Apparent Colors of 2D Materials

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Finding 2D and thin-film layered materials have become essential to develop not only in scientific-related fields, but also in a wide industry, which is constantly feeding from this progress. For electronic devices, thin-film materials are supposed to be a step forward to overcome Moore’s law. In many other technologic areas, the development of tools based on flakes of materials has found new physics, becoming a rising field. Although, destructive techniques are commonly used to characterize the thickness of these materials. Herein, a list of materials is presented, whose thicknesses are characterized by their apparent colors in several substrates, a harmless, fast, and reliable technique that has been already used to determine the number of layers in several works. This list is also enlarged with other materials and substrates.

1. Introduction

The production of 2D materials through mechanical exfoliation is rather straightforward. In fact, it is likely that single-layer thick flakes of different 2D materials were isolated even before the seminal paper of Novoselov and Geim published in 2004.[1] Then why did 2D materials research not bloom until 2004? Even though the production of ultrathin materials by mechanical exfoliation was not an issue, finding these flakes and discriminating them from bulky flakes was an unsolved challenge until 2004. Indeed, mechanical exfoliation produces a random assortment of flakes with different thicknesses, lateral dimensions, and shapes deposited on the surface of acceptor substrate. Therefore, the development of easy, fast, high-throughput, and nondestructive techniques to identify ultrathin flakes of 2D materials and distinguish them from thick flakes was the inflection point for the rapid growth of this research field.

Optical microscopy (OM)-based methods have been proven to be the most suited ones to rapidly identify atomically thin 2D materials flakes.[2–6] Nowadays there are methods based on Raman spectroscopy, photoluminescence, microtransmittance/reflectance, Rayleigh scattering, or optical path interferometry that allow the accurate thickness determination of a wide range of 2D materials. Nonetheless, these more sophisticated OM-based methods are always preceded by a coarse thickness estimation based on the apparent color of the flakes. That is, flakes of different thicknesses have different apparent colors due to a combination of optical absorption and interference color effects. This thickness-dependent color can be further enhanced by depositing the 2D material flakes on top of specific substrates that optimize the interference color effect. Despite the relevance of the coarse thickness estimation through the observation of their apparent color, a comprehensive summary of the reported color versus thickness datasets is lacking in the literature. This is the goal of this work, to gather this information in a single article, unifying the format of the presented datasets to facilitate the reader finding necessary information. We believe that this work will become particularly useful for those researchers starting to work on a new 2D material family. Furthermore, we have added new figures of different materials, by delaminating them using scotch-tape method and placing them on several substrates using deterministic transfer methods,[7] to complement the data that are already published.

The thickness-dependent apparent color of 2D materials can be explained in the basis of a multiple-media optical system (see Figure 1a), in which the incident light reaches a surface, that it could be the substrate or the flake, and it crosses every media until reaching the Si wafer. At this point, the light comes back along the same path (we suppose normal incidence) and reaches the measuring device. The light reflected or transmitted by this system can be calculated by applying the Fresnel law[8] at each...
interface and considering the attenuation and the phase shift introduced while the different light beams propagate along each medium. The reflected intensity for monochromatic light at a normal incidence is written in Equation (1). \[ I = \frac{r_{01}e^{i(\phi_1 + \phi_2)} + r_{12}e^{-i(\phi_1 - \phi_2)} + r_{23}e^{i(\phi_1 + \phi_3)} + r_{01}r_{12}r_{23}e^{i(\phi_1 - \phi_2)}}{e^{i\phi_1} + r_{01}r_{12}e^{-i\phi_1} + r_{01}r_{23}e^{-i\phi_1} + r_{12}r_{23}e^{i\phi_1}} \] where the reflection coefficient is \( r_{ij} = (n_i - n_j)/(n_i + n_j) \), the phase shift in the medium \( i \) is \( \phi_i = 2n_i d_i/\lambda \), \( n_i \) is its respective complex refractive index, \( d_i \) is its thickness, and \( \lambda \) is the wavelength. The subindexes 0, 1, 2, and 3 are assigned as air, flake, SiO\(_2\), and Si, respectively.

The Optical Contrast (C) is defined in Equation (2) and it can be experimentally obtained using an experimental system, as explained by Frienda R. et al.\[10\]

\[ C = \frac{I_f - I_s}{I_f + I_s} \]  

\( I_f \) is the reflected intensity acquired on the flake and \( I_s \) the intensity acquired on the substrate. \( I_f \) can be obtained using Equation (1) and \( I_s \) can be determined replacing the flake for air in medium 1. Figure 1b shows an example of how \( C \) changes using different flake thicknesses from 5 to 93 nm. It has been obtained using values of air as a first medium, with a refractive index \( n_0 = 1 \); a substrate thickness of \( d_s = 297 \) nm of SiO\(_2\), with a refractive index \( n_s = 1.5 \); and a semi-infinite Si media with a refractive index that is dependent on the wavelength.

This method has been seen in several previous works that use silicon substrates with a top SiO\(_2\) layer of specific thicknesses, yielding a strong thickness dependence of the 2D materials’ apparent colors\[2-4\] and thus facilitating their optical identification. The most extended substrates are SiO\(_2\)/Si with thickness of SiO\(_2\) layer in the range of 70–90 nm or 270–300 nm (the specific SiO\(_2\) thickness that optimizes the optical identification depends on the 2D material to be identified).

2. Experimental Section

In Table 1 we present a list of the 2D materials whose apparent color has been reported in the literature. We included the electronic behavior of each material and their bandgap.

2.1. Graphene

Graphene became the first 2D material isolated, by Novoselov and Geim, in 2004 by mechanical exfoliation.\[15\] Its crystal structure is made of carbon atoms, packed in a honeycomb crystal lattice,\[11,12\] with thickness of about 3 Å.\[13\] The carbon atoms are about 1.42 Å from its three neighbors,\[14\] sharing \( \sigma \) bonds; and the remaining electron per atom is used to make \( \pi \) and \( \pi^* \) bonds between layers when they are stacked. Because of its crystal structure (\( P6/mmm \)) space group in international notation), the first Brillouin zone has two inequivalent points K and K’ (called Dirac points), where a band crossing occurs.\[16\] Due to this, graphene is a zero-gap semiconductor and its charge carriers mimic relativistic particles with zero rest mass, and its energy dispersion has a linear relation near the Dirac points, while they move 300 times less than the speed of light.\[17,18\]

The peculiarities of the graphene band structure reflect on its electronic properties: Electronic mobilities up to \( 2.3 \times 10^5 \) cm\(^2\) (V s\(^{-1}\)) has been measured at room temperature\[19\] nearly 200 times the mobility of silicon.\[20\] Moreover, it possesses withstanding mechanical properties, such as a high Young’s modulus of around 1 TPa and a breaking strength of 130 GPa.\[21\]

From these properties and others, graphene has proven to be useful in multiple fields, such as optoelectronics,\[22-31\] flexible electronics,\[32-36\] medicine,\[40,41\] energy storage,\[42,43\] etc.\[44\]

Graphene color ranges for different substrate thicknesses, showcasing that the importance of the flake and the substrate are equivalent for determining the thickness of the flakes. Figure 2a shows a collection of OM images of graphene flakes with thicknesses ranging from single layer to 15 layers, deposited onto 90 nm SiO\(_2\)/Si, with a marked thickness-dependent...
Table 1. (I) indicates that it is an indirect bandgap and (D) indicates a direct bandgap. (E) indicates an experimental value and (T) indicates a theoretical result.

