Sub-surface nanometrology of semiconductor wafers and graphene quality assessment via terahertz route

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Abstract – Modern integrated circuit (IC) packaging faces challenges for higher speed in a smaller dimension achieved due to the 10 nm or smaller process node. While ICs are being packaged in 3D format, it is often not possible to measure features and/or defects in a non-destructive route. This paper reports a technique for nanometrology using bigger wavelengths such as those within the terahertz range. Practical measurements of dot pattern and other patterns on a 3D chip under the surface have been carried out. Two graphene have been imaged for quantifying the number of layers in the exfoliate also the thickness of each graphene sheet in the exfoliate. The results check out well compared to the standard techniques such as the SEM. In addition, a criterion for graphene's quality assessment in terms of direct measurement of number of sheets in an exfoliate has been proposed. Thus, the nanometrology reported here, is a versatile tool for nanoscale measurements.

Keywords—Nano-metrology; terahertz imaging; sub-surface dot pattern; sub-nanometer resolution; layer-by-layer; graphene; exfoliate

I. Introduction

Recently, terahertz metrology has drawn attention from a wider research community for many investigations that are permissible by terahertz approach [1]. However, an approach allowing nanometrology with sub-nanometer resolution by terahertz has been totally overlooked. Terahertz sub-surface imaging and spectroscopy offer an attractive solution for characterization of epitaxial semi-conductors, 0D, 1D and 2D materials for their size, size distribution, defects and chemical nature. Terahertz multispectral 3D reconstructive imaging with minimal sample preparation requirements and its ability to "see" below the surface with a resolution of <1 nm enables lattice level analysis [2]. Another important advantage is the ability to inspect on a layer-by layer basis via a non-contact and non-destructive route. Terahertz 3D imager designed at Applied Research & Photonics (Harrisburg, PA) has been used to demonstrate reconstructive imaging of both surface and 3D (volume) images for the analysis of silver iodide quantum dots, epitaxial semiconductor, and metal lines on Si wafer [3–5]. Layer by layer image analysis has been outlined. Graphical analysis was used for particle size and layer thickness determinations. The results of particle size and layer thicknesses checked out well with those determined by TEM micrograph and powder X-ray diffraction analysis [3]. The reported non-contact measurement system is expected to be useful for characterizing 0D–3D nanomaterials as well as for process development and/or inspection at the production line. Semiconductor wafers' defects may also be analyzed by this technique [5].

Another issue is to find a general technique for graphene quality standardization. Graphene may be produced via different routes, though graphite is the starting material in all cases. As such, the graphene quality is not uniform from all sources. It requires tedious post production characterization to establish the quality of a graphene from a given source [6].

As early as in 1947, graphene was predicted to have extraordinary electronic properties [7]. For years, graphene was considered an academic material that existed only in theory and presumed not to exist as a free-standing material, due to its unstable nature. A. Geim, K. Novoselov, and co-workers were among the first to successfully obtain the elusive free-standing graphene films which was a remarkable achievement [8]. Thus, the 2010 Nobel Prize for Physics was awarded to Geim and Novoselov for "groundbreaking experiments regarding the two-dimensional material graphene."

The unusual properties of graphene make it attractive for a cross-section of applications [9]. A few examples that leverage specific graphene properties, are: (a) the high mobility even at highest E-field-induced concentrations makes the carriers go ballistic giving rise to a ballistic FET device at 300 K; (b) due to its symmetry and linear dispersion it is suitable for RF and high frequency applications such THz detectors and lasers; (c) It also has applications in chemical sensors and MEMS; (d) graphene-based electronics using graphene as a conductive sheet rather than a channel material which could be used to make a single electron-transistor (SET); and (e) graphene is used as transparent electrodes.

It is apparent from this brief review that graphene could be an integral part of electronics manufacturing process. As such, an accurate measurement of its own properties and its properties at the semiconductor interface is important. But as pointed out in ref. [6], to make things complicated, there appears to be no rigorous standard regarding the quality of graphene as of now. As indicated by Intertek, "…recently the International Organisation for Standardisation released their nomenclature which included a definition of a 2D material with respect to graphene, as being up to 10 layers (ISO/TS 80004-13:2017). Whereby the electrical properties effectively become indistinguishable from graphite above this threshold. The question remains though how to determine a graphene's quality. At the face value we might accept that good quality graphene means something like "high purity, low defects"" [6].

