Scanning Electron Microscopy

Volume 1985
Number 1 *1985*

Article 2

11-9-1984

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SCANNING ELECTRON MICROSCOPY/1985/I (Pages 15-20)
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0586-5581/85$1.00+.05

A WIEN FILTER ENERGY LOSS SPECTROMETER FOR THE DEDICATED SCANNING TRANSMISSION ELECTRON MICROSCOPE

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(Paper received March 20 1984, Completed manuscript received November 9 1984)

Abstract

A Wien filter electron spectrometer has been added to a VG Microscopes, Ltd. HB501 STEM to improve the energy resolution and accuracy of energy loss analysis combined with a high spatial resolution. An energy resolution of 130meV is obtained with a 2mR collection angle at the specimen. The 0.28eV wide field emission energy profile therefore dominates the energy resolution for the device. The energy axis is automatically calibrated by the electrostatic method of scanning, yielding an accuracy and stability of 30meV. A preliminary energy resolution of 0.5eV is demonstrated for 20mR full collection angles at the specimen. Results of experiments suggest that, even with a 0.3eV energy resolution, interband losses below 1.5eV will be hard to observe due to the long exponentially decaying field emission profile. Deconvolution procedures will probably be necessary as a result.

KEY WORDS: Wien filter, energy loss spectrometer, oxidation state, inter-band transitions, scanning transmission electron microscopy

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Introduction

There have been some interesting electron energy loss investigations of materials with emphasis on electronic structure (Colliex, et al. (1976), Ritsko and Mele (1981)), and oxidation state (Leapman, Grunes and Fejes (1982)). These investigations have been limited to relatively large areas (several μm and larger) by the lack of a suitable combination of a high quality spectrometer with the high spatial resolution electron microscope. Recently a new magnetic sector spectrometer due to Isaacson (Schienfien and Isaacson (1984)) has been available for the VG Microscopes, Ltd. HB501 STEM. This device obtains about 2eV resolution with greater than 40mR collection angles. For smaller angles, the field emission tunneling asymmetry of the incident beam energy distribution has been demonstrated. This performance is degraded, however, when an attempt is made to integrate weak signals over several minutes of time. The reason is that the STEM acceleration potential is not completely stable, fluctuating by as much as 0.5eV in a period of seconds. Therefore, the useable resolution is poorer than the quality of the spectrometer would suggest. A second disadvantage for studies requiring a highly accurate energy loss calibration is that the magnetic sector energy dispersion is not accurately known. This figure depends strongly on the value of the magnetic field and on the exact electron path length through the field. Hysteresis and day to day mechanical fluctuations which affect alignment necessarily affect the magnitude of the energy dispersion. Thirdly, since the magnetic sector does not have a straight optic axis, it is inconvenient for the addition of further optical systems subsequent to the spectrometer position. These might be used to make available energy filtered diffraction patterns. A fourth problem, associated with the analysis of 100keV electrons, is the extreme mechanical and electrical tolerances required to obtain better than 0.2eV resolution. For instance,

with a typical dispersion of 2 μm/eV, the energy selecting slits must close smoothly to 0.4 μm, and have a straightness of somewhat better than this.

