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Anthony ('Tony') George Cullis was distinguished for his pioneering studies of the microscopic structure and behaviour of semiconducting materials. He provided the first crystallographic details of the complex impurity-iron silicide precipitation processes in electronic device grade silicon, and of the important precipitation of elemental arsenic in bulk gallium arsenide. Studies of high-speed solidification phenomena in silicon, using Q-switched laser-induced melts, revealed notable evidence of constitutional supercooling and a large enhancement of substitutional dopant solubility. He observed conclusively that amorphous silicon melts by a first-order phase transition and obtained the solidification velocity required to amorphize it. He was the first to demonstrate, by transmission electron microscopy, that a quantum-domain crystalline nanostructure exists in porous silicon and can account for its highly efficient light emission, under photo-excitation. Later, his work on epitaxial growth showed that strain waves in surface ripples on mismatched semiconductor layers correlate with segregation of the larger atomic species to the crests of the waves, leading to partial relief of the elastic strain in these parts before eventually plastic relaxation by misfit dislocation generation near the still highly strained surface troughs occurs. This model has revolutionized the explanation of the so-called Stranski–Krastanow growth transition of compressively strained epitaxial layers from two-dimensional flat sheets to three-dimensional islands. As those are important for their use as quantum dots in (opto-)electronic devices such as laser diodes, these studies may be regarded as his technologically most relevant legacy, since they explain why and how real, ternary or

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quaternary quantum dot systems differ chemically and microstructurally from the nominally flat and thin binary layers often deposited.

Education and personal life

Early life

Tony Cullis was born in Worcester on 16 January 1946 as the only child of Doris Mary Cullis (née Bowen), the personal secretary to a managing director, and George Thomas Cullis, a skilled engineer. Tony attended Worcester Royal Grammar School and had a particularly good relationship with his chemistry master, Mr Lammiman, who encouraged him to apply to Wadham College, Oxford, to read chemistry.

At home, Tony was always given the opportunity to develop his own ideas, and he had a small chemistry laboratory in an outhouse in which he often prepared compounds with strange smells or explosive potential. For several years, during the summer holidays, he would work in Bill Bardsley's crystal growth group at the Royal Radar Establishment (RRE), Malvern. In one of these work periods, he designed and built a high temperature furnace, controlled by a saturable reactor, in which he grew several small crystals of beta-SiC from an Si/C melt by slow cooling. No-one was more surprised than Tony himself when the crystals were revealed by dissolution of the excess Si. As a result of his many experiences at RRE, where he became a full-time research worker some years later, he became deeply interested in materials science, which linked well with his chemistry background.

University education: the Oxford days

When Tony went up to Oxford to read chemistry at Wadham College (figure 1), he benefited greatly by having Bob Williams and Jeremy Knowles as tutors. Academic life centred around stimulating college tutorials, with practical classes in the science laboratories in South Parks Road. A lingering memory from the Dyson–Perrins Laboratory recalls the identification of many organic compounds by checking their odours: Tony was convinced that overuse of this technique resulted in subtle but permanent changes in his sense of smell thereafter. Although, with an exacting schedule of laboratory classes, there was not a great deal of free time, he indulged his passion for darts and became secretary of the Wadham darts club, organizing matches against local teams.

After obtaining a Bachelor's degree, Tony went on to carry out DPhil research from 1968 to 1972 in the Department of Metallurgy and Science of Materials at Oxford under the supervision of Roger Booker, with Peter Hirsch as head of department (figure 2). Roger fully resourced the project (in collaboration with the Plessey Company) and gave very strong encouragement as the work went forward. Tony's research covered the growth of silicon (Si) and germanium (Ge) layers by evaporation in ultra-high vacuum, using apparatus that he constructed himself. Initially, this was sited in the departmental annex at 10 Parks Road, but due to its large size it became necessary to move the kit to another annex in Keble Road, requiring its partial deconstruction to fit through the doors. The initial growth of the layers and defect introduction were examined in some detail. In these years, Tony developed his skills in advanced transmission electron microscope (TEM) imaging and analysis, which were to serve him well throughout his research career. In fact, he started his studies using an original Siemens Elmiskop 1: the vacuum was provided by a mercury diffusion pump, and all the electron beam alignment was

Figure 1. Group photograph (1965) taken at Wadham College, Oxford, in the main quad in front of the college chapel and hall. The warden was Sir Maurice Bowra (approximately centre, second row from front) and Tony is centre, second row from back. (From the Cullis family collection.)

Figure 2. Tony collecting his DPhil in 1972. (From the Cullis family collection.)

carried out by mechanically adjusting the column. Beam tilting was performed by manually adjusting 'Gun Knobs 3' while observing the fluorescent screen; however, eventually an attachment to provide electromagnetic beam tilt and shift was purchased. Of course, modern instruments have electronic control of virtually all adjustments, and the Elmiskop is now a museum piece.