So, the topic of "graphene quality" still does not have a satisfactory and quantifiable definition; as is apparent from the above. However, at the simplest (and close to the ideal) is, "lower the number of graphene layers in an exfoliate, better the properties; hence the quality." If, for the moment, one agrees to this argument (and we don't know why anyone shouldn't!), then, one needs to be able to measure the number of layers in a given graphene exfoliate. This is the basis of any graphene standard that are being (or to be) defined. Therefore, it may be proposed that a measurement of the number of graphene layers (i.e., the number of sheets of graphene) in an exfoliate could be used as a direct indication of the respective graphene's quality factor. That is, if an exfoliate has lesser than 10 layers, then the sample is graphene; more than 10 layers is still graphite. Lesser the number of layers (<10), better the quality. Also, the thickness of an individual layer in an exfoliate is another entity to measure. Both of these numbers (i.e. number of layers and the thickness of each layer) are unique for a given graphene sample. For example, high quality graphene is expected to have less than 10 layers in an exfoliate and should have a layer (sheet) thickness of <1 nm. In contrast, graphene oxide's (GO) number of sheets in an exfoliate is higher and so is the thickness of each sheet. Consequently, a 3D image (i.e., volume image) of a given exfoliate can be used for extracting these two parameters. In addition to the number of layers and their thicknesses, the Fourier transform diffraction pattern may also be generated from the 3D image to learn about crystallographic information of a given sample.

In this paper, we demonstrate a multispectral imaging technique with non-contact, continuous wave (CW) terahertz radiation (T-ray) for measuring the graphene quality in terms of the number of sheets in the exfoliate and the sheet thickness in the exfoliate. The technique is illustrated elsewhere with the help of a patterned chip and other known standards [2–5]. Also, a 3D IC chip was analyzed for hidden patterns under a top cover, and lattice images of single-walled carbon nanotube films spun on silicon wafer have also been investigated (unpublished). While terahertz wavelengths are much bigger, in the range of a few microns to a few thousand microns, still a smart scanning and imaging algorithm allow one to accomplish sub-nanometer resolution imaging [2]. In principle, this is not much dissimilar to the imaging scheme by a camera. For instance, in a digital camera, the image of an object is focused by a lens on a focal plane array (FPA) such as a CCD. The output signal from the CCD is processed by a processor and displayed and/or recorded. Here, e have implemented an alternative route by eliminating the focusing lens and the focal plane array but digitizing the object directly in a 3D space. In doing so, there are several advantages that are not available from a focal plane array. For example, one can vary the pixel size (or the voxel size in 3D) from millimeters down to sub-nanometer to suit the measurement needs, while in the FPA, the pixel size is fixed by the CCD. T-ray also gives the ability to see under the surface with layer-by-layer imaging in a non-destructive fashion. In the following, we describe the main steps of camera-less imaging technique followed by exemplary results of graphene films grown on Si substrate via spin coating.

Steps of camera-less high-resolution 3D (volume) imaging technique. As explained elsewhere [2], the main

