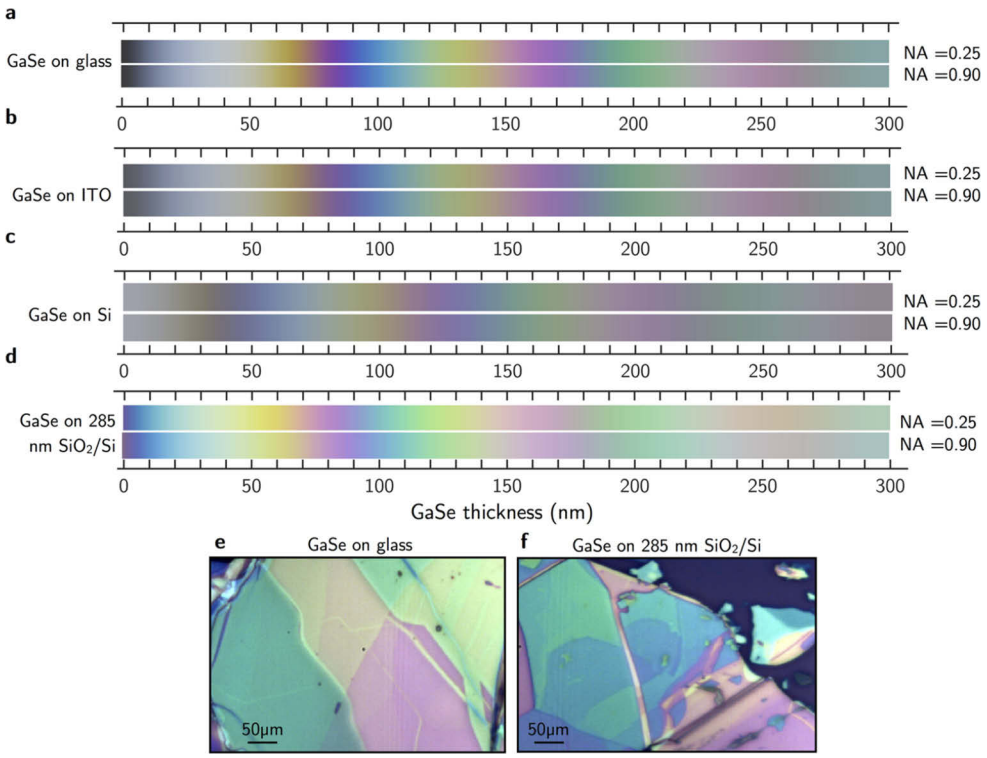

Fig. 5. Color evolution of GaSe thin layers of different substrates as a function of their thickness considering a NA = 0.25 and 0.9. The substrates considered are: (a) glass, (b) ITO, (c) Si and (d) 285 nm SiO_2/Si. Micrograph pictures of the GaSe surface exfoliated on (e) glass and (f) 285 nm SiO_2/Si.

After the favorable agreement between the experimentally measured and theoretically predicted thicknesses on GaS, similar calculations have been performed on GaSe thin layers supported in the different substrates as shown in Fig. 5. Once again, two different numerical apertures have been considered, i.e., NA = 0.25 and 0.90. In this case, we also show the experimental micrograph images of exfoliated GaSe on glass and SiO_2/Si substrates, to highlight that the predicted colors are present in the experimental images, further supporting the results of the modelling proposed here.

5. Conclusions

In summary, a colorimetric reflectometry method based on optical microscopy has been developed to quickly and reliably infer the thickness of flakes of 2D materials. In particular here we focus on addressing the thickness of flakes GaS and GaSe on different substrates. The method has been experimentally validated by comparing the computational estimate of the thickness, as given by the colorimetric approach, with that measured using atomic force microscopy. Generalized colors palettes for GaS and GaSe on various technological substrates are provided that can be used by anyone taking optical micrographs of exfoliated GaS and GaSe as a quick guide for the

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rapid and reliable thickness determination of GaS and GaSe layers on those substrates. The proposed generalized optical identification model and color palettes will facilitate the thickness dependent investigation of 2D semiconductors, expediting their practical applications.

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Disclosures. The authors declare no conflict of interests.

Data availability. The code for generating color palettes on arbitrary multilayer systems and extract the thickness from optical micrographs is available in Ref. [26].

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