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Hamilton Johnson
Ouachita Baptist University, hamiltonjohnson95@gmail.com

Hugh O.H. Churchill
University of Arkansas, Fayetteville, hchurch@uark.edu

Methods of Stacking Atomically Thin Materials without High Temperature Heating

H. Johnson[1] and H. O. H. Churchill[2]

[1]*Department of Physics, Ouachita Baptist University, Arkadelphia, Arkansas 71998, USA*
[2]*Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA*

We present three methods which were attempted for fabricating stacks of atomically thin materials without heating to the high temperatures required by previous techniques. The first two methods were deemed unsuitable for various reasons, but the third was used to create a stack of hexagonal boron nitride (hBN) encapsulated molybdenum disulfide (MoS_2). The method was thus shown to work, but the relative quality of its result has not yet been determined.

Van der Waals heterostructures, made of atomically thin materials, have the potential to form a new class of electronic device, which can continue shrinking past the limits inherent in the currently used materials, as well as being potentially transparent and flexible. Before these sorts of devices can be readily fabricated, there must be a way to reliably assemble 2D materials into heterostructures. The way that has been found is to stack them on top of each other.

The method of stacking that is currently used was pioneered by L. Wang et al. in 2013.[1] Since then a number of different variations on this approach have been suggested, but they all share one step in common: in order to release a completed stack onto the target substrate, the entire stack is heated to $\sim 150^o$C, depending on which materials are used to make the stack.[1–3]

The issue with these procedures is that they require the entire stack to be heated to high temperatures while it is in contact with both a silicon substrate and a silicone stacking stamp. Since the silicone in the stamp expands differently with heat than the Si/SiO_2 substrate does, stress is put on the stack, frequently causing the crystals to break. Therefore it desirable to seek a method of stacking which does not require this heating step. We hypothesized that using a design of stamp which allowed us to locally melt around the stack with a laser without heating the stack itself would result in higher quality heterostructures. The setup we used to test our methods, Fig. 1b, was the same as the traditional method, except for the addition of a 405nm laser and a set of scanning mirrors which served to move the beam in a circle.

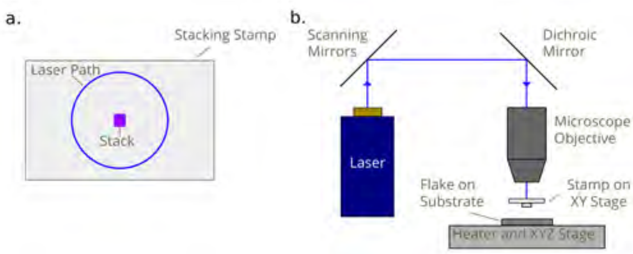

FIG. 1: (a) The laser path around the stack to locally heat the stamp without heating the stack itself. (b) The experimental setup. A 405nm laser which is controlled using two scanning mirrors. It is reflected through the objective onto the stamp. The stamp is on an XY stage to allow it to be aligned with the target flake, which is on a heated XYZ stage.

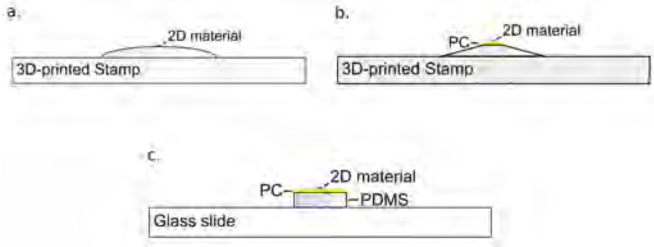

FIG. 2: (a) The first stamp design, composed of a solid 3D-printed polymer structure. (b) The second design, composed of a 3D-printed stamp with a conical hole going through it. The angles of the cone were determined using the numerical aperture of the microscope objective. PC film is on top of the hole. (c) The third design, composed of a glass slide with a PDMS toroid on top of it and PC film on top of that.