All of the above constraints may be relaxed by replacing the magnetic sector with a Wien Filter (described in detail by Boersch et al. (1964)) which is mounted on a high voltage electrode held near the STEM accelerating potential. This system has been built for a transmission electron microscope by Curtis and Silcox (1971). This device has a good quality straight through optical axis and is capable of preserving angular information during the energy loss analysis. Therefore, it is appropriate to consider subsequent optical systems for the recovery of diffraction information. The device is held near the STEM acceleration potential to relax construction tolerances. Since the fast electrons are thus decelerated before analysis, the fractional energy resolution (ratio of desired energy discrimination to the average analysis energy) is decreased (from 10^{-6} to 10^{-3} for 100eV analysis energy). The mechanical and electrical tolerances are similarly relaxed. The Wien filter is remarkably forgiving of construction blunders, as well. Since it is naturally a focussing device, like a lens, variations in object and image distances merely affect the overall system magnification. Therefore, it is not necessary to define these distances to better than about 20 per cent. It is more efficient simply to adjust the filter electrical parameters during operation to produce an optimum focus. A feature of any magnetic device is that the energy dispersion varies inversely with the electron velocity. Therefore, typical dispersions of 50 μm/eV are possible at the lower (100eV) velocities. Magnification by the electrostatic lens, formed by the reacceleration of electrons on leaving the high voltage electrode, produces typical dispersions of 500 μm/eV. Finally, if the filter and energy selecting exit slit are adjusted to accept only the no loss electrons, energy loss scattering may be swept across the slit by adjusting the difference in the potential between the filter and the STEM high voltage. In this way, 10eV loss electrons are passed by adding 10V to the electrode potential. The important result is that, while the dispersion is affected by alignment and magnet variations, the filter center pass energy is determined solely by the value of the scanning voltage generator.

Disadvantages of this system include an uncertain magnification of entrance angles by the deceleration field, necessitating at least a quadrupole lens doublet between the specimen and the spectrometer to control the collection efficiency. Secondly, all driving electronics must reside at high voltage. However, with modern electronic devices, this last problem is not so hard to handle.

Description of the filter

The filter is 4cm long and is designed to operate with 200eV electrons, giving a dispersion inside the electrode of about 60 μm/eV. It is mounted within a high voltage electrode on a standard VG gun flange. The electric field plates are 0.75cm apart. The magnetic field is generated by an iron core yoke enclosed in a sealed stainless steel torus to guarantee the STEM vacuum integrity. The electrode exit aperture is about 0.6cm in diameter and is twice the size of the entrance aperture. Thus the exit electrostatic lens focal length is twice the entrance lens focal length. This condition determines, with the final slit position and the spectrometer center position, the image and object positions for the filter in a way that keeps the deceleration lens demagnification small (about 5x). This is necessary to minimize the magnification of angles within the spectrometer. The quadrupoles are wound on aluminum forms for power dissipation, and have 1.5cm inner diameters. A three element quadrupole would give better, more independent control of focussing properties in the two orthogonal directions. However this system appears adequate, and it seemed prudent to minimize alignment possibilities by restricting the number of lens elements in the system.

The filter electronics consist of an optical data link driven by a computer, and three D/A converters to control the electric field, the magnetic field, and the energy loss scanning supply. This latter supply has a range of 200 to 1200V with a slew rate of 40V/ms. and a stability and accuracy of 30mV. Power is supplied to the high voltage environment by an iron core transformer with plexiglass insulation. The electronics are sited within a high voltage tank using plexiglass and oil for insulation.

Results

Figure 1. shows an electron ray path for the complete system. Both the energy dispersion plane and the non-dispersive plane are shown. Briefly, the system source area (the field of view for optimum operation) on the specimen is about 2 μm in size and comprises about 15mR in angle. The post specimen field in the high excitation lens compresses these exit angles to about 4mR producing an 8 μm virtual source behind the specimen. In the energy dispersion plane, this source is imaged by the field lens with a magnification of about 2x. The deceleration next demagnifies this image by a factor of 5x, producing a filter object source 4 μm in size with an angular divergence of 10mR. With an expected dispersion of 60 μm/eV within the filter, these input conditions roughly balance the angular and source size aberrations at 60meV each. Finally the reacceleration lens images the dispersed spectrum onto the exit slit with a magnification of about 8x, giving 500 μm/eV dispersion there.