While Tony was carrying out his DPhil project, and in coordination with other research students, he developed his style of 'round the clock' working. When the timing phase shift led to overnight attendance, it was somewhat difficult to set up supervisor meetings, but there was never any problem in booking electron microscopes for extended periods. The dedication of the lab community led to vigorous scientific activity and there were always new developments in materials science and electron microscopy to discuss. Tony often found himself working up to deadlines of various types. On one notable occasion, he had to deliver his DPhil thesis for binding on the following day and had decided to work over the last night preparing many of the final figures in the photographic darkroom. Unfortunately, he forgot to tell the departmental photographer, who proceeded to securely lock the darkroom overnight. Upon discovering this problem after all staff had departed, Tony broke the door lock and carried out the required printing. An interview with the head of department followed soon afterwards!

Postdoctoral research as staff member in the USA: the Bell Labs years

After Tony received his DPhil degree at Oxford (Bruce Joyce was his external thesis examiner), in 1972 he took up the post of member of technical staff in Paul Turner's department at Bell Laboratories in Murray Hill, New Jersey, USA, where he remained for almost three years. The work he undertook there shaped much of his subsequent research, and long-lasting friendships that were struck have played a prominent role. In semiconductor device studies, collaboration was with Lew Katz, Tom Seidel and Alan Moline, work involving depth profiling by Rutherford Backscattering of MeV He^{+} ions. This work closely involved John Poate and his group, while some TEM imaging studies were with Dennis Maher and Sho Nakahara.

Bell Labs were then at the heart of the US telecommunications system with responsibility for the design and manufacture of all hard- and software. This unique combination of research and development led, for example, to the storied invention and implementation of the transistor. The labs, when Tony arrived, were investigating and developing the many aspects of silicon integrated circuit technology. The dimensions of these circuits demanded the latest microscopy techniques. This is where his transmission electron microscopy skills were needed and where he made his mark. The transition from Oxford to Murray Hill, the headquarters of Bell Labs, might have been somewhat of a culture shock for Tony, but he fitted in with his English charm and was quite at home. Indeed, there was a significant contingent of scientists and engineers at Murray Hill from the UK and Commonwealth. Tony is remembered for working through the night because of the low noise conditions required for the electron microscope. He would eat huge lunches with his colleagues at the cafeteria to sustain him through the night. His colleagues regarded him as the consummate gentleman with wide-ranging knowledge. Tony was only at the labs for three years, but formed collaborations that lasted throughout his career.

Permanent scientific staff positions: the Malvern decades

In 1975 Tony returned to the UK and joined the team led by Bill Bardsley in the crystal growth division at RRE in Malvern, Worcestershire. Tony set in place an analytical group (including

Figure 3. Tony operating a JEOL JEM 200CX scanning transmission electron microscope. (From the Cullis family collection.)

Doug Coates, Nigel Chew, Hugh Webber, Gerald Williams and Chris Reeves) and established a new facility for TEM and scanning electron microscopy, which permitted many key materials analyses to be carried out. Ultimately, the first 400 kV TEM in the UK was installed (a JEOL JEM 4000EX), which enabled true atomic-scale resolution to be achieved (figure 3). This large instrument came with a built-in superstructure crane used for lifting the huge, high voltage generator tank and the electron gun chamber. This created a problem in that the room chosen for the installation had a rather low ceiling, but nothing daunted Tony—he foresaw the problem and arranged for a large hole to be cut in the ceiling to accommodate the crane! These were exciting times since, in addition to continued collaboration with friends at Bell Labs (especially John Poate and his group), many colleagues in Malvern were investigating new electronic materials that required detailed microscopic analysis; for example, group III–V compound semiconductors (Don Hurle and Brian Mullin) and group II–VI compounds (Brian Cockayne).

In Malvern, Tony also built a laser annealing laboratory embodying novel beam diffusing light guides. His laboratory became a research leader in unravelling the fundamental phenomena of the rapidly solidifying silicon surface layers, which was a new regime of liquid phase epitaxy. It was established, for example, that the solidifying melt front can propagate at velocities up to 15 m/s; above this value the amorphous phase is quenched in. The amorphous silicon melts by a first-order phase transition. Tony's laboratory attracted much international collaboration from the Bell Labs, Cornell University and University of Catania groups.

RRE was renamed several times, first into Royal Signal and Radar Establishment, then Defence Research Agency (DRA) and later Defence Evaluation and Research Agency (DERA), before it was eventually split up into QinetiQ and the Defence Science and Technology Laboratory, both of which ceased most semiconductor research in the 1990s.

In 1978 Tony proposed and initiated a biennial series of international conferences titled Microscopy of Semiconducting Materials (MSM), and he remained as chairman and

Figure 4. Tony at the 2007 MSM conference dinner in Churchill College, Cambridge. Far left Sir Colin Humphreys FRS, left Paul Midgley FRS (co-chairman) and right Archie Howie FRS. (From the Cullis family collection; copyright unknown.)

principal scientific organizer of the series from the first event in 1979 until 2009 (figure 4). Thus, Tony ran the conferences, on each occasion with a selected local co-chair, for nearly a third of a century and had key responsibility for the scientific content. The series started at University of Oxford (with accommodation for delegates in St Anne's, St Catherine's and Keble Colleges), but now alternates between Oxford and Cambridge universities. Each conference has been financially underpinned and provided with advertising facilities by either the Royal Microscopical Society (RMS) or the Institute of Physics (IoP). The 2009 event (Oxford) was the sixteenth in the series.