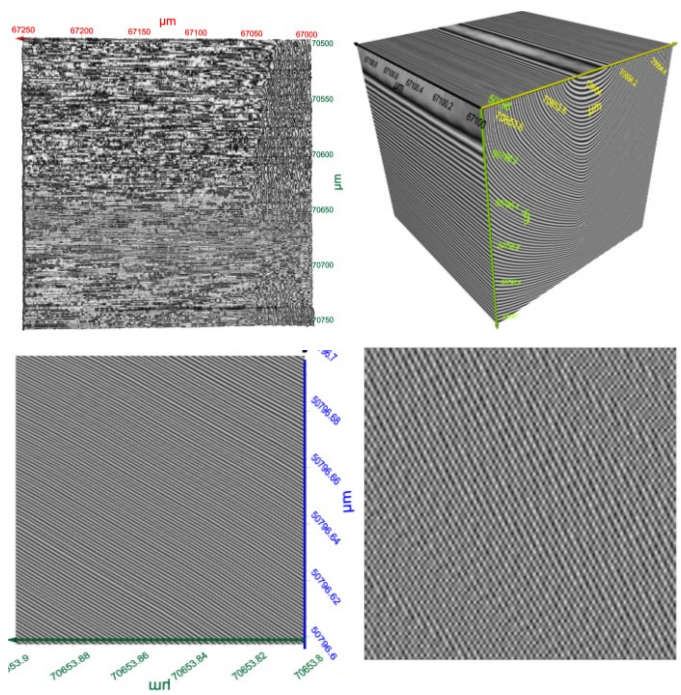

Fig. 1. Images of a sample where metallic nickel is deposited on ceramic via plasma spray; (a) 250 µm × 250 µm, showing patches of ceramic and metallic areas, (b) zoomed over 1 μm^3 volume, (c) 100 nm × 100 nm, and (d) 5 nm × 5 nm.

step is the digitizing of an object to be imaged over a volume via a 3-dimensional scanning scheme when a T-ray beam is vertically incident on the sample. The reflected intensity is stored in a 3D matrix from which images are generated as outlined in detail in ref. [2]. Fig. 1 displays the sequential zooming from a micro-image to nanoscale image of a metal lattice.

II. Experimental

Samples were obtained and measured with the terahertz nanoscanning spectrometer and 3D imager (TNS3DI) system [2]. As received samples were mounted on the machine and scanned with the front end software. The resulting reflectance matrix representing the 3D intensity profile was subjected to the "gridding by inverse power equations" algorithm [2] for generating the images.

Two graphene samples, as received, were prepared on two Si-wafers by spin coating the respective graphene from dilute solutions in N-Methyl-2-pyrrolidone ("NMP"). The wafer was then dried at room temperature for a few hours and mounted on the TNS3DI one at a time. A small volume of each graphene film on Si was digitized by the built-in front-end program. The first sample, referred to as "G95-N," is an older batch that was synthesized on a Branson 450S sonicator (400 Watt), using a microtip in an open container where NMP was used as solvent. Sonication was conducted for 6-8 hours. The second sample, referred to as "G7-12-N," is a different batch that was synthesized on a Hielscher UIP1000 (1000 Watt) unit in a stainless-steel flow-cell (also NMP as the solvent).

The wafers containing the respective films were mounted on the TNS3DI one at a time and scanned. Both graphene samples, viz., G7-12-N and G95-N were processed in an identical fashion. The resulting data were then processed by the same procedure as outlined in ref. [2].

III. Results and Discussion

The imaging technique is illustrated in Fig. 2. Here a section of a 200 mm patterned wafer is imaged. Fig. 2(a) is a photograph of a 200 mm patterned wafer as mounted on the TNS3DI. Fig. 2(b) exhibit the terahertz image of a section of the wafer (200 mm x 100 mm) showing individual dies in course resolution. Fig. 2(c) depicts a 3D close-up of a single die showing materials distribution as varying color, and 2(d) exhibits a surface image of a slice of the single die extracted from 2(c).

Following the same technique, a 3D chip with hidden features was also characterized. Fig. 3(a) shows a surface image of a segment of the 3D test chip and 3(b) shows a graphical analysis. It is evident from 3(a) that while the patterns were supposed to be on a regular grid, however, many irregularities are observed.

