

The MIDAS project at ASU: John Cowley's vision and practical results

J. A. Venables^{1,4}, G.G. Hembree¹, J. Drucker¹, P.A. Crozier² and M.R. Scheinfein³

- 1) Department of Physics and Astronomy, Arizona State University, Tempe AZ 85287-1504
- 2) Center for Solid State Science, Arizona State University, Tempe AZ 85287-1704
- 3) Department of Physics, Simon Fraser University, Burnaby BC, V5A 1S6, Canada
- 4) Also at Department of Physics and Astronomy, University of Sussex, Brighton BN1 9QH, UK

ABSTRACT

A review is given of the conception and development of the MIDAS system at Arizona State University: a *Microscope for Imaging, Diffraction and Analysis of Surfaces*. John Cowley's vision in the early 1980's was ambitious and far-reaching, and he was the reason why the authors came to ASU. We were centrally involved in design and implementation of MIDAS from the mid-eighties onwards; the novel design features are briefly reviewed. Practical results, obtained using this instrument are listed, and the scope for future development and applications are indicated. While it is clear that many new results have been demonstrated, even more possibilities still remain to be explored. Some comments are made about the feasibility of such developments in the light of competing instrumentation.

Keywords: UHV electron microscopy; SEM/STEM, secondary and Auger electrons, nanofabrication, diffraction studies, surfaces, crystal growth, small particle catalysts, magnetic materials.

*Corresponding author: Email: john.venables@asu.edu Fax: (1) 480 965 7954

Journal of Electron Microscopy, submitted (2005); version 6 February 2005

1. Introduction and dedication

The development of new techniques for electron microscopy was a central thread in John Cowley's professional life. This paper describes a particularly ambitious and far-reaching project at Arizona State University, which he initiated in the early 1980's. As all scientists know, having a suitable acronym is one of the first stages of a proposal, and he coined the phrase *MIDAS*, a *Microscope for Imaging, Diffraction and Analysis of Surfaces*. The instrument in question was a fully ultra-high vacuum microscope, with all these analytic tools either in place, or waiting to be developed as the project proceeded.

Not everyone liked this acronym, and of course the same set of letters has been used for many other projects in different fields. More ascetic authors preferred to acknowledge the central role played by the firm VG Microscopes, referring to the microscope as "a new instrument based on the Vacuum Generators HB-501S Scanning Transmission Electron Microscope (STEM)", or words to that effect. The firm's role was indeed central, and some of this involvement is described in section 2. At one point of this development, when the first results should have been available, but were not, the first author gave a talk describing the *SAGUARO*, a *Scanning Auger Giant with Unlimited Applied Research Opportunities*. At a later stage, while waiting for a particularly long bake-out, or equivalent delay, a poster was produced, showing John Cowley in the role of king Midas, and using advertising material from the well-known muffler and brake shop, which had the slogan: *Nobody beats MIDAS*. This poster also did not meet with universal approval, but John liked it, pointing it out to visitors, in what would now be called "outreach". A few years later, after many achievements obtained at a price, this part of the poster received the graffiti: *MIDAS beats everyone!* At this point the poster was taken down and stored out of sight.

The authors of this paper were all centrally involved in the realization of the *MIDAS* project from the mid-80's onwards; in effect, we all came to ASU because of Professor Cowley, either directly or at one remove. Some of the lessons we have learned are discussed in section 8, but in the next few sections we describe the published results obtained with *MIDAS*. Scanning electron and Auger microscopy are described in section 3. Electron Energy Loss Spectroscopy (EELS) and coincidence spectroscopy are described in section 4, and the use of *MIDAS* for nanofabrication and diffraction studies in section 5. Applications to crystal growth and catalysis, and to magnetic materials, are given in sections 6 and 7.

In dedicating this paper to Professor John Cowley's memory, we acknowledge his scientific and inspirational powers, his collaborative fund-raising, and the central, supportive part that he played in our own professional development. John was in his laboratory working until the day he died, and his papers are still appearing as we write. As they say: "he died with his boots on"; there is no better accolade than this in the "wild west". He was a role model for us all.

2. From concept to design and delivery

John Cowley had the concept of an ultra-high vacuum (UHV) Scanning Transmission Electron Microscope for studies of surfaces in the early 1980's, following on his extensive experience with his VG HB5 STEM [1]. The first author had some similar ideas at Sussex, and his group had developed the first UHV-Scanning Electron Microscope (SEM) in the mid-1970's, also manufactured by Vacuum Generators. In 1981, at one of the annual winter workshops John Cowley introduced so successfully, John Venables was invited to speak on "Electron Microscopy of Surfaces" [2]. This led to continued contact with the ASU group and an exchange of ideas, a feature that was also in place with Pieter Kruit and his group in Delft, who was developing related thoughts. The second author, Gary Hembree, had previously worked on a homebuilt surface reflection instrument named REMEDIE, which was Cowley's original move into surface science, using medium energy electrons [3].

The first author tried in 1981 to obtain funds for a European collaboration on a MIDAS-like instrument, and in preparation had produced the outline components for the design; but he basically failed to secure such funding. John Cowley, however, was meanwhile seeking funding from various sources, and had obtained almost all of the money for construction before 1985 [4].

Over 1983-1986 much progress was made on the design, both in Arizona and at VG Microscopes, in East Grinstead, UK. The initial order was placed in September, 1984, with supplemental orders placed over the following 2-3 years. The VG team led by Sebastian von Harrach went to enormous trouble with all the design and development work, fraught decisions about computer control, with many unknowns about sample stages, preparation chambers and all the details needed to prove the vacuum, performance and resolution specifications [5]. In the event, the substantial 100 kV column design was the prototype for a higher voltage (300 kV) STEM, the console was the last instrument constructed with analog electronics, and the solutions for stage design and sample interchange to full UHV standards were obtained against the

pressure of a real time deadline. Thus, as in many cases involving really new instrumentation, the divide between what is done by the firm, and what is done by the purchaser is in the limit arbitrary; the user starts with what is delivered and goes from there.