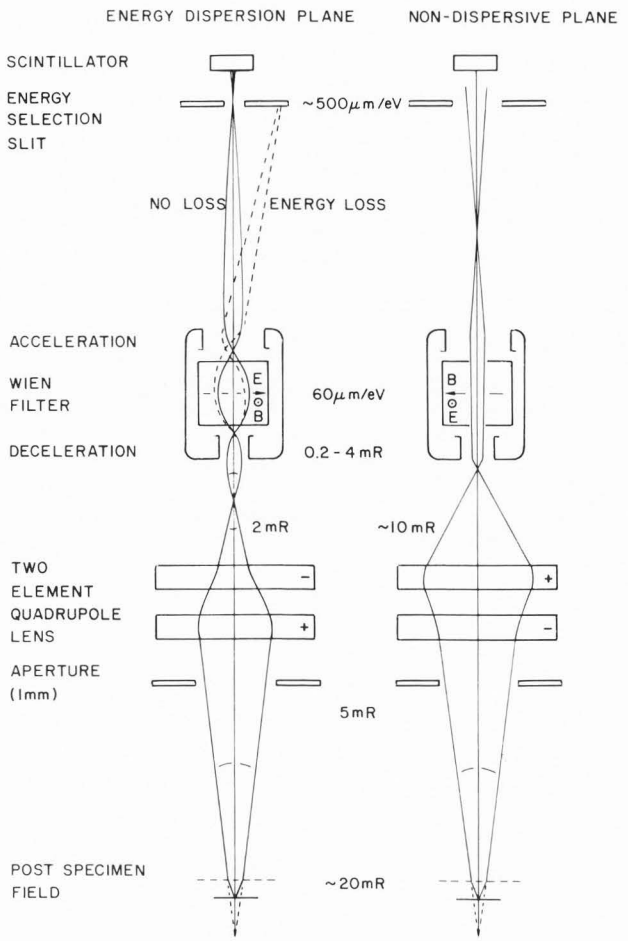

Figure 1. Electron ray paths for the two perpendicular imaging planes in the Wien filter. Electrons originating within a 20mR cone at the specimen are brought to a focus at the entrance of the filter by a doublet quadrupole lens. They are decelerated, dispersed in energy, and reaccelerated to form a spectrum at the energy selecting slit.

In the non-dispersive plane, the doublet quadrupole is adjusted to obtain roughly parallel trajectories within the spectrometer by focussing near the deceleration lens entering focal plane. This provides a line focus parallel to the exit slits. Notice that specimen scattering angles are preserved in some plane behind the energy selecting slits. Therefore, in an appropriately designed system, an energy selected diffraction pattern ought to be available there. This, however, will not be attempted in the present system.

Figure 2 shows a photograph of the apparatus mounted on the VG STEM. The liquid nitrogen trap was extended to allow the addition of a 10cm pumping line (hidden in the photo) for the filter chamber. The chamber itself is mounted about 15cm above the STEM top plate to allow the addition of an isolation valve and to allow the positioning of the quadrupole outside the vacuum. A roughing line is provided, so that the chamber may be vacuum cycled independently from the rest of the microscope.

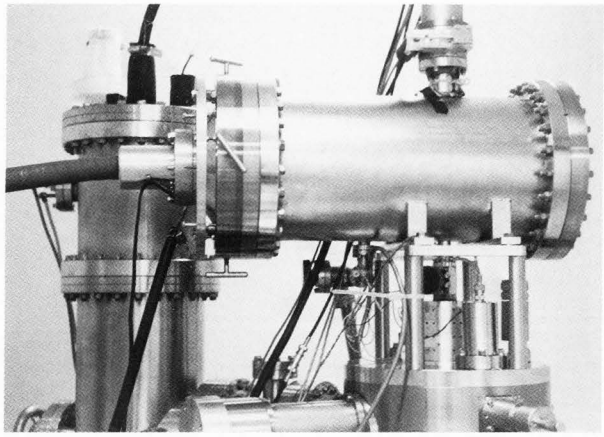

Figure 2. The apparatus is situated physically on top of the STEM. The vacuum components are ultra high vacuum compatible. A base pressure of $3x10^{-10}$ mbar is obtained.