The first method we attempted used a 3D printed transparent polymer stamp in place of the assembly that is traditionally used. The theory was that the stamp would be designed with a raised section and a thin area around it (Fig. 2a). The raised section would be used to pick up the flakes, while the thin section would be where the laser melted the polymer. By making the stamp out of the polymer, we believed it would be possible to cut through it around the completed stack, and then dissolve the part that remained in a solvent, like chloroform.

Many different iterations were designed, but they all suffered from a variety of issues. While the stamps were transparent to the naked eye, under a microscope there were obvious lines and ridges which obstructed a clear view. These were caused by the printer, and marked the areas where two pieces of filament came into contact during printing. The stamp needed to be transparent in order for each layer to be aligned with the rest of the stack. The ridges also disrupted the smoothness of the polymer, making us doubt that it would be able to pick up the atomically thin flakes, which require a very smooth surface. For these reasons, this method was abandoned in favor of a similar one, which removed these problems.

The second technique also used a 3D printed stamp, but the design was such that it would never come in contact with the 2D material, theoretically eliminating the problem with the smoothness of the surface. The stamp was again designed with a raised section for picking up materials, but this time it had a hole running through it (Fig. 2b). This allowed imaging without requiring the stamp to be transparent. Polycarbonate (PC) film, made using a method demonstrated by J.D. Sanchez-Yamagishi,[4] was then placed over the hole using double sided tape to secure it in place. As PC is one of the polymers that is used in the traditional stacking method, we were confident that it would be smooth enough for pick up. Another benefit of having the hole through the stamp was that it allowed the laser to be used to cut a circle through the PC around the stack upon completion without it sticking to anything except the substrate. We tested these stamp designs by bringing them slowly against a substrate in order to see if they formed an obvious fringe between the portion in contact with the substrate and the portion which was not in contact, as was expected.

The first problem we found with this technique came when we first tried to melt the PC. The absorbance of PC over the blue wavelengths is very low, meaning our blue laser had no visible effect. This issue was easily resolved by combining the PC with a type of yellow dye which has a very high absorbance at 400nm. There were concerns that the dye might leave a residue on the stack after the PC was cleaned off, so a dye was found which dissolves in chloroform like PC does. We were able to easily melt a dyed film at low laser powers. The other problems we encountered were not as easy to solve. When bringing the stamp against the substrate, we did not see the expected clean pattern. Instead there were some areas touching the substrate and others not seemingly at random. It was determined that this arose for two reasons. First, because of wrinkles in the PC which caused certain areas to reach the substrate before they were expected to. The wrinkles were caused by imperfections in the stamp around the perimeter of the hole. Due to the resolution of the printer, it was not possible for us to make this edge smooth enough to eliminate all wrinkles in the PC. The other cause of the imperfect contact between the stamp and the substrate was the firmness of the 3D printed material. The silicone layer used in the traditional method allows the stamp to deform somewhat as it comes into contact with the substrate. Without this layer, the stamp was too rigid. Hence, we moved on to a third method based on this one.

The final method we investigated used the same materials that are traditionally used. A glass slide was used to provide support and ease of movement. A layer of PDMS, a type of silicone, was placed on top of this, with a dyed PC film placed over this, and held in place using tape. However, instead of a square of PDMS, we used a 3D printed mold to produce a cylinder with a hole through the center. Having a hole in the PDMS provided the same benefits as having the hole in the 3D printed stamp: we could see through it easily, and the PC could be cut without sticking to anything afterward. Using PDMS provided the deformability that was lacking in the previous method as well as providing a smoother surface for the PC to stick to, cutting down on the number of wrinkles that were observed. A diagram of the stamp is shown in Fig. 2c.

A stamp made in this manner was tested by bringing it slowly against a substrate. An obvious line moved across the surface, as expected. The stamp was then disengaged from the surface. It peeled back smoothly as well. It was then lowered again to confirm that the behavior was consistent. With the PC in contact with the substrate, we turned on the laser to 8.10V and, while keeping the laser focused, slowly raised the stamp. As we were unsure if the laser was successfully melting the PC, the power was increased to 8.70V as the stamp continued rising. Once the stamp had disengaged from the substrate, it was clear that the circle of PC inside the laser path had remained on the substrate as the stamp pulled away. With these tests completed successfully, we began attempting to pick up flakes. We lowered the stamp, with a new piece of PC on it, onto a substrate with a flake of hBN, which had been selected optically for smoothness. After the stamp was fully in contact, it was slowly lifted away. The hBN was not lifted off of the substrate, so the stamp was lowered again. This time once it was in contact the temperature was raised to 70^{o}C, and then cooled back down to room temperature. When the stamp was lifted, it successfully picked up the hBN flake.

