

Final Report on Grant GR/N64250/01
NETWORK FOR ADVANCED MATERIALS THROUGH CHEMICAL VAPOUR DEPOSITION

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1. Background

From 1998 to 2001 the PI lead a highly successful EPSRC Network in the area of optical probes of semiconductor processing (GR/M26084/01, 1998 to 2001), which was eventually rated as 'Tending to Excellent' by the EPSRC review process. As a direct result of feedback generated via this first network, the idea of a second network in the area of Chemical Vapour Deposition emerged. The operation and outcomes arising from this second network are reported here.

Note that following the launch of this second network in 2001, the activities of the PI were severely curtailed such that his involvement in the network was at a much lower level than had been originally foreseen. EPSRC were kept informed of the reasons for this reduction in activity throughout the duration of the award. Despite this, the network has operated successfully, albeit at a reduced level of activity (and with a correspondingly reduced level of financial activity). As might be expected, the level of participation in networking activities by the original named partners has been variable. The lack of activity on the part of some partners may be attributed, in part but not completely, to the problems encountered by the PI in the sense that some activities lacked defined leadership. In order to overcome these problems, the PI enlisted the help of key individuals who contributed extensively in terms of organisational issues.

2. Networking Highlights

- Five formal meetings have been held, including two 'graduate student' meetings.
- Thirty graduate students have received network funding enabling them to attend major international meetings and as such some 33 graduate student papers have been presented.
- Some 24 graduate students were taken on a site visit to Pilkington Glass in St Helens, in order to learn about high volume CVD processes
- Nine research assistants have received conference support, giving in total 12 papers at major international meetings.
- Two graduate students have presented prize-winning work with the partial support of network funding.
- Collaborative work between UCL and Salford in the area of thermochromic systems for windows has resulted in one patent, articles in over 200 newspapers, 6 radio performances and 3 TV interviews.
- Many new collaborations and joint research ventures established
- Extensive European networking has taken place generating new collaborative ventures and EU-funded proposals. In addition this activity resulted in an albeit unsuccessful bid for an EU-funded Network of Excellence entitled NANO-CVD NET, which linked UK researchers with all major players on the field of CVD in Europe.
- At least one new spin-out company has been formed, while 3 others have grown substantially partly through networking activities.
- A major new text edited by network members (Profs Tony Jones and Michael Hitchman) and which includes other network contributors (e.g. Pemble), is currently in preparation.
- The major networking participants have produced some 282 papers over the period of the Network Grant as listed on Web of Science. This figure excludes certain papers and conference proceedings that do not appear on this database. The total number of papers produced by all formal network members is well in excess of 300.
- Network members contributed to a major UK presence at EUROCVD-14, Paris, Spring 2003, giving 13 papers in total, including an invited lecture on in-situ diagnostics for CVD processes (Pemble)

- The major participants in the network have given over 20 invited lectures associated with their CVD-based research, during the operation of the network.
- Prof Ivan Parkin, UCL, was awarded the prestigious Beilby Medal in 2004 by the Institute of Materials, Minerals and Mining, the Royal Society of Chemistry, and the Society of Chemical Industry.

3. Details of Networking Activities

3.1 Networking Meetings

Meetings were held at Salford (1), Pilkington Group Research Lathom (2), UCL (1) and Manchester (1). These ranged from fairly informal gatherings in which network members gave short presentations and posters, to a highly successful graduate student meeting held at Manchester, with 'special guest' Will Rees Jr. (Georgia Institute of Technology). At this meeting, which was organised by Prof Paul O'Brien and staff, only graduate students were permitted to make presentations. It was generally agreed that this type of meeting provided an excellent forum for postgraduate students. Prof Ivan Parkin organised a follow up meeting along the same lines at UCL. Prof Parkin was also responsible for organising a further network meeting held at Pilkington Group Research. At this meeting graduate students were taken for an interesting tour of a float glass facility equipped with CVD coating heads. This was generally perceived to be highly informative, particularly in terms of appreciating the scale of a production glass coating system.

3.2 Strengthening of Existing Networking and Collaboration

In terms of links that were already in place, network members have highlighted the following activities as being supported and enhanced by the network:

Prof Tony Jones and Liverpool University has retained strong links with the groups of Prof. Martyn Pemble (Salford University and Tyndall Institute, Cork) and Prof. Paul O'Brien (University of Manchester).

