Deterministic Dry Transfer of Multilayer h-BN Crystals using Poly Vinylchloride

BSc Thesis

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Abstract

Poly vinylchloride (PVC) is a promising polymer in the use of deterministic dry transfer (DDT) of 2D materials because it has a variable adhesion. Deterministic dry transfer using PVC promises a reliable method of transferring 2D materials and as such, it is ideal for the creation of Van der Waals (VdW) heterosructures. The adhesion of PVC can be controlled by outside conditions, such as temperature or velocity. However current research into VdW heterostructures is hold back by the limitations of the current methods for deterministic dry transfer. Current DDT methods rely on hazardous solvents in cleaning polymer residue after transfer and often have low yield rates. Fortunately, DDT with PVC has no need for hazardous chemicals, as such research into the specific conditions with which PVC can be used in the deterministic transfer method is needed. In this thesis the specific conditions for successful deterministic dry transfer using PVC are tested by developing a reliable and reproducible procedure for stamping h-BN flakes and then using the procedure to test the adhesion of the PVC under different conditions. As such a parameter-space is created within which the transfer of a h-BN flake succeeds without a need for hazardous solvents and a high success rate. We observe however two limitations to the use of the parameter-space namely; only flakes with an area less than 30x30 μm^2 can be successfully dropped and the flakes can only be dropped onto sapphire, which may be due to the high smoothness of sapphire.

Populaire samenvatting

Twee-dimensionele (2D) materialen bestaan uit meerdere lagen van ieder één atoom laag dik waarbij de atomen in de laag met covalente krachten aan elkaar vastzitten, maar de lagen onderling enkel vast zitten met zwakkere Van der Waals krachten. De lagen zijn zonder veel moeite van elkaar af te trekken, bijvoorbeeld door het gebruik van plakband. 2D materialen van maar een laag dik, ofwel monolaag, hebben andere eigenschappen dan als de 2D materialen meerdere lagen heeft, ofwel bulkmateriaal. Wanneer er verschillende typen 2D materialen op elkaar gestapeld worden heet de structuur een Van der Waals heterostructuur, zo genoemd omdat de lagen bij elkaar gehouden worden door Van der Waals krachten. Echter is het bouwen van deze structuren nog niet zo eenvoudig. 2D materialen worden op elkaar gelegd een voor een door middel van een deterministiche overdracht (DO) methode. Echter gebruiken huidige DO methoden polymeren en gevaarlijke chemicalïen om het polymeer residu na de

overdracht op te lossen en te verwijderen. Het gebruik van poly vinylchloride (PVC) als DO methode is volgens literatuur een interessant alternatief omdat het geen gevaarlijke chemicalïen vereist. Het gebruik van PVC als DO methode kenmerkt zich vooralsnog door een lage kans van slagen en onduidelijkheid over de specifieke condities waaronder de overdracht plaatsvind. In onze experminten vonden we een ruimte van condities waarbij oppakken en loslaten met behulp van PVC slaagt. Daarnaast zagen we ook dat de grootte van het stuk 2D materiaal en het ontvangende substraat waar het stuk op gelegd moest worden van groot belang was voor de slagingskans van het loslaten van het stuk 2D materiaal.

Contents

Chapter 1

Introduction

Since the isolation of graphene in 2004 [1], interest and research in 2D materials have grown significantly. Graphene, a 2D materials, has a different band structure than the bulk material it is derived from—graphite, [2]. The difference in band structure leads to different electrical and photonic properties that lead to new physics. [2].

2D materials have a crystal structure with strong in-plane covalent bonds, a so called layer. The layers are held together by comparatively weak out-of-plane Van der Waals forces. Therefore, these materials can be disassembled into mono-, bi-, or multilayers. By combining layers of different 2D materials we can create Van der Waals (VdW) heterostructures.

The heterostructures that can be built with 2D materials constitute an active and growing field of research [2]. As research into heterostructures offers a new and exciting look into the fundamental interactions between light and matter, while also promising outstanding applications in fields such as beam steering, modular mirrors [3], tunneling transistors and other nanophotonic and electronic devices [4].

A method of assembling VdW heterostructures by stacking different 2D materials on top of each other is known as the deterministic dry transfer method (DDTM). According to Castellanos *et al.* [5], the DDTM is preferable to wet methods such as the wedging method [6], the polyvinyl alcohol (PVA) method [7], and the evalcite method [8], due to the lack of hazardous solvents present in order to create a usable application.

The DDTM method uses exfoliated 2D materials, usually referred to as flakes. After exfoliation, flakes are randomly distributed on a donor substrate, the unpredictable nature of exfoliation is unusable for the direct assembly into VdW heterostructures, as such, flakes need to be transferred by a stamp. A stamp is usually made out of various viscoelastic or thermoplastic polymers with variable adhesion. The adhesion of the polymers can be controlled through external factors such as temperature or the velocities used during attaching and detaching of the flake. Consequently, one can readily fabricate VdW heterostructures in the lab with the use of a DDTM.

The most procedures using DDTM have limitations however, the need for hazardous solvents and the low yield of the methods make the construction of VdW heterostructures difficult. A promising polymer that is being used in DDTMs is PVC. PVC is a common, easy-to-use, and inexpensive viscoelastic polymer that needs no hazardous solvents [9–11]. However, in-house trials did not yield the same results as reported by Onodera *et al.* and Wakafuji *et al.* [9–11]. Thus, it is essential to find the specific parameter-space under which these results of a high success rate and no residue can be replicated, which constitutes the main goal of this thesis. Assuming that the viscoelastic and thermoplastic properties of PVC are key to the attachment to and later detachment from the flake, the velocities, acceleration, and temperatures dictate the adhesive behavior of the PVC.

This thesis has the following structure: In chapter 2 a quick overview of the theory and context of the thesis will be given, followed by the methods in chapter 3 used to obtain the results that are explained and discussed in chapter 4. The thesis ends with a conclusion and an outlook on new research directions.

Chapter 2

Background

The creation of Van der Waal (VdW) heterostructures relies on different 2D materials that are assembled with different deterministic transfer methods.

2.1 2D materials

Two-dimensional (2D) materials are comprised of a single plane of atoms that are one atom thick with covalent in-plane forces and weaker outer plane Van der Waals forces in between each plane. The limitation in one dimension gives these materials a different band structure than their bulk (three-dimensional) counterparts due to the effects of quantum confinement. The difference in band structure leads to interesting electrical and photonic properties [1]. Different mono-,bi- or multilayer 2D materials can be assembled into what is called a Van der Waals (VdW) heterostructure, named as such because of the Van der Waal forces keeping the different layers of 2D material together.

2.1.1 Van der Waal heterostructures

A Van der Waal (VdW) heterostructure is a stack of 2D flakes from different materials layered on top each other which can be compared to stacking Lego bricks. In Figure 2.1, 5 different 2D materials are depicted and compared to Lego bricks to illustrate the ease with which, different

2D materials could be combined and assembled into new VdW heterostructures.

Nevertheless, assembling these different layers into one stack requires considerable technical expertise, as the surfaces of each 2D material need to be flat, have no air bubbles, residue or defects for strong Van der Waal forces [2].

The possible applications of VdW heterostructures assembled from 2D materials, include tunnelling transistors, barristors and flexible electronics, as well as optoelectronic devices, including photodetectors, photovoltaics and light-emitting devices with unprecedented characteristics or unique functionalities [4]. These possible applications are however limited by the need for a deterministic way to transfer flakes after exfoliation.

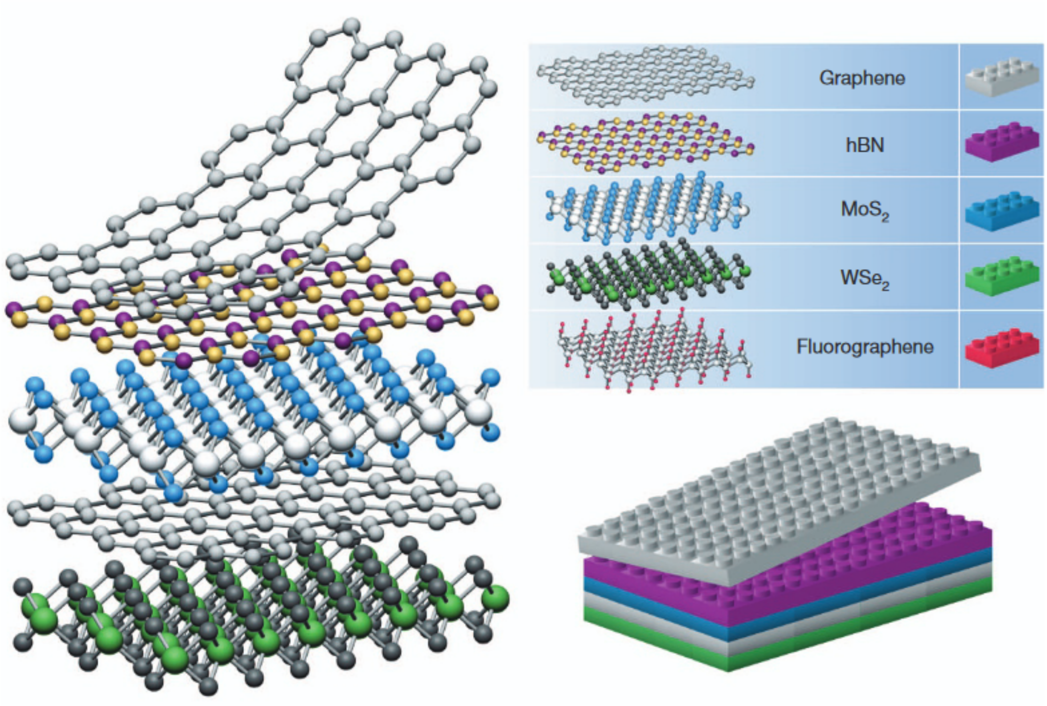


Figure 2.1: A possible construction of a Van der Waals heterostructure, the assembly is compared to building with Lego bricks [2]..