| Material       | Origin      | Electronical behavior | # layers | Bandgap [eV] | Reference |
|----------------|-------------|-----------------------|----------|--------------|-----------|
| Graphite       | Natural     | Semimetal             | Bulk     | 0            | (E)129    |
| Graphene oxide | Synthetic   | Semiconductor, Insulator | 1       | 0.02–2       | (E)52     |
| MoS2           | Natural     | Semiconductor         | Bulk     | 1.2 (I)      | (E)72     |
| WS2            | Synthetic   | Semiconductor         | Bulk     | 1.3 (I)      | (E)79     |
| WSe2           | Synthetic   | Semiconductor         | Bulk     | 1.2 (I)      | (E)72     |
| MoTe2          | Synthetic   | Semiconductor         | Bulk     | 1.6 (D)      | (E)59     |
| 1 T-TaS2       | Synthetic   | Metallic              | Bulk     | 0.19 (D)     | (T)310    |
| 2 H-TaS2       | Synthetic   | Metallic              | Bulk     | 0.39 (D)     | (T)310    |
| 2 H-TaSe2      | Synthetic   | Metallic              | Bulk     | 0            | (E)121    |
| hBN            | Synthetic   | Semiconductor         | Bulk     | 5.9 (I)      | (E)333    |
| γ-InSe         | Synthetic   | Semiconductor         | Bulk     | 1.2 (I)      | (E)155    |
| c-GaSe         | Synthetic   | Semiconductor         | Bulk     | 2.4 (D)      |           |
| FePS3          | Synthetic   | Semiconductor         | Bulk     | 1.59 (D)     | (E)249    |
| MnPS3          | Synthetic   | Semiconductor         | Bulk     | 3 (D)        |           |
| Franckeite     | Natural     | Semiconductor         | Bulk     | 0.7 (I)      | (E)285    |
| CrI3           | Synthetic   | Semiconductor         | Bulk     | 1.2 (D)      | (E)277    |
| PbI2           | Synthetic   | Semiconductor         | Bulk     | 2.41 (I)     | (E)286    |
| MAPbI3         | Synthetic   | Semiconductor         | Bulk     | 1.5 (D)      | (E)295,297|
| (PEA)2PbBr4    | Synthetic   | Semiconductor         | Bulk     | 2.9          | (E)306    |
| BSSCO          | Synthetic   | Superconductor        | Bulk     | 0.042        | (E)314    |

The search of flakes guided by their colors has recently become so common in 2D materials’ thickness identification that even machine learning algorithms have been developed to identify flakes onto SiO2/Si and PDMS substrates in a faster and more reliable way.[46–49] The evolution of these new methods gives science new paths to elaborate everyday measurements faster. We think that the standardization of color charts and the collaborative creation of a color chart repository is indispensable to follow this trend in the future.

2.2. Graphene Oxide

Graphene oxide (GO) is composed of benzene ring regions that are not oxidized and other regions that have aliphatic six-membered rings. The degree of oxidation depends on the relative sizes of these two regions, and they are randomly distributed, meaning that quantifying these values is a complex work. Graphene oxide has different properties when compared with graphene, such as hydrophobicity in GO in contrast to hydrophilicity in graphene,[50] and it is produced easier than its counterpart. The preparation techniques to intercalate oxygen in graphene and synthesize GO are diverse, several reagents are used. Every technique has their particular advantages and disadvantages, producing GO with different properties. By tuning the oxidation degree in graphene the bandgap can be manipulated, opening a direct bandgap due to the disruption of the π electrons.[51] changing from 2 to 0.02 eV.[52] Therefore, it can be used in photodetection for that range of the electromagnetic spectrum. Recently, GO is found to have fluorescent and nonlinear optical properties, being possible to use in short-pulsed high-power lasers.[53] This material has been functionalized, maintaining excellent properties and adding new characteristics, typical of the functional groups.[54] Thus, it has opened a wide path in diverse applications, not only in electronics, photonics, and apparent color. Figure 2b depicts the color bar, with the range that graphene can exhibit from 1L to 125L, paying special attention to the range of 1L–10L deposited on a 100 nm SiO2/Si. Figure 2c shows some flake images but for flakes deposited onto 300 nm SiO2/Si substrates where different apparent colors are clearly observed. In each figure one can notice that, from single-layer to multilayer graphene, the samples’ reflection for their surface is less intense than that from the SiO2/Si substrate, resulting in negative value contrasts. The origin of the contrast can be understood, thanks to Fresnel’s equations, with a physical model like the one depicted in Figure 1, and it is used in several works.[3,4,45]
optoelectronics fields but also, to name some, in biomedical and photocatalytic applications.\cite{54,55} Due to these features, a nondestructible optical characterization is needed. Figure 3 shows flakes of GO from 1L–5L deposited on top of 300 nm of SiO\textsubscript{2}/Si substrate.

2.3. Transition Metal Dichalcogenides

Due to the lack of a bandgap in graphene, other materials became more attractive to researchers,\cite{56} and several kinds of materials have been found attending to different properties, creating a 2D library.\cite{57} Transition metal dichalcogenides, usually named TMDCs, is a family of layered compounds with the typical formula MX\textsubscript{2}, where M = Mo, W, Sn, Hf, and Zr and X = S, Se, and Te. A monolayer of any of these compounds is composed of three atomic layers following the order X–M–X. They possess no dangling bonds on the basal plane and, as it occurs in graphene, the layers are bonded with van der Waals force, which makes them easy to be exfoliated with different techniques. TMDCs possess diverse electronic properties, and most of them are

Figure 2. The number shown on top of each flake corresponds to the amount of monolayers of graphene. a) Color optical images of 1L–15L graphene flakes on 90 nm SiO\textsubscript{2}/Si. The scale bars in each image are 10 μm. Reproduced with permission.\cite{2} Copyright 2013, American Chemical Society. b) Classical numerical color bar for graphene from 1 to 125 layers. Reproduced with permission.\cite{46} Copyright 2019, Elsevier. c) Color optical images of 1L–9L of graphene flakes on 285 nm SiO\textsubscript{2}/Si, scale bar is not included in the original work. Reproduced with permission.\cite{45} Copyright 2013, American Chemical Society. d) Color optical images of 1L–13L graphene flakes on 300 nm SiO\textsubscript{2}/Si taken at the exposure time of 50 ms. The scale bars are 5 μm. Reproduced with permission.\cite{2} Copyright 2013, American Chemical Society.
semiconductors (MoS₂, WSe₂, and MoSe₂), although one can also find semimetals (WTe₂ and TiSe₂), insulators (HfS₂), and even metals (NbS₂ and VSe₂). They have been studied for a long time. In a review, Wilson et al. [58] examined these compounds and the well-known structural, optical, and electrical properties. Moreover, this family of materials have the property of changing their electronic behavior with thickness. Usually, bulk TMDCs semiconductors possess an indirect bandgap while, when they are thinned down to a monolayer, it modifies to a direct one.[59,60]

Moreover, for thick TMDCs (C25/C0 to 100 nm), strong coupling effect between excitons, typical from these materials, and optical modes in Fabry—Perot microcavities due to light confinement is exhibited. In these systems, Rabi splitting can be observed whether placing the TMDC between two metallic mirrors or just onto a well-reflecting substrate, for example, SiO₂/Si.[61,62] These strong coupling between cavity modes and excitons may lead to substantial changes in apparent colors of these materials.

