Institution: University College London (UCL)

Unit of Assessment: 9 – Physics

Title of case study: Enabling Zyvex Labs to develop atomically precise manufacturing processes

1. Summary of the impact

The underpinning research involved modelling the diffusion of hydrogen on silicon surfaces, and the electronic structure of dopant atoms on silicon surfaces. This data was used to inform, guide and develop the atomically precise manufacturing processes of Zyvex Labs. These processes remove hydrogen atoms from a silicon surface to create patterns with atomic precision for later overgrowth. As a result of the UCL research, Zyvex Labs has already obtained funding of $14 million, several jobs have been created, and at least two products are being brought to market.

2. Underpinning research

Techniques for atomically precise manufacturing (APM) – the fabrication of structures with the precision of one atom – are of interest to industry. APM will enable industry to develop new technology ranging from simple quantum dots and atomically accurate metrology standards, to devices for the harvesting and storage of energy and for medical applications. One method of achieving APM involves the growth of structures on the Si(001) surface. A layer of hydrogen on this surface acts as a mask against deposition of further material, so selective removal of hydrogen atoms from the layer enables the selective deposition of new material such as silicon and germanium, as well as dopant atoms for quantum computing devices. The process becomes more complicated, however, if elevated temperatures are required for growth of the new material, since this can also cause hydrogen to diffuse about the surface, reducing the efficiency of the method. The behaviour of hydrogen on the Si(001) surface has therefore become an area of considerable importance, both industrially and academically.

UCL research into the behaviour of hydrogen on Si surfaces has been conducted by David Bowler who joined the Department of Physics and Astronomy at UCL in July 1998. This research was part of a collaboration that started whilst Bowler was at Oxford University and continued when he moved to Keele University and then to UCL. The first key UCL contribution (1998-2000) was part of an extensive joint experimental-theoretical investigation with Oxford University of the behaviour of hydrogen on Si(001) under various conditions [1]. In this work, researchers from Oxford University conducted the experimental work, which consisted of elevated-temperature scanning tunnelling microscope (STM) measurements of hydrogen mobility, and UCL's Bowler conducted the theoretical work, which involved modelling the diffusion barrier for hydrogen on Si(001), both on the perfect surface and near step edges and defects. This modelling of hydrogen diffusion gave a comprehensive picture of the energy surface, including the diffusion barriers and the associated temperatures at which hydrogen becomes mobile.

The next contribution (2001-2003) was performed entirely at UCL and was relevant both to diffusion of hydrogen and growth of new silicon on Si(001) [2]. This research involved modelling the formation of new Si dimers during growth and hydrogen diffusion associated with this process. Later research (2010-2012) performed by PDRA Veronika Brazdova and supervised by Bowler consisted of modelling the electronic structure of Si(110) [3], and understanding the diffusion of hydrogen on Si(110) [4] and around a Si(001)/Si(110) corner. The key findings of this research [1-4] that underpinned the impact were the diffusion barriers for hydrogen on silicon surfaces, both on the perfect surface and near defects and steps.

More recently, UCL researchers have studied the effects of physical structure on the electronic structure of dopant atoms on silicon surfaces [5, 6]. The research involved STM experiments and density functional theory (DFT) modelling of dopants on Si(111) [5] and Si(001) [6], and was performed from 2009 to 2013 entirely within UCL. The effect of the physical structure of the dopants on their electronic properties has been found to lead to very different properties to the standard bulk behaviour: on Si(111), Bi has been found to act as both an electron donor and an electron acceptor, while on Si(001), Bi has been found to form a spin-polarised, local state when coupled with a vacancy. These properties have major implications for the design and construction of quantum information devices built using APM, dopant atoms and silicon surfaces.

Key UCL researchers: David Bowler (PDRA 1998-1999; EPSRC Postdoctoral Fellow 1999-2001; Royal Society University Research Fellow 2001-2009; Lecturer 2002-2006; Reader 2006-present), Veronika Brazdova (PDRA 2006-present) and the UCL STM experimental group (K. Iwaya, P. Studer, S.R. Schofield, C. F. Hirjibehedin and G. Aeppli).

3. References to the research

[1] An experimental-theoretical study of the behaviour of hydrogen on the Si(001) surface, D. R. Bowler, J. H. G. Owen, C. M. Goringe, K. Miki and G. A. D. Briggs, *J. Phys.: Condens. Matter*, 12, 7655-7670 (2000) doi:10.1088/0953-8984/12/35/301

[2] Formation of clean Si dimers during gas-source growth of Si(001), D. R. Bowler, *Phys. Rev. B*, 67, 115341 (2003) doi:10.1103/PhysRevB.67.115341

[3] Electronic structure of Si(110)-(16x2) studied by scanning tunneling spectroscopy and density functional theory, M. Setvin, V. Brazdova, D. R. Bowler, K. Tomatsu, K. Nakatsuji, F. Komori and K. Miki, *Phys. Rev. B*, 84, 115317 (2011) doi:10.1103/PhysRevB.84.115317