2.2 Deterministic stamping

2D materials are commonly exfoliated with the use of tape to create so called 'flakes'. This method, however, while useful in breaking the outer plane Van der Waal forces of the 2D materials, is entirely random in the placement of the flakes. The stochastic placement of the flakes during exfoliation methods means that reliable and direct placement onto the desired substrate, which is needed for the assembly of VdW heterostructures, is unlikely. To solve this problem, deterministic stamping methods have been developed to provide accurate and reliable placement onto 2D materials.

Deterministic stamping is the process of picking up a 2D material (flake) or multiple from a donor substrate and dropping the flake(s) off onto a acceptor substrate. The picking up and dropping off is done by a material (or combination thereof) called a 'stamp'. A stamp is usually built out of viscoelastic and thermoplastic polymers, which have a variable adhesion. The variable adhesion is necessary to drop the flake from the stamp onto the desired location after picking it up. The stamp's size and precise control over its location make it deterministic.

2.2.1 Overview current techniques

The need for deterministic placement of flakes onto a desired location for the assembly into VdW heterostructures has led to a multitude of deterministic transfer methods to transfer flakes. An overview of current techniques is given in the following section.

Deterministic wet transfer methods

There are three popular transfer methods involving wet chemistry and sacrificial polymer layers in the transfer of exfoliated flakes, the wedging method [6], the polyvinyl alcohol (PVA) method [7], and the evalcite method [8].

The wedging method works by creating a sacrificial hydrophilic layer of polymer which transfers the flakes using water as a medium. The hydrophilic polymer layer is dissolved with solvents. The PVA transfer method, requires flakes to be transferred onto a sacrificial polymer layer spin-coated onto a water-soluble PVA layer. After submerging the substrate in deionized water and dissolving the PVA, the polymer layer is brought out of the water and dried. The flakes are transferred onto the desired substrate after which the sacrificial polymer layer is dissolved with solvents. Finally, during the evalcite method, a glass slide is spin-coated with evalcite. The glass slide is mounted into a micromanipulator while the desired substrate is heated to 75-100 °C. After melting the evalcite by touching the heated substrate the flakes are transferred and the evalcite needs to be dissolved with solvents [5].

All three wet methods need to use hazardous solvents to remove polymer residue. The use of solvents means that the selection of 2D materials that can be transferred this way is limited and the use of hazardous solvents is also less favourable if safer methods can be found. Because of these limitations, dry transfer methods were developed.

Deterministic dry transfer methods

Deterministic dry transfer methods (DDTMs) are reliant on the use of polymers and their viscoelastic properties to transfer flakes onto desired substrates. An often used DDTM involves Polydimethylsiloxaan (PDMS). Where exfoliated flakes are transferred onto a layer of PDMS, which is then pressed onto the desired substrate before peeling it off very slowly. This method however leaves a relatively large amount of residue that needs to be cleaned [5].

Another DDTM relies on poly vinylchloride (PVC). According to results from Onodera *et al.* and Wakafuji *et al.* [9–11] PVC leaves no residue and the stamp can even be used multiple times. Because of these promising results, the properties of PVC will be deeper explored in the following section.

2.3 Properties of poly vinylchloride

DDTMs using Poly vinylchloride (PVC) have great results and leave no residue, needs no solvents and the same stamp can even be used multiple times [9–11]. PVC has been shown to have greater surface adhesion to flakes than other polymers [10]. Wakafuji *et al.* [10] and Onodera *et al.* [9] showed that PVC is able to pick up h-BN flakes with no edge contact needed only contact between PVC stamp and the surface of the h-BN flake was necessary for successful attachment to the stamp. It is, therefore, essential to understand what the properties of PVC are.

PVC is a polymer. Polymers are strings of repeating groups, monomers, attached with covalent bonds forming so called macromolecules [12]. Strings formed from these repeating groups can be hundreds of monomers long. In the case of PVC the repeating group is a vinylchloride

($H_2C{=}CHCL$) monomer.

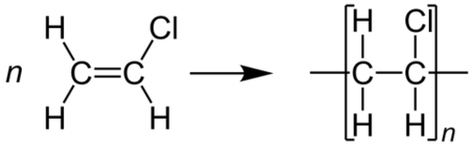


Figure 2.2: A monomer of a vinylchloride group alone (left) and in a chain of poly vinylchloride (right).

The structural properties of PVC are very dependent on the additives added. PVC in the form of cling foil has a high percentage (¿80%) of added plasticizers which make the polymer highly flexibel.
The PVC used in this thesis comes in the form of cling foil. Two brands are used in this thesis: ”Gwoon” and ”Riken”.

2.3.1 Viscoelasticity

Viscoelasticity is a property that PVC exhibits when it undergoes deformation, and it is the property that gives control over the adhesion of PVC which is necassary for DDTM.
Viscosity is the amount of resistance a material has in opposition to an applied external force, whereas elasticity is the ability of a material to return to its original shape after an applied external force disappears. So a viscoelastic polymer, such as PVC, has both viscous and elastic properties and as such exhibits time-dependent strain. The time-dependent strain leads to hysteresis, or the dependence of a system on the system’s history, which can be leveraged to achieve an asymmetric response.
The viscoelastic behaviour of PVC is closely tied to the phase of the PVC. PVC has multiple phases based on the temperature of the material. In Figure 2.3 the deformation of PVC, in response to a static weight as drawn in the middle of the plot, versus increasing temperature is plotted. The deformation is not linear to the temperature, but is instead dependent on the phase of the PVC. Four phases are plotted in Figure 2.3; First, the glassy state where PVC exhibits a more crystal like behaviour and the deformation only changes slightly. Second, the glass transition where PVC exhibits more soft matter like behaviour and the deformation changes sharply. Third, the rubbery state where PVC exhibits high elastic behaviour and

the deformation does not change. And lastly, the viscoelastic flow phase where PVC exhibits viscoelastic behaviour and the deformation changes markedly. The change in viscoelastic behaviour from 80 °C and 130 ° is the basis for the control over the adhesion needed for the deterministic dry transfer method.

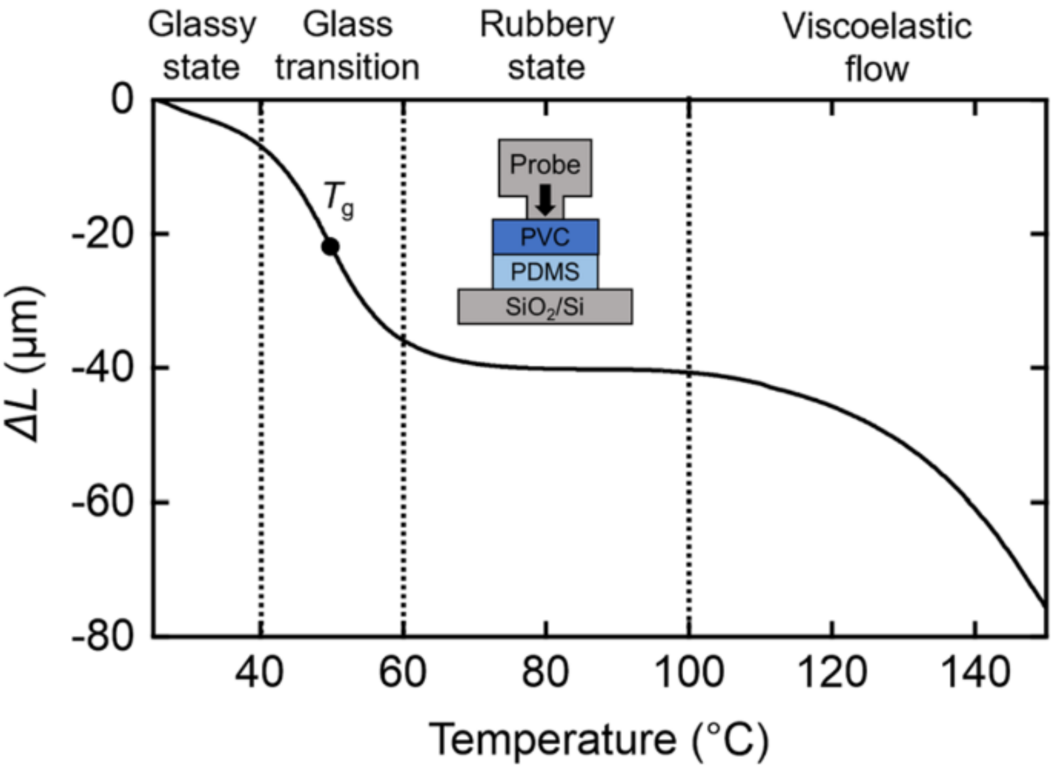


Figure 2.3: Thermomechanical analysis (TMA) results for 130-μm-PVC/PDMS stamp. The vertical axis shows the probe displacement ΔL. T_g is the glass temperature. Inserted is a schematic drawing of the TMA apparatus [9] .