This project required manpower, and John Cowley knew what he was and was not planning to do personally. He had admirable foresight and great generosity. After a couple of years in the planning stage, he offered the first author a position on the faculty at ASU with the disarmingly simple question: ‘How do we continue this collaboration? Have you thought of a half-time job?’ Gary Hembree returned to ASU (he was earlier John Cowley’s PhD student) as a staff scientist, and Jeff Drucker came as a post-doctoral research associate. With students Frank C.H. Luo and Mohan Krishnamurthy, this was first MIDAS team. With generous support from the University, the laboratories were renovated by the time the instrument arrived in June 1988.

The column schematic of MIDAS is shown in Figure 1 [5]. One of the new ideas involved the insertion of “parallelizer” coils in the objective lens bores, both before and after the sample position. These coils have the ability to focus low energy electrons, using the spiraling of their trajectories in the magnetic field that decreases away from the objective lens to a lower value inside the parallelizer, followed by a magnetic aperture that terminates the field abruptly. This topic was researched by Kruit and Venables jointly for their respective projects [6, 7], following earlier work by Kruit and Read. The MIDAS column has surface science “chambers” both above and below the sample. In parallel, a dimensionally similar chamber was constructed at ASU, in order to research the transfer optics for low energy and Auger electron spectroscopy in the STEM column. These transfer optics were thoroughly tested off-line [8, 9] and a commercial concentric hemispherical analyzer (CHA) was purchased from Vacuum Science Workshop to complete the system. The arrangement is shown schematically in Figure 2. A brochure from VG Microscopes Ltd showed the system essentially completed in May 1988, as indicated in Figure 3. But as far as we know, no similar system was actually constructed for any other laboratory. So the MIDAS - HB501S instrument was, and remains to this day, unique.

Computer-based instrument control and data collection was at an early stage, but absolutely necessary for a project of this complexity. We started rather conservatively, using the PDP-11 based systems we knew worked well in the Sussex context [10]. Chris Harland made several visits to ASU to help implement these systems and programs, in collaboration with Mark McIntyre and the second author. Computer systems were evolving with great rapidity, and, in

line with every other experimentalist, we could not afford to change systems with each new advance in memory or speed. In retrospect, the efforts we made to get data acquisition programs down to the memory limit (32kB) of the initial PDP-11's were heroic; anyone who survived that period has a healthy respect, and a certain regret, for the self discipline involved. These computer systems were subsequently replaced by mobile computer stations based on clever use of the PDP-11 architecture, known locally as Rez-mobiles [11], which became the initial basis of the flourishing spin-off company Emispec [12] in the hands of J.K. Weiss and Hans de Ruijter.

3. Biased secondary and Auger Imaging

In the period 1986-1989, there were several visits to conferences to describe the MIDAS project, and to talk about initial experiences [13]. On the first occasion [14] this was to “fly the flag” for the whole of traditional electron microscopy, in the context of the rapidly emerging Scanning Tunneling Microscopy (STM), which won the Nobel Prize in 1986 for Binnig and Rohrer, and in the hands of others was soon to dominate surface studies. The winter workshop at Wickenburg in 1989 was devoted to “Surfaces and Surface Reactions”, and included our paper on biased secondary electron imaging (b-SEI) [15], which demonstrated bright field, dark field and secondary electron images from both surfaces of the same area of thin foils, as shown in Figure 4. Such images had never been seen before, and showed great promise. But the conference also included some of the most beautiful examples to date of surface sensitive STM as well as Low Energy Electron Microscopy (LEEM) [16]; it became clear that the MIDAS project would have to justify itself in a fiercely competitive environment. For the record, it should be noted that this was not clear at the concept stage. MIDAS was John Cowley's stake in the world of Surface Science, the climate was open to instrumental innovation, and we did not know exactly where it would lead.

The combination of secondary electron with Auger spectroscopy and imaging was the first MIDAS development project to be undertaken at ASU, and resulted in several early conference reports and some applications over the period 1989-1992 [17-21]. At the beginning of this period, the papers were development reports [17, 18] but by the end we had good proof-of-concept results in regular journals, and had demonstrated unprecedented secondary electron resolution of <1nm and Auger resolution of <3nm, with sensitivity of 10 atoms for the favorable case of Ag/carbon [19-21]; the case of Ag islands on bulk Si(100) is shown in Figure 5. This

Auger performance has not yet been approached in any other instrument. We also had in hand the first applications to crystal growth and catalysis, as described in section 6. As a byproduct of this interest in crystal growth, Jeff Drucker imaged individual surface steps on Si(100) using b-SEI [22], and had evaluated the contrast on a trajectory model [23] by 1991.

4. EELS and coincidence studies

Electron imaging methods often use secondary electrons to produce high-resolution, low-noise topographic (and work-function) contrast, even on surfaces and at step edges [15, 22, 23 and references quoted]. Secondary electrons (SEs) are produced from a complex cascade process. Energy deposited by the high energy incident electrons gives rise to secondary emission. It was postulated that either SE production resulted from straightforward energy deposition as in the Sternglass model, or, alternatively, that valence shell excitations and plasmons with their large intrinsic cross sections dominated SE production. As secondary emission is extremely sensitive to surface electronic structure and contamination, MIDAS seemed the ideal tool to attempt to resolve the pathways responsible for SE production by using electron correlation spectroscopy (coincidence spectroscopy).

