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Stacking Atomically Thin Materials

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Stacking Atomically Thin Materials

by

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I. Abstract

Atomically thin materials have been an exciting topic of research since graphene was first isolated in 2004. Due to their unique properties, a large amount of research has gone into these materials, but better methods of combining them are still being sought. We present three methods which were attempted for fabricating stacks of atomically thin (or 2D) materials without heating them to the high temperatures required by previous techniques. The first two methods were deemed unsuitable for various reasons, but the third was used to successfully create a stack of hexagonal boron nitride (hBN) encapsulated molybdenum disulfide (MoS₂). While the method was shown to be successful, the relative quality of the product has not yet been determined.

II. Introduction

In terms of scientific fields of research, the field of 2D materials is very young. 2D materials have an atomic structure that is only one to a few atoms thick (Fig. 1a). They do not occur naturally on their own, but they are found as individual layers making up a larger bulk object. For example, graphite is made up of many layers of the 2D material graphene. 2D materials have many unique electrical and mechanical properties compared to normal 3D materials, which have 3D atomic structures and cannot be separated into layers.

Graphene was the first atomically thin material to be observed in 1962 (Boehm, 1962), and in 2004 it became the first 2D material to be isolated (Novoselov et al., 2004). This was done by mechanical exfoliation: sticking a piece of tape to a bulk piece of graphite, and peeling the tape off (Fig. 1b). This left a thin layer of graphite stuck to the tape. The process was repeated on the progressively thinner layers until a single layer was isolated.

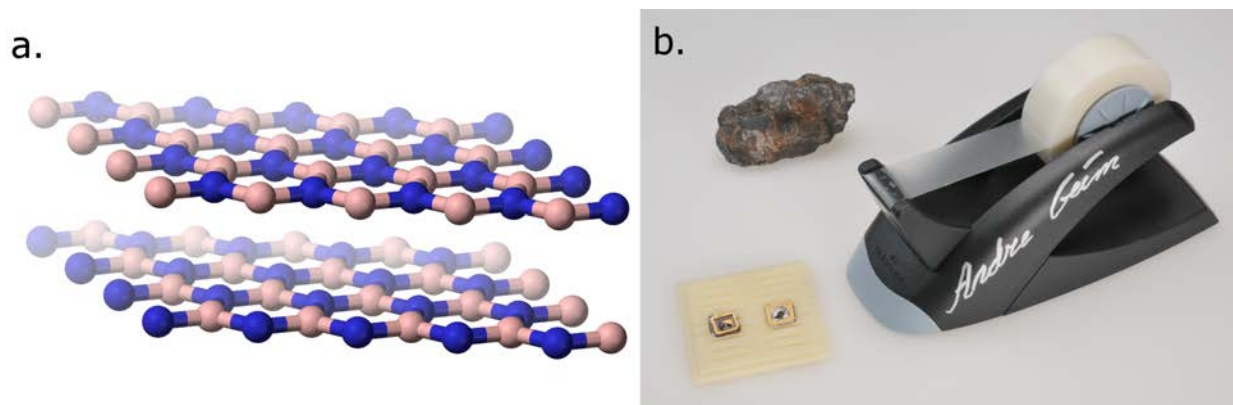


Figure 1: (a) Two layers of hexagonal boron nitride. (b) Bulk graphite (top left), a tape dispenser, and a graphene transistor.

A large amount of research has gone into graphene because of its many unique properties, including high electron mobility and a tensile strength 200 times greater than that of steel (Mrmak, 2014). Because of these characteristics, researchers began searching for other 2D materials with useful properties. This research grew rapidly in 2010, resulting in the discovery and isolation of many different 2D materials. These include allotropes such as graphene, silicene, and phosphorene, which are made up of only one type of element, and compounds like hexagonal boron nitride (hBN), germanane, and molybdenum disulfide (MoS_2), which are made up of multiple elements. Some of these materials function as electrical conductors (like graphene), some as semiconductors (like molybdenum disulfide), and some as insulators (like hBN).

While these materials all have interesting and unique properties on their own, they become even more interesting when combined to form 3D structures. The most widely used method of combining 2D materials was pioneered by L. Wang et. al. in 2013. His group demonstrated a method of stacking 2D materials into layers, using van der Waals forces to keep them together. This method allows 2D materials to be combined into 3D structures, called van

der Waals heterostructures, which can be used in 3D devices while retaining the unique properties of the 2D materials (Wang et al., 2013).

Electronic components generally consist of some combination of conductors, semiconductors, and insulators. Since 2D materials have been found which fulfill each role, they can be used to create much smaller 3D electronic devices than those possible with traditional 3D materials. This is where much of the current research focuses.

