Fast thickness mapping of large-area exfoliated two-dimensional transition metal dichalcogenides by imaging spectroscopic ellipsometry

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Abstract. Two-dimensional transition metal dichalcogenides (2D TMDCs) have gained significant attention from the scientific community due to their exceptional properties, making them extremely attractive for optoelectronic and photonic applications. However, many exfoliation or synthesis techniques yield 2D crystals with limited crystalline quality and/or small lateral size. Here, we report a facile Au-assisted exfoliation method, yielding high-quality, large-area monolayers with lateral sizes of hundreds of micrometers. A self-assembled monolayer of (3-aminopropyl)triethoxysilane (APTES) is employed to improve the adhesion between the 2D material and the target substrate, dramatically improving the yield and reliability of the exfoliation process. The monolayer nature of the final sample is then assessed by means of Imaging Spectroscopic Ellipsometry (iSE), which enables a quick and reliable thickness mapping over millimeter-sized areas.

1 Introduction

Two-dimensional materials play a pivotal role in the fields of optoelectronics and photonics. Thanks to their unique behavior at the atomic scale, they allow to explore novel physical phenomena and to build quantum devices. Among the many 2D materials, semiconducting transition metal dichalcogenides, such as MoS_2 and WS_2, are of particular interest, thanks to their strong excitonic effects, chemical stability, and wide availability. When thinned down to the monolayer form, they exhibit an indirect-to-direct bandgap transition, leading to a strong photoluminescence response in the visible range. The crystalline quality (grain size, density of vacancies) of the 2D TMDC layers and their lateral size are often crucial to successfully integrate these materials into working devices. The traditional mechanical exfoliation methods (scotch-tape) yield a small quantity of monolayers with few-microns lateral size; on the other hand, synthesis techniques, such as chemical vapor depositon (CVD), suffer from spatial nonuniformites, growth of bilayer domains, and yield to a usually lower crystalline quality with respect to exfoliation methods.

Recently, gold-assisted exfoliation methods emerged as an effective way to isolate millimeter-sized monolayers of TMDCs from bulk crystals [1, 2]. These methods exploit the affinity between gold and sulphur to overcome the van der Waals attraction between adjacent layers of the bulk TMDC. However, the gold film employed to pick up these monolayers is rarely a good final substrate. Indeed, a conducting substrate quenches the photoluminescence due to a charge transfer mechanism.

Here, we present a novel exfoliation technique based on the gold-assisted exfoliation method. (3-aminopropyl)triethoxysilane (APTES) is exploited to functionalise a SiO_2/Si substrate, enabling a successful transfer of hundreds-of-micron-sized TMDC monolayers from the Au film adopted for the gold-assisted exfoliation to the functionalised substrate.

Imaging Spectroscopic Ellipsometry (iSE) is employed to quickly assess the thickness of the exfoliated film over millimeter-sized areas, while Raman and photoluminescence (PL) spectroscopies can confirm the high crystalline quality of the monolayer.

2 Materials and methods

2.1 Exfoliation method

A 150 nm-thick gold film is deposited onto a silicon wafer, and is peeled off with a thermal release tape (TRT) immediately before the exfoliation. The resulting Au/TRT stack, exposing a hydrophilic, pristine Au surface, is then

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gently pushed onto a freshly cleaved bulk TMDC crystal, thereby picking up a monolayer. Afterwards, the TMDC/Au/TRT stack is pushed onto a previously functionalised SiO_2/Si substrate, and the TRT is detached by heating the system at the TRT release temperature. Substrate functionalisation, carried out by immersing them in an APTES/ethanol solution, is crucial to ensure that the TMDC/Au layer properly sticks to the substrate, preventing it from being pulled away by heating-induced deformations of the TRT. The gold film is etched away from the Au/TMDC/APTES/SiO_2/Si stack by a KI/I_2 gold etchant; finally, the samples are rinsed with deionized water and isopropyl alcohol [3].

2.2 Characterisation

Imaging Spectroscopic Ellipsometry (iSE) allows to quickly map the ellipsometric quantities Ψ and Δ with lateral resolution down to 1 µm over areas up to 1 mm^2. Through a proper optical modeling of the sample stack, it is possible to convert these quantities into a thickness map of a known thin film. We employ iSE to quickly assess the thickness of our MoS_2 or WS_2 crystals over very large areas, confirming the presence of monolayer domains with lateral scales of hundreds of microns. iSE thickness mapping relies on the dielectric functions of MoS_2 and WS_2 adopted from our previous work [4].

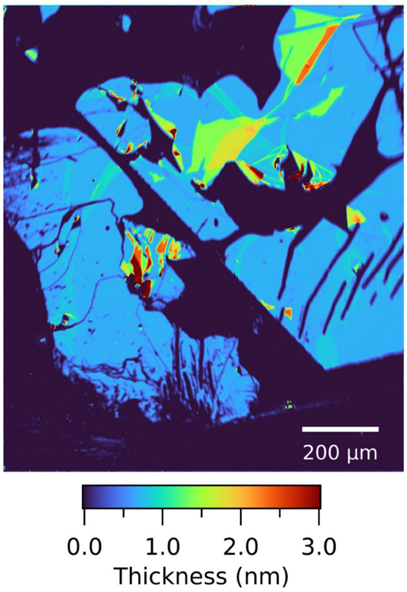

Figure 1. Thickness map of an exfoliated crystal of MoS_2 on a SiO_2/Si substrate, obtained by fitting imaging spectroscopic ellipsometry (iSE) data. The map shows a large area of MoS_2 with a thickness of about 0.7 nm, corresponding to the monolayer crystal, as well as some bilayer and multilayer areas.

Figure 1 shows the thickness map of a MoS_2 monolayer onto a silicon substrate with thermal oxide. This clearly demonstrates the effectiveness of our process in yielding large-area monolayers and the unique capability of iSE as an optical, fast, non-damaging technique to reliably assess the thickness of 2D materials over large areas.

3 Conclusions

We developed a reliable method to exfoliate large-area, high-quality monolayers of transition metal dichalcogenides. We showed the potentiality of iSE to optically assess the number of TMDC layers over millimeter-sized areas. Our approach tackles two prevalent challenges in the field of semiconducting 2D materials: reliably fabricating large-area crystals and quickly characterizing them over their entire surface.

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