In order to perform the experiments we needed to measure the time between specific energy loss events and SEs. The “Rez-mobile” used within HREM for data acquisition and control [11] was not flexible enough to measure the time-correlation spectra and extract coincidence spectra in single-electron counting mode. Post-doc J.K. Weiss built the very first windows based data I/O system, specifically designed around National Instruments cards and using Windows 3.0, to conduct the coincidence studies. The production of this prototype system helped him (and later Hans de Ruijter) in crossing the bridge to private enterprise and the creation of EmiSpec systems [12].

The electron coincidence work was conducted in three stages: (1) Studies on simple amorphous carbon films focusing on valence band excitation and energy deposition in general; (2) Studies on single crystal silicon, so that band effects might be identified in the correlation spectra; and finally (3) Studies looking at large momentum transfer energy loss events as a means of explaining the intrinsically high spatial resolution available in SEM images. The low count rates and weak signals in time correlation spectra led to extended experiments, thereby dominating the up-time on MIDAS for almost 6 months. The results indicated that while well

defined electronic structure could be identified as being responsible for individual SE events, by and large, the data confirmed that SE production was indeed directly proportion to the total energy deposited in the film [24-27]. Further, the k -space measurements confirmed that indeed large momentum transfer events were more efficient at producing SEs, a conclusion that supports the observation of high spatial resolution in SEM images.

The MIDAS work on correlated electron spectroscopy closely followed the work of Pieter Kruit's group in Delft on amorphous carbon (conducted in a non-UHV environment) [28]. Our own work was followed by experiments in the Cambridge group by Mullejans *et al.* [29], where our results were essentially confirmed. Although our efforts to elucidate SE production pathways were successful, the complexity and poor statistics implicit in this type of experiment forced us to abandon further work in this area on MIDAS.

5. Nanofabrication and diffraction studies

One of the initial uses of the unique capability of MIDAS to image simultaneously the upper and lower surfaces of a sample with secondary electrons [15] was to electron-irradiation damage in Transition Metal Oxides (TMO). Peter Crozier, Molly McCartney and David Smith wrote a series of papers in 1990-91 outlining the results [30-31]. These studies were in part stimulated by a notion developed by Colin Humphreys and coworkers in the mid-eighties, that the extremely fine damage features produced by the STEM probe in TMO could be used in some way to either produce novel physical phenomena for research, or in practical applications of nano-lithography (still to be determined) [32]. In the latest development of the MIDAS instrument system the second author, in collaboration with John Spence's research group, has been enhancing the capabilities of the machine to do large scale patterning of inorganic resists of several types, including TMO-doped silicate glasses. The initial stages of this work have been reported in a recent publication by Nan Jiang *et al.* [33].

A parallel recent development of the HB-501S in collaboration with John Spence has been in the area of nanodiffraction. The instrument has from the beginning produced spectacular Convergent Beam Electron Diffraction (CBED) patterns from a single crystal YAG screen. Since the electron-optical column was the first ever delivered from VG with a full post-specimen lens stack, including a strong projector lens at the output, the range of camera lengths available at relatively low image distortion is very large. However, the method of recording the CBED

patterns as delivered, on 35mm camera film, left much to be desired when it came time to extract real data from them. Initial experiences with an add-on 512x512 pixel CCD camera were equally frustrating, due to the primitive state of computer interfacing at the time.

We have now largely solved these problems and at the same time increased the size and resolution of the recorded CBED pattern, by replacing the serial energy loss spectrometer at the top of the column with a large diameter phosphor screen, which is fiber-optically coupled to a 2048x2048 pixel, 16 bit CCD camera. This development is reported along with some initial applications in the 2003 publication by Hembree *et al.* [34]. One of these applications made use of electron Ronchigrams to measure the spherical aberration coefficient of the objective lens. Cowley coined this term around 1980 to describe the distorted lattice fringe images which appear in large angle shadow images of crystals oriented in strongly diffracting directions. He then developed and demonstrated a method to accurately measure several electron optical properties of a STEM by measuring geometric ratios in these patterns [35]. Figure 6 shows an electron Ronchigram produced by three beam interference from a [100]-oriented Beryl crystal in MIDAS. One of the many lasting legacies of John Cowley is the routine daily use of shadow images and Ronchigrams by microscopists world-wide to align and optimize their STEM instruments.

6. Applications to crystal growth and catalysis

Initial applications were to crystal growth and catalysis, as these topics were close to the core interests of the initial MIDAS team. Some systems were chosen for their importance to semiconductor materials physics, with the growth of Ge/Si(100) being a hot topic at the time, and subsequently. Jeff Drucker and Mohan Krishnamurthy worked hard on this system, and produced some of the important early results using MIDAS [20], as well as Krishnamurthy's PhD thesis [36]. He was so successful in applying for scholarships during this period that our vitae became saturated with conference proceedings [37]. This material was boiled down to a major paper [38] in which the results were distilled, as illustrated in Figure 7. Mohan went on to start a brilliant career in electronic materials, which was tragically cut short in 1998 in a freak drowning accident; volume 570 of the MRS Symposium series is dedicated to his memory [39].

Another initial system was Ag/Si(100), since there had been a lot of prior work in the first author's Sussex group; it was an excellent test system for Auger spectroscopy and imaging and provided some new results [20, 21], not least on the stability of the intermediate layer [9,

40], which had been variously measured to be between 0.25 and 1 monolayer (ML) thick in previous experiments. Silver in small particle form has interesting catalytic properties, as well as having a strong Auger signal in a useful (350 eV) energy range. Thus Jingyue Liu, supported on a post-doctoral fellowship by Gerard Spinnler of Shell, was able to demonstrate both the resolution and sensitivity of the Auger signal, as well as the applicability of MIDAS to both publishable [41] and proprietary studies of model and real catalysts. Dr Liu went on to a distinguished career with Monsanto, where he is a major expert on catalysts [1]; comparisons of MIDAS and other techniques for such studies have been published more recently [42, 43].

