Optimization of Mechanically Assembled Van Der Waals Heterostructure Based On Solution Immersion and Hot Plate Heating

Xunyong Lei

International Center for Quantum Design of Functional Materials (ICQD), Hefei National Laboratory for Physical Science at the Microscale, and Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

xunylei@mail.ustc.edu.cn

Abstract. Layers of two-dimensional material are bonded together by van der Waals force, as a result, there is no need to take into consideration of the lattice mismatch in the formation of heterojunction, which is endowed with the characteristics of simple stacking in method, free of limitation to the type of materials and diverse changes. However, although the Van Der Waals heterojunction is relatively easy to stack, it is still difficult to generate inter-layer coupling between the thin crystal layers that form the Van Der Waals heterojunction. In most cases, the stacked heterojunction is simply stacked together without any new effects. Therefore, the realization of heterojunction coupling is a difficult problem to be considered in the process of preparing Van Der Waals heterojunction. In this paper, a method based on solution immersion and hot plate heating is proposed to optimize the mechanical stacking of Van Der Waals heterojunctions. It is found that the heterojunctions prepared by normal mechanical stacking method are usually uncoupled before treatment, but they can be stably coupled after treatment. Our method, simple, fast with low-cost, has been repeatedly verified to have a high success rate of coupling, which is suitable for most experimental groups to use and reproduce.

Keywords: Van Der Waals Heterojunction, Transition Metal Chalcogenides, Mechanical Stacking, Interlayer Coupling.

1. Introduction

Two-dimensional materials have become a hot area of research in condensed matter physics after graphene is discovered. The two-dimensional material based inter-layers are bonded together by Van Der Waals force, as a result, it is easy to form many thin layers and monolayers by mechanical stripping method. At the same time, these thin layers and monolayers can also be stacked together using a micro-optical manipulator by mechanical stacking method, which are bonded together by Van Der Waals forces to form a van der Waals heterojunction [1]. Since there is no need for lattice matching between layers of the Van Der Waals heterojunction, so any two kind of materials can be bonded together in theory.

At present, the achievements pertinent to Van Der Waals heterojunction emerge one after another in an endless manner. The Van Der Waals heterojunction has become one of the most productive research objects in the field of two-dimensional materials from enhancement of graphene properties on
the ultra-flat surface of HBN in HBN-graphene heterojunctions [2], to Interlayer excitons in double layer transition metal chalcogenides [3], and then to twisted Angle transition metal chalcogenide heterojunctions and magic angle graphene [4-6] in recent years. However, it is not easy to achieve the coupling of the heterojunction in the experiment, and many experimental groups failed to achieve the coupling of the heterojunction in the process of studying the heterojunction. Therefore, how to realize the coupling of heterojunction is a long-standing experimental problem.

Currently, in order to enable the heterojunction coupling, there have been some processing methods, such as to remove the organic defective gum on the material surface in order to get a clean surface by using acetone [2], to get a better adhesion of the heterojunction through long time annealing [7], and to use hydrophilic/hydrophobic transfer of samples [8]. These methods have been popularized and used to a certain extent with good results.

We have improved the traditional stacking method using PDMS as the stacking medium [9]. In the process of sample preparation using mechanical stacking method, the monolayer sample is prepared on PDMS and then transferred to silicon wafer. The sample is then cleaned with acetone, isopropyl alcohol and deionized water. After initial drying, the coupled heterostructures are stabilized by heating. Our improved method, with simple processing, is operable for all laboratories with low cost and easy repetition, which saves time and efforts. It is suitable for general experimental sites and can greatly improve the coupling probability of heterojunction. Taking the transition metal sulfur compounds (TMDs) as an example, this paper describes double transition metal sulfur compounds heterojunction by using our preparation method, and a new interlaminar exciton emission peak and a new interlaminar Raman model have been measured in the region of heterojunction, confirming that interlayer couplings exist in heterojunctionafter processed. We stack different types of heterojunctions by changing the types of transition metal chalcogenides, and the interlayer coupling phenomenon can be found in all of them, which proves that our experimental method is universal.