2.3.2 Adhesion

In order to understand the control over the adhesion of PVC, it is essential to understand adhesion at an intermolecule level.

Adhesion describes the group of interatomic and intermolecular forces that act between two surfaces [13]. Adhesion forces are researched in multiple disciplinary topics such as: surface chemistry, surface physics, rheology, polymer chemistry, polymer physics and fracture analysis [13]. Awaja *et al.* [13] describes multiple forces of adhesion that may be the main force for driving the adhesion between the inert and flat h-BN flake and PVC stamp.

The hypothesis for this thesis is that the viscoelastic behaviour of the PVC influences the adhesion by changing the conditions between attachment en detachment. According to Awaja *et al.* [13] molecular bonding is the most widely accepted theory of adhesion. Molecular bonding is the intermolecule bonding created by dipole-dipole interactions, Van der Waals forces and chemical interactions (that is, ionic, covalent and metallic bonding). Molecular bonding mechanism need close direct contact between adhesive and flake [13], as such, defects, cracks and air bubbles can lessen the adhesion between the adhesive and the flake.

Chapter 3

Methods

In the following section the methodology, setups and experimental procedures, that are essential in finding a parameter-space for the successful transfer of flakes using PVC, are discussed and summarized.

3.1 Stamping

In order to create a parameter-space with which the DDTM using PVC is successful each time, it is essential to have a standardized experimental procedure. As such the standardized process of creating and using stamps made with PVC is discussed in detail in this section.
The stamping stage and microscope setup is detailed in Figure 3.1. The stamping stage used a Thorlabs KDC101 Kinesis K-Cube Brushed DC Servo Motor Controller to control the z-axis, while the x-,y-plane could be varied by a Piezo stage. The acceptor or donor substrate was laid on a copper heating element on top of another Piezo stage to align the stamp and substrate under the long working distance (LWD) objective.

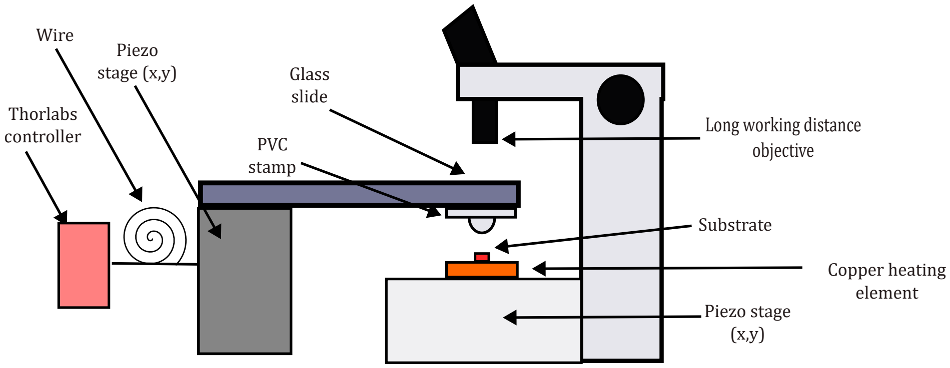


Figure 3.1: A schematic of the stamping set up used for DDTM.

The standardized procedure for creating stamps with PVC is done as follows:

- Prepare a clean microscope glass slide and place a cube of 5 x 5 x 2 mm^3 PDMS on top.
- Drop a glob of superglue on a separate glass slide.
- Using a pair of tweezers or another small tool, detach small drops of superglue from the larger glob onto the PDMS cubes to form domes, let the superglue cure for 1 hour.
- Take a clean part of the cling foil (PVC) roll to prevent contamination and place it over a clean workstation, see Figure 3.2 (a).
- Cut with a scalpel as many small squares of PVC as stamps you want to assemble, see Figure 3.2 (b).
- Cut with scissors small strips (10 x 2 mm^2) of one sided tape and place these on a separate clean glass slide.
- Place the strips of one sided tape over three of the sides of the PVC covering half of the strips with PVC so half the strip can attach to the glass slide.
- Stretch the PVC over the dome, and attach PVC square to the glass slide with the tape. Attaching the PVC squares to the glass on three sides, stretched over the dome, see Figure 3.2 (d).

- First attach the strip of tape to the still unattached side of the PVC before attaching it to the glass while stretching the PVC over the dome as tight as possible.
- Bake the stamps in a vacuum oven at 80 °C over night.

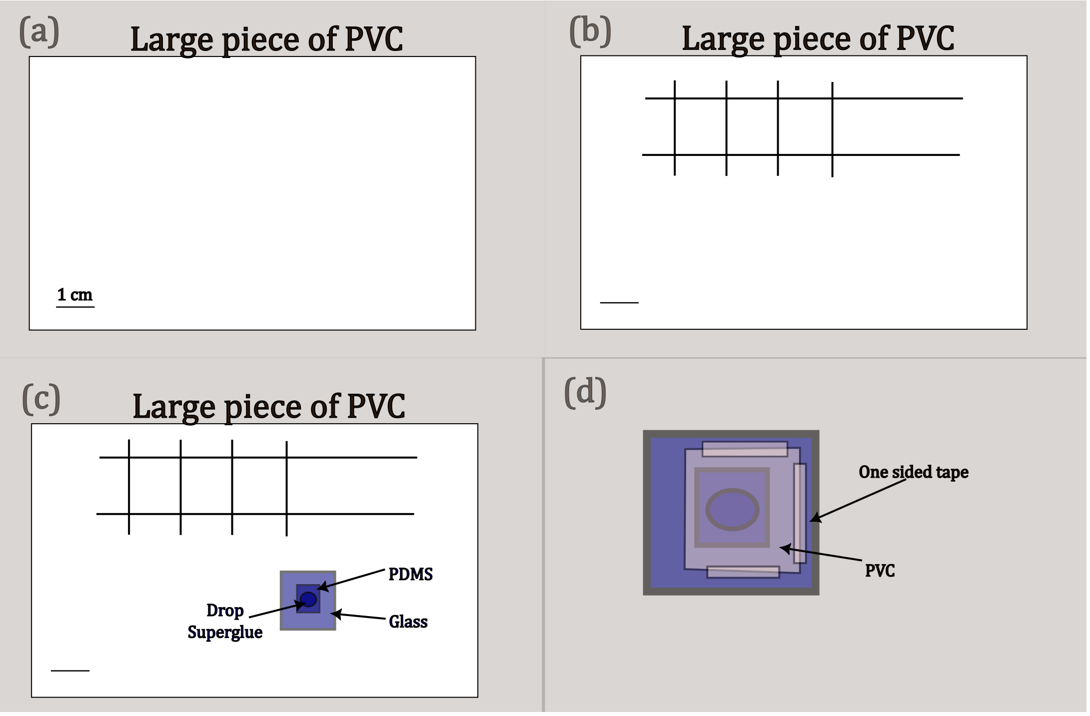


Figure 3.2: Four schematic drawings of cutting and layering the PVC cling foil ontop of the PDMS and superglue stamp. (a) A large piece of untouched PVC on a clean surface. (b) Squares cut into the large piece of PVC. (c) The stamp with PDMS and superglue on top of the large piece of PVC. (d) The stamp with PDMS and superglue being covered by a cut square of PVC attached with one sided tape at three sides.

In Figure 3.3 the standardized process of the deterministic dry transfer method can be seen. The dome created with a drop of superglue ensures a relatively small and thus precisely controlled contact area that can increase by lowering the stamp further, if needed.

The experimental procedure for deterministic dry stamping is detailed here.

- Find a flake with a surface area of around 30 x 30 μm^2 or less and 30 to 40 nanometers thick on the donor substrate. See Figure 3.3 (a).
- Hover the lower part of the domed structure on the stamp around 100 μm away on the x-,y plane from the desired flake so when you lower the stamp it does not hit the flake directly. Use the brightest spot on the dome to roughly locate the lowest part.
- Make contact with the substrate, this is visible by the change in colour. Lower the stamp further until the contact front fully covers the h-BN flake at a velocity of $V_{pick-up,attachment}$, an acceleration of $\alpha_{pick-up,attachment}$ and a temperature of $T_{pick-up}$.
- Wait 2 minutes while the flake is fully in contact with the stamp, see Figure 3.3 (b), before detaching the stamp at a velocity of $V_{pick-up,detachment}$, an acceleration of $\alpha_{pick-up,detachment}$ and a temperature of $T_{pick-up}$ until the contact front is no longer visible.
- Check to see if the flake is attached to the stamp by slightly moving the stamp and seeing if the flake moves along with the stamp.
- Replace the donor substrate with the acceptor substrate, and find an empty and clean location on the acceptor substrate.
- Attach the stamp with the picked up flake to the acceptor substrate at a speed of $V_{drop,attachment}$, $\alpha_{drop,attachment}$ and a temperature of T_{drop}, see Figure 3.3 (e).
- Wait 2 minutes before detaching the stamp at a speed of $V_{drop,detachment}$, $\alpha_{drop,detachment}$ and T_{drop}.
- See if the h-BN flake detached from the stamp, like in Figure 3.3 (f).

