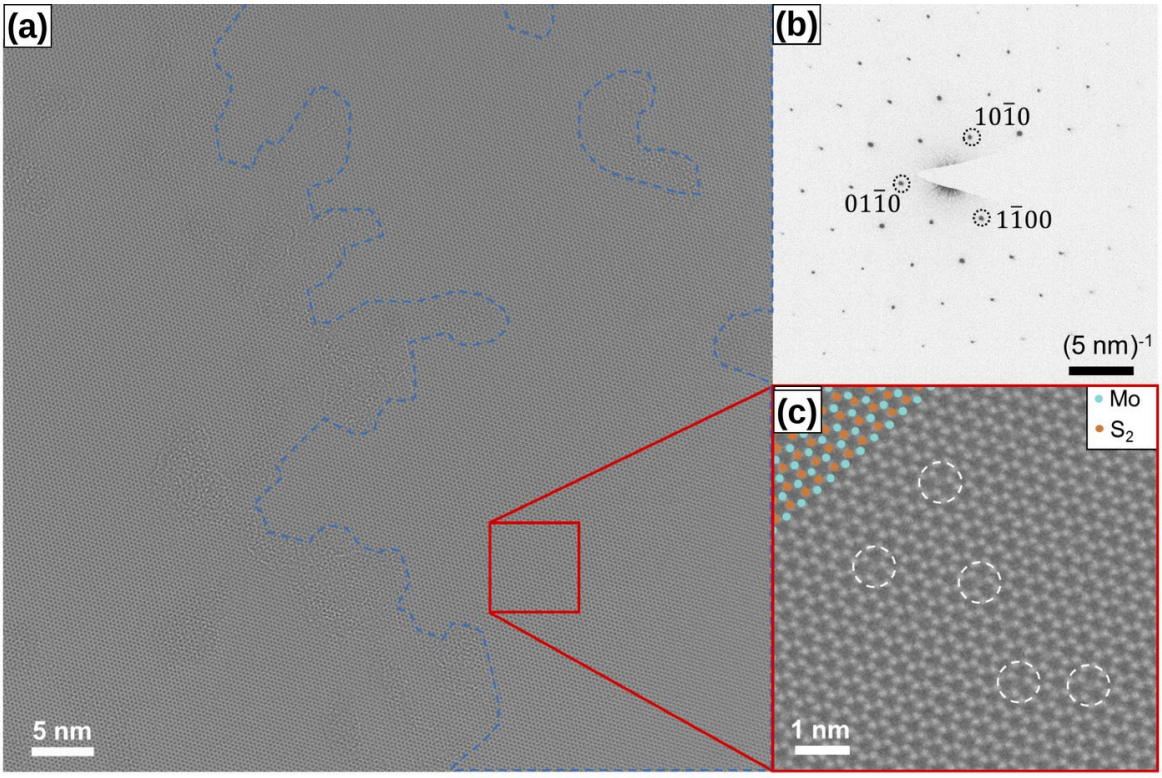

Fig. 1: Grown MoS_2 monolayer at atomic resolution.

High Optical Quality of MoS_2

January 1, 2020 · salve-project.de/newspress/high-optical-quality-mos2.html

January 1, 2020 – MoS_2 monolayers grown by chemical vapor deposition can match exfoliated ones. Researchers from Toulouse, Jena, Ulm and NIMS Tsukuba counted the vacancies in the grown layers atom by atom with the C_c/C_s-corrected SALVE microscope at 60 kV and found a defect density of the same order as in exfoliated monolayers. Encapsulated in hBN, the grown layers emit light with lines as narrow as those of the best exfoliated samples.

A semiconductor only three atoms thick can be grown over large areas on a cheap silicon wafer, but for years such grown layers were thought too imperfect for careful optical work. Monolayers of transition metal dichalcogenides (TMDs) such as MoS_2 and WSe_2 are semiconductors with a direct band gap in the visible to near-infrared[1],[2]. Their strong interaction with light and their transport properties make them candidates for a range of future devices[3]–[6]. To show their intrinsic properties, they usually have to be encapsulated in hexagonal boron nitride (hBN), which shields them from their surroundings[7]–[11]. Many applications also need layers hundreds of micrometres across, many flakes on one substrate or even continuous films[12]–[14].

Such large areas come from chemical vapor deposition (CVD), while monolayers peeled from bulk crystals, the usual choice for fundamental studies, are only tens of micrometres wide. A team from the Université de Toulouse, FSU Jena, Ulm University and the National Institute for Materials Science (NIMS) in Tsukuba has now shown that conventional CVD can deliver MoS_2 monolayers of high quality. With the C_c/C_s-corrected SALVE microscope at 60 kV, the Ulm group counted the missing atoms in the grown layers directly, one by one, and found a defect density of the same order as in exfoliated monolayers.