2. Experimental Results and Discussions

TMDs is a two-dimensional semiconductor material with direct band gap luminescence in a single layer. The chemical formula is Mx2, where M is a transition metal element, M=Mo, W; X is a chalcogenide element, X=S, Se, which is characterized with a hexagonal lattice structure (Fig. 1 (a)). Coupling may occur when different TMDs monolayers are stacked using the mechanical stacking method, intercambium excitons [3] are made by overlapping of energy bands, as shown in Fig. 1 (c). However, in actual experimental operations, due to insufficient stacking or excessive fluctuation of the sample surface, the layer spacing between the upper and lower TMDs is too large, and the electronic states between the upper and lower TMDs fail to overlap, so the failure in coupling is generated. At this time, the heterojunction is in an uncoupled state [10].
Figure 1. (a) Crystal structure of single-layer TMDs; (b) Uncoupling between layers caused by excessive layer spacing; (c) Interlaminar excitons generated by interlaminar coupling in a bilayer TMDs heterojunction.

The distortion and undulation of the thin layer samples during mechanical stacking are the important reasons for no coupling. As shown in Figure 2 (a), in the process of transferring samples to the silicon wafer by PDMS, the samples on the PDMS are generally intact and flat. However, in the process of fitting with the silicon wafer, there is a gap between the thin layer sample in general conditions and the substrate because PDMS fails to reach a complete and uniform contact with the silicon wafer [9]. This effect persists as other thin layers of samples are transferred to the wafer for stacking, so that the thin layers of samples on the wafer do not touch each other well. The result is a heterojunction with poor coupling and poor contact.

Figure 2. (a) Interlayer decoupling caused by sample fluctuation; (b) Mechanical stacking using solution immersion and hot plate heating.

Our method is an optimization of the above mentioned mechanical stacking method using PDMS as the transfer medium. After preparing the thin layer sample on PDMS, we have to transfer the
samples to the silicon chip, and it is soaked with acetone for 10 minutes to remove the residual glue brought by PDMS on the thin layer surface. Isopropyl alcohol was used for 3 minutes to remove acetone, and deionized water was used for 3 minutes to remove isopropyl alcohol. After soaking, air was used to gently blow the surface of the silicon wafer as soon as possible to slightly remove the deionized water of the silicon wafer to prevent residual water stains. After rapid blow-drying, there is still a certain amount of solution in the gap between the thin layer sample and the substrate, the sample and the substrate will adhere closely to the solution due to the presence of the solution. The solution gradually evaporate and dissipate by heating the hot plate. In this process, the material and the substrate will always maintain good contact with the solution until the solution evaporates, and the material can be combined with the substrate more evenly and closely.

![Figure 3](image_url)

**Figure 3.** (a) Flat hBN sample on silicon wafer; (b) Stacking single layer WSe₂ on the surface of hBN; (c) Washing and soaking WSe₂ in solution; (d) Heating WSe₂; (e) Stacking a single layer of MoS₂ on the surface of WSe₂; (f) WSe₂-MoS₂ heterojunction after cleaned and soaked; (g) WSe₂-MoS₂ heterojunction after heated; (h) Position of WSe₂ and MoS₂

In order to verify the reliability of our experimental method, we initially prepared a relatively thick (hundreds of nm) but clean and flat hBN sample on the silicon wafer, as shown in Figure 3 (a). We stripped a single layer of WSe₂ samples on the PDMS and stacked them on the hBN samples, as shown in Figure 3 (b). In can be found that there are areas of different contrast on the surface of hBN, which is the result of the bubbles and wrinkles due to stress, uneven bonding and other factors. We then soaked it with the three solutions described above, as shown in Fig. 3 (c), and we found that bubbles still existed on the surface of WSe₂, with no visible difference from Fig. 3 (b).

However, after being heated by a hot plate at 150°C for 3 minutes, the bubbles and wrinkles on the surface of WSe₂ disappeared, as shown in Figure 3 (d), which indicated that the surface of WSe₂ was greatly stretched and evenly fitted to the flat surface of hBN, so there were no bubbles and wrinkles. Then we continued to prepare single-layer MoS₂ samples in PDMS and repeated the mechanical stacking process to stack MoS₂ on the surface of WSe₂, as shown in Figure 3 (e). We found that there were not many bubbles and folds in the WSe₂-MoS₂ heterojunction region at this time. As shown in Figure 4, we measured the PL spectrum (yellow line) of the WSe₂-MoS₂ heterojunction at this time, and it is discovered that the signal of the yellow line was equal to the simple superposition of the PL spectrum of the monolayer MoS₂ (red line) and the PL spectrum of the monolayer WSe₂ (blue line), and no PL peak of interlayer excitons was found, nor any other phenomena were found.