The MSM conferences, usually each of three to four days duration, address the state-of-the-art across the complete scientific field of semiconductor studies by microscopy methods, primarily electron-based but also covering X-ray and scanning probe approaches. The scientific work presented ranges from elucidation of the behaviour of novel quantum nanostructures and materials at the atomic level to the understanding of cutting-edge giga-scale silicon devices and the determination of the properties of compound semiconductors such as the very important gallium nitride (the blue laser material). These conferences have been recognized around the world as providing the pre-eminent venue for the presentation of the latest analytical work by leading researchers. The conferences have also been noted for the often cerebral games conducted at the conference dinners: the delegates have been involved in activities such as portrait naming, identification of invited speakers from photographs of them at three to five years of age and delicate egg balancing on straws! The MSM conferences have typically attracted around 160–220 attendees from about 20 countries. The general interaction and knowledge exchange that resulted from the conferences have directly injected important new dynamism into the corresponding sections of the scientific community, leading to increased research activity in semiconducting materials, processes and devices, together with publication of additional associated research papers.

Permanent records of the meetings have been published, containing papers of all contributions, these being peer-reviewed during the meeting and comments/recommendations given to the authors before they left. The success of these volumes, produced by IoP Publishing and later by Springer, has been due to Tony's superb organizational and editing skills, along with a very fine eye for detail. The volumes contain more than 1800 fully refereed papers presented in approximately 10 000 published pages. This success in definition and organization, over a very extended period, of a prominent international conference series has been a unique contribution by Tony to the scientific community.

University professorship: the Sheffield years

After two decades of materials research in Malvern, in 1995 Tony moved to the Department of Electronic and Electrical Engineering (EEE) at the University of Sheffield to take up the chair of Semiconductor Nanocharacterization. He then led the successful application to the Engineering and Physical Sciences Research Council (EPSRC) in a national competition for the first UK fully analytical thermal field-emission gun transmission electron microscope (FEG-TEM). The installation of this instrument has permitted a sequence of PhD students and postdocs to carry out atomic-scale imaging together with nanometre scale analysis using X-ray microanalysis, electron energy-filtered imaging (EFI) and Z-contrast imaging, which were applied to a range of critical materials problems, with a particular focus on advanced semiconductor structures. Just over a decade later, with Thomas Walther now in post, further- funding was secured (this time from the university and EPSRC) to install a world-leading aberration corrected 300 kV cold-field-emission gun instrument offering an outstanding 0.05 nm resolution and providing many exciting opportunities for materials studies on the atomic scale (figure 5). The factory acceptance test at the manufacturing plant in Akishima near Tokyo, Japan, went well in 2009 and the huge instrument was disassembled, shipped and re-assembled the following year in Sheffield, where in the meantime an appropriate building annex had been built that enabled operation of the microscope both within the lab itself and remotely from an adjacent control room.

During his time in EEE, Tony was head of the Semiconductor Materials and Devices Group (1999–2009), which also contained the National Centre for III–V Technologies. He had primary responsibility for a number of major organizational activities, including the 1998 Teaching Quality Assessment exercise in which the department scored a maximum 24 points. He also organized the departmental submission to the 2001 Research Assessment Exercise where, again, a maximum five star award was achieved.

Tony also made sure that John Rodenburg moved over from Sheffield Hallam University and was supported in the development of diffractive imaging by ptychography, a method that has in the last decade revolutionized X-ray imaging, which had previously suffered from the lack of high-quality lenses to focus X-rays into suitably small spots.

Outline of scientific research activities and achievements

Tony's wide-ranging and often pioneering research work was directed primarily towards the elucidation of the microscopic structure and behaviour of semiconducting materials

Figure 5. Inauguration of the double aberration corrected electron microscope at the University of Sheffield in June 2010. From left to right: Sir Harry W. Kroto FRS KBE (Nobel Prize in chemistry 1996); Alan Law, then lord mayor of Sheffield; Tony; Michael J. Hounslow, then head of the Faculty of Engineering; Geoffrey Tomlinson, then PVC for research; Thomas Walther. (Photograph courtesy of Ian Spooner.)

principally using TEM methods, often in conjunction with other advanced analytical techniques. These research studies led to the publication of more than 370 refereed scientific papers, which have received more than 15 000 literature citations. This exceptional citation total demonstrates the impact of Tony's studies on the work of other researchers around the world.

It has been remarkable that Tony not only had an enormous scientific output but that he achieved this despite the modest size of his own research group, which consisted, for most of the time, of just one senior experimental officer, one postdoctoral researcher, a technician and a few PhD students. He supervised all together 14 PhD students between 1995 and his retirement in 2010, so took on about one each year on average. His successful approach was to provide detailed guidance both on sample preparation and data analysis, while supporting all students to regularly attend scientific conferences at which they could present and discuss their own research with their peers.

