專題研究計畫成果報告

一、背景與目的

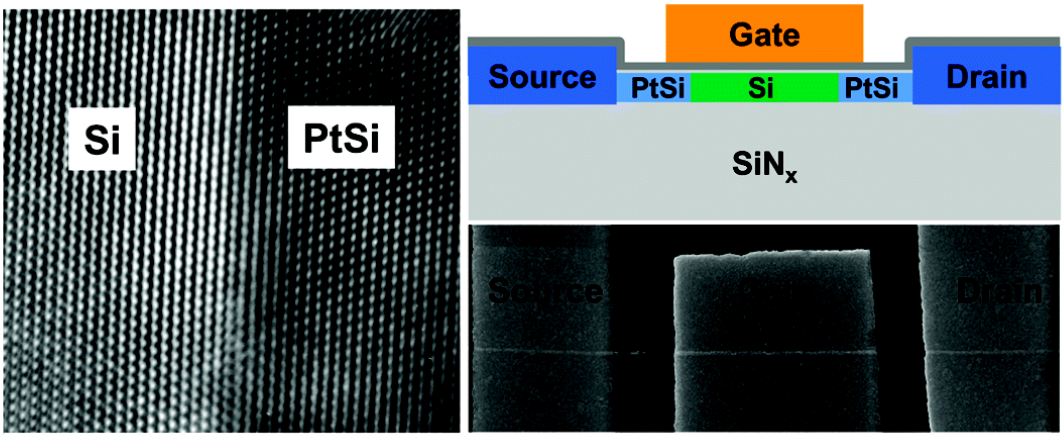
近年來電子元件微小化的發展，使得具奈米尺度之功能性材料結構及其光電特性益受重視。在新世代奈米元件中，奈米點可望應用於單電子電晶體、高密度記憶體、半導體雷射。而一維奈米結構則被看好應用於導線及具發光特性之奈米元件。尤其以矽奈米線為基礎，應用於微電子奈米元件之研究，一直是各個相關領域相當重視的研究方向。在矽晶上，自動對準低電阻率金屬矽化物仍為下一世代電子元件所需之重要材料。近年來許多矽化物奈米線之研究亦由於在新世代奈米元件中可望取代金屬導線而成為重要焦點。在此趨勢下，更發展出利用矽奈米線製作奈米尺度之電晶體，使其具有取代積體電路上金氧半電晶體之潛力，並對微電子工程及高敏度的生物檢測器帶來新的契機。為了達成此目標，矽化物/矽奈米線異質結構(heterostructure)成為重要的研究課題。在相關金屬矽化物奈米線之研究領域中，近年來有許多重要的成果刊登於知名頂尖期刊，顯見其重要性。而近期，本研究團隊亦在此領域發表幾項重要研究成果，也在世界上居於領先的地位，並且持續往更深入與重要的主題進行研究。另一方面，在現代積體電路元件技術中，由於銅導線具有較低之電阻率，訊號傳遞延遲效應(RC delay)較小，所以在超大型積體電路元件製程中正逐漸取代原有之鋁導線製程。隨著電子元件之持續微小化，通過元件連結導線之電流密度亦隨之持續升高，當銅導線中電流密度高達約 10^6 A/cm^{2}時，銅原子即可能受電流驅動沿導線產生遷移之現象，此稱之為電遷移(electromigration)效應。電遷移現象造成連線中許多孔洞(void)的生成，導致連結導線產生開路或短路的問題。而隨著元件尺度下降到奈米等級，此一問題亦預期將會更加嚴重。

二、結果與討論

本研究計畫針對上述研究主題，至今已有許多成果產出，且部分成果都發表在知名國際期刊上。本研究主要分兩大部分，一是金屬矽化物的奈米結構成長、特性、及動力學研究。另一部分為銅導線電遷移之行為研究。兩部分都有極佳的成果分別發表在 Applied Physics

Letters、Nano Letters 以及 Science 期刊，其摘要及主要成果分別描述如下:

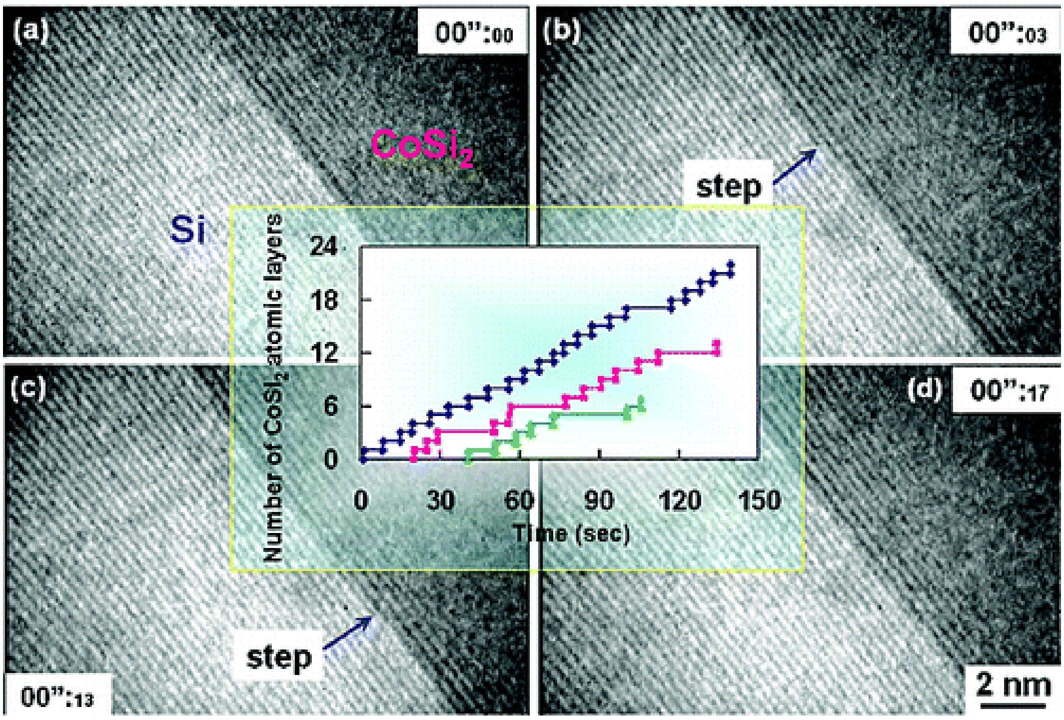
1. Y.C. Lin, K.C. Lu, W.W. Wu, J. Bai, L.J. Chen, K.N. Tu, and Y. Huang, “Single Crystalline PtSi Nanowires, PtSi/Si/PtSi Nanowire Heterostructures and Nanodevices,” *Nano Lett.* **8**, 913-918 (2008).



We report the formation of PtSi nanowires, PtSi/Si/PtSi nanowire heterostructures, and nanodevices from such heterostructures. Scanning electron microscopy studies show that silicon nanowires can be converted into PtSi nanowires through controlled reactions between lithographically defined platinum pads and silicon nanowires. High-resolution transmission electron microscopy studies show that PtSi/Si/PtSi heteorstructure has an atomically sharp interface with epitaxial relationships of Si$[1\bar{1}0]$//PtSi[010] and Si(111)//PtSi(101). Electrical measurements show that the pure PtSi nanowires have low resistivities of ~28.6 μΩ·cm and high breakdown current densities $> 1\times10^8$ A/cm^2. Furthermore, using single crystal PtSi/Si/PtSi nanowire heterostructures with atomically sharp interfaces, we have fabricated high-performance nanoscale field-effect transistors from intrinsic silicon nanowires, in which the source and drain contacts are defined by the metallic PtSi nanowire regions, and the gate length is defined by the Si nanowire region. Electrical measurements show nearly perfect p-channel enhancement mode transistor behavior with a normalized transconductance of 0.3 mS/μm, field-effect hole mibility of 168 cm^2/V·s, and on/off ratio $>10^7$, demonstrating the best performing device from intrinsic silicon nanowires.