We soaked the prepared heterojunction in solution, as shown in Fig. 3 (f), and we found that the bubbles and folds increased, indicating that the solution immersion made the bonding between WSe₂ and MoS₂ closer. We repeated the measurement in Fig. 3 (e) for the sample in Fig. 3 (f), and there was no significant difference in PL spectra before and after immersion in the solution. We put the soaked
WSe$_2$-MoS$_2$ heterojunction on a hot plate and heated it at 150°C for 3 minutes, as shown in Fig. 3 (g). It is shown as:

![Image](image_url)

**Figure 4.** MoS$_2$, WSe$_2$, and PL spectra of WSe$_2$-MoS$_2$ heterojunction before and after heating. Among them, MoS$_2$ is 1/3 of the actual luminescence intensity, and WSe$_2$ and WSe$_2$-MoS$_2$ heterojunction before heating is 1/40 of the actual luminescence intensity.

The bubbles and wrinkles are slightly darker in color, indicating that the solution (deionized water) is removed in heating process, which allows the upper and lower layers of the sample to bond more closely. According to the characteristics of heterojunction coupling that have been mentioned, a large number of bubbles and wrinkles tend to appear at the interface of heterojunction coupling. We re-measured the PL spectrum of the WSe$_2$-MoS$_2$ heterojunction region, as shown in the green line in Figure 4, and found that the following changes occurred in PL spectrum: 1. The luminescence intensity is equal to 1/40 of that of WSe$_2$-MoS$_2$ heterojunction before heating, and the luminescence intensity is greatly reduced. 2. Interlayer exciton signals are generated, and the luminescence intensity is much higher than that of monolayer WSe$_2$ and MoS$_2$. These phenomena are consistent with the reports of interlaminar excitons in the double-layer TMDs heterojunction.

![Image](image_url)

**Figure 5.** Raman mode comparison of WSe$_2$, MoS$_2$, and WSe$_2$-MoS$_2$ heterojunction before and after heating.
To further verify our conclusion, we also measured the Raman spectra of monolayer MoS$_2$, monolayer WSe$_2$, WSe$_2$-MoS$_2$ heterojunction before heating, and WSe$_2$-MoS$_2$ heterojunction after heating, as shown in Fig. 5. The single-layer WSe$_2$ enjoys a degenerate $E''_{2g}$ and $A_{1g}$ characteristic Raman mode (255 cm$^{-1}$). Single layer MoS$_2$ is characterized with a $E'_{2g}$ mode (387 cm$^{-1}$) and a $A_{1g}$ mode (405 cm$^{-1}$). We found that the Raman mode of WSe$_2$-MoS$_2$ heterojunction before heating was basically the same as the simple superposition of Raman mode of single-layer WSe$_2$ and MoS$_2$ in the whole wave-number range, while the WSe$_2$ $E'$ mode of WS$_2$-MoS$_2$ heterojunction after heating showed an obvious red shift (about 5 cm$^{-1}$) compared with that of single-layer WSe$_2$, as shown in Fig. 5 (a). At the same time, a 2LA(M) pattern near 260 cm$^{-1}$ exists for WSe$_2$, which produces a red shift (about 7 cm$^{-1}$) in the heated WSe$_2$-MoS$_2$ heterojunction. This shows evidence that WSe$_2$ is affected by MoS$_2$.

Most notably, two new Raman modes appeared in the WSe$_2$-MoS$_2$ heterojunction at the 280-320 cm$^{-1}$ wave-number segment. The new mode with a wave number of 284 cm$^{-1}$ is a $E''_1$ mode that only appears in the odd-numbered multilayer MoS$_2$[11]. In the even-numbered multilayer MoS$_2$, this mode will be transformed into a $E'_{1g}$ mode due to the change of symmetry, which will not appear in the single-layer MoS$_2$. The new mode with a wavenumber of 309 cm$^{-1}$ is the Raman $B^{1}_{2g}$ mode of WSe$_2$[12]. It is an out-of-plane Raman pattern that only exists in two or more layers of WSe$_2$. Therefore, we can confirm that inter-layer coupling does exist between WSe$_2$ and MoS$_2$.