Solid-phase precipitation

A significant part of the early analytical work performed by Tony at Bell Labs focused upon the investigation of solid-phase precipitation phenomena in semiconductors. Impurity iron (Fe) is occasionally present as an unwanted and sometimes devastating contaminant in device-processed Si. In the early 1970s Bell Labs had a serious problem in Si processing, which had been correlated with the presence of a materials defect that gave a characteristic, kite-shaped, etching feature. However, the nature of the defect was unknown. In order to resolve this problem, in collaboration with Lou Katz, Tony examined the detailed structure of the defect using advanced TEM methods (1). This work was the first to crystallographically identify the ζ_a -$FeSi_2$ (α-lebolite) precipitate phase, which can form in the Si lattice due to the presence of Fe impurity.

Having determined the impurity responsible, the source of the Fe was identified as impure pyrolytic boron nitride discs used during diffusion doping. The presence of the precipitate defect severely depressed electronic device yields and so it was essential not to expose Si wafers to any source of Fe during processing. The analytical work also demonstrated that, if Fe is accidentally introduced up to modest levels into processed device wafers, it can be removed by phosphorus diffusion gettering of the Si. As a second example of solid-state precipitation, later studies of bulk GaAs (6), in collaboration with Peter Augustus and Derek Stirland (Plessey Caswell, UK), identified the nature of precipitate defects often found in bulk ingots of the compound semiconductor. The studies provided the first demonstration that the precipitation of crystalline elemental As commonly occurs in the GaAs during ingot growth prior to the preparation of device wafers. This identification is important because the presence of such precipitates can have a very deleterious effect upon electronic devices subsequently fabricated. Indeed, the work has given substantial insight into general defect formation and diffusion processes in GaAs by highlighting the high mobility of As interstitial point defects in the crystal lattice.

Ion implantation

Ion implantation is a vital step in the processing of semiconductors, and a great deal of Tony's research work was aimed at obtaining a fundamental understanding of the technique and extending it to new areas of application. His first work in the area was in collaboration with Tom Seidel and colleagues at Bell Labs and focused upon inert gas implantation into Si for external gettering applications (3). This was followed by extended collaborative investigations with John Poate of metal miscibility, where ion implantation was employed, for the first time, as an extremely rapid quenching technique to prepare metastable alloys in the surface layers of Cu crystals (2). Substitutional solid solutions (for Ag and W in Cu) and amorphous alloys (for Ta and W in Cu) were produced.

In all this work, studies by Rutherford backscattering of He^+ ions complemented data obtained by TEM work, and the metastability of the quenched alloys was demonstrated in studies of phase separation upon annealing. When Tony moved back to RRE in 1975 he maintained his strong links with John Poate's group at Bell Labs and performed studies of ion implantation in III–V AlGaAs/GaAs multilayer structures. These showed, for the first time, the great and unexpected resistance of AlAs to lattice damage under ion bombardment (21). The mechanism of in-situ recrystallization mediated by highly mobile point defects was identified, and the work enabled unique crystal (AlAs)/amorphous (GaAs) multilayer stacks to be fabricated. Separate investigations (13) of low voltage ion milling for TEM thin specimen preparation (with Nigel Chew at RRE) gave the first demonstration that the technique of reactive I_2^+ ion bombardment would suppress unwanted defect formation in II–VI semiconductors and artefactual disproportionation of In-containing III–V materials. This technology was patented and commercially licensed to Ion Tech Ltd.

Laser annealing and ion implantation

In the later 1970s, news emerged from Russia describing the use of Q-switched laser pulses to anneal the lattice damage produced in ion-implanted semiconductors (Khaibullin *et al.* 1977). This important advance took semiconductor physicists in the West by surprise and immediately a lot of work on laser processing was started. A Q-switched laser is a laser with a modulator where energy is stored in the gain medium for a while and then released in an extremely short, typically nanosecond scale, high-power laser pulse by rapidly switching the cavity quality factor (Q) from low to high. The annual Boston Fall meetings of the Materials Research Society (MRS) evolved to become the major venue for reporting progress. Tony's group at RRE rapidly initiated work in this area in collaboration with John Poate and colleagues at Bell Labs, together with Mike Thompson (Cornell University) and Ugo Campisano and colleagues at Catania, Italy. Ultimately, the studies were broadened to cover other major forms of transient annealing, including electron beam annealing.