[4] H atom adsorption and diffusion on Si(110)-(1x1) and (2x1) surfaces, V. Brazdova and D. R. Bowler, *Phys. Chem. Chem. Phys.*, 13, 11367-11372 (2011) doi:10.1039/C1CP20108E

[5] Site-dependent ambipolar charge states induced by group V atoms in a silicon surface, P. Studer, V. Brazdova, S. R. Schofield, D. R. Bowler, C. F. Hirjibehedin and N. J. Curson, *ACS Nano*, 6, 10456 (2012) doi:10.1021/nn3039484

[6] Half-filled orbital and unconventional geometry of a common dopant in Si(001), K. Iwaya, D. R. Bowler, V. Brazdova, A. Ferreira da Silva, C. Renner, W. Wu, A. J. Fisher, A. M. Stoneham and G. Aeppli, *Phys. Rev. B*, 88, 035440 (2013) doi:10.1103/PhysRevB.88.035440

References [5], [1], and [3] best indicate the quality of the underpinning research.

Relevant research grant:

(i) Si(110): (16x2) Reconstruction and Adatom Diffusion, EPSRC, January 2009-June 2010, PI: David Bowler, £140,000

4. Details of the impact

Zyvex Labs is a leading company in the area of APM in the US. It is part of Zyvex Corporation, which carries out fundamental research into APM, often building its own tools. Zyvex now takes that technology to market by developing commercial products in the nanomaterials and nanomanipulation areas. The company has already developed a system that is in wide use throughout the semiconductor industry (a nanoprobe, used to characterise chips at 90nm and below); the UCL research has underpinned development of a new system to be brought to market around 2015. It has also helped generate new employment and $14 million in funding for the company [A].

Zyvex Labs is developing techniques to create nanoscale patterns with atomic precision by manipulating hydrogen on Si(001), and then growing new material on top of the patterns. The company is developing products for market based on this patterning: control electronics for STMs, to allow patterning; and turn-key systems to be added to STMs, to give a complete patterning and growth system. Both of these systems will allow other companies to produce patterns in hydrogen-terminated Si(001) and grow new materials within the patterns.

While developing early ideas for APM based on hydrogen lithography and subsequent growth, the President (at the time Chief Technical Officer followed by Vice President) of Zyvex Labs realised the importance of theoretical underpinning for the process. He writes, “I did an extensive literature search on the subject. Your theoretical work stood out as the best available data and in excellent agreement with the published experimental data” [A]. Zyvex Labs and UCL set up a collaboration, under a non-disclosure agreement, in May 2007.

UCL’s data on hydrogen diffusion and epitaxial growth of silicon improved Zyvex Labs’ development process by giving important limits on the atomically precise process being developed: during the early stages of development, in early 2008, it indicated that the approach was feasible; later, it was used to identify the temperatures at which hydrogen becomes mobile, which were used to control and manage the growth processes [A]. This last point is particularly important: the growth of new silicon requires elevated temperatures, and so the atomically precise control would be impossible without UCL’s data on the temperatures at which the hydrogen mask would degrade. The UCL research findings in section 2 were therefore used to set maximum annealing and growth temperatures for the APM process, to ensure fidelity of patterns. As Zyvex Labs’ entire process and hence product relies on control of the position of the atoms on the surface, the UCL results underpin its approach, and hence the products that are being brought to market. The President writes: “Further, your research on hydrogen mobility on silicon and epitaxial growth of silicon is still very relevant and is referenced on a very regular basis as we are carrying out this research” [A].

In addition to underpinning Zyvex Labs’ approach, the UCL research has helped the consortium led by Zyvex Labs to obtain just over $14 million in funding between January 2008 and July 2013 [A]. This consists of two research contracts from the US Defense Advanced Research Projects Agency and a matching grant from the State of Texas, awarded to enable the accelerated commercialisation and market adoption of atomically precise devices and manufacturing approaches. These contracts started in August 2008 and have resulted in the hiring of at least five new employees at Zyvex Labs, including one of the original experimentalists from Oxford [A]. The UCL research underpinned the funding as it enabled Zyvex Labs’ development of atomically precise processes, which in turn allowed the contracts to be awarded. The President of Zyvex Labs writes that UCL’s “work on the mobility of hydrogen on silicon surfaces has been enormously influential on the research at Zyvex Labs and the funding of that research” and that the funding was “made possible in no small measure by your research” [A].

In 2013, UCL research has also been informing the approaches used by Zyvex Labs in a new area: the development of manufacturing techniques for quantum computing devices. This process will use hydrogen depassivation to deposit dopant atoms with atomic precision, and Zyvex Labs is using the recent UCL research on the electronic structure of dopants on silicon surfaces to understand the effects of physical structure on dopant properties and hence to design the devices [A]. [text removed for publication]

5. Sources to corroborate the impact

[A] Correspondence from the President of Zyvex Labs – corroborates all claims about the impact of UCL research on Zyvex Labs, including the use of UCL research findings in the development of techniques, the amount of funding received and the generation of new employment. Available on request.