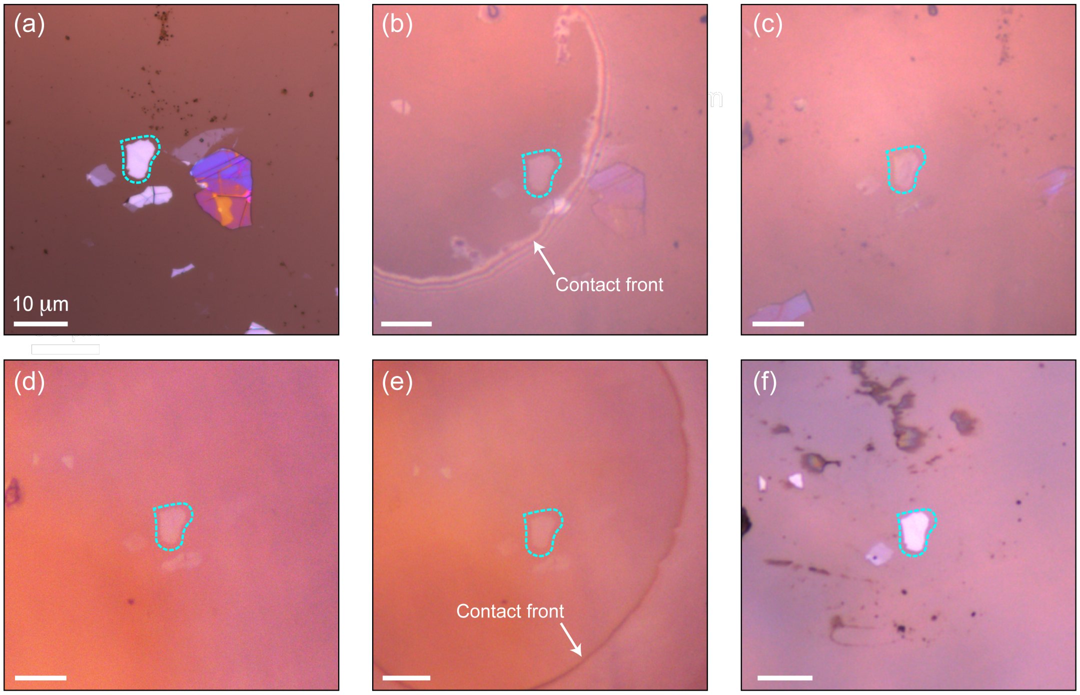


Figure 3.3: Six microscope images taken with 5x magnification. (a) The desired flake is located on the silicon substrate. (b) The contact front, between the PVC stamp and the silicon substrate, is visible while picking up the desired flake. (c-d) The desired flake is attached to the stamp which is no longer in contact with the silicon. (e) The contact front, between the PVC stamp and the sapphire substrate, is visible while dropping the desired flake. (f) The desired flake is successfully dropped on the sapphire substrate.

3.2 Optical spectroscopy

3.2.1 Fabry-Pérot Reflectrometry

To understand the thermalmechanical behaviour of PVC under different temperature regimes and to observe the phase transitions of PVC mentioned in Onodera *et al.* [9], Fabry-Pérot reflectrometry was performed.

Fabry-Pérot reflectometry uses thin-film interference, where light is reflected at normal incidence or under a slight angle α, the light passes through the thin-film and is reflected by the substrate beneath, see Figure 3.4. The substrate is assumed to be infinitely thick. The thickness of the film d and the phase differences between $R1$, $R2$,... and Rn can thus be related to each other. These different reflections will have different phases and as such interfere constructively or destructively with each other, showing periodicity in the spectrum like Figure 4.7.

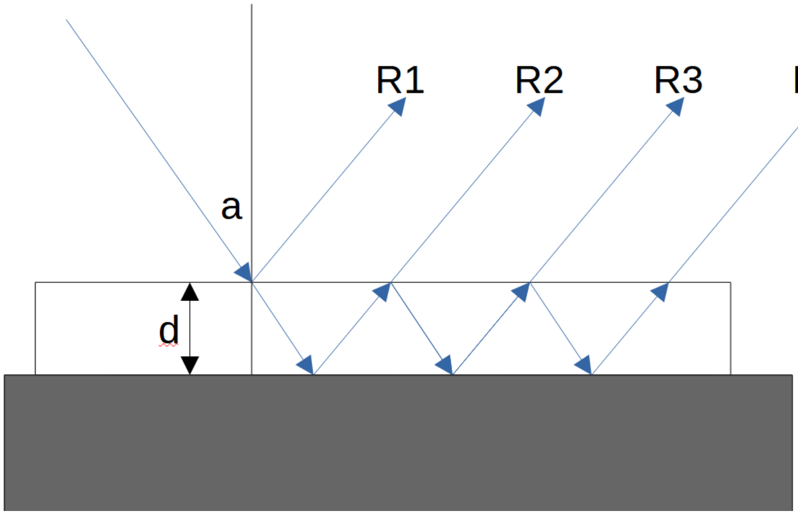


Figure 3.4: A schematic explanation of Fabry-Perot interference in thin films, with d the thickness of the thin-film and α the incoming angle of the light.

With the amount of fringes and the knowledge that destructive interference happens when waves are half out of phase, the path length difference and thus the thickness can be calculated using the known refractive index of the material and fitting the data to simulations using the transfer-matrix method (TMM) [14] and the differential reflectivity equation:

$$\frac{dR}{R} = \frac{R_{PVC} - R_{Substrate}}{R_{Substrate}} \tag{3.1}$$

The thickness of the polymer is calculated assuming the refractive index of the polymer remains constant over the temperature range, which is an approximation. The substrate used is silicone which has a strongly defined refractive index for the used wave length range and can as such be used for differential reflectivity.

Using the WITec alpha300 microscope and laser equipment, measurements of the charged coupled device (CCD) counts over a range of wave lengths were made, while slowly changing the temperatures of the sample stretched over a silicon-oxide substrate in discreet steps.

A LED light was used at 20% illumination power to prevent over-saturation of the CCD spectrometer. The measurements were done with 30 accumulations and 0.5 seconds integration time.

3.2.2 Raman spectroscopy

The deterministic dry transfer method relies on the viscoelastic and adhesive properties of the specific polymer that is being used to transfer the flakes as such it is essential to distinguish the polymers that are being used. The method used to distinguish the polymers in this thesis is Raman spectroscopy.

Raman spectroscopy is a way to measure the Raman scattering and as such the Raman shift of a material. Raman scattering is a form of inelastic scattering that occurs when the light of the laser hits the material and excites electrons to a virtual energy state, creating excitons. The electron immediately falls back a lower energy state, this state often has a different energy than the original energy state based on the type of scattering, as can be visualized in Figure 3.5. The different types of scattering are caused by phonons, where each phonon mode causes a different Raman shift. Phonons are quasi-particles that are used to define the vibrations in the lattice of a material. Each material has distinct and different Raman peaks due to the different phonon modes. As such we can use it to identify the material that is being used. The spectral shift is usually measured in cm^{-1}.

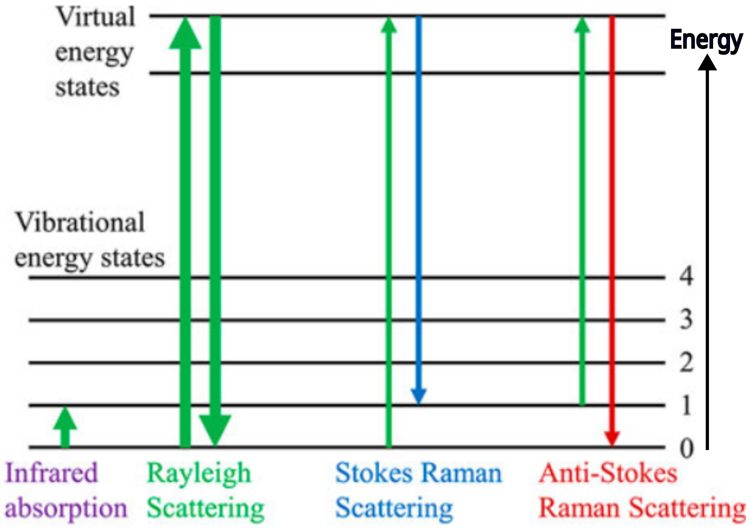


Figure 3.5: Energy level diagram of Raman scattering, Rayleigh scattering and infrared absorption with energy on the y-axis [15].