This was an exciting time, as it was clear that much fundamental and applied work would be necessary in this new field. At the time of the earliest investigations (1978/1979), the area was one of the most active regions of research in solid-state physics, although Q-switched laser work worldwide was severely impeded by problems of laser beam nonuniformity. It is, therefore, especially significant that Tony invented a novel light-guide diffuser/homogenizer (4) suitable for use with high-power Q-switched laser beams. The diffuser device was patented and licensed for manufacture by JK Lasers Ltd: its development was a breakthrough that led to advances in the science and technology of laser processing which would not otherwise have been possible on the timescales achieved. The impact of the device can be judged by the response of colleagues to the first news of its existence. The events to be recounted took place at the MRS meeting in the Sheraton hotel, Boston, in 1978. At this point in time, Tony was patenting the diffuser device and no details of it had been made known. A keynote talk at the MRS meeting was given by Chris Hill, from the former Plessey Company (Caswell, Northants, UK). He had shown a graphical representation of the electrical activation of ion implants in Si by the use of Q-switched laser pulses. However, his results differed from those of everyone else in the field, since they showed a smooth relationship between laser pulse energy density and level of activation: all previous results showed a poor correlation between these parameters due to the effects of severe laser spot nonuniformity, which could not so far be improved to the extent necessary. Chris Hill's work took a large step forward in this respect, as was evident to the *ca* 1000 attendees at his presentation. At the end of his talk, a forest of hands shot up because there was one key question in peoples' minds: how could he obtain such a close energy density/activation correlation implying such a high order of laser beam uniformity? When Walter Brown from Bell Labs was selected, he pointedly asked this question. Chris Hill's response was that all his anneals had been carried out at DERA, Malvern, UK, using a new technique and that Tony Cullis would need to elaborate on the details. At this instant, heads began to scan the audience and Tony felt that it might be sensible to leave the auditorium. He had positioned himself near an exit to beat the crush at the end of the session, but, after Chris's answer to the question, he felt that he should leave immediately. Tony got up and walked through the exit and heard a scurrying noise behind him. He walked fast enough to stay ahead of his pursuers and, after travelling a short distance, he found a lift with the doors open. He stepped quickly inside and turned to face the doors, which were then closing, and he felt that he had made a satisfactory escape. However, just before the doors came together, an umbrella was thrust between them and forced them open again. The owner of the umbrella then stepped inside, introduced himself to Tony and demanded to know how he homogenized his laser beams so effectively! Needless to say, Tony did not tell him, although he let him down gently!

The experimental laser annealing work that Tony undertook was often in collaboration with long-standing colleagues at Bell Labs, including John Poate, and led to important fundamental advances in the understanding of the annealing method. In the early days, there was much

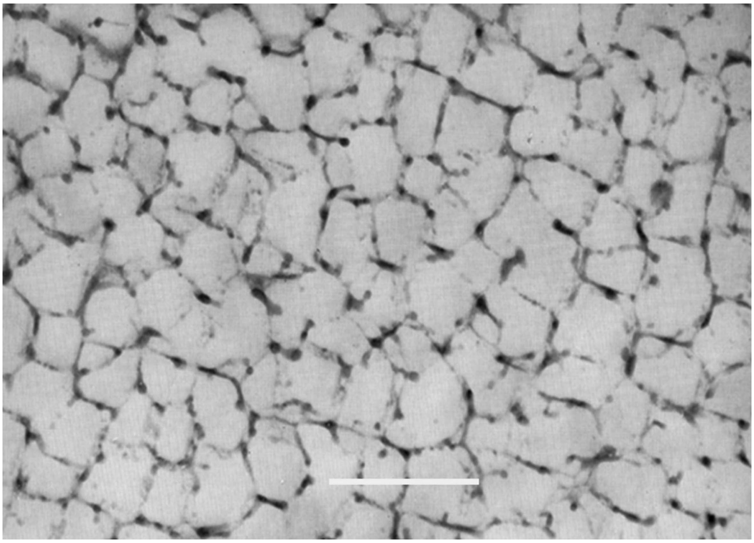

Figure 6. Indium cell structure in laser annealed Si layer due to constitutional supercooling in the resolidifying transient melt. Scale bar is 0.2 µm. (Reproduced from (7) with permission from AIP Publishing.)

argument about the way in which the process of Q-switched laser annealing occurred. One group, led by Jim VanVechten (IBM), argued vociferously that the process was non-thermal and relied upon intense electronic excitation. A second group based around Bell Labs, Oak Ridge, Catania (Italy), and DERA researchers maintained that the process was indeed thermal and relied upon rapid pulse melting and resolidification. The arguments in this area raged for several years and were channelled, to a large degree, through the annual MRS meetings in Boston. Tony occupied a position at the core of this debate and carried out collaborative experiments that ultimately settled the question in favour of pulsed melting. A notable first observation was that of large solubility enhancements for certain low-solubility impurities in Si—up to three orders of magnitude for Pt in Si (5)—due to non-equilibrium solute trapping during very high speed solidification of the laser-induced melt. Very importantly, a proportion of a low-solubility dopant is in general swept out to the Si sample surface by segregation in the transient melt, and Tony's TEM work first established that a characteristic cellular distribution of segregated impurity was formed due the occurrence of constitutional supercooling (5) in the resolidifying liquid. These studies benefited greatly from collaboration with the leading crystal growth theoretician Don Hurle, and led to the first quantitative theoretical description of the observed phenomenon by the application of full morphological stability theory (7). The importance of these solidification impurity cell structures was such that a key example (In impurity in Si) found its way on to the cover of the proceedings of the 1979 Microscopy of Semiconducting Materials Conference (figure 6). These studies, as much as any, demonstrated that Q-switched laser annealing took place by transient melting and contributed directly to the ending of the world-wide argument on this topic.

