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Mechanical Metallurgy for Two-Dimensional Crystals

Exceptional electronic transport and quantum oscillations in thin bismuth crystals grown inside van der Waals materials
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Wafer-scale fabrication of 2D nanostructures via thermomechanical nanomolding
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Recommended with a Commentary by Joe Checkelsky, Massachusetts Institute of Technology

The notion that new physics comes from new materials has long been a tenant of synthesis driven research in condensed matter science [1,2]. The realization of two-dimensional materials is a prominent illustration of this. Breakthroughs in the development of molecular beam epitaxy (MBE) starting in the mid-20th century [3] to create new two-dimensional interface systems in semiconductor heterostructures led to the discovery of the fractional quantum Hall effect [4]. The development of techniques to mechanically exfoliate and manipulate van der Waals (vdW) materials in recent decades [5] has enabled the assembly of heterostructures found to support new correlated and topological electronic phases [6]. From such discoveries also arise possible applications such as the thin-film based high electrotonic mobility transistor [7] or vdW platforms for neuromorphic devices [8]. Viewing these remarkable developments as being in part enabled by new synthesis methodologies, a natural question is if there are other methods that might enable the realization of additional two-dimensional materials.

In the field of metallurgy, there is a long history of shaping materials to a particular form [9]. The most historic example is forging, originating in the handwork of blacksmiths in *e.g.* crafting tools. A modern forging apparatus mechanizes the work of the blacksmith mechanically or hydraulically with a drop hammer combined with a press to compressively shape a material. The process is often carried out at high temperatures where the metal has improved ductility. Conventional forging is used to produce mechanical parts ranging in size from small bolts to power plant steam turbines. A related method for shaping materials is extrusion, wherein a block of material (the feedstock) is heated and pushed through a die of particular cross section. These typically form rods or hollow tubes such as I-beams or toothpaste tubes. Just as modern metallurgy research leverages many tools of nanoscience familiar to condensed matter physics to investigate the structure of materials (*e.g.* electron microscopy), how then about leveraging these paradigms for shaping materials to synthesize new two-dimensional materials for condensed matter studies?

The two works highlighted here present recent advances in addressing this question- in particular in developing two-dimensional morphologies of non-vdW crystals. In the first, L. Chen *et al.* have investigated the synthesis of ultrathin crystals of Bi using a van der Waals press that in construction resembles a micro-scale forge (see Fig. 1(a)). Using established vdW transfer techniques, they place a flake of Bi several microns in lateral size and up to half a micron thick in between two sheets of hexagonal BN (hBN). Applying pressures of GPa order to this assembly, this structure is then heated to temperatures as high as 300 °C to initiate two-dimensional molding of the flake and then cooled (see Fig. 1(b,c)). A key distinction with previous work [10] (and from the conventional operation of a forge) is that here the apparatus is heated beyond the melting point of Bi (271 °C) so that this is a high pressure melting and recrystallization process in a confined geometry. In fact, the authors report they observe a rapid expansion of the lateral size of the material near 220 °C at high pressure, consistent with the reduction of the melting temperature known for Bi [11] (Bi is similar to water in that the liquid phase is denser than the solid phase in the vicinity of the melting point).