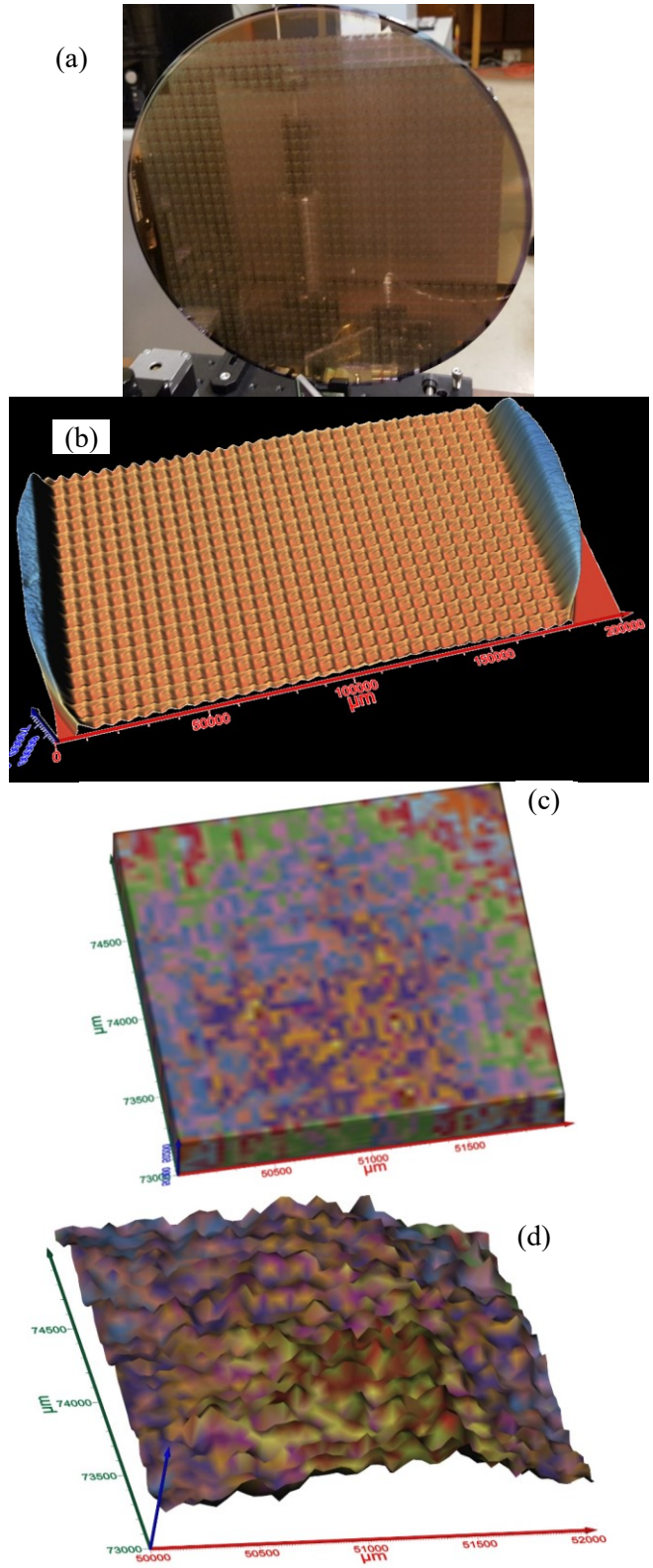

Fig. 2. (a) Photograph of a 200 mm patterned wafer mounted on the nanoscanner. (b) Terahertz image of a section of the wafer (200 mm x 100 mm) showing individual dies. (c) Close-up 3D image of a single die showing materials distribution, and (d) Surface image of a slice of the single die extracted from (c).