Clean light from a grown layer

The team removed the grown MoS_2 monolayers from their growth substrate, encapsulated them in hBN and measured their photoluminescence (PL) and reflectivity at T = 4 K. The result was unexpected: the optical transitions were as narrow as in exfoliated samples, about 5 meV wide, compared with about 50 meV for the layers still on their silicon oxide[8],[15]. The emission came from free excitons, not from defects. The layers even showed excited exciton states that appear only in high-quality material[16],[17], and polarized laser light created large valley coherence and valley polarization[18]. Spin and valley physics, so far studied almost only in small exfoliated flakes, can thus be explored in CVD-grown samples of large area.

Which defects, and how many

Whether a grown layer can match an exfoliated one depends first of all on its crystal. Which type of defect is present is not always clear[19]. In naturally occurring MoS_2 and in CVD-grown films, sulfur vacancies often dominate, whereas metal vacancies and anti-

sites prevail in synthetic crystals grown by chemical vapor transport (CVT)[2]. The crystals of this study were grown in a modified CVD process in which a Knudsen-type effusion cell delivers a controlled flow of sulfur[12]. For comparison, the researchers also prepared monolayers by exfoliation from bulk MoS_2 with adhesive tape and identified them under an optical microscope by their contrast on silicon oxide[20].

Counting vacancies with SALVE

The SALVE microscope images both kinds of sample at atomic resolution over a wide field of view (Fig. 1a). The diffraction pattern shows that the whole imaged area is a single, highly ordered crystal (Fig. 1b). In the enlarged view, the molybdenum atoms and the pairs of stacked sulfur atoms can be told apart, and missing sulfur atoms, mostly double sulfur vacancies as typically found in MoS_2 monolayers[12],[21]–[23], can be recognized directly (Fig. 1c).

The team counted these vacancies in clean areas of the images and divided their number by the area. In the CVD-grown monolayers, the density was 7.9×10^{13} vacancies per cm^2; the values of three areas ranged from 6.9 to 9×10^{13} cm^{-2}. In the exfoliated monolayers, four areas gave between 3.4 and 4.1×10^{13} cm^{-2}. How the vacancies were made visible and how the uncertainty was estimated is explained in the box below (Figs. 2 and 3).

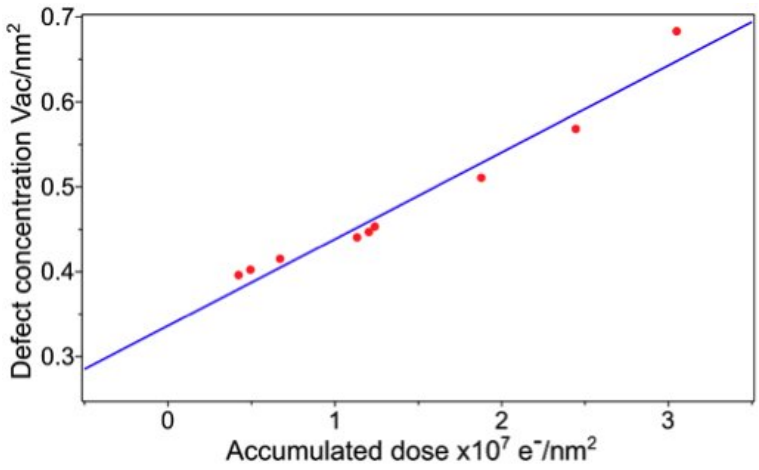

Fig. 3: Vacancy density versus electron dose.

SALVE: counting vacancies at 60 kV

The images were taken with the C_c/C_s-corrected SALVE microscope at 60 kV. This voltage lies below the knock-on threshold of sulfur atoms[23], so the beam does not knock them out directly, yet it still gives sub-Ångström resolution[24]. Chromatic and spherical aberration were both corrected to between −10 and −20 µm, and typical dose rates were about 10^5 electrons/(nm^2 s). The CVD-grown MoS_2 was recorded with bright atom contrast on a 4k × 4k camera, the exfoliated MoS_2 on a 2k × 2k camera, both with exposure times of 1 s.

The exfoliated flakes were transferred to Quantifoil TEM grids by placing a grid with a drop of isopropyl alcohol on the flake; as the alcohol evaporates, the grid touches the flake. The silicon oxide was then etched away with KOH, which releases the MoS_2 onto the grid, and the sample was rinsed with double-distilled water.