Nowadays, the family of TMDCs is very attractive in applications such as photonics, electronics, optoelectronics,[63] sensors,[64,65] and so on.[66,67] 2.3.1. MoS₂

Among the TMDCs, molybdenum disulfide (MoS₂) has been the most studied material. It has been identified as 2D after the discovery of graphene. MoS₂ is formed by stacking layers, bonded with van der Waals forces, and it possesses three polytypes. In this work, we are going to focus on the 2H one (hexagonal polymorph), with an in-plane hexagonal P6₃/mmc crystal structure, in which the molybdenum atoms are in the centers of trigonal prisms formed by sulfur.[68] MoS₂ is already well known for its applications in the fields of lubrication,[69] catalysis,[70] and petroleum desulfuration[71] for a long time, but in the last years, its optical, electronic, and optoelectronic properties have also started to be intriguing to the scientific community. When the MoS₂ is exfoliated to one layer (of thickness around 0.7 nm[72]), its energy bandgap changes from indirect, with a value of ≈1.2 eV at its Γ point, to a direct bandgap of 1.8 eV at its K point.[60,73,74] Moreover, it has been proven that this bandgap can be tuned by applying strain, as it happens with various TMDCs.[75–77] Thus, the electronic properties of monolayer MoS₂ make it a suitable candidate for applications in transistors, achieving higher on/off ratio than that of graphene, and in optoelectronic devices.[78]

Figure 4 shows the calculated C of MoS₂ from 1 L to 8 L using substrates of 100 nm SiO₂ (Figure 4a) and 300 nm SiO₂ (Figure 4b). Here, it is well depicted how the maximum and minimum values of the function move along the wavelength for MoS₂ flakes with different thicknesses on the same substrate. Figure 5 shows OM images of few-layer MoS₂ flakes of different thicknesses deposited onto 90 nm (Figure 5a) and 300 nm SiO₂/Si (Figure 5b,c). The panels (b) and (c) come from two different works, showing a change of apparent color due to the different parameters that the authors have used in their experiments. As we have already seen, these flakes show a marked thickness-dependent apparent color that depends on

![Figure 3](image1.png)

**Figure 3.** GO flake on top of 300 nm of SiO₂/Si substrate from 1L–5L. Below panel shows the apparent color chart made from these thicknesses. Reproduced with permission.[131] Copyright 2013, Elsevier.

![Figure 4](image2.png)

**Figure 4.** Plots of calculated C for 1L–8L MoS₂ on a) 100 nm SiO₂ and b) 300 nm SiO₂ as a function of wavelength. Adapted with permission.[46] Copyright 2019, Elsevier.
the specific SiO2 thickness used. In addition, these figures can be used to build up color charts that correlate the thickness of MoS2 flakes with their apparent color on SiO2/Si substrates with 90 and 300 nm SiO2 capping layer.

Chemical vapor deposition (CVD) method is the most common technique to grow monolayer MoS2 on different substrates, and it is well developed and reproducible. Figure 6 shows MoS2 monolayer flakes grown by CVD using sapphire (panel (a)) and 280 nm SiO2/Si (panel (b)) as substrate as well as monolayer MoS2 on quartz substrate (panel (c)) using mechanical exfoliation method.

2.3.2. WS2

Tungsten disulfide (WS2) is another material that has become very interesting to the scientific community due to many intriguing assets, such as high spin–orbit coupling (SOC), high-emission quantum yield, and large exciton and trion binding energy. Hexagonal polymorph type (2 H) structure, the most stable one with a monolayer thickness of 0.6 nm, has an indirect bandgap of \( \approx 1.3 \) eV in bulk. When it is thinned down to a monolayer, a direct bandgap of \( \approx 2 \) eV is obtained, similar to that of MoS2. This change in bandgap is useful in renewable energy conversion and storage fields, such as electrocatalysis, photocatalysis, batteries, and supercapacitors. Moreover, monolayer WS2 has become as a promising material for fields like valleytronics, photonic, and photoluminescence enhancement. However, it also features intriguing properties when it is studied in few layers, paving a way in electronics, optoelectronics, photovoltaics, and thermoelectricity applications.

Figure 7 shows WS2 flakes deposited onto three different Si substrates with SiO2 capping layers of 88, 215, and 297 nm,
respectively, building the apparent color charts to identify thin films of WS$_2$ on these substrates.

Figure 8 exhibits WS$_2$ flakes deposited onto 300 nm SiO$_2$/Si substrate, displaying the apparent color of 1L–4L WS$_2$ on this substrate.

2.3.3. WSe$_2$

Tungsten diselenide (WSe$_2$), in its 2H polytype,$^{[90]}$ is another renowned member of the TMDCs family, which also experiments a transition from indirect ($\approx$1.2 eV in bulk$^{[73]}$) to direct

![Figure 6. MoS$_2$ monolayer flakes grown by CVD technique on a) sapphire. Adapted with permission$^{[314]}$ Copyright 2015, Springer Nature. b) 280 nm SiO$_2$/Si. Scale bar corresponds to 10 μm. Adapted with permission.$^{[315]}$ Copyright 2015, Springer Nature. c) Mechanically exfoliated MoS$_2$ monolayer deposited on quartz. Scale bar corresponds to 5 μm. Adapted with permission.$^{[316]}$ Copyright 2016, John Wiley and Sons.](image)

![Figure 7. WS$_2$ flakes and corresponding color charts onto Si substrates with a) 88, b) 215, and c) 297 nm SiO$_2$ capping layers from top to bottom, respectively.](image)
(≈1.6 eV\(^5\)) bandgap and an increase in the photoluminescence intensity when it is studied as monolayer, with a thickness of ≈0.63 nm.\(^{91}\) In this material SOC is more enhanced in comparison with other TMDCs,\(^{92}\) making it a promising candidate for spintronic applications. WSe\(_2\) is useful in similar applications as is WS\(_2\), which are electrocatalysis, batteries, photocatalysis, solar energy conversion, etc.\(^{93}\) Moreover, bulk and mechanically exfoliated monolayers or thin-film WSe\(_2\) flakes present a p-type electrical conduction, which makes it very interesting for electronic applications\(^{91,94}\) and high-carrier mobility transistors using WSe\(_2\) monolayer flakes.\(^{95}\) Thus, characterization of few-layer tungsten diselenide is mandatory for its use in these applications.

Figure 9 shows two collections of OM images and corresponding color charts of few-layer WSe\(_2\) flakes with different thickness deposited onto 90 nm (Figure 9a) and 300 nm (Figure 9c) SiO\(_2\)/Si substrates, respectively. Below the flakes’ OM pictures, one can

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**Figure 8.** The optical image and color charts of 1L–4L WS\(_2\) flakes deposited onto 300 nm SiO\(_2\)/Si substrate. Reproduced with permission.\(^{182}\) Copyright 2017, John Wiley and Sons.

**Figure 9.** The numbers indicate the amount of layers of WSe\(_2\) flakes. Color optical images of 1L–14L WSe\(_2\) flakes on a) 90 nm and c) 300 nm SiO\(_2\)/Si substrates. The scale bars shown in (a) and (c) have a length of 5 \(\mu\)m and 2 \(\mu\)m, respectively. Reproduced with permission.\(^{2}\) Copyright 2013, American Chemical Society. b) Color chart built from WSe\(_2\) flakes on 287 nm SiO\(_2\)/Si substrate. Reproduced with permission.\(^{317}\) Copyright 2021, AIP publishing.
find their respective color charts, correlating the thickness of WSe₂ flakes with their apparent color when they are placed onto 90 and 300 nm SiO₂/Si substrates. Figure 9b shows the color charts of few-layer WSe₂ flakes on 287 nm SiO₂/Si substrate with thickness ranging from 1L to 50 nm.

### 2.3.4. MoTe₂

Molybdenum ditelluride (MoTe₂) crystal structure is organized in a honeycomb lattice and it has an indirect bandgap of 0.93 eV when it is measured in bulk, increasing to a direct one of 1.08 eV when it is a monolayer, with stronger photoluminescence. Similar to GaSe and InSe, it has been found that MoTe₂ samples are not stable in air. Chen et al. noticed that monolayers, around 0.7 nm thick, of MoTe₂ flakes are stable for up to 8 days in ambient exposure, but their optical properties are largely affected, that is, optical contrast and photoluminescence intensity. This aging process is related to the binding of O₂ molecules to Mo and Te atoms, absorbed at defect sites. In addition, other studies using theoretical investigations have suggested that adsorption of nonmetal atoms on the surface of MoTe₂ may create a magnetic moment locally, and MoTe₂ monolayers might adsorb long-range antiferromagnetic ordering due to adsorption of H atoms onto it. The apparent colors of 1L, 4L, and 5L MoTe₂ deposited on 300 nm SiO₂/Si substrate are extracted from the picture shown in Figure 10.

