

摘要

自 2004 年從高定向熱裂解石墨中首度分離出單層的石墨烯以來，二維材料的穩定存在已被實驗所證實。由於其獨特的二維晶體結構，石墨烯表現出諸多與傳統三維材料相異的優異物理性質，如極高的載子遷移率、光耦合強度及導熱性等，因此被許多國家及產業視為是次世代光電子元件的重點材料發展項目之一，如何合成出高品質石墨烯也成為元件上游的關鍵技術。其中，以銅與鎳等固態金屬催化劑的化學氣相沉積法因可合成出單、多層大面積且高品質的石墨烯連續薄膜，最為被廣泛研究。經由適當的製程調整，不同品質需求的石墨烯可以磊晶/析出於銅/鎳金屬層上方。然而，為了製作成以石墨烯為主要做動層的各种光電子元件，需要一個額外的轉移製程將石墨烯轉移至氧化物基板上，以迴避石墨烯與底層金屬的並聯電路效應。不幸的是，此一轉移製程將會創造大量各種缺陷，大幅地降低石墨烯的品質；此外，轉移過程繁雜且不易控制，大幅的增加製程的難易度且直接地影響元件良率。因此，如何開發將石墨烯直接成長於氧化物基板上的製程，將成為本論文的研究重點。

本論文分兩個研究重點，其一為利用微波直接加熱析出成長石墨烯與高度結晶化之石墨；另一則為利用氣相鎳輔助催化沉積石墨烯於氧化物基板之技術開發。由於材料對微波吸收選擇性的差異，微波源所挾帶的電磁能可以有效地集中在欲加熱的區域並達到快速升降溫的特性，在此研究中我們以具強偶極性的碳化矽作為微波吸收源加熱預先蒸鍍的無序碳/鎳/氧化矽基板的試片，使鎳層在高溫時固溶碳原子，並於冷卻過程中析出石墨烯。值得一提的是，由於無序碳對鎳層的還原效應的貢獻，與氧氣的氧化作用達到平衡，鎳層將可保留其金屬特性，因此系統能在常壓下製備石墨烯。此外，氧化鎳層與金屬鎳層的體積來回劇烈變化，將可迫使鎳表面的無序碳持續不斷的被導入鎳層之中，並於鎳層與基板間析出具有高度結晶特性的石墨層，其轉換率更可高達約 80%。

在氣相鎳輔助催化沉積石墨烯製程技術方面，我們利用鎳蒸氣對甲烷的催化效應，使之解離成碳原子，並自組裝成具穩定相的六連環結構後沉積於氧化物基板上，形成大面積的連續石墨烯薄膜。以此沉積方式得到的石墨烯薄膜，可以透過改變沉積時間線性的改變石墨烯厚度，且由於氣相系統的均勻性，石墨烯能均勻的附著在具有高縱深比奈米結構的矽奈米柱陣列的表面，表現出不具有空間依賴的特性。我們也以場發射元件測試了此石墨烯/矽奈米柱陣列複合結構在高放射電流密度下的操作，間接佐證以此方式製備的石墨烯結構的高度穩定性。仰賴此製程的自組裝過程，硼蒸氣的引入也可以有效的對石墨烯做出具有化學鍵生成的取代性摻雜，且其摻雜濃度能藉由調控石墨烯的沉積速率而調整，並得到相對應不同的功函數特性，可望用以做為光電元件中具有功函數調控匹配特性的透明電極。



Abstract

In 2004, graphene, a stable 2D material with only one atomic thickness, has been first synthesized from a highly ordered pyrolytic graphite by mechanical exfoliation. Due to the two-dimensional nature, graphene exhibits a lot of outstanding physical properties such as extremely high mobility for both electrons and holes, extremely high thermal conductivity, and extremely high optical adsorption rate and is considered as one of candidates of materials for the next generation optoelectronics industry. Until today, many different processes to synthesize graphene have been developed. The chemical vapor deposition process by using Cu or Ni as the catalysts is the most famous process since it can grow graphene with high quality and large area by adjusting the growth conditions. Unfortunately, the graphene grown on the Cu or Ni foils/films by the CVD process needs an extra transfer process to transfer the graphene onto oxide substrate for devices. The transfer processes are complex and usually damage graphene to significantly decrease the quality of graphene. In this thesis, development of new processes on directly growing graphene on the arbitrary metal oxide substrates by using microwave heating process and Ni vapor-assisted CVD processes, respectively.

Due to the strong dipole nature, SiC was used as the susceptor to absorb microwave and transfer into heat to heat the α -C/Ni/SiO₂ sample prepared by E-xbeam evaporation. Since the microwave can be focused on the target, the process is fast with high temperature increase/decrease rate. The balance between oxidation and reduction by oxygen and amorphous carbon keeps the Ni layer to remain the metallic nature and allows graphene segregate on the surface. Besides, the highly order graphite was found at the interface between Ni and SiO₂ with the almost 80% transformation ratio from amorphous carbon. For the graphene deposition process, Ni

vapor was used as a gas phase catalyst to decompose the methane and release carbon atoms during the annealing process. The thickness of graphene can be tuned linearly by adjusting the deposition time. In addition, we also demonstrated direct growth of graphene on a high aspect ratio Si nanorod arrays. The endurance of field emitted test also shows the high stability performance of this graphene/Si nanorod hybrid structure even under a large current. Depending on the self-assembly process, we also introduce a boron vapor into the growth system to achieve the boron doping of the graphene during the graphene deposition to change the work functions by carefully adjusting the deposition rate of graphene.