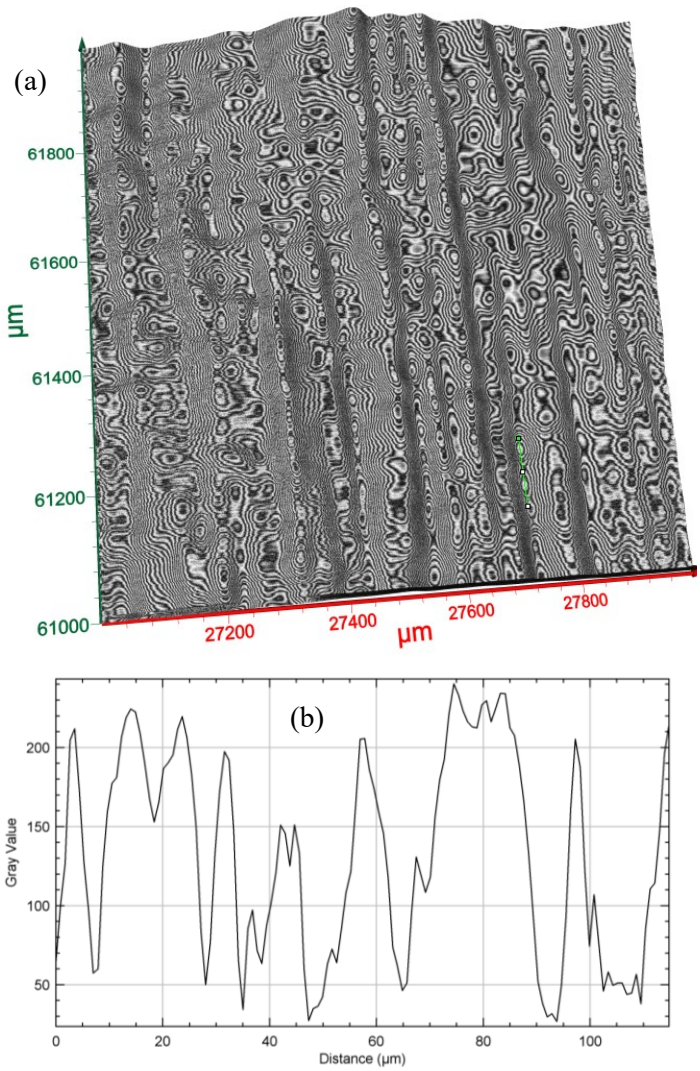

Fig. 3. (a) Pattern revealed under the surface of 3D test chip (1 mm × 1 mm). (b) Graphical analysis of the pattern along the cursor (green line) for dimensional quantification.

Fig. 4(a) shows a silicon wafer with the above described graphene film mounted on the nanoscanner. Fig. 4(b) exhibits a wide area (~2 × 4 µm^2) image of the graphene film. Fig. 5(a) shows a terahertz volume image (200 nm x 200 nm x 200 nm) of graphene sample G7-12-N exfoliates and Fig. 5(b) exhibits a volume image (200 nm x 200 nm x 200 nm) of sample G95-N. From Fig. 5(a) it is evident that there is formation of graphene sheets, as expected for the exfoliates. All the sheets, however, are not of uniform thickness across the depth. The topmost layers are thicker and of non-uniform shape. Since a single graphene sheet's thickness is expected to be <1 nm, the top sheets indicate imperfections, likely due to impurities or some kind of defects. Below the top sheets, there is an intermediate band of sheets, with thickness of each sheet <1 nm. Below this intermediate band, there is another band of graphene sheet with finer structure.

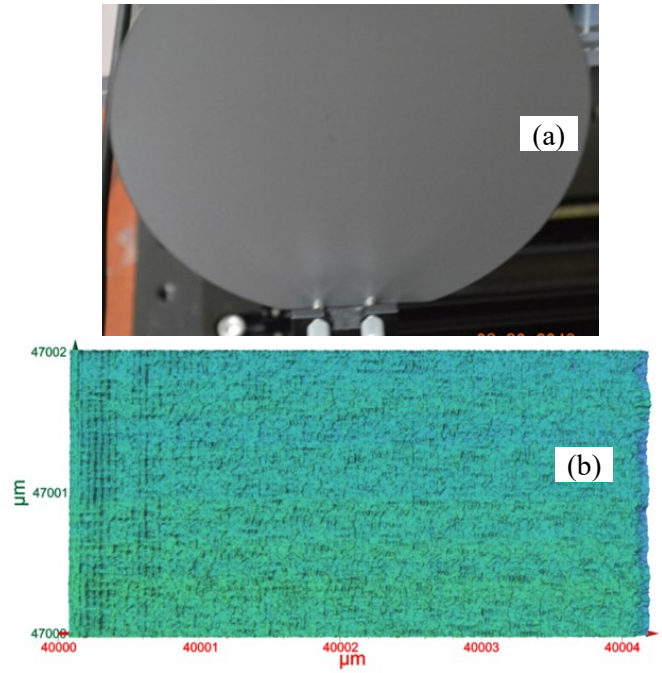

Fig. 4 (a) Graphene film spun on silicon wafer from dilute suspension in NMP. (b) A wide area terahertz image of the graphene on the silicon wafer.

The thickness of each sheet in this band is ~0.95 nm. The total thickness of all 3 bands is ~38 nm. Below this, the layer thickness increase, presumably due to the structure of SiO_2 on the top of the Si-wafer.

From the volume image (Fig. 5(b)) of the sample G7-12-N it is evident that this sample also exhibits formation of graphene sheets, as expected for the exfoliates. Here also not all the sheets are of uniform thickness across the depth. The topmost sheets are thicker and of non-uniform shape, likely due to impurities or some kind of defects. Below the top band, there is an intermediate band of graphene sheets with finer structure. The thickness of each sheet in this 14-sheet band is ~0.93 nm. Below this, the layer thickness increase, presumably due to the structure of SiO_2 on the top of the Si-wafer. Further analysis is necessary for a quantitative interpretation of these samples. However, because the are 14 sheets of graphene in the sample G7-12-N exfoliate, it can be assumed that this sample does not qualify as a higher quality graphene that requires <10 sheets in the exfoliate.