### 2.4. TaS₂

Tantalum disulfide (TaS₂) presents two typical crystal polytype structures: octahedral (1T) and hexagonal (2H) with complex electronic behaviors, showing dependence on the temperature and the number of layers. Recently, 2D charge density wave materials, such as 1T-TaS₂ and 2H-TaS₂, among other TMDCs, have attracted interest as high-performance functional materials. A charge density wave is a ground state led by the interaction of electrons and phonons and it is associated with a periodic distortion of the crystal lattice in 1D.

The 1T polytype shows a metal–insulator transition at a temperature of 350 K and another one at 190 K involving two semiconducting phases. Although 1T-TaS₂ is not a superconductor, it shows superconductivity when a pressure of dozens of GPa is applied. This behavior depends on the temperature. In addition, 1T-TaS₂ has been developed as a catalyst when it is placed on a nanoporous gold substrate, achieving high hydrogen evolution reaction performance, reaching values comparable with that of commercial Pt–C catalyst. This compound can be synthesized in quantum dots (QDs), changing its properties when the grain size of 1T-TaS₂ QDs is reduced. It features a monolayer thickness of ≈0.8 nm. It exhibits an increase in bandgap from indirect to direct due to confinement effect in the electronic structure.

Figure 11 shows a collection of OM images of few-layer 1T-TaS₂ flakes of different thicknesses deposited onto 90 nm SiO₂/Si substrate. The bottom panel of Figure 11 shows the color charts correlating the thickness of 1T-TaS₂ flakes with their apparent color.

Figure 12 shows two OM images of thin-film 1T-TaS₂ flakes deposited onto 285 nm SiO₂/Si substrate. Along with it, atomic force microscopy (AFM) measurements are included to provide a coarse value of the thickness of the 1T-TaS₂ flakes. The 2H polytype shows charge density waves (at a critical temperature of 75 K and superconductivity transitions (below 1.75 K), with a metallic electronic behavior at low temperatures. It has been observed that superconductivity persists when the material is thinned down to 3.5 nm thickness, the equivalent to five covalent planes, the thickness being ≈0.6 nm. It has been observed that this polytype possesses chiral charge density waves, which coexist with superconductivity. Moreover, the superconducting state can be tuned, increasing its transition temperature when Na atoms or pyridine molecules are intercalated in 2H-TaS₂. This polytype has also found its place on the solar cell field, obtaining high efficiencies when thin films are used as an electron transport layer in perovskite-based devices.

In Figure 13, the color chart of a single-layer 2H-TaS₂ flake on a 285 nm SiO₂/Si substrate is shown, exhibiting a thickness of 1.2 nm.

### 2.5. TaSe₂

2H-Tantalum diselenide (TaSe₂) is a layered polytype, having a hexagonal crystal symmetry with metallic behavior at room temperature. However, it shows up to three orders of magnitude to values for classical metals. When the material is in bulk, it has proved to have phase transitions at certain temperatures: from metallic to incommensurate charge density wave, at 90 K. This polytype has also found its place on the solar cell field, obtaining high efficiencies when thin films are used as an electron transport layer in perovskite-based devices.

Recently, Raman measurements at low temperatures exhibited the existence of incommensurate charge density waves’
phase transition in thin layers (less than five layers) of 2H-TaSe$_2$. This material in thin films is currently used in the fabrication of field-effect transistor and it has proved to have potential for optoelectronic applications.\cite{122}

Figure 11. Color optical images of 1L-28L and 32L 1T-TaS$_2$ flakes on 90 nm SiO$_2$/Si. The scale bars are 5 μm. The numbers indicate the number of 1T-TaS$_2$ layers. The bottom panel shows the corresponding color charts of 1T-TaS$_2$ flakes. Reproduced with permission.\cite{2} Copyright 2013, American Chemical Society.

Figure 12. a,d) Color optical images of thin-film 1T-TaS$_2$ flakes on 285 nm SiO$_2$/Si. b,c,e,f) Images corresponding to AFM measurements of the flakes. The scale bars are 10 μm. Adapted with permission.\cite{318} Copyright 2021, American Chemical Society.

Figure 13. OM image of an atomically thin 2H-TaS$_2$ flake deposited onto a 285 nm SiO$_2$/Si substrate, along with the respective color chart of the monolayer flakes in the dashed square. Adapted with permission.\cite{99} Copyright 2016, Springer Nature.

Figure 14. Color optical image of 2L–5L 2H-TaSe$_2$ flakes on 300 nm SiO$_2$/Si. The scale bar is 10 μm. The bottom panel shows the corresponding color charts of 2H-TaSe$_2$ flakes. Adapted with permission.\cite{319} Copyright 2013, Springer Nature.

Figure 14 depicts the apparent color for 2L–5L 2H-TaSe$_2$ flakes deposited onto the 300 nm SiO$_2$/Si substrate and the corresponding color charts.
2.6. hBN

Hexagonal boron nitride (hBN) is a very stable, highly anisotropic crystal with strong covalent bonds between boron and nitrogen in the in-plane direction and vdW bonds between layers.\textsuperscript{[123–125]} It exhibits an indirect wide bandgap of $\approx 4-7$ eV,\textsuperscript{[124–129]} which is independent of the thickness of hBN when it is varied from bulk to monolayer. For several decades, hBN has been used as a thermally stable ceramic.\textsuperscript{[130]} Later, it has also been used as substrate, due to its atomically smooth surface with almost free dangling bonds.\textsuperscript{[131]} This property is commonly used to encapsulate graphene, TMDCs, and other 2D materials, considering that it protects them from degradation and enhances electronic transport.\textsuperscript{[131–135]} In addition, it is used to enhance the photoluminescence of TMDCs (i.e., MoS$_2$) in microcavities.\textsuperscript{[136]}

hBN is known to be a hyperbolic material, meaning that it has different values of refractive indices along different directions and also the permittivity is opposite in sign.\textsuperscript{[130]} Related to this property of hBN, phonon polaritons’ propagation has been observed,\textsuperscript{[137]} using it for a broad variety of potential applications.\textsuperscript{[138–142]} Moreover, hBN thin film is a very promising candidate for quantum photonics working along 2D vdW materials\textsuperscript{[143–148]} but also nonlinear optical properties have been observed in this material.\textsuperscript{[149,150]}

Figure 15a shows an AFM measurement of hBN flake deposited onto SiO$_2$/Si substrate. Figure 15b–f shows a collection of OM images of the same few-layer hBN flakes deposited onto 88, 148, 215, 271, and 297 nm SiO$_2$/Si, respectively. Figure 15g exhibits the corresponding color charts, built up to correlate the thickness of the hBN flake with their apparent color on the 50, 88, 148, 215, 271, and 297 nm SiO$_2$/Si substrates.