Prof Ivan Parkin has strengthened his already substantial links to Pilkington Glass and the University of Salford and as such there are several new joint funding applications planned involving Prof David Sheel.

Dr Philip Martin contributed extensively to the EU Integrated Project application, MULTICOAT lead by the Salford group, which was unsuccessful. As a result, several smaller bids are now in preparation.

Dr Peter Haycock has extended his collaboration with Dr Kieran Molloy at Bath University regarding MOCVD of tin oxide and antimony oxide based films. This has benefited significantly from discussions at network meetings and with network members outside meetings. Two further joint applications to EPSRC are in preparation.

Dr Clare Carmalt has established an enhanced interaction with Epichem due to more regular meetings with the network. Epichem have now given more support in the form of chemicals and will part fund a CASE PhD award next academic year

Drs Chris Rego and Waqar Ahmed have strengthened their collaborative links with the University of Rome (Tor Vergata), Italy. University of Aveiro (Portugal), and Micro Materials (Wrexham). These links have all benefited from meetings at conferences, which were funded through the CVD Network.

Dr Ian Watson cites the network as providing a useful forum for pursuing his pre-existing industrial collaboration with Epichem Metalorganics. There is currently one refereed journal paper from joint work with Epichem, plus one conference presentation on work so far unpublished elsewhere.

3.3 The Development of New Collaborations

Prof Martyn Pemble has undertaken new collaborative work in the field of novel photonic band gap materials, which was specifically cited in the original proposal. The Salford group established direct links with the Institute of Photonics in Strathclyde (Dr Ian Watson), with a view to the fabrication of novel GaN-based photonics systems. In November 2002 a Salford graduate student, Ms (now Dr) Debra Whitehead, worked in Strathclyde using the state-of-the-art MOCVD system to attempt to infill synthetic opaline materials with GaN. These experiments, although interesting, did not result in infill but rather produced surface coatings. The Salford group also performed a series of experiments with the group of Dr Clare Carmalt at UCL, who had prepared a range of very novel azo-precursors potentially suitable for the

growth of GaN by CVD. Mr John Mileham (UCL) visited Salford on a number of occasions supported by the network. Although it was not clear as to whether the experiments actually produced GaN impregnated opals, this work has provided the impetus for a new series of experiments that the PI is currently undertaking in Cork in collaboration with other researchers within the newly formed Tyndall National Institute (see www.tyndall.ie).

Prof Pemble was invited to join the EU funded Coordinated Action DESHNAF (Deposition of Super Hard Coatings) as 'CVD' expert. This has provided some interesting new networking links to partners mainly in Germany and Israel.

Prof David Sheel has forged innumerable new networking links via his invited membership of the Joint European-Japanese Photocatalysis Forum.

Profs Sheel and Pemble have now taken over from Prof Roy Gordon as 'CVD Teach-in experts' at the ICCG (International conference on Coatings on Glass) series of meetings. Attendance at these meetings has been supported at a very low level by the network and has led to the establishment of many new contacts across Europe.

Prof Kieran Molloy has established new links with Qinetiq, who are providing some external sponsorship for an EPSRC studentship entitled 'CVD Precursors for the Deposition of Ferroelectric Sb(S)I Thin Films'.

Professor Tony Jones has formed new collaborative links with the group of Prof Ivan Parkin.

Prof Ivan Parkin, related to the links established with Prof Tony Jones at Liverpool, the UCL group has forged new links with Epichem, through which Epichem have agreed to provide UCL with a substantial quantity of precursor materials. Prof Parkin's group has also established new links with a lens manufacturer – Norville Lens.

Dr Philip Martin has submitted a joint funding application with Dr Krikor Ozanyan to EPSRC on Temperature Tomography (awaiting outcome). He has also prepared a successful joint funding application with James Bradley (UMIST now University of Liverpool) to EPSRC on 'Diagnostic study of pulsed magnetron plasmas: a route to advanced engineering coatings'. This work is now in progress.

Dr Peter Haycock has described how complementary research at Keele and UCL has been identified and led to useful discussions with potential for future joint work that has not yet been realised.

Drs Chris Rego and Waqar Ahmed have established new collaborative links with several Universities in the UK, including: University of Paisley, Imperial College, Cambridge University and the University of Salford. The group has also established links with the industrial company Advanced Energy through contacts made at a conference, attendance at which were partially funded by the Network. The MMU CVD group has also founded a number of international links with the universities including The University of Purdue (U.S.A), Tennessee Technological University (U.S.A), Clemson University (U.S.A) again via contacts made at conferences (see section 3.5). Access to characterisation facilities, which are not available at MMU, have been obtained as a result of contacts made at CVD Network meetings and conferences. In total, 7 papers arising from new collaborations have been presented.