IV. Conclusions

This paper outlines the use of terahertz reconstructive multispectral imaging based nanometrology for characterization of semiconductor chips and graphene exfoliate. In particular, hidden line and dot patterns on a chip under the surface coating were imaged and graphical

analysis used for quantification. In addition, two samples of graphene film on silicon wafer were imaged and quantified. The 3D image of the graphene exfoliates reveals that the current graphene samples form distinguishable bands when spun on Si-wafer from dilute solution in NMP. A criterion for determining a given graphene's quality has been proposed in terms of the direct measurement of the number of sheets in the graphene exfoliate. It was found that the sample G7-12-N has 14 sheets in the measured exfoliate; as such it is assumed that this sample does not qualify for a high-quality graphene, because, to be distinguishable from graphite's property an exfoliate must have <10 sheets. In addition, a criterion for distinguishing between the graphene and the graphene oxide has also been demonstrated by measuring the individual sheet thickness in the exfoliate. Graphene must have a sheet thickness of <1 nm while the graphene oxide will have a thicker sheet. Further investigation is necessary for confirmation of these proposed criteria.

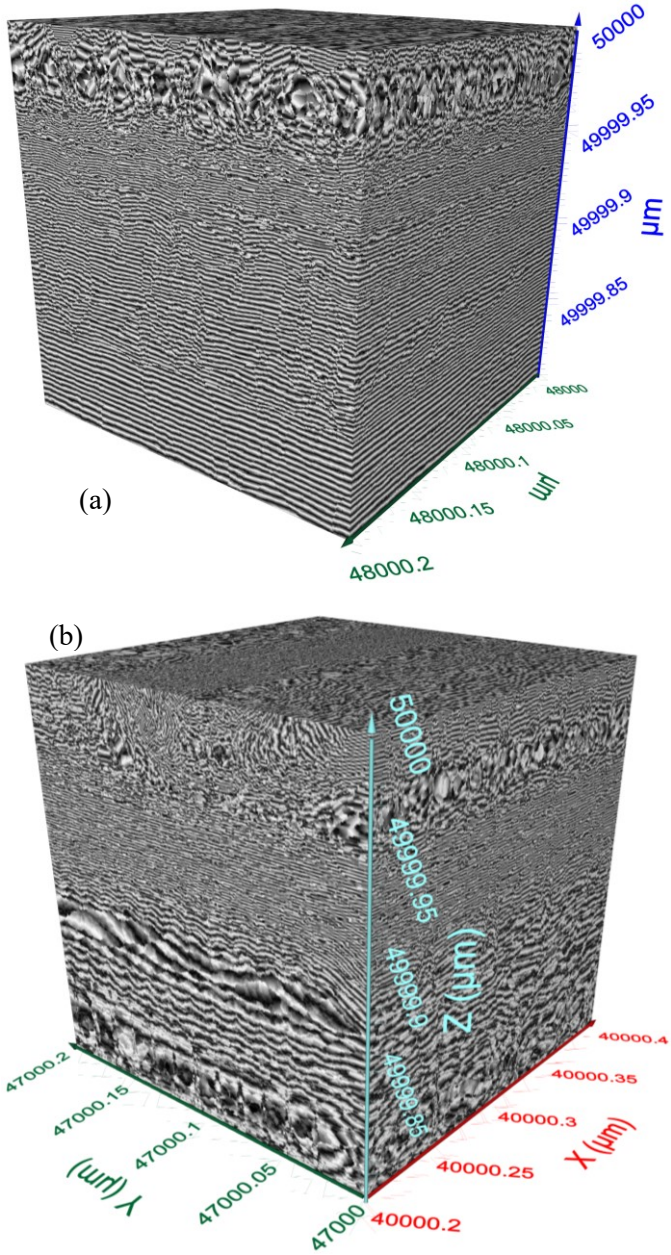

Fig. 5. Volume image of graphene showing the exfoliate structure. (a) Sample G95-N exhibits smallest thickness ~1 nm per exfoliate layer. (b) Sample 7-12-N exhibits smallest exfoliate thickness <1 nm.

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