The most extreme conditions of Si Q-switched laser annealing were subjected to careful scrutiny to provide unique information on phase transitions between a transient melt and the amorphous state. By correlation of experimental observations and computer simulations, Tony's work was first to quantitatively determine (8) the different solidification velocities required to amorphize (001)- and (111)-Si. This work relied upon a first derivation of the correct functional form of the thermal conductivity/temperature dependence of amorphous Si (11). A new defect formation regime was identified for (111)-Si at solidification velocities just below the amorphization threshold. This work was extended by high resolution TEM studies which, for the first time, directly correlated crystal growth breakdown during very high speed solidification with atomic-scale growth processes (including twin formation) at the melt/solid interface (12). Subsequent collaborative work (10) with John Poate and Mike Thompson (Cornell) employed nanosecond resolved, transient conductivity measurements to provide the first direct experimental measurement of the (001)-Si amorphization threshold velocity, giving confirmation of the earlier calculations (8). John and Mike came over to DERA for these experiments since Malvern was producing the most uniform Q-switched ruby laser pulses available at that time. They managed to secure a seat on a military flight into Brize Norton for John (listed as Dr Poate), but, interestingly, on the return journey he was called last to board the flight. On checking why this might have happened, he was informed that this was the correct ranking position for Driver Poate!

Detailed investigations of indium-implanted amorphous Si layers subjected to ultra-high speed melting and solidification were employed by Tony (9) to demonstrate a new type of explosive crystal growth process during laser annealing. Of special importance, this work provided the first evidence to show that amorphous Si melts by a first-order phase transition to form an undercooled, normal, low-viscosity liquid and that the amorphous phase is not itself a glassy state.

Porous silicon

More recently at Malvern, Tony's work focused on in-depth collaborative studies, with Leigh Canham, of luminescent porous Si formed by anodization. Porous Si itself has a long history. It was first formed in the 1950s at Bell Labs (Uhlir 1956) and later exploited in Japan to produce thick Si oxide for electronic device isolation (Imai 1981). However, there was a massive increase in interest when Leigh demonstrated (Canham 1990) the tuneable, highly efficient, room temperature luminescent light output from the material. One of the driving forces for detailed study of the material was the early worldwide uncertainty regarding its structure and the mechanism of highly efficient multi-colour luminescence emission; this situation impeded many potential advances and there was a priority need to clarify the situation. In fact, over a period of time, at least 20 different mechanisms (involving postulated hydrogenated amorphous Si, surface hydrides, luminescent molecules, Si or oxide defects, surface states, etc) were put forward worldwide to explain the observed luminescence. Tony's detailed TEM studies demonstrated conclusively (15), for the first time, that anodized luminescent porous silicon is composed of quantum-domain crystalline Si nanostructures, principally (~2–4 nm wide) quantum wires, which account for its light emission, under photo-excitation, by recombination of quantum-confined excited carriers (figure 7). This luminescence mechanism has stood the test of time and has been overwhelmingly supported by independent scientific evidence. Of particular importance, resonantly excited photoluminescence has characterized the phonon structure of the luminescent material and has shown that it has the electronic and vibrational band structure of crystalline Si (Calcott *et al.* 1993). Tony's TEM work also established that thickness fluctuations exist in the quantum wires present in the porous material, and it was pointed out that this would lead to carrier trapping due to band-gap variations, a

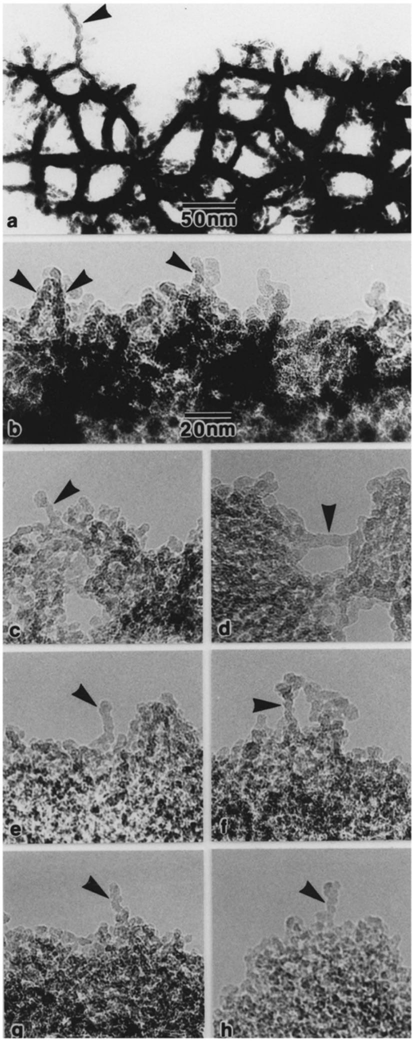

Figure 7. TEM images (with slight underfocus) of thin porous Si layers showing narrow undulating Si quantum wires (arrowed) protruding beyond the matrix edge. (Reproduced from (15) with permission from *Nature*.)

phenomenon of great significance in accounting for the high luminescence efficiency of the material. The importance of the reported work derives from the materials understanding obtained, which strongly underpinned the very rapid expansion of this field and excluded the many other proposed but incorrect luminescence mechanisms. Indeed, the *Nature* paper (15) has received more than 1200 literature citations (as of 2025) from around the world, thus demonstrating the tremendous impact that this research advance generated in a field that proved to be one of the most active in solid-state science.