3.4 Dissemination and Exploitation Activities

3.4.1 Papers and Presentations

As noted earlier, the network partners have published well in excess of 300 papers during the course of the grant, including some 20 invited papers. These statistics serve to illustrate the very high levels of activity that has been maintained by network partners. In terms of public dissemination, some lectures of note are those given by Profs Pemble and O'Brien at the BA Festival, university of Salford, 2003, those given by Dr Carmalt and Prof Parkin at the ACS Meeting, Anaheim, California, 2004 and a series of lectures given by Prof Parkin at key US institutions including Purdue, Caltech, UCLA and Ohio State.

3.4.2 Commercially Significant Research Outputs and Spin-out Companies

Possibly the most widely publicised result to emerge from the laboratories of network partners was that associated with the deposition of thermochromic VO₂ thin films by CVD as presented by Prof Ivan Parkin and his student Mr (now Dr) Troy Manning, of UCL. As noted earlier, this finding attracted enormous media attention. This work was part of a collaborative EPSRC funded venture involving UCL, Salford and Pilkington Group Research. Although it is not possible to equate success stories such as this to networking directly, it demonstrates the

potential achieved when individuals from varying backgrounds are brought together- *one of the primary aims of this particular network*. A press release describing this finding may be found by following the media and news links on the UCL website.

The significance of this work in terms of potential energy cost reduction should not be underestimated. As acknowledged experts in coated glass technologies, key network members feel that thermochromic windows may be the next major product to be commercially launched worldwide.

Also well publicised at the time of launch was the development of TiO₂-based self-cleaning windows. Pilkington developed this product in close collaboration with Prof Ivan Parkin and Prof Andrew Mills with the definitive work being performed before the onset of the networking activities. However, work in the area now continues and has benefited from networking discussions. Via the EU funded project PHOTOCOAT, the Salford group, together with the group of Prof Andrew Mills and other partners, is now striving to achieve significant improvements in photocatalytic activity without loss of optical quality. This has led to enhanced European networking links to organisations such as St Gobain Glass, EADS and Berndorf Band.

Under this heading it is also appropriate to address the activity of spin-out companies associated with network members. Although the network grant was not instrumental in creating these new commercial ventures, some benefits may have arisen indirectly as a result of networking discussions. In this respect it is noteworthy that *Profs Pemble and Sheel* and their spin-out company CVD Technologies Ltd have continued to expand their portfolio of activities, such that not only do they participate in EU funded research (e.g. Activated CVD, ASSYST, PHOTOCOAT) but also perform custom R&D activities, manufacture specialised products and most recently, have expanded the business activity to include high volume coated glass systems. This most recent venture, in which CVD Technologies are working closely with 2 major US organisations, is described in detail on the CVD Technologies web pages. See www.cvdtechnologies.com. There is no doubt that networking activities associated with conference and meeting attendance, while primarily benefiting the academic activities at Salford, have also contributed enormously to the successful expansion of the commercial activities.

Prof Ivan Parkin has been instrumental in creating a new spin-out company via his activity at UCL. This company, Novosense, takes advantage of CVD for making gas sensor materials. Associated with this development is patent number GB 2403295 published in Dec 2004, entitled 'Gas Sensor'.

Prof Paul O'Brien established the company Nanoco in December 2001 in order to commercialise unique, proprietary and widely patented methods of synthesizing quantum dots developed by his group. See www.nanoco.biz/.

Dr Philip Martin's company TDL Sensors Ltd continues to grow in strength and has now developed a range of diode laser monitoring systems that are specifically designed to probe the often-harsh environment of a CVD reactor. Details of this and other products may be found at www.tdlsensors.co.uk. TDL maintains strong links with CVD Technologies and as such Dr Martin's group and TDL sensors are currently partners with the Salford group and CVD Technologies on the EU project ASSYST.

3.5 Noteworthy Graduate Student Performance

For his work on the thermochromic coatings on glass described above in 2003, Dr Troy Manning was awarded the Ramsay prize at UCL. Also from UCL, Dr Emily Peters was winner of the Apley Prize 2004. This prize is given to students in their final year and is awarded on the basis of evaluation of drafts of their thesis.