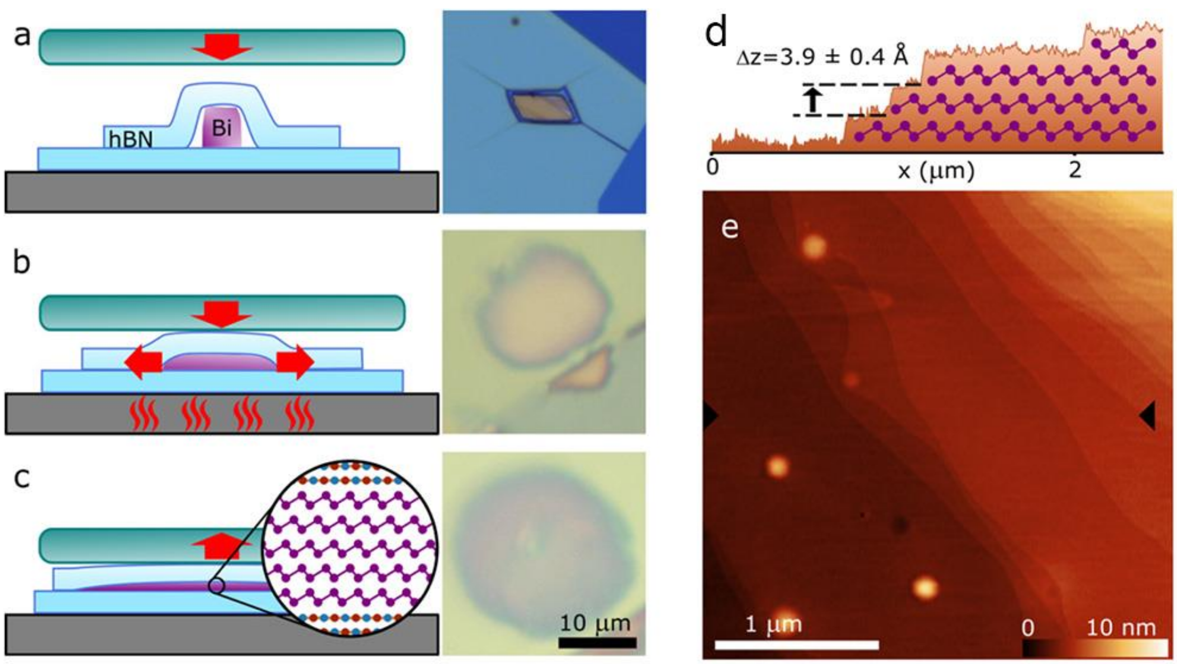

Figure 1 – Schematic (left) and top-down optical image (right) of (a) encapsulation of a flake of Bi in a vdW press, (b) its heating and compression, and (c) crystallization of thin crystals of Bi. (d) Cross-sectional and (e) topographic view of resulting thin Bi crystal. All adapted from L. Chen et al., arXiv:221107681 (2022).

The resulting Bi flakes are as thin as 5 nm and exhibit step heights consistent with single atomic layers of the buckled Bi network (see Fig. 1(d)). Laterally, the flakes have exceptionally large terraces exceeding a micron and are extremely flat (see Fig. 1(e)). The authors observe that the latter is closely related to the surface roughness of the mold material, with hBN providing a lower surface roughness compared to SiO_2, graphite, sapphire, and mica. The materials are morphologically thin enough that size quantization strongly affects the electronic structure and electrical transport has a strong surface state contribution. In device structures, the authors are able to measure Shubnikov-de Haas oscillations of the surface states, which they can further modulate with an electrostatic gate. This has proven challenging for MBE grown Bi films and demonstrates this as a new method to realize high quality 2D crystals of Bi.

There is significant motivation to realize Bi in the atomic two-dimensional limit. Known in the bulk as one of the electronically cleanest semimetals in which various quantum oscillatory phenomena were discovered [12,13], it has been shown that as a monolayer that so-called Bismuthene has a large topological insulating gap (approximately 0.8 eV) [14]. Previously grown using MBE, a challenge has been to create materials of sufficient lateral size for device structures. Extending the present method to thinner films is thus of great interest. While this may be challenging for a number of reasons including changes in melting dynamics [15], the optical access of the present setup may aid in a relatively rapid evaluation of the growth process. It seems possible that even the flakes currently studied might find improved quality if other techniques for preparing high quality bulk Bi such as annealing and zone refining were to be employed. The authors also report that other soft materials such as Au, Sn, and In show promise with this method, suggesting its potential broader use.