Using the Witec alpha300, a 532 nm laser, 100x magnification and a copper heating stage with a sticky patch the Raman peaks of the samples were measured. See Figure 3.6.
The focus was calibrated by observing the changes to the largest peak until the peak did not grow. The strength of the illumination of the 532 nm laser was lowered to 20% to prevent the over-saturation of the CCD spectrometer, which happens around 64000 counts.
With the movable camera a spot was found on the LDPE substrate with no folds or other deficiencies. The camera was removed from the optical path before the measurements.
The measurements were again made with an integration time of 0.5 seconds, 30 accumulations and at room temperature.

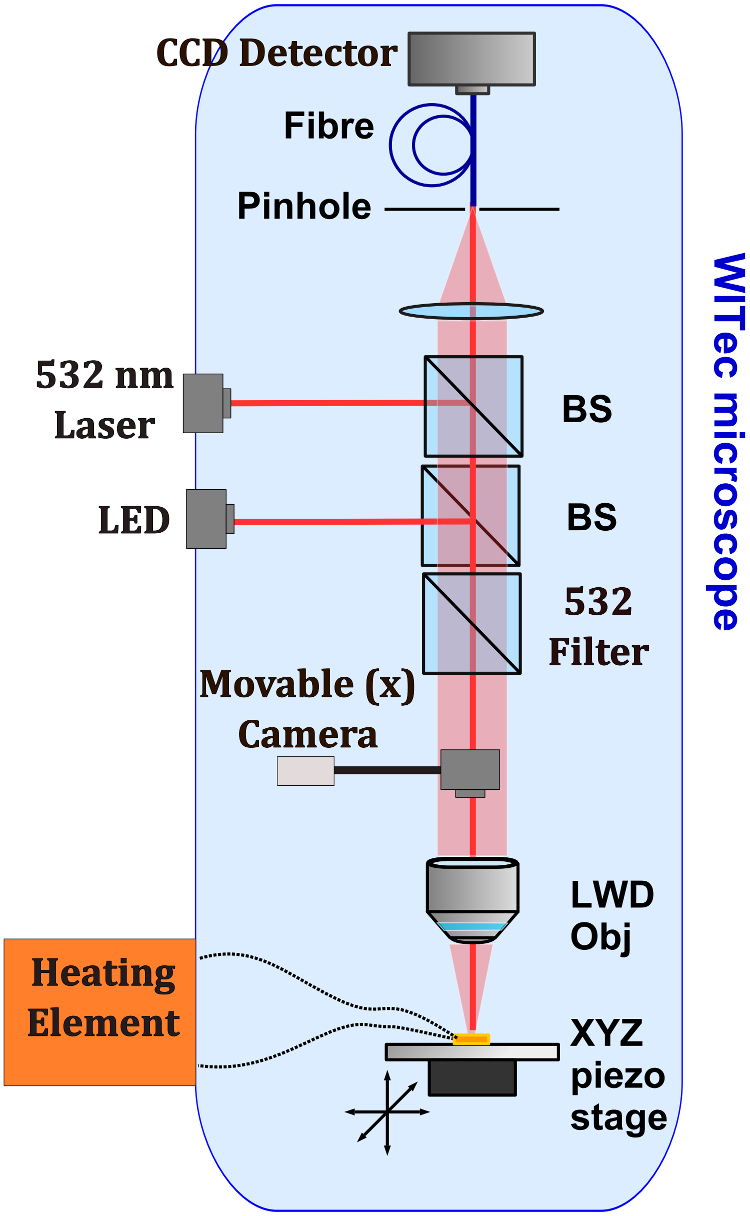


Figure 3.6: A schematic of the Witec alpha300 setup used, with beamsplitter (BS) and 532 nm filter. The camera can be moved in and out of the beam path in the x-axis.

Chapter 4

Results and discussion

In this section the results will be presented and interpretation of these results will be given. First, the results using cling foil of the "Gwoon" brand will be presented. Second, the results using "Riken" cling foil will be presented. And lastly the results and interpretations will be summarized.

4.1 Thermalmechanical analysis of "Gwoon" cling foil

Again the goal of this thesis is to find a parameter-space with a high yield and a high rate of success for the deterministic dry transfer method with PVC. It is essential that more is known about the thermalmechanical properties (TMP) of cling foil, to narrow down on the desired parameter-space. In order to know more about the TMP of PVC, Fabry-Pérot interferometry was performed with cling foil from the "Gwoon" brand as thin-film.

The temperatures used for the Fabry-Pérot interferometry range from 20 to 150 °C,in discrete steps of 10 °C. The thickness was calculated using the transfer-matrix method mentioned in Chapter 3. The best fits are then plotted in Figure 4.1, the thickness was calculated in discrete steps of 0,1 μm.

Plotting the thickness versus the temperature in Figure 4.1 was done to emulate the thermal-mechanical analysis (TMA) in Figure 2.3 and in order to illustrate the thermal properties of the material.

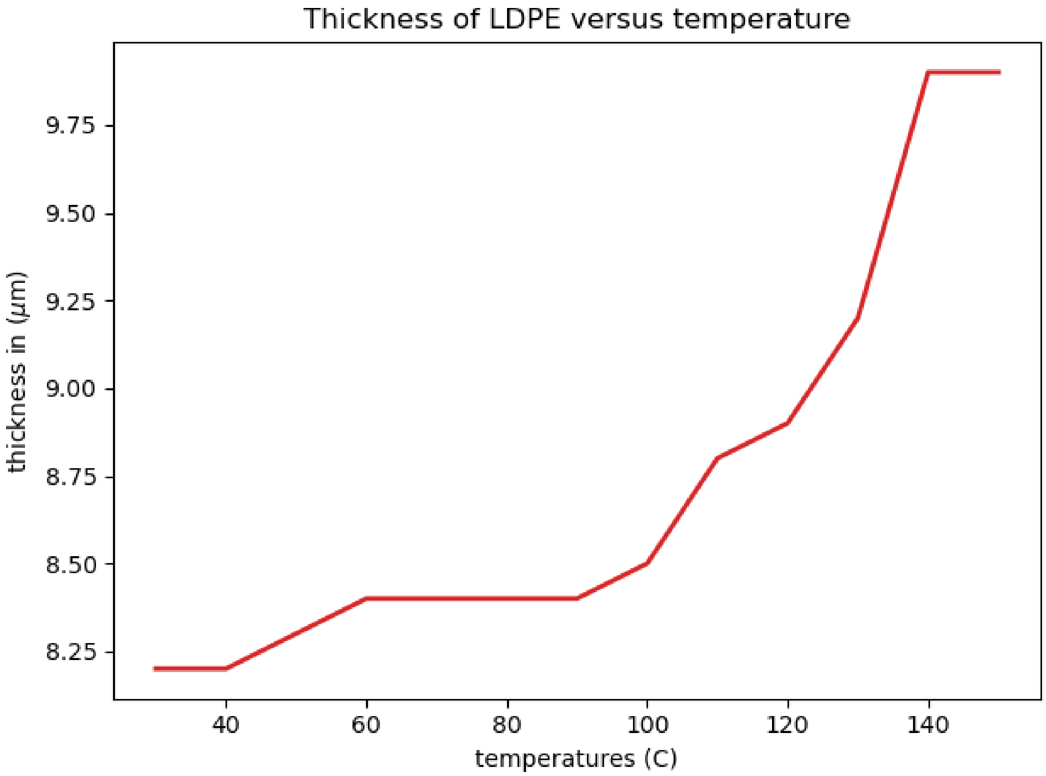


Figure 4.1: A graph plotting the thickness of LDPE (μm) as a function of temperature (°C), ranging from 30-150 °C.

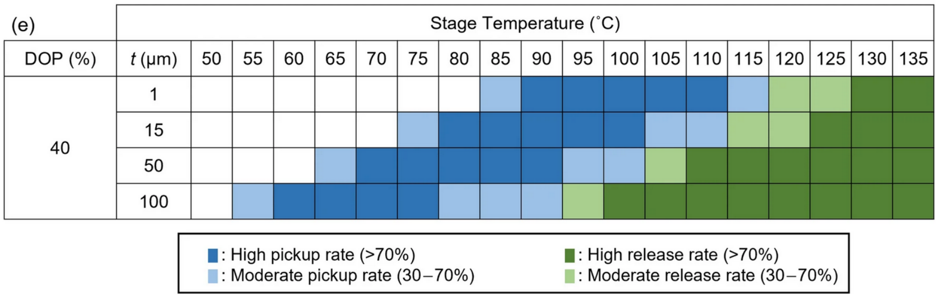
Observable from Figure 4.1 is an almost exponential jump in the thermal expansion around the 110-120 °C range, this jump may correspond to a phase change of the ”Gwoon” cling foil. The trend observable in Figure 4.1, does not compare very well to the results depicted in Figure 2.3. As there seems to be only one phase transition visible in Figure 4.1 unlike the four phase transitions depicted in Figure 2.3. The difference may be because the measurements were not performed under the same conditions, as there was no external force deforming the polymer during the Fabry-Pérot measurements.

4.2 Stamping with ”Gwoon” cling foil

After assuming the difference in phase transitions between Figure 4.1 and Figure 2.3 was from the difference in measurement. The deterministic dry transfer method using the ”Gwoon” cling foil began with the stamp creation procedure described in Chapter 6 and the deterministic dry transfer procedure described in Chapter 3.