Another student, Yun Li, also worked with us on Ge/Si(100) in the early 90's, though not on MIDAS, and reminded us that not all surface work requires a microscope; in her case she used AES on Si/Ge/Si(100) sandwich structures to determine the segregation energy of Ge at the surface of Si(100) to be 0.24 ± 0.02 eV [44, 45], very close to that subsequently calculated by others [46]. In the same time period, Krishnamurthy and Drucker used MIDAS to extend their interest in related systems by exploring Ag/GaAs(110) [47] and Ag/InP(100) [48] for comparison with Ag/Si(100). Jeff Drucker, who returned to ASU as a faculty member in 2000, has made the Ge/Si system his own, with extensive work on the growth, inter-diffusion and properties of quantum dots [49] using many techniques, but especially atomic force microscopy (AFM) in conjunction with HREM and EELS.

7. Applications to magnetic materials

The renaissance in research in magnetism in the late 1980s was largely stimulated by the ability to fabricate monolayer metallic films. Amongst the most important synthesized magnetic properties were giant magneto-resistance and exchange coupling between ferromagnets through non-magnetic metallic spacers, effects that depend very sensitively on the lattice type and spacing. An important report set the agenda for magnetism research in the nineties [50].

Magnetic films grown in registry with the substrate produce lattice distortions (or pseudomorphic phases) with unusual properties, but metallic-monolayer film growth might also be influenced by defect and step edge nucleation, and vertical site exchange across interfaces since the atoms in metal surfaces are relatively loosely bound. These magnetic monolayer systems were ideal candidates for high spatial resolution studies in MIDAS. We added preparation facilities, including electron beam metal evaporators, and characterization facilities,

including a surface magneto-optic Kerr effect (SMOKE) station, to the MIDAS preparation chamber in 1991. A schematic drawing of these facilities is shown in Figure 8. We aimed to correlate high spatial resolution structural and chemical information from b-SEI and Auger electron imaging, obtained in the same UHV ambient in which the films were grown, with macroscopic magnetic properties obtained by SMOKE.

The first system we studied was (in 1991) the most investigated, and perhaps complex metal-metal system: f.c.c Fe/Cu(100). The f.c.c phase of Fe, stable in bulk above 911° C, could be grown on Cu(100) with 0.83% lattice mismatch at room temperature. For f.c.c (f.c.t) Fe, a non-magnetic, high and low spin, or an anti-ferromagnetic phase can be stable depending upon the lattice constant [51]. Our Fe/Cu(100) studies, both on and off MIDAS, lasted nearly 3 years, resulting in the theses of Kevin Heim [52], Zhijun Yang [53] and many papers [54-59], with the participation of Masters student Sean Healy. A set of hysteresis loops taken with the SMOKE system is shown in Figure 9.

Our most notable findings were observations of sub-surface Fe-island formation in room temperature grown films, identified using nm-resolution Auger imaging, and a weak field-dependent metastable phase, that was probably the result of low level carbon contamination in our films. We were able to demonstrate, using the unparalleled sensitivity of MIDAS, that defect (oxygen) densities well below the broad beam Auger sensitivity limit had a dramatic impact on film growth. But we were unsuccessful in correlating specific nanometer-scale film structure with measured bulk magnetic behavior. The definitive work on Fe/Cu(100) may still be in the future, but measurements using STM at the same time elegantly displayed how mobile Cu atoms on (100) surfaces impacted film growth [60]. Subsequent work extended the same type of approach to Co/Cu(100), with Steve Coyle's thesis [61] and related papers [62].

With the trials of Fe/Cu(100) still fresh in our minds, we realized that we needed to focus on magnetic systems that played to the obvious strength of MIDAS, unparalleled transverse spatial resolution. We shifted to small particle magnetism, specifically order-disorder transitions induced by geometrical ordering on surfaces on nm-length scales [63-66]. CaF₂/Si(111) was selected as a technologically relevant material, one that should yield small islands of transition metal (Fe, Co) on the insulator, and, perhaps might be patterned in-situ. Locally modifying the surface of the CaF₂ using the electron beam in MIDAS, producing Ca-rich areas, might more effectively nucleate the transition metal deposit. Important results were obtained on random 2D

particulate magnetism [63-65], and it was convincingly shown that film growth was dominated by defect nucleation [66]. Our efforts to produce lithographically defined structures in-situ stopped at that point, and further progress was not made until Akira Sugawara arrived as a post-doctoral fellow, and introduced us to his NaCl(110) reconstructed surface-templates. This very successful work, however, did not use the MIDAS instrument, but relied on a combination of Kerr microscopy, SMOKE and standard ex-situ TEM analysis [67].

8. Discussion and conclusions

This article has introduced the MIDAS project at Arizona State University, emphasizing John Cowley's vision for the instrument, and the authors' experiments with it, especially in the initial period. Cowley himself was always interested in the extension of microscopy to surfaces, in the context of what one could achieve with electron beams in related configurations. His frequent conference invitations typically surveyed this project among the many other topics he was interested in; he usually wrote these invited talks on his own [68], and used them for publicity for MIDAS, but he did not engage extensively in the surface science done with it, or in any way interfere with the program. That was very characteristic of him; he had his own agenda to the end, and this project had been passed to the authors of this article, so he let it fly.

Following that initial vision and our practical results, this instrument has had to compete with a large range of surface and near surface analytical techniques, most notably STM and AFM that have come to dominate microscopy of surfaces. This historical accident meant that the initial vision came to be modified, as we concentrated on demonstrating the capabilities of MIDAS, and establish that it could be used in specialist ways, essentially in a niche market as a complement to other techniques. Chemical analysis on a microscopic scale was developed for the case of Auger electron spectroscopy, AES, as described in section 3. Scanning Auger Microscopy, SAM, was also developed, and MIDAS achieved the highest spatial resolution anywhere (<3 nm), with, as mentioned in section 1, *Unlimited Applied Research Opportunities*. What has been achieved so far is really only a start of what is, in principle, possible with this system.