Students Ms Abbie Jones and Mr Mohammed Amar from MMU were runners up in the IOM³ National postgraduate lecture competition, 2nd March 2004. Ms Jones also received an invitation to work at the University of Purdue for one month in 2004, while her colleague at MMU, Mr Htet Sein, received a similar invitation to work at the university of Tennessee in June 2003. Via partial support from the network, these two students gave 4 papers at the ASM International conference on surface coatings, 2-5th August 2004.

4. Comments by Network Members

Since possibly the best persons to ask about the effectiveness or otherwise of the network would be the members themselves, some comments are provided here as extracted from a summary questionnaire circulated by the PI.

Please provide any comments that you wish to see included in the Final Report. These will be included without editing.

Prof Tony Jones, Liverpool- 'I found the Network an extremely useful vehicle for meeting CVD technologists, and I believe this has strengthened the position of the UK in an extremely competitive worldwide technology'.

Dr Peter Haycock, Keele- 'The network was extremely useful for bringing together academics working on a range of aspects of CVD and sharing ideas and experiences to a level that was much more difficult beforehand. It was also excellent for providing broad background training in aspects of CVD for graduate students. Discussions at network meetings about analytical and diagnostic techniques were particularly useful'.

Drs Chris Rego/Waqar Ahmed, MMU- 'The Postgraduate students at the MMU are most appreciative to the CVD Network for its support. They are very grateful for the opportunity to present their research across the world and also the networking opportunities, which have helped them to establish strong national and international collaborative links'.

Dr Ian Watson, Strathclyde- 'My own PhD students researching III-nitride semiconductor growth work in an environment heavily focused on semiconductor physics and photonic device applications. Therefore I believe that attendance of the network's own meetings gave them valuable exposure to the more diverse applications of CVD technology'.

Dr Peter Gardner, Manchester- 'Coming from a surface science/catalysis community my knowledge of CVD was limited prior to joining this network. However it was clear from discussions with Prof. Pemble that we have a technique that could possibly benefit the CVD community. With help of resources provided by the network I attended the 256 WE-Heraeus-Seminar (Workshop) on Optical Spectroscopy at Interfaces in Germany. As a direct result of that meeting I was able to develop our ideas concerning RAIRS on non-metallic substrates. Two papers were subsequently published jointly with Prof. Pemble's group on our work related to CVD precursors for SnO₂ thin film production. A further three papers relating to the theory of the experiment have been published or are in the review process. The work has also been presented at six national and international conferences'.

5. Summary and Conclusions

The Network has spent approximately 2/3 of its allocated budget (some £40k), with the vast majority of the funding being used to enable researchers to attend major scientific meetings. This has provided invaluable experience for graduate students and has also helped to maintain the world lead that UK researchers possess in the field of CVD. The fruits of the collaborations fostered by the Network are now being harvested in terms of further research grant income, increased research publication outputs and the expansion of entrepreneurial activities such as the formation of spin-out companies. Direct benefits to industry are likely to arise. Good examples of these are work from UCL and Salford, on potential thermochromic windows (see section 3.4). A further example concerns improved self-cleaning windows, which were originally developed by Pilkington with direct input from UCL (Prof Ivan Parkin) and Strathclyde (Prof Andrew Mills). These systems are now undergoing further development via EU funding (Salford, Strathclyde and others).

In terms of electronic materials and coatings, Epichem continues to work closely with academia and has established several new collaborations during the course of the Network (see sections 3.2 and 3.3). This is likely to lead to the development of a range of new precursors capable of the growth of complex oxide systems and other materials, which will have many potential applications.

In terms of photonic materials, work is now proceeding at a significant pace with CVD methods being used to modify and tune photonic gaps. Although still a relatively young field, this area possesses enormous potential for the creation of novel device systems.

Our understanding of CVD processes is now higher than it has ever been. It is predicted that this is an area that will continue to grow in terms of both academic research and economic benefits.

Overall, despite unexpected events that strongly influenced the management of the Network, there can be little doubt that the grant has been successful. The planning and operations

should have been better, as should the level of specific training supplied to graduate students. These factors have been reflected in the self-assessment document supplied.

6. Acknowledgements

The PI wishes to thank all participants for their invaluable contributions and the EPSRC for financial support.

Martyn E Pemble 01/02/2005