T_{drop} was taken from Figure 4.2 to be $T_{drop} = 130°C$, assuming a thickness of 8-9 μm based on results from Figure 4.1. The initial $T_{pick-up} = 70°C$ was assumed from in-house trials with successful pick-ups. Initial $V_{pick-up,attachment}$, $V_{pick-up,detachment}$, $V_{drop,attachment}$ and $V_{drop,detachment}$ were chosen based on in house trials to be $V_{pick-up,attachment} = 10\mu m\ s^{-1}$,$V_{pick-up,detachment} = 1\mu m\ s^{-1}$, $V_{drop,attachment} = 10\mu m\ s^{-1}$ and $V_{drop,detachment} = 1\mu m\ s^{-1}$, the acceleration ($\alpha_{pick-up}, \alpha_{drop}$) was set to the minimum possible on the Thorlabs Controller, $\alpha_{pick-up}, \alpha_{drop} = 10\mu m\ s^{-2}$.

Figure 4.2 depicts a table containing the amount of plasticizer, dioctyl phthalate (DOP), within the PVC and four thicknesses versus temperature. It also contains the results of the pickup/release success chance at those parameters.



(e)		Stage Temperature (˚C)																	
DOP (%)	*t* (μm)	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120	125	130	135
40	1								🔹	🟦	🟦	🟦	🟦	🟦	🔹	🟢	🟢	🟩	🟩
	15						🔹	🟦	🟦	🟦	🟦	🟦	🔹	🔹	🟢	🟢	🟩	🟩	🟩
	50				🔹	🟦	🟦	🟦	🟦	🟦	🔹	🔹	🟢	🟩	🟩	🟩	🟩	🟩	🟩
	100		🔹	🟦	🟦	🟦	🟦	🔹	🔹	🔹	🟢	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

🟦: High pickup rate (>70%)
🔹: Moderate pickup rate (30–70%)
🟩: High release rate (>70%)
🟢: Moderate release rate (30–70%)

Figure 4.2: Test results for pickup/release using PVC stamps. PVC-thickness dependence of pickup/release for PVC with 40% DOP. Blue (green) cells indicate conditions under which pickup (release) is possible [9].

The results from the stamping with ”Gwoon” cling foil, using $T_{pick-up} = 70°C$, $V_{pick-up,attachment} = 10\mu m\ s^{-1}$, $V_{pick-up,detachment} = 1\mu m\ s^{-1}$, $\alpha_{pick-up}, \alpha_{drop} = 10\mu m\ s^{-2}$, are however, not similar as those reported in literature [9–11]. The values for $V_{drop,detachment}$ and T_{drop} that have been tested are recorded in Table 4.1, with the success rate.

All detachment tests done with ”Gwoon” cling foil were done with flakes larger than 30 x 30 μm^2 in area and with silicon as acceptor substrate. Picking up flakes was successful with the initial values assigned for T$_{pick-up}$, $\alpha_{pick-up}$ and V$_{pick-up}$.

$\mathbf{V}_{drop,detachment}$ / $\mathbf{T}_{drop}$	120 (C)	130 (C)	135 (C)	150 (C)
1 (μm s^{-1})	⬜	⬜	🟥	🟩
0.1 (μm s^{-1})	🟥	🟥		

Table 4.1: A table listing the combination of parameters used for each detachment test onto a silicon substrate. T$_{drop}$ refers to the temperature of the substrate and the immediate surroundings during detachment and V$_{drop,detachment}$ to the detachment velocity of the stamp from the substrate.
Light-gray cell are the combinations not tested. Red cells are failed drops. Green cells are successful drops.

In Table 4.1 can be seen, that only detachments of the desired flake from the stamp done at a temperature of 150 °C are successful. These successful detachments are, however, not dry, the polymer melts at that temperature leaving a large amount of residue, as can be seen in Figure 4.3. The residue shown in Figure 4.3 needs to be cleaned off before the dropped h-BN flake can be used. The cleaning is most often done with air plasma.

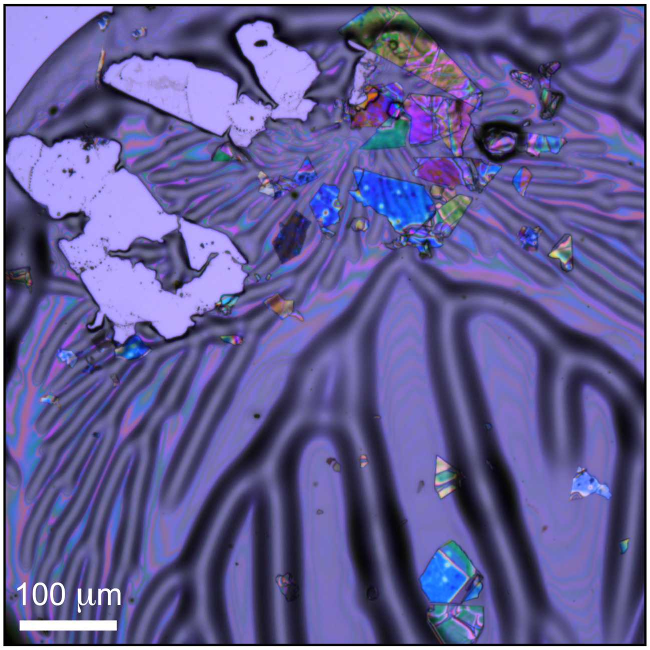


Figure 4.3: A microscope image with 5x magnification of the polymer residue and detached h-BN flakes after dropping a h-BN flake on a silicon substrate.

4.2.1 Difference in results

The findings in using a deterministic dry transfer method with ”Gwoon” cling foil are summarized as follows. Firstly, the trends in Figures 4.1 and 2.3 do not agree. Secondly, the only successful drop parameters recorded in Table 4.1 are when the cling foil melts and leaves a large amount of residue, which does not agree with literature [9–11].
The difference in results could be based on the false assumption that ”Gwoon” cling foil is made from PVC.

4.3 Raman spectroscopy of ”Gwoon” cling foil

In order to prove if ”Gwoon” cling foil is made out of PVC, a Raman spectral shift measurement was done. The results are explained in the following section.
A large stretch of untouched ”Gwoon” cling foil was unrolled from the roll and cut off. The

large piece was laid down on a clean surface to prevent contamination and the silicon substrate was laid on top with the polished surface touching the cling foil while pressing hard to prevent the forming of air bubbles. A square of the cling foil was cut away with an utility knife around the silicon substrate. The substrate with cling foil was pressed with a special cotton swab to push out air-bubbles, this process did create scratches as the special cotton swab was very firm. See Figure 4.4.

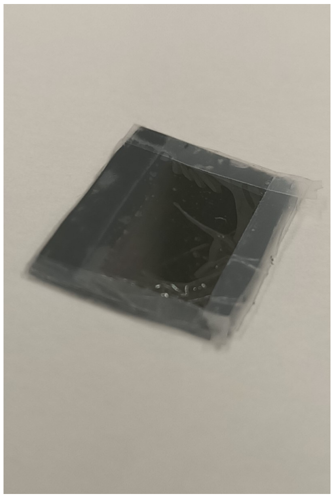


Figure 4.4: A picture of the "Gwoon" cling foil stretched over silicon substrate and attached with tape on all four sides.

In Figure 4.5, the total CCD counts are plotted versus the relative Raman shift in $1/cm$. There are numerous significant peaks with which the material can be identified. Especially noteworthy are the peaks at 1064, 1129, 1297, 1440, 2850, and 2883 cm^{-1}. The large peaks at 520 cm^{-1} and around 935-990 cm^{-1} are from the silicon substrate. Figure 4.5 was compared to existing literature [16, 17] in order to determine that "Gwoon" cling foil is not made from PVC but from low density polyethylene (LDPE).