Although the technology is still in its infancy, there are practically limitless possible applications of structures made of 2D materials. It has only been 13 years since graphene was first isolated (Novoselov et al., 2004), and it will be many more years before devices based on 2D materials are in wide use. However, some applications can be predicted.

The biggest field these materials will affect is electronics. The size of traditional silicon-based electronics have decreased fairly constantly for many years, but they are now almost as small as they can be without exhibiting quantum effects (Markley, 2016). This is because they depend on 3D molecular arrangements. Using heterostructures made of 2D materials, researchers have already made electronic components, such as transistors, that have a thickness of only a few atoms (Das et al., 2014). Components like these will be much smaller and thinner than traditional ones, enabling the creation of electronics which are much smaller or more powerful, as well as bendable or transparent (Markley, 2016).

One potential application of these electronics is prosthetics. The technology exists for controlling prosthetics or implants using electrodes embedded in the brain. However, current materials tend to leave scarring. Because of their flexibility, 2D materials could be used as electrodes for these interfaces without the danger of scarring. Combined with smaller, thinner,

and more flexible electronics, this could allow for much better implants and prosthetics which patients can directly control using their brain (Markley, 2016).

These smaller components will also greatly improve the power of computers because they can be placed much closer together. The copper wires currently used to connect components can also be replaced with 1-atom thick wires, saving more space, and helping to distribute heat. This will allow traditional computers to be both smaller and more powerful (Markley, 2016).

Besides traditional computers, these heterostructures also open up the possibility of improved quantum computers. While traditional computers use binary to store information in bits, quantum computers store information in quantum bits, or qubits. Using the quantum effect of superposition, multiple bits of information can be stored in a single qubit. Because of this, they can be used to solve problems which are impractical or impossible to do otherwise. The small scale of atomically-thin materials allows for the easy creation of controlled quantum effects, which can be used to form qubits (Paiste, 2015). While several other methods of

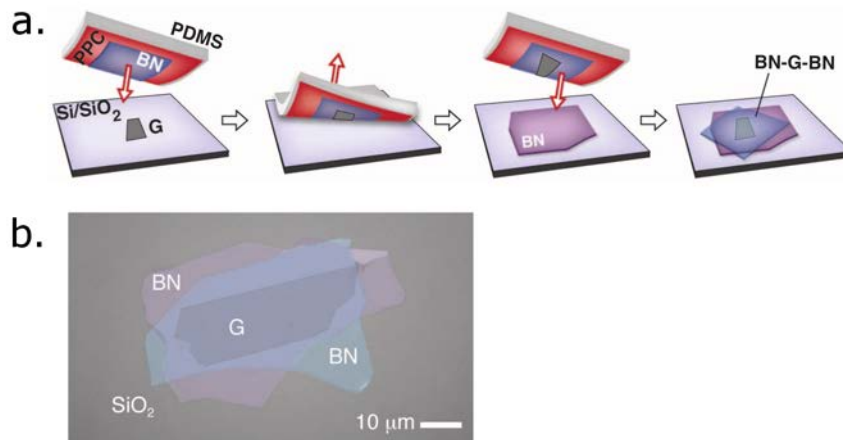


Figure 2: (a) A schematic of the method used to create van der Waals heterostructures. A stamp made of a layer of polymer (PPC) on a layer of silicone (PDMS) is brought into contact with each layer of material to create a stack. (b) A stack of graphene between two layers of boron nitride. Reprinted from Science 342, 614-617 by L. Wang, et al., 2013.

producing quantum computers are also being researched, 2D materials are a very promising candidate.

Because they are so thin and have such a large surface area compared to their volume, 2D materials also are excellent candidates for power generation and storage. The amount of energy that can be stored in a capacitor is mainly limited by the internal surface area. Since 2D materials are so thin, they can have a very large surface area for a given volume, allowing much more energy to be stored (Markley, 2016). Since capacitors are used to store and rapidly discharge energy, higher capacity capacitors could be used to rapidly charge electric cars or other large devices.

These are a but few of the many examples of ways 2D materials could be used to greatly improve current technology.

III. Background

However, before electronics made of 2D materials can become widespread, more effective ways of stacking the materials must be found. The original method (Fig. 2a) uses a microscope connected to a micro-manipulator (with micrometer or nanometer precision). A heater is connected to the micro-manipulator. The small pieces, or flakes, of the 2D material are located using the microscope and aligned and stacked using the micro-manipulator, using a sacrificial polymer layer. The heater is then used to heat the polymer to around 150°C, melting it and releasing the stack onto a substrate (Wang et al., 2013). The polymer is cleaned off using chloroform, or some other solvent, leaving a clean stack on the substrate.