2.7. Group III–VI Compounds

The group III–VI family, with the typical formula M$\text{III}$X$\text{VI}$ (M = Ga, In; X = S, Se, Te), is found to be very interesting because of their intriguing optoelectronic and electronic properties. In addition, M$\text{III}$X$\text{VI}$ family has been used in flexible devices and, in contrast to TMDCs, they exhibit thickness-independent direct bandgap, second harmonic generation (SHG), and p-type electronic behavior (infrequent property in TMDCs), among other assets. In addition, it has been observed that strain can be used in these materials to modify their properties.\textsuperscript{[151,152]} Because of these and more features, M$\text{III}$X$\text{VI}$ group forms

![Figure 15. a) AFM image of hBN flake with thickness ranging from 9 to 102 nm. b–f) The corresponding optical images of the hBN flake placed onto 50, 88, 148, 215, 271, and 297 nm SiO$_2$/Si substrates, respectively. g) AFM thickness bar and color bars of hBN flakes deposited on 50–297 nm SiO$_2$/Si substrates.](image-url)
promising candidates to be used in optics, electronics, and optoelectronics applications.\[^{[153]}\]

2.7.1. InSe

Exfoliation of few-layer indium selenide (InSe) has been achieved recently by Mudd et al.\[^{[154]}\] who discovered the thickness-dependent bandgap of the material (from 1.2 eV for ten layers to 2.4 eV for monolayer\[^{[155]}\] with 0.8 nm of thickness\[^{[156]}\]). This striking discovery is explained by the interlayer coupling effect, which has impact on other properties in thin films.\[^{[155]}\] Indium selenide can adopt various complex stoichiometries and several phases.\[^{[157]}\] Specifically γ-rhombohedral InSe (whose unit cell is made of four layers of monoatomic sheets in the way: Se–In–In–Se\[^{[157]}\]) is a direct-bandgap semiconductor, which owns anisotropic electronic properties and a high carrier mobility. When its thickness is thinned down, the direct bandgap changes to an indirect one, opposite in behavior compared with MoS\(_2\).\[^{[158]}\] The scientific community focused on the fabrication of InSe-based optoelectronic devices, due to its ease of use and the good features, showing very high responsivities in photodetectors.\[^{[153,159–167]}\] This material has proven to possess superior responsivities and fast responses when it is used in photodetectors.\[^{[153]}\] Furthermore, it can be combined with other 2D materials, forming heterostructures. Zhao et al. enhanced \(I–V\) behavior by building Schottky diodes based on Au/graphite/InSe heterostructures\[^{[168]}\] when compared with Au/InSe heterostructures. Also, photoreponsivity performance and external quantum efficiency (EQE) can also be improved by introducing graphene flakes.\[^{[169]}\]

Overall, InSe flakes are advantageous to work with electronic and optoelectronic applications. Figure 16 shows a color chart of InSe deposited onto a 271 nm SiO\(_2\)/Si substrate.

2.7.2. GaSe

Gallium selenide (GaSe) is another compound that belongs to the M\(^{\text{III}}\)X\(^{\text{VI}}\) group. The monolayer, with a value of 0.8 nm thickness,\[^{[170,171]}\] consists of four atomic layers as Se–Ga–Ga–Se. Several modifications in the stacking sequence can lead different space groups, the most important polytypes being β-GaSe, ε-GaSe, and γ-GaSe.\[^{[172]}\] The ε-GaSe polytype is the main stacking order when it is found in bulk.\[^{[173]}\] It has an indirect bandgap of 2.1 eV and another direct bandgap of only 25 meV higher.\[^{[174]}\] Furthermore, the bandgap gets larger to 3 eV when its thickness decreases to monolayer,\[^{[175,176]}\] which is useful in optoelectronics.\[^{[175]}\] As its counterpart InSe, GaSe has been constantly used in photodetectors, achieving outstanding values of photoresponse times, which are comparable, and even faster, with those devices made with other currently used materials.\[^{[17,177–180]}\] In addition, GaSe owns nonlinear optical properties as a result of an absence of the inversion symmetry center. A work carried out by Karvonen et al. found nonlinear optical features of SHG and third harmonic generation in thin films of GaSe.\[^{[181]}\] Moreover, SHGs in InSe and GaSe are produced in odd and even numbers of layers,\[^{[156]}\] in comparison with 2D TMDCs and hBN, in which this property has a dependence on the number of layers.\[^{[182]}\] One of the drawbacks of GaSe is its environmental degradation, which can be easily overcome by encapsulating it with hBN.\[^{[183]}\]

Figure 17 shows a color chart of GaSe flakes with thicknesses ranging from 8 to 41 nm deposited onto a 271 nm SiO\(_2\)/Si substrate.

2.8. Metal Oxides

Metal oxides (MOs) are very abundant in the Earth’s crust, and they are known for centuries to the humanity. They have different electronic structures, charge transport mechanisms, or defect states, to name some, when compared with silicon and III–V compounds. Wide-bandgap MOs have been widely used as transparent conductive oxides (TCO) electrodes in p–n junctions or photovoltaics. MOs can be used as collectors of electrons or holes, depending on the semiconductor/electrode arrangement. If the transparent electrode collects holes and the metal electrode electrons, it is named as conventional architecture. If the MO collects electrons, it is named as inverted architecture.\[^{[184]}\]

2.8.1. MoO\(_3\)

Molybdenum trioxide (MoO\(_3\)) is a MO which has different phases with different crystal structures. In its α phase, it is a vdW material, with a single-layer thickness of 0.7 nm\[^{[185]}\] and a direct bandgap of nearly 3 eV.\[^{[186–188]}\] It is widely used in optical applications such as anode buffer layer in organic photovoltaics,\[^{[189]}\] commonly used as a hole selective layer,\[^{[190]}\] enhancing the open-circuit voltage and fill factor parameters. It has also been used in perovskite solar cells\[^{[191]}\] and in silicon heterojunction solar cells.\[^{[192]}\] By adding MoO\(_3\) layers from 3 to 20 nm as

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**Figure 16.** The top panel shows InSe flakes ranging from 4 nm to 90 nm placed onto a 271 nm SiO\(_2\)/Si substrate. The bottom panel shows the corresponding color chart of InSe flakes. Adapted with permission.\[^{[3]}\] Copyright 2020, John Wiley and Sons.
buffer layer in organic light-emitting diodes, it has improved the efficiency, the stability, and the lifetime, reaching the 5000 h of use.\textsuperscript{[192,193]} Its $\alpha$ phase consists of an orthorhombic structure, which is formed by a double-layer stacking of linked MoO$_6$ octahedra in the $b$-direction, along which the layers are bounded by vdW forces. Its crystal structure possesses an in-plane anisotropy with different unit cell parameters.\textsuperscript{[194–198]} Recently, we studied its mechanical and optical anisotropy in thin films, using a new optical method to identify the orientation of the material based on the change of the refractive index and finding one of the largest in-plane anisotropic Young’s modulus so far.\textsuperscript{[199]} Anisotropic optical materials show diverse and complex optical properties.\textsuperscript{[142,200,201]} $\alpha$-MoO$_3$ exhibits a highly anisotropic propagation of phonon polaritons,\textsuperscript{[202–205]} which can be used to reduce optical losses and improve light confinements.\textsuperscript{[206–209]} Recently, a theoretical study has shown that the bandgap of MoO$_3$ can be modified by distorting its crystal lattice, and these variations are different when the strain is applied along the three axes.\textsuperscript{[210]} Figure 18a–d shows several flakes of MoO$_3$ deposited onto 88, 148, 271, and 297 nm SiO$_2$/Si substrates, respectively.