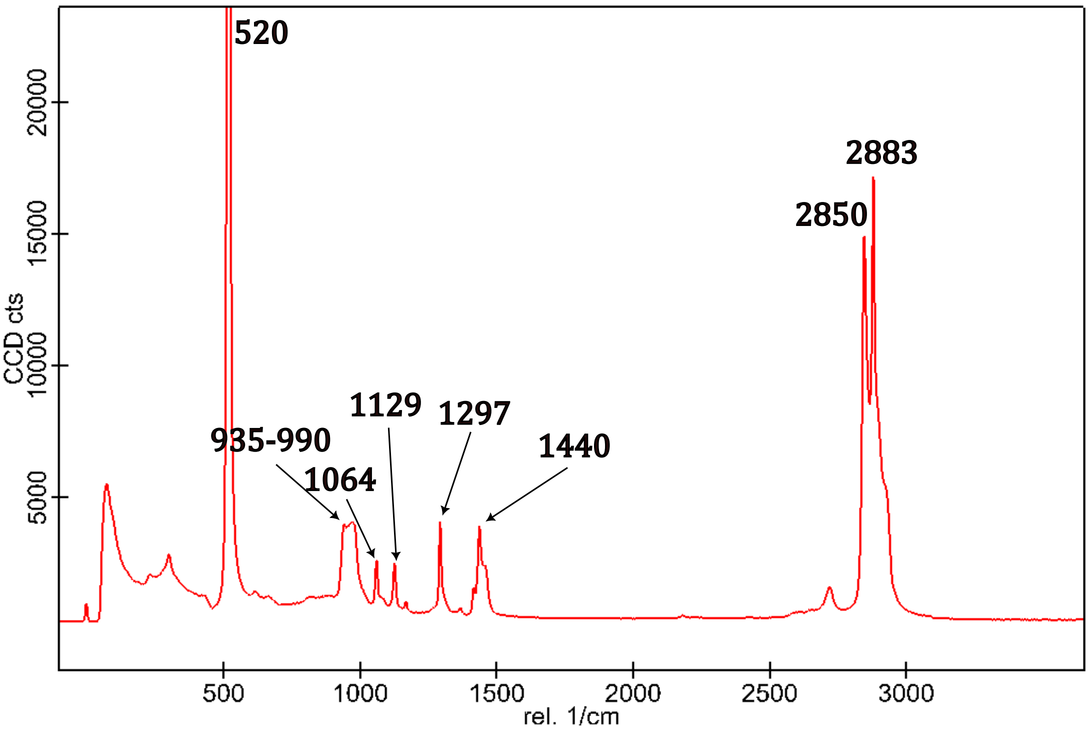


Figure 4.5: The measured Raman peak of LDPE stretched over a Silicon substrate, measured at room temperature. The result was compared with the measurements of [16].

The difference in between the in-house results and the literature can thus be explained by the difference in polymers.”Riken” cling foil mentioned in Onodera *et al.* [9] is instead being used as PVC.

4.4 Raman spectroscopy of ”Riken” cling foil

To ensure ”Riken” cling foil was indeed made from PVC the Raman spectral shift measurement was repeated. The results are explained in the following section.
In Figure 4.6, the total CCD counts are plotted versus the relative Raman shift in cm^{-1}. There are numerous significant peaks with which PVC can be identified but especially the peaks at 360, 635, 695, 1329, 1428, and 2916 cm^{-1}. The peak at 520 cm^{-1} is from the silicon substrate. The measurement was compared to [17] to determine that ”Riken” cling foil is made from PVC.

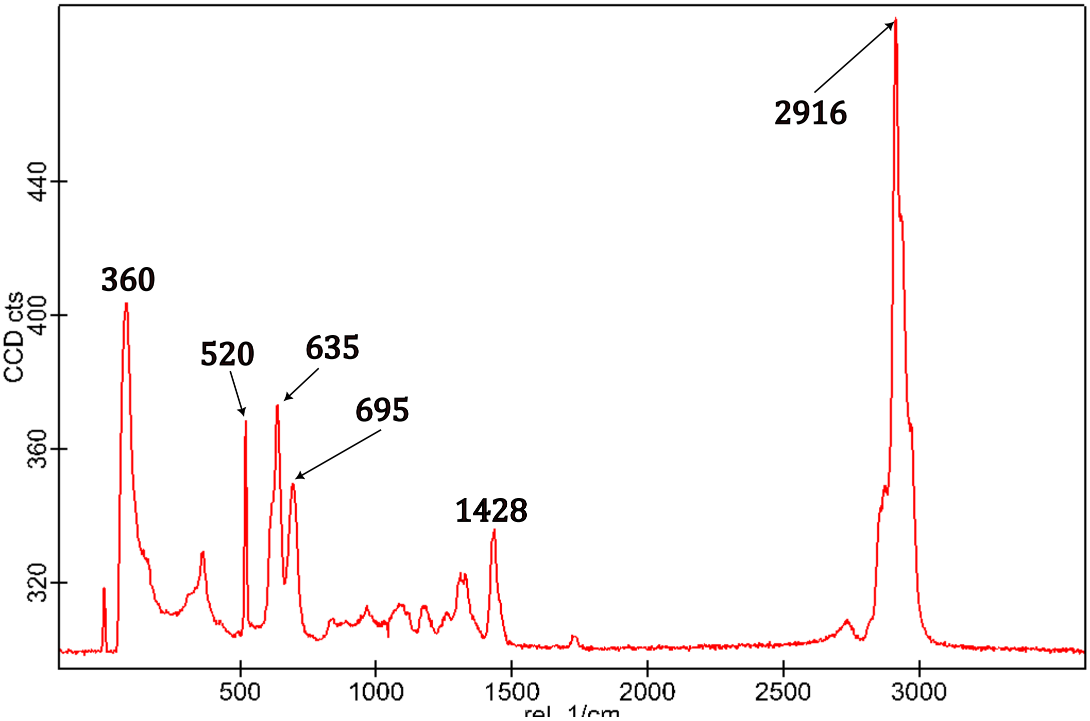


Figure 4.6: The measured Raman peak of PVC stretched over a Silicon substrate, measured at room temperature. The result was compared with the measurements of [17].

4.5 Thermalmechanical analysis of "Riken" cling foil

It is again essential to narrow down on the desired parameter-space before the DDTM using the "Riken" cling foil is tested. In order to know more about the TMP of "Riken"cling foil, Fabry-Pérot interferometry was again performed with the polymer as thin-film.
In Figure 4.1 the fitted thicknesses of the PVC, that were calculated using the TMM, are plotted versus the temperature. The calculated thickness was fitted along the differential reflection, as shown in Figure 4.7.

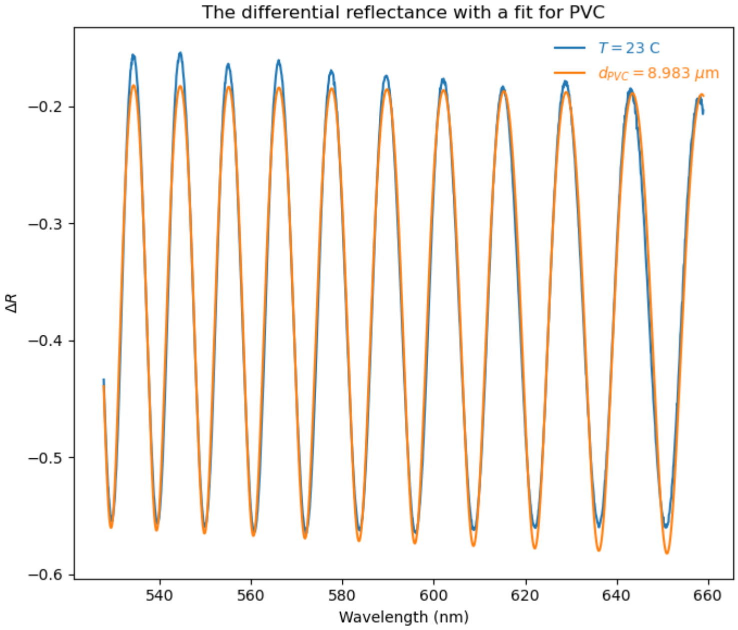


Figure 4.7: A plot of the differential reflectance versus wavelength using eq.3.1 at room temperature, with the fitted thickness calculated using the transfer-matrix method.

In Figure 4.7 the differential reflectivity of the ”Riken” cling foil on top of the silicon substrate at 23 °C is plotted in blue, while the orange plot is of the fitted differential reflectivity 3.1 calculated using the transfer-matrix method (TMM) [14] and a thickness of 8.983 μm. The thickness was fitted with smaller steps to create a more gradual plot of the best fits, see Figure 4.8. The Fabry-Pérot measurements were done in discrete steps of 3 °C.

There is a clear tipping point in the thermal expansion around the 100-110 °C range, after which the PVC shrinks. This transition may correspond to the phase transition from the rubbery to the viscoelastic state mentioned in Onodera *et al.* (2022) [9] and as shown in Figure 2.3. The possible phase change may be relevant as it is hypothesized that the phase change of PVC from rubbery to viscoelastic decreases the adhesion.