At one time, argument also raged over the significance of luminescence given by highly oxidized porous Si. However, Tony's work (18) once again gave the first demonstration that crystalline Si nanostructures in this material could straightforwardly account for its luminescence, and dispute in this area has since become inconsequential. A leading review (20) presented a detailed and very comprehensive survey of worldwide work in this scientific area.

Epitaxial layers and devices

In recent years, there has been considerable interest in epitaxial growth phenomena and, in particular, stress relief in heteroepitaxial structures. For compressively strained epitaxial layers, morphological distortion in the form of surface ripples can occur. The TEM work carried out by Tony studied such a system, namely epitaxial SiGe alloy layers grown on Si (16). These investigations were the first to provide direct measurement of the form of the local strain variations (strain waves) within microscopic ripple arrays upon the SiGe layers. The results demonstrated that such surface morphology evolution is expected to be a general phenomenon for heteroepitaxy with high compressive stress since, in accord with theory derived by others, surface ripples are produced when their presence yields a low free-energy state of the epitaxial system. Subsequent investigations by Tony gave quantitative measurements of the microscopic ripple strain and showed that stress relief in the ripple crests is essentially complete in the direction of the periodic field (normal to the ripple rows). A consequence of this behaviour is that considerable additional compression is induced at troughs in the ripple structures. Tony's work in the InGaAs/GaAs system was the first to experimentally demonstrate (19) that misfit-relief defects preferentially nucleate in such strained trough regions—the first observation of this new misfit defect formation mechanism. The theme of heteroepitaxial layer studies was continued in a wide collaboration between the DRA (Colin Whitehouse, Tony), the Universities of Sheffield, Durham and Hull and the Daresbury Laboratory (later, the European Synchrotron Radiation Facility in Grenoble). This group undertook molecular beam epitaxy (MBE) growth investigations by in-situ, real-time X-ray topography observations using the electron synchrotron (17). The work employed a unique UHV MBE apparatus that could be inserted into a synchrotron beamline to monitor epitaxial growth as it took place. For a two-year period, Tony led the DRA activity before moving to University of Sheffield. The project focused on the InGaAs/GaAs system and produced a number of key achievements, including observation of a two-stage activation of misfit defects (14).

After moving to Sheffield in 1995, Tony aimed his TEM-based research in several distinct directions. A first important TEM application related to the 'SiGe/Si Heterostructure MOS' EPSRC-funded programme with seven university and three industrial partners, together initially with DERA. Here, for p-channel devices, the precise profiles of 10 nm SiGe alloy channels were measured, since these controlled device characteristics and were required for device modelling. This work, in collaboration with David Norris, pushed the available analytical techniques to the limit and showed, principally by EFI, that the SiGe alloy channels had 2–3 nm compositional asymmetries due to the effects of elemental segregation during growth (22). By using a kinetic segregation model, it was then shown in leading work that the experimental results were in accord with theoretical expectations.

A second important TEM application focused upon determination of the exact distribution of B dopants introduced into Si by then state-of-the-art low-energy ion implantation. This was required by integrated circuit manufacturers for device modelling, and their reliance for measurement on secondary ion mass spectrometry (SIMS) had begun to give problems with such shallow dopant distributions. Tony's studies, in collaboration with Teh-Sheng Wang, measured by EFI for the first time the precise buried B distribution with nanoscale accuracy (23). For

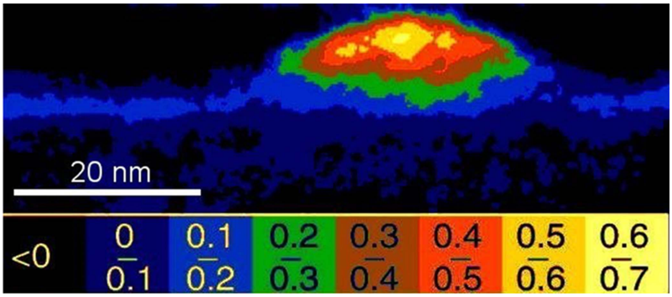

Figure 8. Indium distribution within InGaAs/GaAs quantum dot measured by energy-filtered TEM (24). (Image provided by Thomas Walther.)

as-implanted material, the distribution was shown to be smooth with no surface peak, contrary to all previous determinations by SIMS, which were relied upon by the semiconductor industry and which were now seen to require reinterpretation. For annealed material, the first direct observation was made of nanoscale dopant clustering, which gave fundamental insight into dopant behaviour and was important for process modelling by computer simulation.