The stacking stamp used to fabricate the stacks is made of silicone, and the substrate is made of silicon. The heating causes uneven expansion of the silicone and silicon, causing the

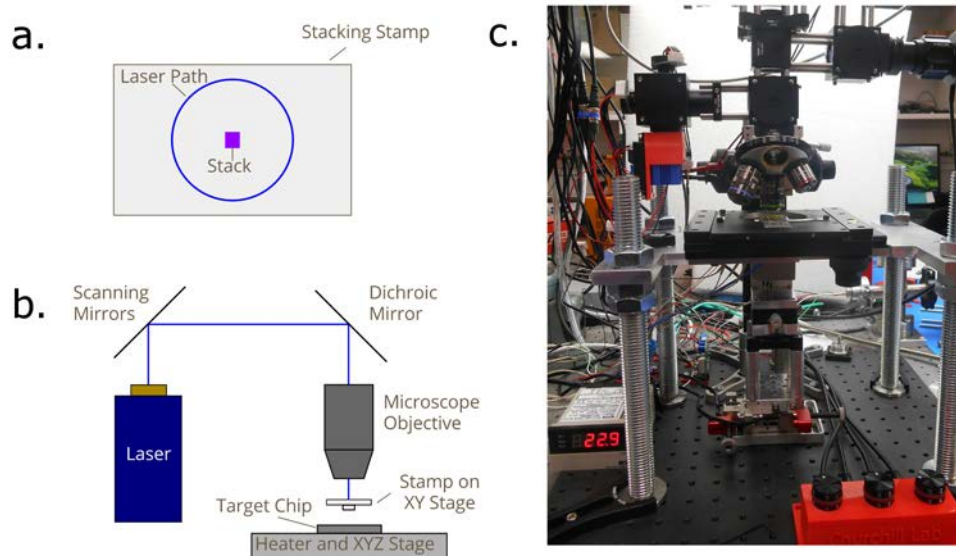


Figure 3: (a) The path the laser travels around the stack. (b) A diagram of the experimental setup. (c) The experimental setup.

stack to break. While several other researchers improved on the original method in various ways (Pizzocchero et al., 2016; Zomer et al., 2015), none of them removed this heating step. For this reason a large number of the stacks created using these methods break.

In order to more reliably produce heterostructures for quantum devices, it was theorized by H. Churchill that a 3D-printed stamp combined with a laser cutter could allow heating to be confined to a circle around the edge of the stack, preventing the stack itself from being heated. This would remove the stress on the stack, increasing the quality of the resultant heterostructure and improving the reliability of the method. Three variations of this method, each using a different family of stamp design, were investigated to determine their viability.

IV. Experimental Procedure

Three different methods, each using a different stamp design, were tested. The

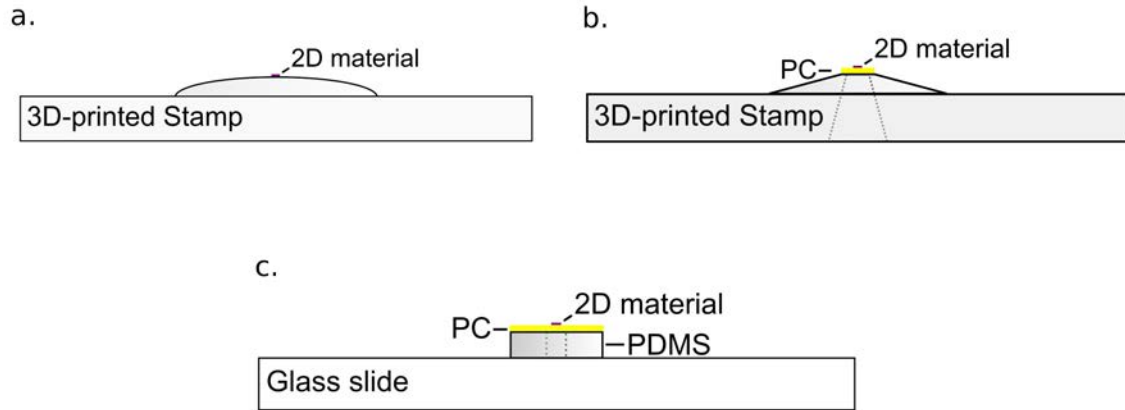


Figure 4: (a) The first stamp design, composed of a solid 3D-printed structure. (b) The second design, composed of a 3D-printed stamp with a conical hole going through it and PC film over the hole. (c) The third design, composed of a toroid of PDMS with PC over it, supported by a glass slide.

experimental setup used here was the same as the traditional one, with two additions. A 405 nm laser was mounted to the side of the microscope, and a set of scanning mirrors were positioned to move the laser beam in a circle around the completed stack (Fig. 3).