Our first goal for using this method was to create a stack of hBN encapsulated MoS_2. Thus, our next step was to attempt pick up of a MoS_2 flake using the hBN flake on the stamp. We used the same method, bring the stamp slowly into contact with the substrate which held the flake. This time we had to be careful to keep the flake on the stamp lined up with the flake on the substrate, so that they would form a stack. However, when we brought the stamp down this time it did not come fully into contact with the substrate as it had before. We tried two different substrates, using several different flakes on each one, but were unable to make a smooth contact. After this, we determined that the PC film had most likely been damaged between the pick up of the hBN and the attempted pick up of the MoS_2, and restarted.

We picked up a hBN flake in the same was as before, except with only raising the temperature to 50^{o}C. A smaller flake picked up at this temperature, but the slightly larger flakes did not. Thus we determined that a higher temperature is preferable. After picking up the first flake, we attempted using it to pick up a MoS_2 flake. We brought the stamp most of the way into contact, but there appeared to be a bubble next to the flakes that led us to believe they were not fully touching. However, after we heated to 70^{o}C and cooled back down to room temperature and lifted the stamp, the MoS_2 flake remained attached to the hBN. This hBN-MoS_2 stack was then lowered onto a final hBN flake using the same method. Again a bubble appeared to form next to the flakes. Once in contact, the stack was again heated to 70^{o}C and cooled back down. Next the laser was turned on to approxi-

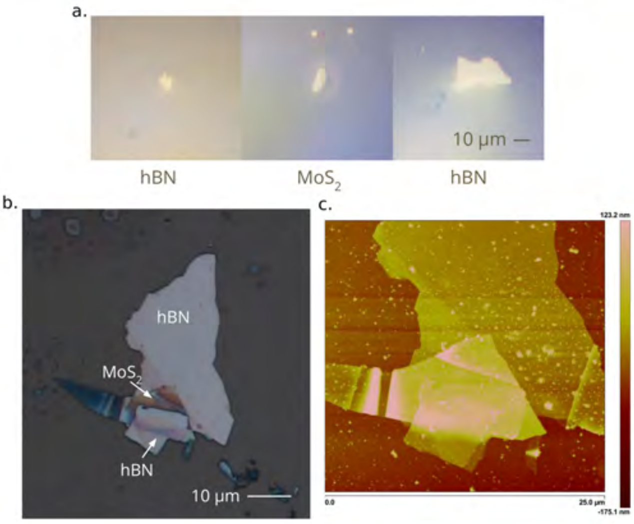

FIG. 3: (a) The three flakes on substrates before pick up. (b) An optical view of the completed stack. (c) AFM view of the completed stack. Image by J. Stacy.

mately 8.50V and kept in focus as the stamp was raised. This resulted in a circle of PC on the substrate with the stack under it. The final step was to remove the PC by first soaking in chloroform for 10 minutes, then soaking in IPA for 1 minute, then blowing dry using nitrogen. This resulted in a hBN-MoS_2-hBN stack on the Si/SiO_2 substrate (Fig. 3b).

We have shown that it is possible using the final method presented here to produce stacks of atomically thin materials while heating only to 70^{o}C, a decrease of more than 50% from the temperatures required by most techniques. This should allow higher quality heterostructures to be fabricated, leading to better devices based on those structures. Before that point comes, ways of cleaning the stacks will be required. An AFM image (Fig. 3c) made it clear that there is a large amount of unwanted material around and on the stack, which will need to be removed. After this, research into the quality of the stacks fabricated using this method will be required to see how they compare to stacks made using the traditional methods. If they compare favorably, then further optimization will be carried out on the stamp design.

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