In a particularly important area of work, unique information about the nature of the Stranski–Krastanow (S-K) epitaxial growth instability (Stranski & Krastanow 1938) was obtained by Tony in collaborative work with Thomas Walther using nanoscale measurements of composition gradients following initial growth and island formation in the InGaAs/GaAs epitaxial system. The S-K transition is widely used to produce nanoscale islands (or quantum dots) for use in (opto)electronic device fabrication and in ranges of advanced research. For the first time, this work identified the process of elemental segregation as generically underlying the S-K islanding transition in heteroepitaxial layer growth (24, 25). The process of segregation had not previously been identified in this role; indeed, the newly devised mechanism is potentially applicable to all strained-layer systems exhibiting the transition (except under restricted conditions where, for example, an Asaro–Tiller–Grinfeld morphological instability occurs). The work (25) directly addressed the important InGaAs/GaAs layer growth system and specified the way in which the islanding transition is fundamentally controlled by surface segregation of indium in the initial ultra-thin flat 'wetting' layer, causing surface strain and elevating the adatom number density, which ultimately leads to island nucleation. The quantitatively accurate description of islanding in the InGaAs/GaAs system by the new mechanism was demonstrated (25). This new mechanism provides a fundamental explanation for the 60-year mystery concerning the nature of the islanding transition, including the reason for initial flat layer growth before island formation. The great importance of understanding the transition mechanism is emphasized by the fact that, as indicated above, the transition is employed in the production of virtually all self-organized epitaxial semiconductor quantum dots that have paved the way to more efficient light emitting diodes and better solid-state lasers that were studied in the nearby physics department of the university, so understanding the basic crystal growth was key to making better (opto-)electronic devices. Highly detailed and optimized control of the process depends crucially upon understanding the underlying mechanism. In addition, the studies (24) provided the first direct 2D composition measurements within individual nanoscale InGaAs quantum dots (figure 8) and confirmed that there is an alloy gradient (with a 'trumpet' profile having excess indium at the dot apices) in accord with the results of independent indirect scanning tunnelling microscope (STM) and optical spectroscopic measurements. Knowledge of the precise composition gradient is vital for accurate modelling of quantum dot characteristics. Indeed, in collaboration with Max Migliorato and Dave Powell, modelling of the complex composition variations in quantum dots was carried out using the Tersoff potential in order to determine the extent of structural relaxation in cross-sectional samples (26)—for comparison with STM measurements—and to describe the anisotropic electron energy levels exhibited (27).

External activities

In the area of scientific publishing, Tony was a founding editor board member and, from about 1990, editor (with S. S. Lau) of the review journal *Materials Science and Engineering Reports* (Elsevier). In the years 2000 and 2002 the journal had the highest citation impact factor of all journals in the worldwide materials science area.

In addition, Tony served on many organizational committees of professional bodies; these posts included the chairmanship of the Electron Microscopy and Analysis Group of the IoP and membership of the council of the RMS. In 2001 Tony was elected president of the Scientific Council of the Tecnologie Avanzate e nanoSCienza (TASC) national laboratory (Trieste, Italy), with direct responsibility to the president of Istituto Nazionale per la Fisica della Materia and to the director of TASC for conducting formal annual reviews of TASC activities, including work on several beamlines of the ELETTRA synchrotron.

Finally, Tony's work on the MSM series of conferences has already been outlined earlier.

Family life and personal interests

During his student years at Oxford, Tony impressed his fellow students not only with his quiet, hard work but also by (nearly) always wearing a bow tie and driving an MGB sports car. On 6 October 1979 he married Ruth Edith Allen, a Guy's trained nurse, in the parish church of Broadheath in Worcestershire.

Bow ties remained Tony's hallmark over several decades. He also enjoyed charismatic cars and even owned a Ford Mustang during his time in New Jersey. Later on, he drove a Rover Vitesse, a Nissan Skyline GT-R and finally a fun Mini Cooper.

A further long-standing interest was philately, and Tony especially enjoyed looking out for rare stamps with printing errors to add to his collection. He also collected many vinyl pop records, particularly during the 1960s and 1970s.

Tony sadly passed away on 9 December 2021 after a long battle with Parkinson's disease, leaving behind his wife Ruth, daughter Elizabeth, a scientist in the field of cancer research, and Richard, a car designer. Tony also left three grandchildren: May, William and Clara.

Awards

1984 Leslie Holliday Prize, the Institute of Materials, Minerals & Mining, London
2004 Fellow, the Royal Society
2016 Honorary Fellow, the Royal Microscopical Society

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The frontispiece portrait photograph was taken in 2004 by Prudence Cuming Associates and is © the Royal Society.

Author profiles

Thomas Walther

Thomas Walther is a trained physicist and has been reader in advanced electron microscopy at the University of Sheffield since 2006/7, having spent postdoctoral years in both France and Germany. He first met Tony at the MSM conference in Keble College, Oxford, in 1993.

John L. Hutchison

John L. Hutchison has been reader in materials in the Department of Materials, University of Oxford, and has known Tony closely since the 1970s. He worked with Tony for many years as co-chair and proceedings editor of the MSM series of conferences in Oxford. He retired in 2010.

John M. Poate

John M. Poate is emeritus senior vice-president of research at the Colorado School of Mines. He previously served as a Harwell fellow of the UK Atomic Energy Authority, head of the Silicon Processing and the Interface Physics Research departments at Bell Laboratories (where he met Tony) and dean of the New Jersey Institute of Technology.

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