### 2.9. BP

Phosphorus has several allotropes and the most stable one is called black phosphorous (BP), which is a layered material with strong in-plane anisotropy, each layer forming a puckered surface due to $sp^3$ hybridization. It has a layer-tunable direct energy bandgap that varies from 2 eV for monolayer, which has been predicted theoretically and measured experimentally,\textsuperscript{[211,212]} and a value of 0.3 eV in bulk,\textsuperscript{[213]} as it happens to III–VI compounds, changing monotonically with the addition of layers. This property makes BP a promising candidate in applications such as optoelectronic in the wavelength range from $\approx$0.6 to 1.5 $\mu$m. Its use in photodetectors yielded high EQEs and avalanche gain.\textsuperscript{[214]} These kinds of photodetectors have been carried out using other 2D materials, and they show higher responsivity values, although most of them cannot be used in the IR range of the spectrum, and BP-based photodetectors show faster response time.\textsuperscript{[129,175,215]} Photodetectors using few-layer BP flakes have achieved broadband detection and fast response.\textsuperscript{[216]} This difference may be due to the origin of the photoresponse in BP phototransistors, showing that it is dominated by thermally driven thermoelastic and bolometric processes, not photovoltaic effect as usual.\textsuperscript{[217,218]} In photothermoelectric devices, a difference in temperature is built in the detector, driving the charge carriers from the hot end to the cold end, thus setting an electrical field on the device (process known as Seebeck effect). Therefore, an ideal photothermoelectric detector should have a big light absorption coefficient and a small heat capacity. In addition, a large Seebeck coefficient and a small resistance are required to achieve high responsivity.\textsuperscript{[219]}

A high drawback of BP is its chemical instability when it is exposed to ambient conditions. An increase in 200% in the volume of few-layer BP flakes due to the condensation of water molecules in the surroundings is observed.\textsuperscript{[220]} Usually, an encapsulation process is used to protect this material from degradation, while it has been found that chemical doping also improves the stability.\textsuperscript{[221]}

As shown in the top panel of Figure 19, it depicts BP flakes of thickness ranging from 4 nm to 98 nm placed on 88 nm SiO$_2$/Si substrate using deterministic transfer methods. As shown in the bottom panel, the BP flakes are deposited on the 297 nm SiO$_2$/Si substrate, with thickness ranging from 9 nm to 94 nm. Color charts are extracted from BP flakes with thickness ranging from 4 nm and 9 nm, respectively, up to 100 nm. Figure 20 shows other BP flakes deposited on 300 nm SiO$_2$/Si substrate, including the color bar up to 80 nm and paying special attention to the first 10 layers. The difference between the apparent color of SiO$_2$ shown in Figure 19 and 20 is due to the different parameters in both works when taking the pictures, as we have already discussed.

### 2.10. TiS$_3$

Transition metal trichalcogenides (TMTCs), with the formula MX$_3$ (where M = Ti, Zr, Hf, etc. and X = S, Se, Te), is another 2D family with members that present many different electronic properties. This group of materials possess a wide range of bandgap values, making them suitable for applications including field-effect transistors, a broad range of photodetectors, and others attending their anisotropic properties.\textsuperscript{[222,223]} TMTCs are also layered materials, with layers bonded by vdW forces.\textsuperscript{[224]} TiS$_3$ is a well-known material from this family, and its atoms in the single layer are arranged in a crystal structure of the trigonal prism, showing in-plane anisotropic properties, such as linear dichroism and different mobility values.\textsuperscript{[225,236]} TiS$_3$ is characterized to have an optical bandgap of 1 eV\textsuperscript{[227]} in bulk (and another energy gap of 1.4 eV appears when this material...
is presented in thin films or powders\cite{228}. Recently, it started to be interesting to the scientific community due to its attractive properties such as low-cost production, abundance and nontoxic elements, and the easiness of the process of synthesis.\cite{224,229} TiS$_3$ has been also studied as a thermoelectric material,\cite{230} whose thermal conductivity can be enhanced by adding impurities atoms.\cite{231} The aforementioned properties can be tuned by inducing an external strain\cite{232} in few-layer TiS$_3$, finding a change in the bandgap from direct to indirect when the strain is applied along a certain axis. Moreover, electrical and photovoltaic devices have been built with this material\cite{233} featuring high mobility. These properties, combined with the direct bandgap and its in-plane anisotropy, are enough to prove that TiS$_3$ is a good candidate for photodetectors.\cite{234}

Therefore, characterizing the thickness of this material prior to the applications mentioned before is critical for the advances in this field. Figure 21 depicts TiS$_3$ nanoribbons with thickness ranging from 5 nm to 110 nm and its color chart on 90 nm SiO$_2$/Si substrate.

2.11. Bi$_2$Te$_3$

Bismuth telluride (Bi$_2$Te$_3$) is a layered material with a rhombohedral lattice\cite{235,236} and a semiconductor crystal with a direct bandgap of 0.15 eV.\cite{237} It is a well-known thermoelectric material that has been widely used for decades and thoroughly developed to enhance its thermoelectric properties, such as reducing its dimension and shapes.\cite{238} Currently, the investigations in thermoelectric materials are focused on the high-temperature region, although Bi$_2$Te$_3$ works in the low-temperature region of 200–500 K, usually in microenvironmental cooling and Peltier effect.\cite{239} Bi$_2$Te$_3$ is synthetized with several techniques, depending on the process used, the product material can vary from nanoparticles to single crystals with a wide range of thicknesses from a few nanometers to hundreds of them.\cite{240–242} Thus, a characterization presented in Figure 22 is needed to accurately determine the thickness of this material with the optical method.
2.12. Metal Phosphochalcogenides

Another family of layered materials has emerged, phosphochalcogenides, with the typical formula of MPX$_3$ (M = Mn, Fe, Co, Ni, etc. and X = S, Se). These materials tend to crystallize in a monoclinic structure, shaping a honeycomb lattice,[243–245] and having a small cleavage energy between planes,[246] thus indicating they can be easily exfoliated. This class of chalcogenides is used in catalytic and optoelectronic applications, with a wide bandgap ranging from 1.3 to 3.5 eV. A family of MPX$_3$ can be intercalated with alkali ions in its van der Waals gap and pave a way for batteries applications, being used as cathode and anode materials.[247] Using monolayers of phosphochalcogenides in lithium-ion batteries, stability and specific capacity are enhanced when compared with other layered materials.[248] Nowadays, the possible use of these materials as cathodes in batteries of future NASA’s missions to Venus is being studied.[247]

2.12.1. NiPS$_3$

Among the MPX$_3$ compounds, nickel phosphorus trisulfide (NiPS$_3$) is an important element in this family of materials. It has proven to possess antiferromagnetic properties and it possesses an experimental indirect energy bandgap of 1.7 eV.[249] Interestingly, when the material is thinned down, its monoclinic crystal structure changes to the hexagonal D$_{3d}$ in a monolayer, and the change of the lattice constant of the material yields a change in the energy bandgap to 1.8 eV.[250] The antiferromagnetic behavior also changes when the material becomes single layer and the zigzag and Néels orders are virtually degenerated, thus facilitating large magnetic fluctuations. Recently, the first fabrication of field-effect transistors with NiPS$_3$ is reported, revealing an n-type semiconductor. Using few-layer-oriented crystals of NiPS$_3$, on/off ratios of orders of magnitude similar to the ones found in graphene have been obtained.[251] In addition, the mobility variation with thickness is comparable with the devices using TMDCs. Chu et al.[252] built UV photodetectors with few layers of NiPS$_3$, using the shift of typical Raman peaks to quickly identify the thickness of the samples used. The ultrathin NiPS$_3$ flakes exhibit comparable photoresponse with other 2D materials-based devices, that is, MoS$_2$, MoSe$_2$, graphene, and graphene oxide.

As shown in Figure 23, the apparent color of 1–4L and 7L of NiPS$_3$ is extracted when it is deposited on a 90 nm SiO$_2$/Si substrate.

2.12.2. FePS$_3$

Iron phosphorus trisulfide (FePS$_3$) is a magnetic semiconductor with an energy gap of 1.59 eV[249] and intrinsic antiferromagnet when the temperature is below its Néel temperature (120 K).
Its structural properties change with dimensionality; when this material is studied in its bulk form, it has a monoclinic structure, with the point group C2h, whereas when it is found in monolayer, it belongs to the D3d factor group. When the material is thinned down, the positions of Raman peaks P4 and P5 move away, which can be useful to determine the thickness of the sample. Its intrinsic magnetism makes this material a suitable one for magneto-optics and 2D spintronics applications.