Figure 3 shows the field emission gun energy distribution following Crewe et al. (1971). The theoretical tunneling profile (line) can be deconvoluted from the measured profile (dots) to find a spectrometer energy resolution of 130meV with a 100 μm collector aperture (2mR at the specimen). The inset shows the same profiles plotted as log intensities to illustrate the long exponential tail.

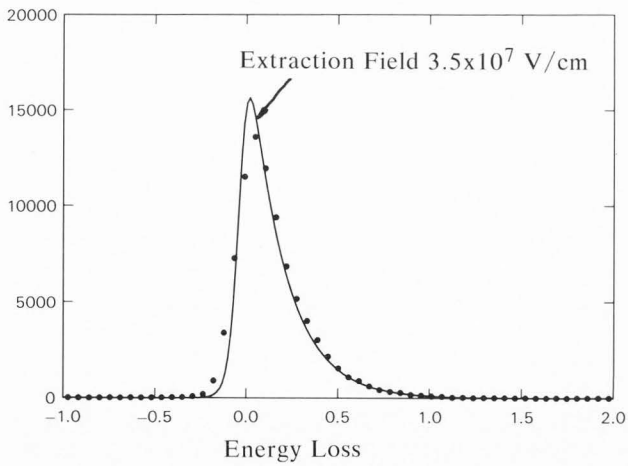

Figure 3. Measured field emission energy profile (dots) compared to the theoretical tunneling curve. The implied energy resolution is about 130meV.

Figure 4 shows the first energy loss plot for Al showing the plasmon and $L_{2,3}$ edge structure. The 1mm collection aperture was used, giving a resolution of 1.5eV. This resolution is largely limited by poor alignment in the quadrupole lenses. This figure has been recently improved to 0.5eV with further improvements in the lenses. The 73 and 74eV positions are marked. There is an instrumental peak near 18eV that results from no loss electrons hitting the electric field plates as the spectrum is scanned.

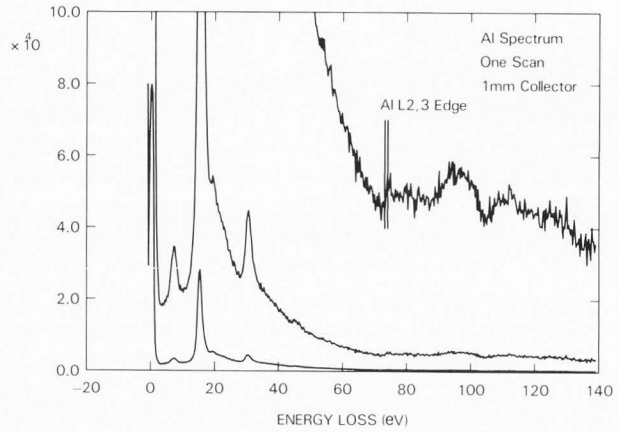

Figure 4. The first experimental energy loss plot for Al with this filter. The energy calibration is demonstrated to be good. A resolution of 1.5eV with a 20mR collection angle at the specimen was used. The probe size was about 1nm.

Figure 5 begins to bring us back to the point of all this work. Here is shown a preliminary look with higher accuracy at the Al $L_{2,3}$ excitation. The energy resolution here was about 1.5eV as in Figure 2. Seven 0.5sec scans were averaged for this result. The edge position is measured to be 72.70±.04eV (limited by the counting statistics), in agreement with the value 72.73eV obtained by Olson and Lynch (1979) from x-ray absorption measurements. Upon moving the 1nm probe to the edge of a crack in the Al foil, we find a shift in the energy to 76.5eV. This is likely a result of the presence of the insulator bandgap in the Al_2O_3 on the edge of the foil. This result was noted in the x-ray results also, where they found a value of 76eV. The discrepancy in energy is probably related to the lower visibility of the edge onset in the oxide. This lack of a sharp edge was also noted in the earlier work. Therefore, the oxidation state on a 1nm size scale is accessible.