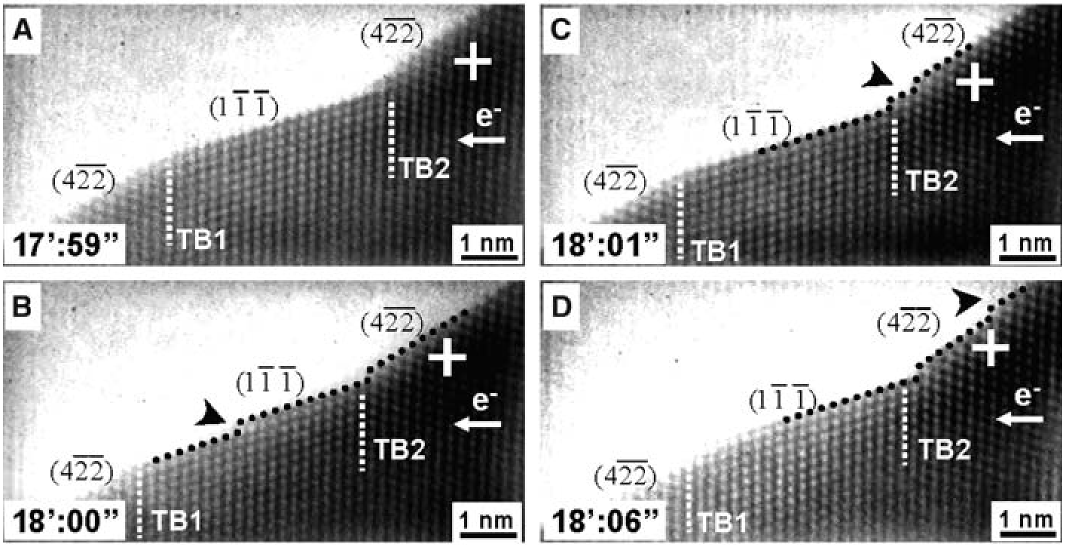
2. Y.C. Chou, W.W. Wu, S.L. Cheng, B.Y. Yoo, N. Myung, L.J. Chen, and K. N. Tu, “In–situ TEM Observation of Repeating Events of Nucleation in Epitaxial Growth

of Nano $CoSi_2$ in Nanowires of Si," *Nano Lett.* **8**, 2194-2199 (2008).



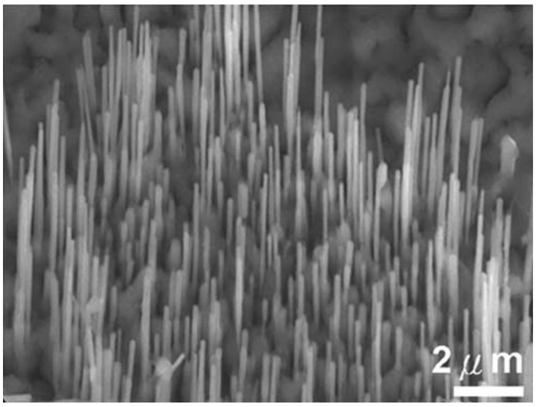
The formation of CoSi and $CoSi_2$ in Si nanowires at 700 and 800°C, respectively, by point contact reactions between nanodots of Co and nanowires of Si have been investigated in situ in a ultrahigh vacuum high-resolution transmission electron microscope. The $CoSi_2$ has undergone an axial epitaxial growth in the Si nanowire and a stepwise growth mode was found. We observed that the stepwise growth occurs repeatedly in the form of an atomic step sweeping across the $CoSi_2$/Si interface. It appears that the growth of a new step or a new silicide layer requires an independent event of nucleation. We are able to resolve the nucleation stage and the growth stage of each layer of the epitaxial growth in video images. In the nucleation stage, the incubation period is measured, which is much longer than the period needed to grow the layer across the silicide/Si interface. So the epitaxial growth consists of a repeating nucleation and a rapid stepwise growth across the epitaxial interface. This is a general behavior of epitaxial growth in nanowires. The axial heterostructure of $CoSi_2$/Si/$CoSi_2$ with sharp epitaxial interfaces has been obtained. A discussion of the kinetics of supply limited and source-limited reaction in nanowire case by point contact reaction is given. The heterostructures are promising as high performance transistors based on intrinsic Si nanowires.

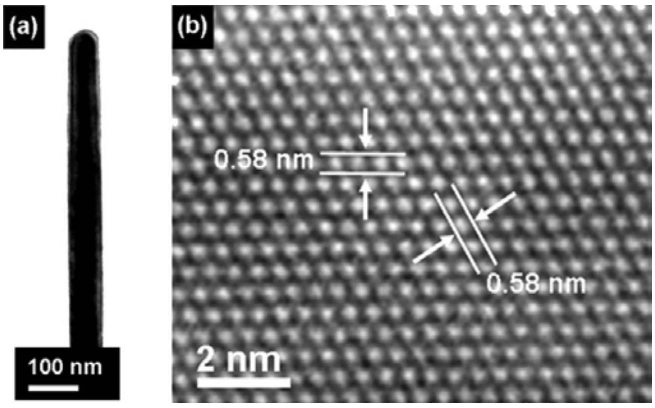
3. K.C. Chen, W.W. Wu, C.N. Liao, L.J. Chen, and K.N. Tu, "Observation of Atomic Diffusion at Twin-modified Grain Boundaries in Copper," *Science* **321**, 1066-1069 (2008).