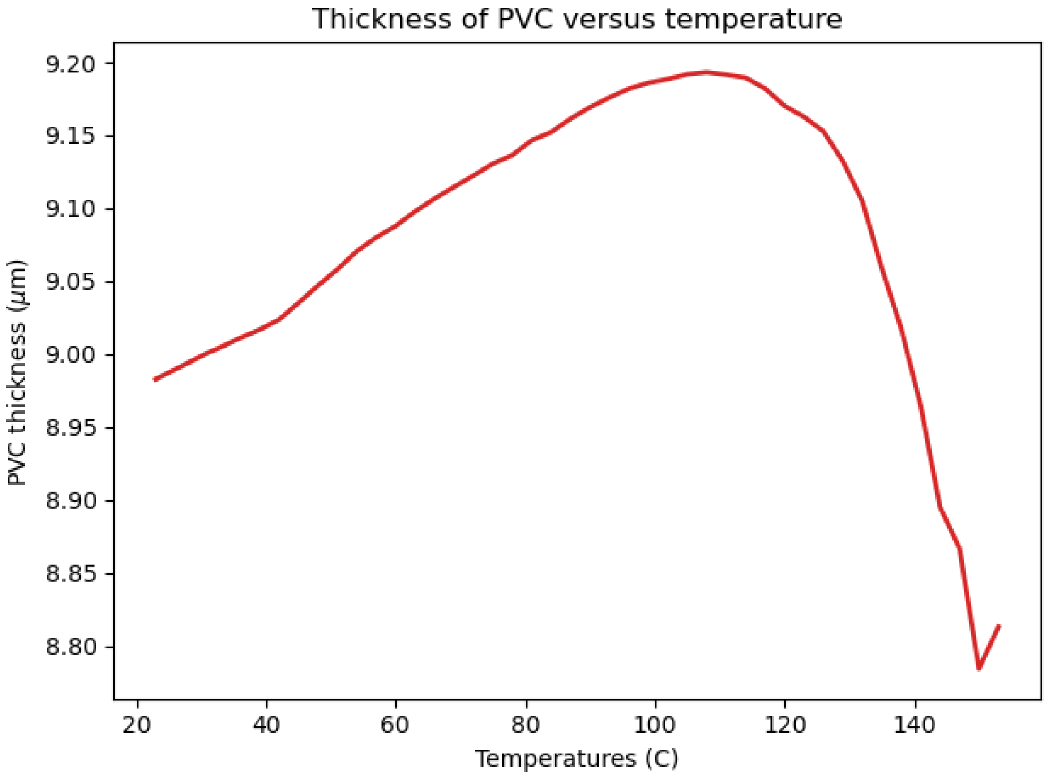


Figure 4.8: A graph plotting the thickness of PVC (μm) as function of temperature (°C), ranging from 30 °C to 150 °C.

4.6 Stamping with "Riken" cling foil

Initial $T_{pick-up}$ T_{drop} were chosen based on the results from Figure 4.2, Figure 4.8 and a thickness of 9 μm to be equal to 90 °C and 135 °C.

The results from the DDTM using PVC, with the following values, $T_{pick-up} = 70$°C, $V_{pick-up,attachment} = 10\mu$m s^{-1}, $V_{pick-up,detachment} = 1\mu$m s^{-1}, $\alpha_{pick-up}, \alpha_{drop} = 10\mu$m s^{-2}, are recorded in Table 4.2.

In Table 4.2 there seems to be a clear parameter-space (green) in which drops/detachments are successful. The 2nd attempt cell recorded at 5 μm s^{-1} and 150 °C refers to the fact that the detachmnet only succeeded on the 2nd attempt. From the parameter space in Table 4.2 it may be that the success rate of the dropping flakes is on T$_{drop}$ = 150°C. Yet it also may be that the success rate is dependent on V$_{drop,detachment}$ = 0.1μm s^{-1}. The success rate may also be dependent on parameter-space (green) and not V$_{drop,detachment}$ or T$_{drop}$ alone.

The drop success rate may also be dependent on the size of the flake as all detachment recorded in Table 4.2 were done with flakes smaller than 30 x 30 μm^2 onto a substrate of sapphire. All attempts done with flakes larger than 30 x 30 μm^2 failed to detach from the PVC stamp onto the sapphire substrate even while using the parameters that yielded success when using smaller flakes were used. All successful drops were done on a sapphire substrate, all detachments done on other substrates failed, as recorded in Table 4.3.

The substrates in Table 4.3 are listed in alphabetical order and in the second column is stated whether the detachment of the h-BN flake (smaller than 30x30 μm^2) failed or succeeded. The hypothesis for the failing of the detaching on non sapphire substrates is that the smoothness of the substrate is a deciding factor in the detachment this could be explained with Van der Waal forces. For strong VdW forces between surfaces the contact area between the surfaces needs to be as large and flat as possible, and thus as smooth as possible. The hypothesis is as such that sapphire has the largest smoothness of the substrates listed and used in Table 4.3.

V$_{drop,detachment}$ / **T**$_{drop}$	130 (C)	140 (C)	150 (C)
15 (μm s^{-1})	▨	▨	🟥
10 (μm s^{-1})	▨	▨	🟩
5 (μm s^{-1})	▨	▨	🟩 2nd attempt
1 (μm s^{-1})	▨	▨	🟩
0.1 (μm s^{-1})	🟩	🟩	🟩

Table 4.2: A table listing the combination of parameters used for each detachment test onto a sapphire substrate.

Light-gray cell are the combinations not tested. Red cells are failed drops. Green cells are successful drops.

Gold contacts	fail
Gold contacts with dodecanol	fail
h-BN crystal	fail
Sapphire	success
Silica (cleaned with IPA and ethanol)	fail
Silicon (not cleaned)	fail
Silicon (cleaned with IPA and ethanol	fail
Silicon with dodecanol on both sides	fail

Table 4.3: A list of substrates, where detachment of a h-BN flake of 30 x 30μm^2 was attempted. The success condition is if a flake detached from the PVC stamp onto the respective substrate with the parameters used in Table 4.2

The attachment of the flake to the stamp in the pick up phase of the stamping procedure did not succeed 100% of the time. On around half of the pick ups, a second or third attempt was needed before the flake attached to the stamp. Moving the initial contact point, the lowest part of the dome, around the flake, so the contact front came from a different angle in between each attempt may be the reason behind the success of the final pick up. In rare cases changing the initial contact front did not succeed in attaching the flake to the stamp on a second, third or even fourth attempt. The hypotheses for the cause of these failures is that the stamp was not clean or smooth enough for good adhesion to the flake. This is supported by the following observation, when the stamp was changed with another unused stamp the flake would be picked up successfully within 4 attempts.

4.7 To summarize

The goal of this thesis was to find a parameter-space using the deterministic transfer method with PVC and understand why deterministic dry transfer happens within a certain parameter-space. The parameter-space in which the transfer is successful, is recorded in Table 4.2. However, the goal behind the creation of parameter-space was for the use of creating VdW heterostructures. For the creation of VdW heterostructures there needs to be a high success rate in the deterministic transfer method to not waste too many precious 2D materials or too much time. It seems however that the results mentioned in Onodera *et al.* (2022) and Wakafuji *et al.* (2022) and (2020) [9–11] which, are contradicted here, are not reproducible or only with limitations, such as the smoothness of the substrate or the size of the flake. The failed attempts of dropping a h-BN flake on gold contacts or on a larger h-BN flake limit the possible uses of PVC as a useful polymer in deterministic transfer methods.

Chapter 5

Conclusion and outlook

5.1 Conclusion

To conclude this thesis, where the goal is to find a parameter-space with a high success rate for the deterministic dry transfer method using PVC to transfer h-BN flakes we record the results as follows. The DDTM using PVC to transfer h-BN flakes is a safe alternative to wet and dry DTMs with no need for hazardous solvents. The method leaves almost no residue in contrast to other DDTMs, such as with LDPE or PDMS. The use of PVC stamps in picking up h-BN flakes is reliable as long as a clean and smooth PVC stamp is used. Based on the results the successful transfer only succeeds if $V_{drop,detachment}$ and T_{drop} are within the found parameter-space. This parameter-space, however, has two limitations: the flake size and the acceptor substrates smoothness.

The deterministic dry transfer method using PVC transfers h-BN flakes with a high yield and a high success rate as long as the acceptor substrate is as smooth as sapphire, the parameter-space, for $V_{drop,detachment}$ and T_{drop}, is used and the flakes are smaller than 30 x 30 μm^2 in area.

According to Onodera et all [9] the use of poly vinylcholoride (PVC) as a polymer for deterministic stamping is very promising and can be used for the creation of interesting heterostructures. The results that the detachment is only successful on sapphire as is observed here is, however, in contrast with the findings from Ondera *et al.* and Wakafuji *et al.* [9–11] and does put certain limits on the use of PVC in the DDTM.

These limits however could be broadened and may even be stretched with research into the specific forces of adhesion that are present at the surface of PVC. Awaja *et al.* [13] and Wakafuji *et al.* [10] hypothesize that the main adhesion force of PVC may be static-electricity. Further research into the influence of the PVC phase on the strength of the electrostatic force and the importance of smoothness on the interatomic force, might explain or even stretch the limits found the deterministic dry transfer method using PVC in this thesis.

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Chapter 6

Supplementary

6.1 LDPE / ”Gwoon” cling foil

The method to prepare the stamp using LDPE or ”Gwoon” cling foil follows the following steps:

- Prepare a clean microscope glass slide, and layer a thin (0.5 mm) square (5 x 5 mm^2) sheet of Polydimethylsiloxaan (PDMS) on top.
- Lay a cube of 5 x 5 x 5 mm^3 PDMS on top of the glass slide next to the thin PDMS. Air plasma etch the glass slide with PDMS up to 2 minutes before placing the air plasma etched side of the PDMS cube on the thin film of PDMS for good adhesion.
- Drop a small bubble of superglue on the PDMS cube, let it cure for 1 hour.
- Stretch out the LDPE cling foil from the roll and press a large glass microscope glass on top of the LDPE, before cutting away the sides of the cling foil with a utility knife or scalpel.
- Cut small strips of double sided tape and create the borders of a square.
- Air plasma etch the LDPE and exposed superglue dome for up to 2 minutes before cutting the LDPE squares. Place them with the air plasma etched surface towards the superglue.
- Air plasma etch the created stamps up to a maximum of 30 seconds directly before use.