In the second work, M. T. Kiani *et al.* extend the use of current state of the art for nanoscale extrusion (known as thermomechanical nanomolding) to synthesize nanoribbons of Cu. It has been previously established that the extrusion of crystalline nanowires is possible [16] and that such wires can be single crystal in nature. This appears to occur as a single crystal grain is seeded at the nanoscale die which the material is pressed through [17]. Instead of one-dimensional extrusion, the authors study two-dimensional extrusion of Cu through trenches of Si_3N_4 coated Si (see schematic in Fig. 2(a)).

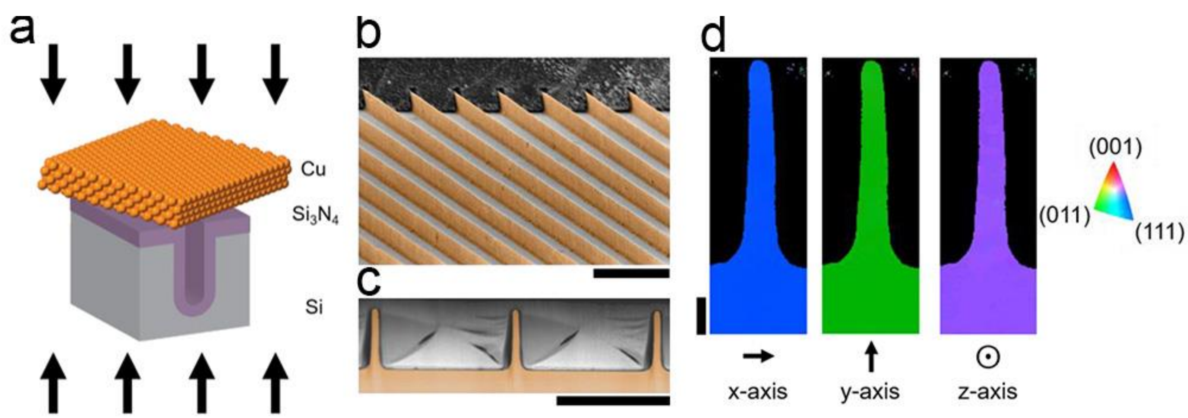

Figure 2 – (a) Schematic of extrusion of single crystal Cu through Si_3N_4 coated Si. (b,c) False color scanning electron microscope images of extruded Cu ribbons (scale bars are 2 μm and 1 μm, respectively). (d) Grain orientation map of ribbons matching that of single crystal feedstock (scale bar is 100 nm). All adapted from M. T. Kiani et al., arXiv:2306.10167 (2023).

The authors prepared trenches tens of nanometers wide and up to a micron deep using conventional lithographic techniques. Cu feedstock with different grain size (from nanocrystalline to bulk single crystal) was then pressed at pressures of 10-100 MPa and temperatures up to 400 °C (half the melting point of Cu in an absolute scale). While the crystallinity of the extrusion from polycrystalline feedstock was not improved (as it was in nanowire extrusion), remarkably the extruded sheets from single crystal feedstock retain their crystallinity and orientation (see Fig. 2(b-d)). This appears to work for specific crystal orientations and enables the rapid synthesis of nanometer thickness scale sheets of single crystal Cu.

These extruded single crystal sheets of Cu have immediate potential impact for applications: such materials are expected to have dramatically reduced resistance due to lack of grain boundaries and could improve the performance of interconnects [18]. At the same time, thermomechanical nanomolding has been shown to work for a range of materials [16] such that it is considered "materials agnostic" process relative to *e.g.*

MBE. This suggests the immediate application of this process to other materials from elemental metals to complex systems may offer pathways to new 2D morphologies of many materials.

A common theme of these two works is the use of a confined growth space. It is noteworthy that other methods such as confinement heteroepitaxy [19] have also recently reported successes in realizing 2D morphologies near the atomic limit of non-vdW materials using such restricted vessels. To what degree the present techniques can realize crystals at the atomic two-dimensional limit is a key question for this subfield. The promise of realizing a dramatically expanded class of two-dimensional crystals beyond vdW systems- perhaps of potentially any given material- will continue to motivate these and other new approaches for novel material synthesis.

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