In Figure 24, FePS3 flake with thickness from 8 to 32 nm is shown, deposited onto a substrate of 272 nm of SiO2 thickness of capping layer.

2.12.3. MnPS3

Manganese phosphorus trisulfide (MnPS3) shares the same crystal structure of the other phosphochalcogenides discussed before and a magnetic behavior similar to them, with an indirect bandgap of \( \approx 3 \text{ eV} \). MnPS3 shows an antiferromagnetic behavior, showing the same magnetic ordering performance down not just to bilayer MnPS3 flakes, but even to the monolayer limit, paving a way to the 2D antiferromagnet material field. Its Néel temperature decreases slightly from 78 K, when it is studied in bulk, to 66 K, when it is thinned down to three layers; implying that the van der Waals interaction between the layers stabilizes the magnetic order. In addition, a broadening of its P2 Raman mode occurs when the material is close to the...
Néel temperature. It is worth to highlight the fields where it can be useful, such as electrocatalysis,\textsuperscript{(260)} photocatalysis,\textsuperscript{(261)} electron tunneling,\textsuperscript{(262)} valleytronics,\textsuperscript{(263)} and devices applications.\textsuperscript{(264)}

Figure 25 shows a MnPS$_3$ flake with one, two, and four layers thick, deposited onto 90 nm SiO$_2$/Si substrate.

2.13. Franckeite

Fabrication of van der Waals heterostructures is a way to build devices with outstanding optical, optoelectronic, and electrical properties, among others. Nonetheless, the correct delamination/deposition of the materials and the following fabrication of these devices are large engineering challenges that must be overcome. These problems have led to find other naturally occurring van der Waals heterostructures as materials for those devices, such as franckeite. Franckeite is a layered material, and its crystal structure is a complex composition of stacks of pseudohexagonal (H) and pseudotetragonal (Q) layers. The H layers are formed by four atomic layers of sulfide compounds with molecular formula MS, being M = Pb$^{2+}$, Sn$^{2+}$, or Sb$^{3+}$. The Q layers are formed by MS$_2$ formula, where M = Sn$^{4+}$ or Fe$^{2+}$.\textsuperscript{(265)} The alternation of this slab gives material anisotropy properties although the material itself is made by alternating isotropic layers.\textsuperscript{(266)} This superlattice system exhibits interestingly a transversal modulation along the $b$ direction and a nonmodulation in the $a$ direction.\textsuperscript{(267)} The $c$ direction is perpendicular to the plane ($a-b$), in which the layers are bonded with van der Waals forces.

Frisenda et al.\textsuperscript{(268)} recently studied the rippling that this material exhibits an inhomogeneous in-plane strain profile and anisotropic vibrational properties, using linearly polarized light with Raman spectroscopy measurements. They investigated also anisotropic electrical and optical properties, showing linear dichroism. Due to this odd structure, franckeite has an experimental monolayer thickness of 2.4 – 3.5 nm measured with an AFM, which is in agreement with the single unit cell of 3.8 nm using cross-section transmission electron microscopy measurements\textsuperscript{(269)}.

Franckeite has been thoroughly examined by several groups, finding an experimental electronic indirect bandgap of 0.7 eV in bulk.\textsuperscript{(265)} Electronic and structural properties changes have not been correlated with the number of sheets, as it happens in other materials, although it exhibits a change in the intensity of Raman peaks with the thickness.\textsuperscript{(269)} The lack of change is explained by the large thickness of a monolayer in this material and thus the weak interactions that franckeite layers’ feel to each other. Moreover, franckeite exhibits a superior stability after exfoliation in ambient conditions (up to six months)\textsuperscript{(269)} although the degradation becomes very fast when it is thinned down to a monolayer. Its small bandgap and high stability make this material a candidate to replace BP in optoelectronic applications and solar cells, showing a fast response with light.\textsuperscript{(270)} Furthermore, this material can be used in other applications, such as surface plasmon resonance sensors, biological analysis, environmental monitoring, food safety, or chemical sensors.\textsuperscript{(271–274)}

Figure 26 shows the apparent colors of franckeite flakes on 292 nm (Figure 26b) and 92 nm (Figure 26e) SiO$_2$/Si substrates.

2.14. CrI$_3$

Chromium iodide (CrI$_3$) belongs to the family of chromium trihalides CrX$_3$ (X = Cl, Br, I), which are magnetic layered materials.\textsuperscript{(275)} It has a phase transition from the monoclinic to the rhombohedral type upon cooling from room temperature.\textsuperscript{(276)} CrI$_3$ has a direct bandgap of $\approx$1.2 eV,\textsuperscript{(277)} lowering to a theoretical indirect bandgap of 1.1 eV\textsuperscript{(278)} when it is thinned down to monolayer. From the CrX$_3$ family, it possesses the highest ferromagnetic Curie temperature,\textsuperscript{(277)} with a value of $T_c = 68$ K. The stacking-dependent effect of the magnetization is strong, changing from antiferromagnetic when studied as a bilayer,\textsuperscript{(279)} and ferromagnetic, when presented as a monolayer, besides lowering its $T_c$ down to 45 K.\textsuperscript{(280)} This ferromagnetic behavior in monolayer samples can transition to antiferromagnetic when a compressive strain is applied.\textsuperscript{(281,282)} For a bilayer system, if a tensile strain is applied, the antiferromagnetic phase stabilizes, while a compressive strain transforms the system ferromagnetic; in addition, a change in $T_c$ is observed when a strain is induced.\textsuperscript{(283)} The magnetism exhibited in a bilayer system can be controlled with electrical currents by tuning the gate voltage, showing magnetoelectric effects.\textsuperscript{(284)} These aforementioned properties make this material suitable for spintronic and optoelectronic applications.

Figure 27 shows the characteristic apparent color chart of CrI$_3$, deposited on top of a 285 nm SiO$_2$/Si substrate; the respective colors have been extracted from the study by Huang et al.\textsuperscript{(280)}

2.15. PbI$_2$

Another family of compounds is transition metal halides, whose properties in ultrathin samples are complementary to other 2D groups of materials, that is, the range of the bandgap spans a region not covered by the TMDCs. Lead iodide (PbI$_2$) belongs to that family, whose structure consists of a layer of Pb atoms sandwiched between two layers of I atoms with van der Waals forces acting as the interlayer interactions, while the intralayer interactions are covalent, shaping a hexagonal crystal structure. This material possesses a shift in its energy bandgap when it is studied in monolayer. The bandgap increases monotonically from a direct value of 2.26 eV in its bulk form to an indirect
bandgap of 2.64 eV in single layer,[285] according to theoretical calculations. It is consistent with experimental measurements, which yield values from 2.41 eV in bulk to 2.47 eV in monolayer, observing the change of bandgap from direct to indirect.[286] Thus, the thickness dependence of the optoelectronic properties is a great asset of this material. Another one is that it shows higher absorption than others in the UV range.[287–290] Although a common way to grow this material is in its bulk form, the synthesis of 1D or 2D PbI₂ is mandatory for its later use in devices.[291] It has been used in a photodetector, observing high responsivity and photogain. In other works, PbI₂-based photodetectors prepared on polyethylene terephthalate have shown superior mechanical stability and durability, also showing high photore sponsivity and fast response time when compared with others prepared on SiO₂/Si substrate.[290] In addition, PbI₂ has been used in optononlinear devices.[292] Other applications of PbI₂ exist apart from the optoelectronic applications, for example, nuclear radiation detectors.[293] Also, intercalation of other species between its layers is useful to generate new materials with novel properties that can be used in multiple applications.[294]

Figure 27. Experimental color chart from 1L to 6L of a CrI₃ flake deposited on a 285 nm SiO₂/Si substrate, whose apparent colors have been extracted from the study by Huang et al.[280]

Figure 26. OM images of franckeite flakes a) on a gel-film carrier substrate with transmission mode. b) 292 nm SiO₂/Si substrate, after transfer, with epillumination OM and c) atomic force microscopy images. The color chart below (a–c) serves as a guide to determine the thickness of franckeite flakes on 292 nm SiO₂/Si substrates. d–f) Same images as shown in (a–c) but for a franckeite flake transferred onto a 92 nm SiO₂/Si substrate. The color chart below (d–f) serves as a guide to determine the thickness of franckeite flakes on 92 nm SiO₂/Si substrates. Reproduced with permission.[327] Copyright 2017, Beilstein-Institut.