In section 4 we described some fundamental studies on electron scattering, and in section 5 initial studies of nanofabrication and diffraction. Specialist diffraction studies are ongoing with John Spence's group at ASU [34], and nanofabrication is also a possible area for future application. In sections 6 and 7, we described initial applications to crystal growth, catalysis and

magnetic materials. There is scope for many more such studies. High resolution biased Secondary Electron Imaging (b-SEI) is very powerful, as demonstrated using MIDAS; b-SEI can also in principle be done on a new generation of commercial field-emission, lower voltage commercial (user-friendly) SEMs, combined with backscattered electron imaging, as discussed recently by Venables and Liu [43].

There are several avenues for further technical development left to explore in future. First, there are related analytical techniques at high beam voltage (100-300 kV), in which state of the art imaging of bulk samples, or especially thin films, is combined with analytical spectroscopy: AES, EELS, X-ray spectroscopy, in addition to 'Z-contrast' imaging. All these techniques are in need of more incident electrons at a given spatial resolution, in order to improve the signal to noise ratio (SNR). Some spectroscopies, EELS especially, have been transformed by parallel recording of the energy spectrum and associated spectrum-imaging techniques, but these have not yet been applied systematically to AES/SAM with *in-situ* experimentation as on MIDAS. The recent development of aberration correctors and their deployment in STEM instruments enable higher beam currents to be delivered to a small probe. It is at present uncertain where the major effort using such correctors will be deployed, since these instruments are also in the process of transforming atomic resolution imaging.

These new developments will be expensive and available in (at most) a few centers of expertise. In surface analysis, strong end-product applications are needed to justify investment in new instrumentation; in effect, what may be interesting for wide-spread application is the availability of less expensive, easier to use, instrumentation. MIDAS, however, will still have a role for testing out new developments. It is a tribute to John Cowley's vision that interesting and challenging experiments are still being done, some twenty years after the MIDAS project was conceived.

Acknowledgements

We acknowledge the initial funding received for construction [4] and subsequent support by several research grants and by Arizona State University, for personnel, operations and development costs. The figures used have all been published previously in the original literature, in review articles and in a graduate teaching book [69], where there is more discussion of the papers listed here. We thank VG Scientific Ltd for permission to reproduce figure 3 from a brochure promoting the MIDAS - HB501S instrument.

References

- [1] For an early account, see Cowley JM (1986) Electron microscopy of surface structure. *Prog. Surf. Sci.* **21**, 209-250. For a detailed account of this HB5 work, see Liu J (2005) Scanning transmission electron microscopy and its application to the study of nanoparticles and nanoparticle systems. *J. Electron Microscopy*, this volume.
- [2] Venables JA (1981) Electron microscopy of surfaces. *Ultramicroscopy* **7**, 81-98.
- [3] Elibol C, Ou HJ, Hembree GG and Cowley JM (1985) Improved instrument for medium energy electron-diffraction and microscopy of surfaces. *Rev. Sci. Inst.* **56**, 12-15-1219.
- [4] Construction was supported by the Office of Naval Research (Award #N-00014-84-g-0203), the National Science Foundation (Grant # DMR-8500659) and by Arizona State University.
- [5] Venables JA, Cowley JM and von Harrach HS (1987) A field-emission STEM for surface studies. *Inst. Phys. Conf. Ser.* **90**, 85-88; for electron optical calculations relevant to the MIDAS column, see Venables JA and Cox G (1987) Computer modelling of field emission gun scanning electron microscope columns. *Ultramicroscopy* **21**, 33-46.
- [6] Kruit P and Venables JA (1987) An electron optical comparison of spectrometer systems for high spatial resolution Auger microanalysis. Proc. 5th Pfefferkorn Conf. Brüggen, *Scanning Microscopy Suppl.* **1**, 115-122.
- [7] Kruit P and Venables JA (1988) High spatial resolution surface sensitive electron spectroscopy using a magnetic parallelizer. *Ultramicroscopy* **25**, 183-194
- [8] Hembree GG, Luo CH, Bennett PA and Venables JA (1988) Transfer optics for high spatial resolution electron spectroscopy. *Proc. EMSA* **46**, 666-667; Hembree GG, Luo FCH and Venables JA (1990) Secondary and Auger electron spectroscopy and energy-selected imaging in a UHV-STEM. *Microbeam Analysis - 1990*, 249-252.
- [9] Luo Frank CH (1990) PhD Thesis, Arizona State University.
- [10] Harland CJ and Venables JA (1985) Digital data acquisition, display and analysis of signals from surfaces. *Ultramicroscopy* **17**, 9-20.
- [11] Weiss JK, Rez P and Higgs AA (1992) A computer system for imaging and spectroscopy in analytical electron microscopy. *Ultramicroscopy* **41**, 291-301.

