Fast and reliable identification of atomically thin layers of TaSe₂ crystals

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ABSTRACT
Deposition of clean and defect-free atomically thin two-dimensional crystalline flakes on surfaces by mechanical exfoliation of layered bulk materials has proven to be a powerful technique, but it requires a fast, reliable and non-destructive way to identify the atomically thin flakes among a crowd of thick flakes. In this work, we provide general guidelines to identify ultrathin flakes of TaSe₂ by means of optical microscopy and Raman spectroscopy. Additionally, we determine the optimal substrates to facilitate the optical identification of atomically thin TaSe₂ crystals. Experimental realization and isolation of ultrathin layers of TaSe₂ enables future studies on the role of the dimensionality in interesting phenomena such as superconductivity and charge density waves.

1. Introduction
Experimental isolation of graphene by mechanical exfoliation [1] has unleashed interest in a whole family of atomically thin materials which exhibit a variety of interesting properties ranging from topological insulator behavior to superconductivity [2–15]. Only a few two-dimensional (2D) crystals have been fabricated and thoroughly characterized [16–20], and most of the other possible 2D crystals with attractive properties remain barely explored. For instance, layered transition metal dichalcogenides with the formula MX₂ (M = Mo, W).
W, Nb, Ta or Ti and X = Se, S or Te) present a broad variety of electrical properties ranging from wide band-gap semiconductors to superconductors. As in the case of graphene, while fabrication by mechanical exfoliation from bulk crystals of these layered materials is rather simple [2], identification of atomically thin flakes requires fast, reliable and non-destructive characterization techniques [21–27].

The realization of ultrathin superconducting layers would enable one to employ the electric field effect to control physical properties such as the superconducting transition temperature or to study the interplay between the superconductivity and the sample dimensionality. However, among the family of transition metal dichalcogenides, studies of atomically thin superconducting layers are scarce and mainly focused on NbSe2 and TaS2 crystals [3, 4, 28]. TaSe2 is a good example of a layered material which has not been studied in its atomically thin form so far, while it is very interesting. In fact, in its bulk form, TaSe2 is among the most studied charge density wave (CDW) systems as it shows both incommensurate and commensurate density-wave phases and a superconducting transition below 0.15 K [29, 30].

In this work, we report the fabrication of atomically thin two-dimensional TaSe2 crystals on SiO2/Si wafers. We perform a combined characterization by atomic force microscopy (AFM), quantitative optical microscopy and Raman spectroscopy. We also determine the optimal SiO2 thickness to optically identify ultrathin TaSe2 crystals. This work constitutes a necessary step towards further studies on other properties of atomically thin TaSe2 sheets.

2 Experimental

Starting elemental materials were used as received from commercial suppliers with no further purification.

2.1 TaSe2 single-crystal fabrication

TaSe2 crystals were synthesized from the elemental components in a two-step process. Firstly, polycrystalline TaSe2 was obtained by ceramic combination of stoichiometric ratios of Ta and Se. Ta powder, 99.99% trace metals basis and Se powder, ~100 mesh, 99.99% trace metals basis were used. Powdered starting materials were intimately mixed, placed inside an evacuated quartz ampoule and reacted at 900 °C for 9 days. The resulting free-flowing glittery grey microcrystals were then transformed into large single-crystals using the chemical vapor transport (CVT) methodology. For that purpose, 1 g of TaSe2 polycrystalline material together with 275 mg of I2 were loaded into a 500 mm long quartz ampoule (OD: 18 mm, wall-thickness: 1.5 mm). The mixture was placed at one end of the ampoule which was exhaustively evacuated and flame-sealed. The quartz tube was finally placed inside a three-zone split muffle where a gradient of 25 °C was established between the leftmost load (725 °C) and central growth (700 °C) zones. A gradient of 25 °C was also set between the rightmost and central regions. The temperature gradient was maintained constant during 15 days and the muffle was eventually switched off and left to cool down to ambient conditions. Millimetric TaSe2 crystals were recovered from the ampoule’s central zone, exhaustively rinsed with diethyl ether and stored under a N2 atmosphere.

2.2 Viscoelastic-stamp based exfoliation

The viscoelastic stamps employed during the TaSe2 micromechanical exfoliation were based on poly (dimethylsiloxane) (PDMS) stamps, a viscoelastic material commonly used in microimprint lithography. The PDMS stamps were cast by curing the Sylgard® 184 elastomer kit purchased from Dow Corning [26].

2.3 Atomic force microscopy

AFM was used to characterize the thickness of the fabricated flakes. A Nanotec Cervantes AFM (Nanotec Electronica) was operated in contact mode under ambient conditions. We selected contact mode AFM instead of dynamic modes of operation to avoid artifacts in the determination of the flake thickness [31]. The piezoelectric actuators of the AFM have been calibrated by means of a recently developed calibration method to provide a determination of the flake thickness as accurate as possible [32].

2.4 Optical microscopy

The quantitative measurements of the optical contrast