2.16. MAPbI₃

The organic–inorganic hybrid perovskite CH₃NH₃PbI₃’s, commonly known as methylammonium lead iodide (MAPbI₃), structure suffers a phase transition with the temperature, from orthorhombic (10–130 K), tetragonal (190–300 K), to cubic phase (from 350 K).[295] It belongs to the family of methylammonium lead halides, which have attracted the interest of use in light-energy conversion devices due to the low-cost production and the ease of processing. MAPbI₃ is known to be a semiconductor with a direct bandgap of 1.5 eV[296,297] but with a weakly indirect bandgap of 60 meV below the direct one. It has proven to possess superior features when used in perovskite solar cells, such as photoconversion efficiencies more than 20%.[298] It has been observed that, by applying a hydrostatic pressure from ambient conditions, the direct transition and the radiative efficiency are enhanced.[298] It has proven to possess superior features when used in perovskite solar cells, such as photoconversion efficiencies more than 20%.[299] Although its major drawback is thermal degradation, several studies have been carried out to improve this behavior to be competitive with commercial solar cells.[300] Recently, it has been found out that this material, in its tetragonal phase, is also ferroelectric,[301] and it needs to be determined if this property plays a role when used in room-temperature solar
cells. It has been demonstrated that, controlling the thickness of thin films, MaPbI3-based solar cells and other optoelectronic devices is relevant for its performance.\textsuperscript{302–304}

Spina et al.\textsuperscript{305} calculated the apparent colors of MAPbI3 nanowires up to 200 nm as a function of SiO\textsubscript{2}/Si and TiO\textsubscript{2}/Si substrates. Rods of different colors shown in Figure 29a are MaPbI\textsubscript{3} samples on a 280 nm SiO\textsubscript{2}/Si substrate. Figure 29b,c shows the 2D color charts, in which the vertical axis is the substrate thickness and the horizontal axis is the MaPbI\textsubscript{3} thickness.

2.17. (PEA)\textsubscript{2}PbBr\textsubscript{4}

Other perovskites have attracted the interest in photovoltaic applications; these are phenethylammonium lead bromide compounds (C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{4}NH\textsubscript{3})\textsubscript{2}PbBr\textsubscript{4}, usually shortened as (PEA)\textsubscript{2}PbBr\textsubscript{4}, with an optical band gap of 2.9 eV.\textsuperscript{306} These

![Figure 28. a–j Optical images of PbI\textsubscript{2} flakes with thickness ranging from 10 to 173 nm on 285 nm SiO\textsubscript{2}/Si substrate. The bottom panel shows the corresponding color chart of PbI\textsubscript{2} flakes. Adapted with permission.\textsuperscript{305} Copyright 2017, IOP Publishing.](image)

![Figure 29. a) Optical image of MAPbI\textsubscript{3} nanowires on 280 nm SiO\textsubscript{2}/Si substrate. b,c) Calculated apparent colors of MAPbI\textsubscript{3} nanowires up to 200 nm on 200–500 nm SiO\textsubscript{2}/Si and 50–300 nm TiO\textsubscript{2} substrates, respectively. Adapted with permission.\textsuperscript{305} Copyright 2017, John Wiley and Sons.](image)

![Figure 30. a) Optical image of (PEA)\textsubscript{2}PbBr\textsubscript{4} flakes deposited on 300 nm SiO\textsubscript{2}/Si substrate with the respective apparent color chart of this material from 1–3L, 6L, and 7L. b) AFM image of the dashed red box shown in (a), showing the number of layers of the respective flake. Adapted with permission.\textsuperscript{328} Copyright 2021, American Chemical Society.](image)
organic–inorganic perovskites are typically prepared using thermal ablation because they are compatible with the deposition of other materials and, in this way, heterostructures such as LEDs and microcavities can be prepared.[307] During the preparation process, the perovskites are stacked in layers bonded with van der Waals forces; thus, they can be easily delaminated with typical methods. Because of the energy bandgaps between the organic and the inorganic sheets, this kind of perovskites behaves as a quantum well, with strong quantum confinement effects. (PEA)$_2$PbBr$_4$ has also been thoroughly studied in photonics and optoelectronic applications due to ultralow dark current, high detectivity, and ON/OFF ratio properties, among others.[306,308]

Figure 30a shows optical image of a (PEA)$_2$PbBr$_4$ flake on 300 nm SiO$_2$/Si substrate. The color chart below it shows the apparent color of layers from 1 to 3, 6, and 7L, measured with the AFM technique, as shown in Figure 30b.

2.18. BSCCO

Bi$_2$Sr$_2$CaCu$_2$O$_8$ (BSCCO) belongs to the copper oxide high-temperature superconductor family, in which some of them possess a layered crystal structure. It is a type-II superconductor with a critical temperature of 105 K[309] and shows an intermediate phase of ordinary and superconducting properties at temperatures above that critical temperature. BSCCO needs to be doped with holes by an excess of oxygen to be a superconductor. It was the first high-temperature superconductor that did not have rare-Earth compounds.[309]

The most promising application of superconductors is electrical power transport. BSCCO has already been used in the development of a long-length transmission voltage cable to operate in an electrical grid, with a total length of 600 m, carrying a current of 2400 A and a voltage of 148 kV.[310] Furthermore, the thickness dependence of the superconductivity state has been studied, showing that decreasing the thickness of the sample leads to an increase in the stability of type-II superconductor state against flux jumps.[311] A flux jump consists of thermomagnetic avalanches that occur in superconductors, which can destroy the critical state. The flux jump can be induced by a small fluctuation in temperature or by an external magnetic field. A new fabrication of BSCCO process has been developed, in which monolayers of BSCCO can be obtained with tunable properties, displaying all the fundamental physics of high-temperature superconductivity.[312]

Figure 31 shows several flakes of BSCCO delaminated with the scotch-tape method and placed onto a 271 nm SiO$_2$/Si substrate. The color chart below the optical images shows the apparent color of BSCCO flakes with thickness ranging from 10 to 100 nm.

3. Conclusion

2D and thin van der Waals materials have changed our perspective of technology in just a few years. Since the discovery of graphene in 2004, many breakthroughs and studies have been carried out in this subfield of research, unveiling new physical phenomena. Dealing with these kinds of new materials’ physical properties and applying them to new functionalities are of great importance. Several ways to assess the thickness of exfoliated flakes have been developed, but using the thickness-dependent apparent colors of flakes, when deposited onto a SiO$_2$/Si surface, is still one of the most convenient and widespread ones. Here we have presented a review that summarizes the reported thickness-dependent apparent color data for a wide range of these new materials. The list of these materials can be expanded continuously by adding new substrates’ thicknesses, other substrates different from SiO$_2$/Si (such as Si$_3$N$_4$/Si, Au/Ti/Si, etc.), and other layered materials. Furthermore, the color charts that are made from these studies can be useful to be implemented in machine learning systems to make the work of thickness identification even faster and more reliable.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, apparent colors, flakes, optical contrasts, SiO₂ thin films

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