- [12] Emispec, a local company in Tempe, now also called FEI Company Tempe, was founded by J K Weiss and W J (Hans) de Ruijter, following their PhD work on EELS in the Center for HREM at ASU around this time. See <http://www.emispec.com/> for current details.
- [13] See, for example, Venables JA (1988) Electron microscopy in surface Science. *Proc. EMSA* **46**, 678-679; Venables JA, Flora PS, Harland CJ, Luo CH and Hembree GG (1989) New developments in electron spectroscopy and imaging. *Inst. Phys. Conf. Ser.* **98**, 289-294 (EMAG '89).
- [14] Venables JA, Smith DJ and Cowley JM (1987) HREM, STEM, REM, SEM- and STM. *Surface Sci.* **181**, 235-249. A full list of MIDAS-related publications, including conference proceedings, has been posted at <http://venables.asu.edu/research/midas.html>
- [15] Hembree GG, Crozier PA, Drucker JS, Krishnamurthy M, Venables JA and Cowley JM (1989) Biassed secondary electron imaging in a UHV-STEM. *Ultramicroscopy* **31**, 111-115.
- [16] This 1989 issue of *Ultramicroscopy* **31**, 1-157 (Guest Eds. Smith DJ and Venables JA), contained STM papers by RJ Hamers *et al.* (pp 10-19), MG Lagally *et al.* (pp 87-98) and a LEEM/ PEEM paper by E Bauer *et al.* (pp 49-57).
- [17] Drucker JS, Krishnamurthy M, Hembree GG, Luo CH and Venables JA (1989) High spatial resolution secondary and Auger imaging in a STEM. *Proc. EMSA* **47**, 208-209; *Inst. Phys. Conf. Ser.* **98**, 303-307 (EMAG '89).
- [18] Venables JA and Hembree GG (1991) *Inst. Phys. Conf. Ser.* **119**, 33-38 (EMAG '91).
- [19] Hembree GG, Luo FCH and Venables JA (1990) Secondary and Auger electron spectroscopy and energy-selected imaging in a UHV-STEM. *Proc 12th International Cong. for Electron Microscopy (Seattle)* **2**, 382-383; (1991) Auger electron spectroscopy and microscopy in STEM. *Proc. EMSA* **49**, 464-465.
- [20] Hembree GG, Drucker JS, Luo FCH, Krishnamurthy M and Venables JA (1991) Auger electron spectroscopy and microscopy with probe-size limited resolution. *Appl. Phys. Lett.* **58** 1890-1892.
- [21] Hembree GG and Venables JA (1992) Nanometer-resolution scanning Auger electron microscopy. *Ultramicroscopy* **47** 109-120.
- [22] Drucker J, Krishnamurthy M and Hembree GG (1991) Biassed secondary electron imaging of monatomic surface steps on vicinal Si(100) in a UHV STEM. *Ultramicroscopy* **35** 323-328.

- [23] Drucker J (1991) Topographic contrast of monatomic surface steps on Si(100) in secondary electron microscopy. *J. Appl. Phys.* **70**, 2806-2811.
- [24] Scheinfein MR, Drucker J and Weiss JK (1993) Secondary-electron production pathways determined by coincidence electron-spectroscopy. *Phys. Rev. B* **47**, 4068-4071.
- [25] Scheinfein MR, Drucker J, Weiss JK, Liu J, Hembree, GG and Cowley JM (1993) The origins of high spatial resolution secondary electron microscopy. *Mater. Res. Soc. Symp. Proc.* **295**, 253-259.
- [26] Drucker J and Scheinfein MR (1993) Delocalized secondary electron generation studied by momentum-resolved coincidence-electron spectroscopy *Phys. Rev. B* **47**, 15973-15975
- [27] Drucker J, Scheinfein MR, Liu J and Weiss JK (1993). Electron coincidence spectroscopy studies of secondary and Auger electron generation mechanisms. *J. Appl. Phys.* **74**, 7329-7339.
- [28] Pijper FJ and Kruit P (1991) Detection of energy-selected secondary electrons in coincidence with energy-loss events in thin carbon films. *Phys. Rev. B* **44**, 9192-9200; Kruit P (1993) Nanometer resolution analysis of surfaces *Surface Sci.* **287**, 1067-1069.
- [29] For a review, see Howie A (1995) Recent developments in secondary electron imaging. *J. Microscopy* **180**, 192-203; Mullejans H, Bleloch AL, Howie A and Tomita M (1993) Secondary electron coincidence detection and time-of-flight spectroscopy. *Ultramicroscopy* **52**, 360-368.
- [30] Crozier PA, McCartney MR and Smith DJ (1990a) The effect of electron-irradiation on rutile crystals. *Inst. Phys. Conf. Ser.* **98**, 227-230. (EMAG '89); (1990b) Observation of exit surface sputtering in TiO₂ using biased secondary-electron imaging. *Surface Sci.* **237**, 232-240.
- [31] McCartney MR, Crozier PA, Weiss JK and Smith DJ (1991) Electron-beam-induced reactions at transition-metal surfaces. *Vacuum* **42**, 301-308.
- [32] For a summary, see Humphreys CJ, Bullough TJ, Devenish RW, Maher DM and Turner PS (1990) Electron beam nano-etching in oxides, fluorides, metals and semiconductors. *Scanning Microscopy Supplement* **4**, 185-192.
- [33] Jiang N, Hembree GG, Spence JCH, Qiu J, Garcia de Abajo FJ and Silcox J (2003) Nanoring formation by direct-write inorganic electron-beam lithography. *Appl. Phys. Lett.* **83** 551-553.