To confirm that van der Waals heterostructures could be created using one of these methods, the goal of the experiment was to fabricate a stack of hBN encapsulated MoS₂, meaning a layer of MoS₂ between two layers of hBN.

The first method used a 3D-printed transparent polymer stamp in place of the glass slide, silicone stamp, and sacrificial polymer which are traditionally used. The stamp was designed with a raised section with a thinner area around it (Fig. 4a). It was hoped that the raised section would come in contact with the flakes of 2D material to pick them up, and the thin section would be cut with the laser after the stack was complete. The polymer remaining on the stack could be dissolved using chloroform. The stamp had to be transparent so that flakes could be aligned visually prior to stacking.

The second method was very similar in design to the first in that it utilized a 3D-printed stamp with a raised section, but included a hole through the center (Fig. 4b). Polycarbonate (PC) film was placed over the hole, using a method demonstrated by J. D. Sanchez-Yamagishi in 2015. PC is one of the polymers traditionally used to pick up flakes, so it was believed that it would remove the issues with the rough surface. Since PC is also transparent, the microscope could see through it, removing the need for the 3D-printed portion of the stamp to be transparent. This design fixed the main problem of roughness with the previous version. In addition, because the stack would be created on the polymer, which goes over the hole, it was anticipated that the laser would easily cut through the thin PC layer to release the stack onto the final substrate.

The third and final method used a doughnut-shaped piece of PDMS, which is a type of silicone, attached to a glass slide and covered with PC film (Fig. 4c). The PDMS was formed using a 3D-printed mold to give it the hole in the center, which provided the same benefits as having the hole in the 3D-printed stamp: it could easily be seen through, and the PC could be cut without sticking to anything except for the substrate and stack. It was expected that using PDMS would provide the deformability that was lacking in the previous design, as well as provide a smoother surface for the PC to stick to, reducing the number of wrinkles.

V. Results and Discussion

Many iterations of the first stamp design (Fig. 4a) were tried, but they all suffered from a variety of issues. The main problem was the roughness of the surface of the stamps. Microscopic ridges left behind by the 3D printer disrupted the surfaces and prevented the stamps from smoothly picking up atomically-thin flakes. The ridges also kept the stamps from being

transparent under the microscope, even though they were to the naked eye. For these reasons this design was abandoned.

While the second stamp design (Fig. 4b) improved on the first method, the polymer did not smoothly come into contact with the substrate when they were brought together for two reasons. First, there were wrinkles in the PC film stretched over the hole. These wrinkles were caused by imperfections in the perimeter of the hole, left by the 3D printer. Due to the resolution of the printer, these imperfections could not be removed. Second, the rigidity of the 3D-printed material prevented smooth contact. The silicone stamp used in the traditional method allows the stamp to deform as it comes into contact with the substrate, which increases the smoothness of the contact. Without this layer, the 3D-printed material was too rigid.

During initial testing, a version of third and final stamp design (Fig. 4c) was successfully brought into smooth contact with the substrate and lifted off again. It was also confirmed that the laser, at an applied voltage of between 8.10 V and 8.70 V, was able to cut a circle through the PC, leaving the circle behind on the substrate when the stamp was removed. After these successful tests, attempts to pick up flakes of material began.

The flakes were placed on a substrate using mechanical exfoliation (a piece of tape) (Fig. 5a). The hole in the PDMS on the stamp was aligned with a flake of hBN, which had been selected optically for smoothness, and the stamp was lowered into contact with the flake. The stamp did not initially pick up the flake. The stamp was brought back into contact with the flake, and the temperature was raised to 70°C and cooled to room temperature. This allowed the stamp to pick up the flake when it was removed. The pick up process was repeated for the MoS₂ flake, with care being taken to keep it aligned with the hBN flake on the stamp using the microscope.