Grain boundaries affect the migration of atoms and electrons in polycrystalline solids, thus influencing many of the mechanical and electrical properties. By introducing nanometer-scale twin defects into copper grains, we show that we can change the grain-boundary structure and atomic-diffusion behavior along the boundary. Using in situ ultrahigh-vacuum and high-resolution transmission electron microscopy, we observed electromigration-induced atomic diffusion in the twin-modified grain boundaries. The triple point where a twin boundary meets a grain boundary was found to slow down grain-boundary and surface electromigration by one order of magnitude. We propose that this occurs because of the incubation time of nucleation of a new step at the triple points. The long incubation time slows down the overall rate of atomic transport.

4. C.Y. Lee, M.P. Lu, K.F. Liao, W.W. Wu, and L.J. Chen, “Vertically Well-Aligned Epitaxial Ni31Si12 Nanowire Arrays with Excellent Field Emission Properties,” *Appl. Phys. Lett.* **93**, 113109 (2008).

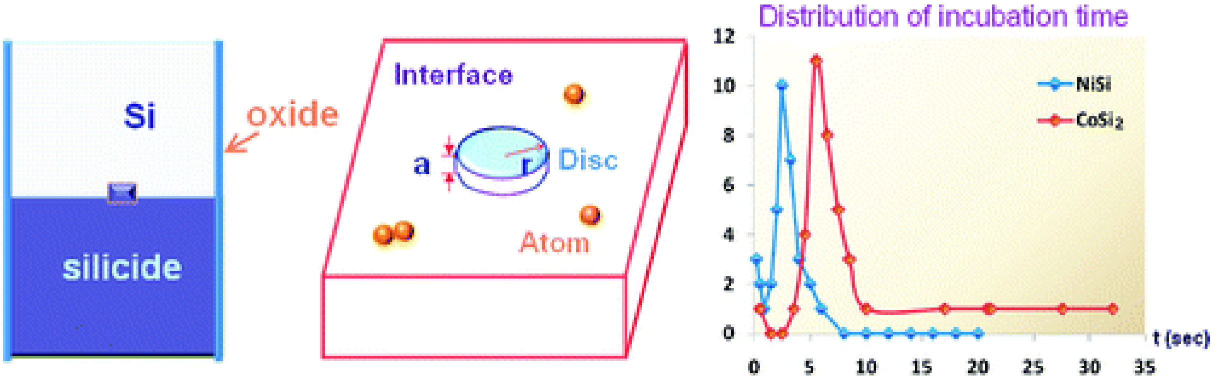




Vertically well-aligned single crystal $Ni_{31}Si_{12}$ nanowire (NW) arrays were epitaxially grown on $Ni_{31}Si_{12}$ films preferentially formed on Ni foil substrates with a simple vapor phase deposition method in one step. The $Ni_{31}Si_{12}$ NWs are several micrometers in length and 50–80 nm in diameter.

The resistivities of the Ni31Si12 NWs were measured to be 51 μΩ·cm by four-terminal electrical measurement. The NWs can carry very high currents and possess excellent field emission properties. The growth of vertically well-aligned $Ni_{31}Si_{12}$ NW arrays shall lead to significant advantages in the fabrication of vertical Si nanodevices.

5. Y.C. Chou, W.W. Wu, L.J. Chen, and K.N. Tu, "Homogeneous Nucleation of Epitaxial $CoSi_2$ and NiSi in Si Nanowires," *Nano Lett.*, ASAP doi: 10.1021/nl900779j (2009).



Homogeneous nucleation is rare except in theory. We observed repeating events of homogeneous nucleation in epitaxial growth of $CoSi_2$ and NiSi silicides in nanowires of silicon by using high resolution TEM. The growth of every single atomic layer requires nucleation. Heterogeneous nucleation is prevented because of non-microreversibility between the oxide/Si and oxide/silicide interfaces. We determined the incubation time of homogeneous nucleation. The calculated and the measured nucleation rates are in good agreement. We used Zeldovich factor to estimate the number of molecules in the critical nucleus; it is about 10 and reasonable. A very high supersaturation is found for the homogeneous nucleation.

三、參考文獻

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四、計畫成果自評

本計畫承蒙國科會微電子學門給予大力支持，特此感謝。近一年來之研究成果也所幸能發表於部分優質期刊，希望貴會能繼續支持我們新人，也期許後續相關的研究能持續能拿出更好的科研成績。另外在材料與半導體領域，材料分析仍是相當關鍵且重要的一環，因此電子顯微鏡扮演著舉足輕重的角色，陳力俊教授的臨場超高真空穿透式電子顯微鏡提供了重要的實驗平台，對於新穎材料的熱、電行為將會是日後繼續努力研究的方向。