Single vacancies are hard to spot even in a magnified raw image. A Fourier filter that removes the frequencies of the MoS_2 lattice makes them stand out as small black dots (Fig. 2).

The electron beam itself slowly creates new vacancies. The team therefore followed the vacancy density over the accumulated dose in exfoliated MoS_2 and fitted a straight line, valid while fewer than 5 % of the sulfur atoms are displaced (Fig. 3). Its slope gives the error of the measured density. Because every area is exposed to the beam for a few seconds before the first image, an earlier irradiation of 10 s was included in the uncertainty of the dose; the true starting density is therefore probably slightly lower than measured.

As good as exfoliated

The defect density of the CVD-grown monolayers is thus of the same order of magnitude as that of exfoliated monolayers[2],[25],[26], and it agrees well with values reported for MoS_2 from naturally occurring bulk[27],[28]. A low density of sulfur vacancies means high structural quality, and that is what made the high optical quality in emission and absorption expected in the first place.

What it opens up

Counting defects atom by atom in low-voltage HRTEM proves to be a direct way to measure the structural quality of new TMD materials right after growth. The study shows that large-area CVD-grown MoS_2, once lifted from its growth substrate and encapsulated in hBN, can be used where so far only exfoliated flakes would do, and opens new possibilities for (opto-)electronics and spintronics.

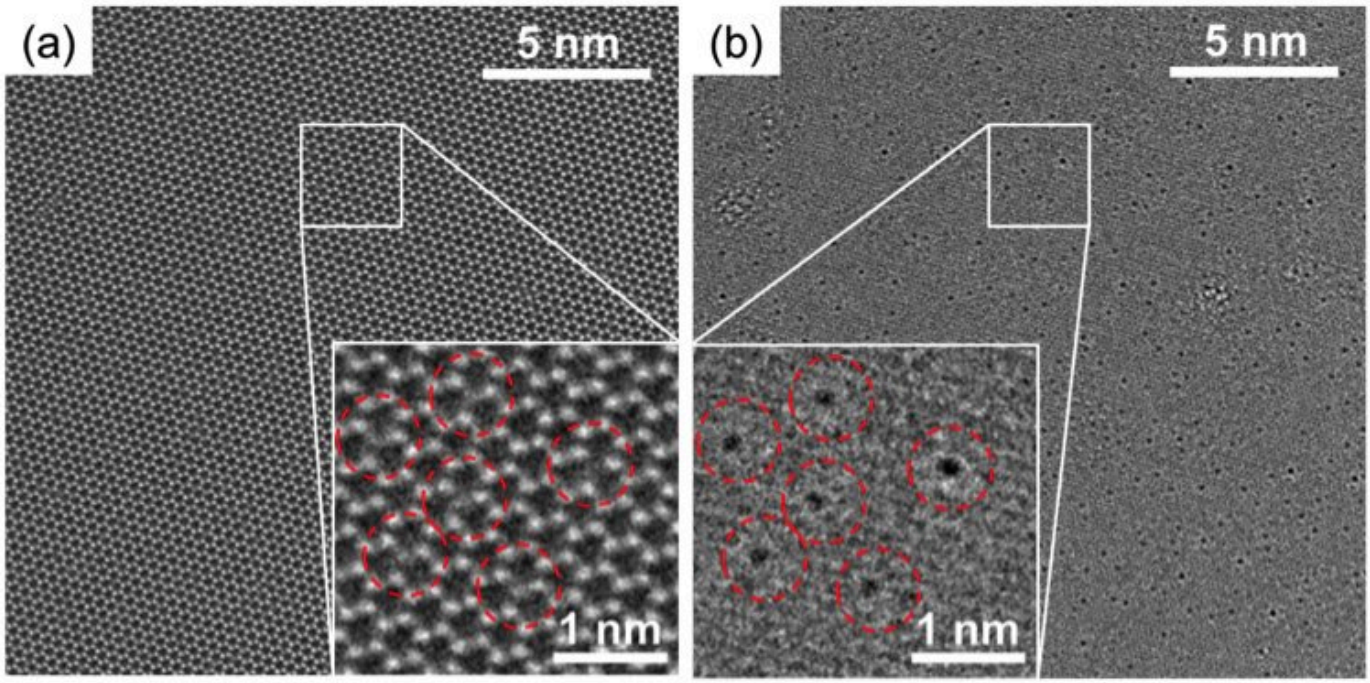

Fig. 2: Raw and Fourier-filtered HRTEM of MoS_2.

Resource

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