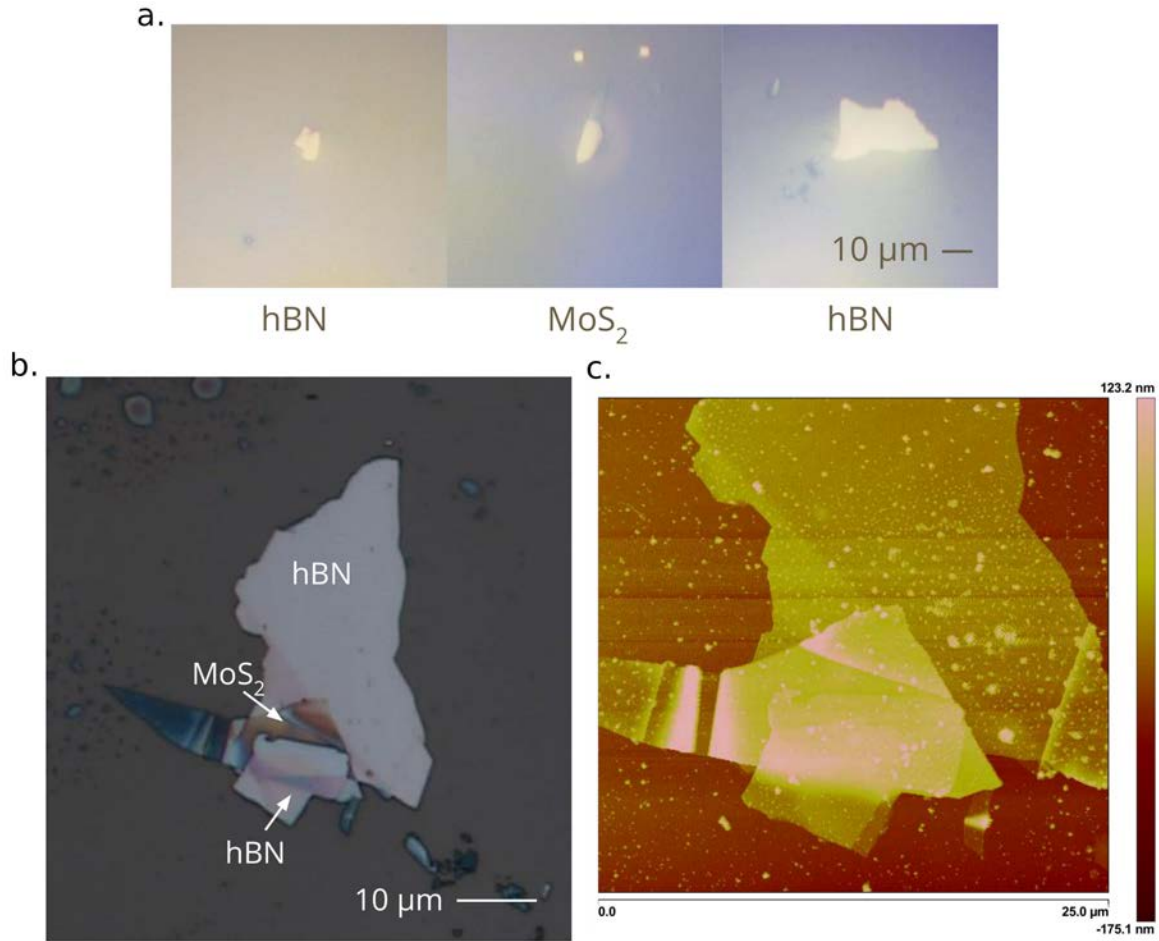


Figure 5: (a) The three flakes on their respective substrates before pick up. (b) An optical view of a completed hBN-MoS₂-hBN stack. (c) An AFM view of the completed stack. Image by J. Stacy.

For the final hBN flake, which was the bottom layer, the stamp was brought into contact with the substrate and heated as before. However, as the stamp was lifted away from the substrate, the laser was turned on at an applied voltage of approximately 8.50 V and kept in focus in a circle around the stack. As hoped, this resulted in the circle of PC with the stack in the center remaining on the substrate after the stamp was removed. The PC was removed using chloroform, then the stack was cleaned by soaking it in isopropyl alcohol, and blown dry with nitrogen. The final result was a hBN- MoS₂-hBN stack on a silicon substrate (Fig. 5b).

VI. Conclusions

Using this stamp design, a van der Waals heterostructure was fabricated while heating the stack to only 70°C, a decrease of more than 50% from the temperatures required by most current techniques. However, further research is required to analyze the quality of the stack. An AFM (atomic field microscopy) image of the stack (Fig. 5c) showed a large amount of unwanted material on and around the stack. Because of this, a better method of cleaning the heterostructure must be developed. Also, the quality of the stack compared to those made with the more traditional methods must be tested. If the stack compares favorably to those fabricated using traditional methods, then further optimization will be carried out on the stamp design. The glass slide used in the final method will be replaced with a 3D-printed slide with a hole in it. This will remove the optical distortions from the glass slide, improving both imaging and cutting quality. It is hoped that this method will allow better quality heterostructures to be formed more reliably, leading to better devices based on those structures.

VII. Acknowledgments

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