- [34] Hembree GG, Koch C and Spence JCH (2003) A quantitative nanodiffraction system for ultrahigh vacuum scanning transmission electron microscopy. *Microsc. Microanal.* **9** 468-474.
- [35] Lin JA and Cowley JM (1986) Calibration of the operating parameters for an HB5 STEM instrument. *Ultramicroscopy* **19** 31-42.
- [36] Krishnamurthy Mohan (1991) PhD Thesis, Arizona State University.
- [37] Krishnamurthy M, Drucker JS and Venables JA (1990a) Studies of Ge/Si(100) and observation of atomic steps on Si(100) using biased secondary electron imaging in a UHV STEM; Proc 12th International Cong. for Electron Microscopy (Seattle) **1**, 308-309; (1990b) Heteroepitaxy of Ge on Si(100). *Mater. Res. Soc. Symp. Proc.* **198**, 409-414; (1991) Nanometer resolution studies of microstructural evolution during the heteroepitaxy of Ge on vicinal Si(100). *Mater. Res. Soc. Symp. Proc.* **202**, 77-82.
- [38] Krishnamurthy M, Drucker JS and Venables JA (1991) Microstructural evolution during the heteroepitaxy of Ge on vicinal Si(100). *J. Appl. Phys.* **69**, 6461-6471.
- [39] Venables, JA (1998) *Materials Research Society Bulletin* **23** (11), 13; (1999) *Mater. Res. Soc. Symp. Proc.* **570**, preface, ix-x.
- [40] Luo FCH, Hembree GG and Venables JA (1991) Initial growth of Ag/Si(100) studied with high spatial resolution AES and SEM. *Mater. Res. Soc. Symp. Proc.* **202**, 49-54.
- [41] Liu J, Hembree GG, Spinnler GE and Venables JA (1992a) High resolution Auger electron spectroscopy and microscopy of a supported metal catalyst. *Surface Sci.* **262**, L111-L117; (1992b) High resolution Auger electron spectroscopy and microscopy of small metal particles. *Catal. Lett.* **15**, 133-143; (1993) Nanometer-resolution surface analysis with Auger electrons. *Ultramicroscopy* **52**, 369-376.
- [42] Liu J (2000) Contrast of highly dispersed metal nanoparticles in high-resolution secondary electron and backscattered images of small metal particles. *Microsc. Microanal.* **6**, 388-399.
- [43] Venables JA and Liu J (2004) High spatial resolution studies of surfaces and small particles using electron beam techniques. *J. Elect. Spect.* (in press, published online 9 Nov 2004).
- [44] Li Yun (1995) PhD Thesis, Arizona State University.
- [45] Li Y, Hembree GG and Venables JA (1995) Quantitative Auger electron spectroscopic analysis of Ge segregation in Si/Ge/Si(100) heterostructures *Appl. Phys. Lett.* **67**, 276-278.

- [46] Boguslawski P and Bernholc J (1999) Segregation effects at vacancies in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and $\text{Si}_x\text{Ge}_{1-x}$ alloys. *Phys. Rev B* **59**, 1567-1570; (2002) Surface segregation of Ge at $\text{SiGe}(001)$ by concerted exchange pathways. *Phys. Rev. Lett.* **88**, 166101.
- [47] Drucker J and Krishnamurthy M (1995) Microstructure Evolution of Ag/GaAs. *Mater. Res. Soc. Symp. Proc.* **355**, 101-106.
- [48] Krishnamurthy M and Drucker J (1996) Microstructural evolution during epitaxial growth of Ag on vicinal $\text{InP}(100)$ surfaces. *J. Appl. Phys.* **80**, 174-182.
- [49] Drucker J (2002) Self-assembling Ge(Si)/Si(100) quantum dots. *IEEE J. Quantum Electronics* **38**, 975-987 and references quoted.
- [50] Falicov LM, Pierce DT, Bader SD, Gronsky R, Hathaway KB, Hopster HJ, Lambeth DN, Parkin SSP, Prinz G, Salamon M, Schuller IK and Victora RH (1990) *J. Materials Res.* **5**, 1299-1340.
- [51] Kraft T, Methfessel M, van Schilfgaarde and Scheffler M (1993) Effect of substrate-imposed strain on the growth of metallic overlayers calculated for fcc and hcp iron. *Phys. Rev. B* **47**, 9862-9869.
- [52] Heim Kevin R (1994) PhD Thesis, Arizona State University.
- [53] Yang Zhijun (1994) PhD Thesis, Arizona State University.
- [54] Yang ZJ and Scheinfein MR (1993) Combined 3-axis surface magneto-optical Kerr effects in the study of surface and ultrathin-film magnetism. *J. Appl. Phys.* **74** 6810-6823.
- [55] Heim KR, Healy SD, Yang ZJ, Drucker JS, Hembree GG and Scheinfein MR (1993) Correlations between ultrathin-film microstructure and magnetic properties in epitaxial-films of fcc Fe/Cu(100). *J. Appl. Phys.* **74**, 7422-7430.
- [56] Hembree GG, Drucker J, Healy SD, Heim KR, Yang ZJ and Scheinfein MR (1994) Field-induced metastable states in ultrathin films of fcc Fe/Cu(100). *Appl. Phys. Lett.* **64**, 1036-1038.
- [57] Scheinfein MR, Healy SD, Heim KR, Yang ZJ, Drucker JS and Hembree GG (1994) Structural and magnetic properties of epitaxially grown fcc Fe/Cu(100) and Fe/CaF₂/Si(111). *Mater. Res. Soc. Symp. Proc.* **332**, 473-482.
- [58] Yang ZJ, Healy SD, Heim KR, Drucker JS, Hembree GG and Scheinfein MR (1994) Surface magnetization processes investigated by the combined surface magneto-optical Kerr effects in Fe/Cu(100) thin films. *J. Appl. Phys.* **75**, 5589-5591.