For the wave-number segment of single-layer MoS$_2$, characteristic Raman mode, the wave-number of single-layer MoS$_2$ is the same as that of WSe$_2$-MoS$_2$ heterojunction before heating, but after heating, both $E''_{2g}$ modes and modes $A_{1g}$ appear red shift. The change of $E'_{2g}$ mode of MoS$_2$ after heating also verifies the existence of inter-layer coupling between MoS$_2$ and WSe$_2$.

We also changed different TMDs materials to stack MoS$_2$-WS$_2$ heterojunction and WS$_2$-WSe$_2$ heterojunction for repeated experiments, as shown in Figure 6. We found the presence of interlayer excitons in the low energy region of PL spectrum in the final heterojunction region. Therefore, our experimental method is universal and effective for different types of materials.

A hot plate is heated and treated in the same way as annealing, but the physical process is completely different. According to the reported work, annealing treatment is generally carried out in the environment of 100-300°C and high vacuum, and the duration lasts usually 3-12 hours, and the strategy of low temperature/long time natural cooling is usually adopted. Annealing treatment can be considered to provide energy to the heterogeneous junction which is not completely stacked. In the continuous heating process, the lattice slowly stretches, passes the energy barrier from one system to another, and slowly changes from a disordered stacked state to an orderly flat contact state. Therefore, long heating and high vacuum environment are required. But the physical process of combination of solution immersion and hot plate heating are quite different.

The solution acts as a adhesive, transforming the thin layers of the upper and lower layers from untightly bonding to tightly bonding. It can quickly evaporate from the gap between the upper and lower layers during a brief heating process. But, until it evaporates, it continues to hold the upper and lower layers together through the tension of the liquid. Therefore, high vacuum is not required in heating process, and nor several hours of heating is required. Only a short period of low temperature heating is sufficient to complete the process of heterojunction uncoupling to coupling.
Figure 6. (a) MoS$_2$-WS$_2$ heterojunction and its interlayer excitons after processed; (b) WS$_2$-WSe$_2$ heterojunction and its interlayer excitons after processed.

3. Conclusion
This paper introduces a simple mechanical stack based optimization method, the methods of solution soaking and hot plate heating is combined with the PDMS based mechanical stacking method. Taking the two-layer TMDS heterojunction as an example, it is proved that our method can effectively realize the interlayer coupling of heterojunction, and the time and consumption are made with relatively low cost, so it is suitable for the ordinary heterojunction stacking process.

References
[1] Geim A K, Grigorieva I V. Van der Waals heterostructures. Nature, 2013, 499(7459): 419-25.
[2] Dean C R, Young A F, Meric I, et al. Boron nitride substrates for high-quality graphene electronics. Nature Nanotech, 2010, 5(10): 722-6.
[3] Fang H, Battaglia C, Carraro C, et al. Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides. Proc Natl Acad Sci USA, 2014, 111(17): 6198.
[4] Tran K, Moody G, Wu F, et al. Evidence for moiré excitons in van der Waals heterostructures. Nature, 2019, 567(7746): 71-5.
[5] Seyler K L, Rivera P, Yu H, et al. Signatures of moiré-trapped valley excitons in MoSe2/WSe2 heterobilayers. Nature, 2019, 567(7746): 66-70.
[6] Jin C, Regan E C, Yan A, et al. Observation of moiré excitons in WSe2/WS2 heterostructure superlattices. Nature, 2019, 567(7746): 76-80.
[7] Kunstmann J, Mooshammer F, Nagler P, et al. Momentum-space indirect interlayer excitons in transition-metal dichalcogenide van der Waals heterostructures. Nature Phys, 2018, 14(8): 801-5.
[8] Li H, Wu J, Huang X, et al. A universal, rapid method for clean transfer of nanostructures onto various substrates. ACS Nano, 2014, 8(7): 6563-70.
[9] Castellanos-Gomez A, Buscema M, Molenaar R, et al. Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. 2D Materials, 2014, 1(1):
[10] Xue J, Sanchez-Yamagishi J, Bulmash D, et al. Scanning tunnelling microscopy and spectroscopy of ultra-flat graphene on hexagonal boron nitride. Nature Mater, 2011, 10(4): 282-5.

[11] Molina-Sánchez A, Wirtz L. Phonons in single-layer and few-layer MoS2 and WS2. Phys Rev B, 2011, 84(15): 155413.

[12] Ataca C, Topsakal M, Aktürk E, et al. A Comparative Study of Lattice Dynamics of Three- and Two-Dimensional MoS2. J Phys Chem C, 2011, 115(33): 16354-61.