- [59] Healy SD, Heim KR, Yang ZJ, Drucker JS, Hembree GG and Scheinfein MR (1994) The initial phases of epitaxy of fcc Fe/Cu(100): supersurface and subsurface island formation, *J. Appl. Phys.* **75**, 5592-5594.
- [60] For a review, see Besenbacher F (1996) Scanning tunneling microscopy studies of metal surfaces *Rep. Prog. Phys.* **59**, 1737-1802.
- [61] Coyle Steven T (1998) PhD Thesis, Arizona State University.
- [62] Coyle ST, Hembree GG and Scheinfein MR (1997) Growth, morphology, and magnetic properties of ultrathin epitaxial Co films on Cu(100). *J. Vac. Sci. Tech. A* **15**, 1785-1790; Coyle ST and Scheinfein MR (1998) Magnetic ordering in Co films on stepped Cu(100) surfaces. *J. Appl. Phys.* **83**, 7040-7042, and references quoted.
- [63] Heim KR, Hembree GG and Scheinfein MR (1994) Ultrahigh-vacuum scanning electron microscopy characterization of the growth of Fe on CaF₂/Si(111) - selective nucleation on electron-beam modified surfaces. *J. Appl. Phys.* **76**, 8105-8112.
- [64] Heim KR, Hembree GG, Schmidt KE and Scheinfein MR (1995) Enhanced superparamagnetism in two-dimensional arrays of nanometer sized Fe islands, *Appl. Phys. Lett.* **67**, 2878-2830;
- [65] Scheinfein MR, Schmidt KE, Heim KR and Hembree GG (1996) Magnetic order in two-dimensional arrays of nanometer-sized superparamagnets. *Phys. Rev. Lett.* **76**, 1541-1544.
- [66] Heim KR, Coyle ST, Hembree GG, Venables JA and Scheinfein MR (1996) Growth of nanometer-size magnetic particles on CaF₂(111). *J. Appl. Phys.* **80**, 1161-1170.
- [67] Sugawara A, Coyle ST, Hembree GG and Scheinfein MR (1997) Self-organized Fe nanowire arrays prepared by shadow deposition on NaCl(110). *Appl. Phys. Lett.* **70**, 1043-1045; Sugawara A and Scheinfein MR (1997) Room-temperature dipole ferromagnetism in linear self- assembling mesoscopic Fe particle arrays. *Phys. Rev. B* **56**, R8499-R8502; Sugawara A, Hembree GG and Scheinfein MR (1997) Self-organized mesoscopic magnetic structures. *J. Appl. Phys.* **82**, 5662-5669.
- [68] Cowley JM (1987a) High-resolution imaging and diffraction studies of crystal surfaces. *J. Electron Microscopy* **36**, 72-81; (1987b) High-resolution electron microscopy. *Ann. Rev. of Phys. Chem.* **38**, 57-88; (1989) Imaging and analysis of surfaces with high spatial resolution. *J. Vac. Sci. Tech. A* **7**, 2823-2838; (1997) Applications of stem instruments for surface studies. *Surface Rev. Lett.* **4**, 567-575.

[69] Venables JA (2000) Introduction to surface and thin film processes, *Cambridge University Press*, Cambridge and New York, especially sections 3.5, 5.3, 6.3, 7.3 and 8.3.

Figure Captions

Figure 1: Schematic scale drawing of the MIDAS column, indicating the main operational features (adapted from ref [5] as published in ref [15]). VOA = virtual objective aperture.

Figure 2: Cross sectional diagram of the specimen region of the MIDAS column, showing the relationship of parallelizer coils, objective lens, extraction optics (comprising a Wien filter and the CMA sector) and the specimen (from ref [15]).

Figure 3: a) MIDAS column as in figure 1, showing upper SE detector, diffraction pattern viewing camera, and EELS spectrometer at the top of the column. The sample exchange mechanism is on the right of the photograph; b) View of the preparation chamber as delivered, with sample exchange mechanism on the left and airlock entry on the far right. In between are the two sample preparation and analysis stations which were subsequently developed, as for example shown schematically in figure 8.

Figure 4: Biased SE images from (a) upper (exit) and (b) lower (entrance) side of a composite gold-decorated carbon film and carbon black sample, with bias voltage $V_b = -90$ V; (c) corresponding annular dark-field detector image. We see from (a) and (b) that the gold particles are on the lower side of the film, whereas the carbon-black particle spans both sides through the hole in the film; this topographic information is entirely absent in (c), which, however, does have the highest lateral resolution on the gold particles [15].

Figure 5: (a) Ag MNN Auger electron peak and (b) biased SE images of thin silver island on bulk Si(100) substrate. 128*120 line digital images, with 0.2 nA, 100keV probe of ~2 nm diam.; line scans and more details are given in ref. [21], where <3nm Auger resolution is demonstrated. There is some drift in (a) relative to (b) due to greater frame time in (a). Scale bar = 10 nm.

Figure 6: Electron Ronchigram obtained from beryl [100] at room temperature. Note the ellipses of zero contrast that are used to measure the spherical aberration coefficient $C_s = 2.6 \pm 0.2$ mm for the MIDAS column, with a probe diam. about 2 nm. More details are given in ref. [34].

Figure 7: Simultaneously collected (a) b-SE and (b) Bright-Field STEM images of Ge islands on vicinal Si(100). Note that edges of the islands are highly visible in (a), whereas the terminated moiré fringes in (b) are indicative of misfit dislocations. These fringes are absent in islands below about 10-nm radius. Island densities and size distributions are given in ref [38], and the island illustrated would now be referred to as a “dislocated dome”.

Figure 8: The MIDAS-HB501S column and preparation chamber arranged for magnetic studies. The column shows the position of the sample (S), objective lens (OL), electron parallelizers (P) and secondary electron detector (SE), plus the field emission gun (FEG). The sample can be transported from the airlock to the sample preparation station, which has multiple ports used as shown, plus those for sample heating (H) and extra Knudsen cell evaporators (K1-K3); the YAG screen (Y) is for viewing the RHEED pattern. After preparation, the copper sample (C) can be transported to the SMOKE station before being examined by high resolution SEM and AES analysis (After ref. [55]).

Figure 9: Polar and longitudinal hysteresis loops from Fe/Cu(001) grown and measured at room temperature, taken with the SMOKE setup shown in figure 8, with an angle of incidence of 45° : a) and b) 2.1 ML, no remanent magnetization; c) and d) 3.5 ML, remanent, mostly out of plane; e) and f) 4.7 ML remanent, in plane; g) and h) 10 ML, non-magnetic f.c.c Fe film [56].