Figure 6 shows the low energy loss region for Al with the resolution limited by the field emission distribution. The attempt here was to decide how small an energy loss we may reasonably expect to be able to measure. Thirteen 0.5 second scans were averaged for this result. Clearly, more integration time will be necessary to obtain unambiguous results.

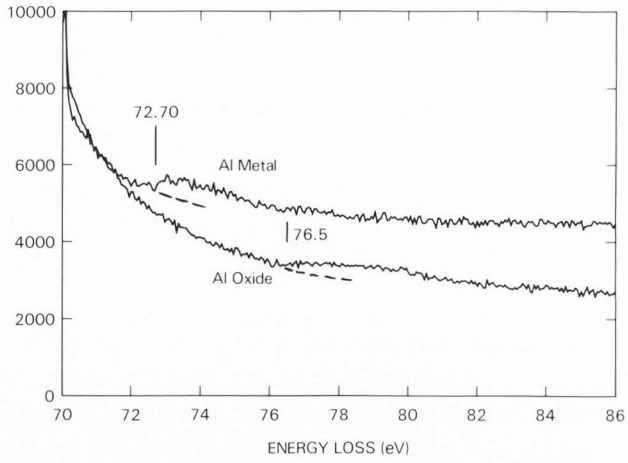

Figure 5. Higher accuracy energy loss plot for the Al $L_{2,3}$ edge for the metal and for the oxide. The two areas were within 2nm of each other. The nearly 3.5eV shift in the edge is caused by the opening of a bandgap in the oxide. The probe size was about 1nm.

However, two points may be made here. First, since the tunneling distribution decreases exponentially in the energy loss direction, there is a significant instrumental background even 1.5eV away from the 0.28eV wide zero loss. Secondly, the cross sections for inter-band transitions, except in rare cases, are small and coexist with a continuous background of intra-band excitations. Therefore interpretation in this region is expected to be difficult.

However, if the spectrometer resolution can be made small, we may be able to characterize the field emission profile accurately. Then this shape may be

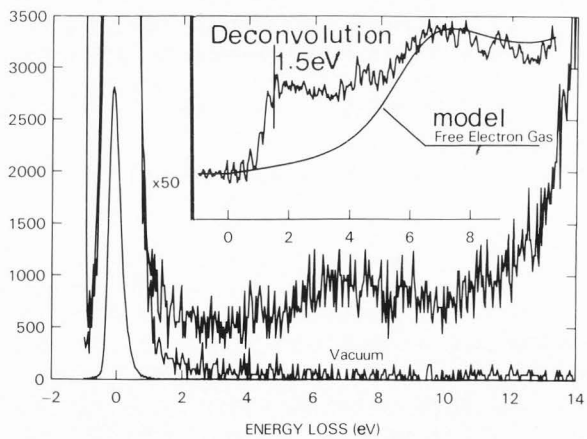

Figure 6. The low energy loss region with a resolution of about 0.28eV. The exponential tail of the no loss distribution produces difficulties in interpretation for losses below about 1.5eV. Deconvolution procedures are probably going to be necessary. The probe size was about 1nm.

deconvoluted from the data. If this is possible, the zero loss may be cleanly removed from the data by fourier transform techniques. Some optimal filter will then be used to control noise as was discussed by Ray (1979). This idea was applied to the data of Figure 6 to check for the visibility of the 1.5eV bandgap which exists in only a very small portion of the Al Brillioun Zone. The result does show a small peak at 1.5eV, but the statistics of the measurement need to be better for a confident assessment.

With some further refinements, this device will be useful for investigations with high spatial resolution of chemical shifts, oxidation states and defect electronic structures. In addition, it possibly promises the ability to combine the energy loss capability with the parallel recording of micro-diffraction information.

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Discussion with Reviewers

Note added in proof: The performance of the system at the time the revised paper was submitted was as follows: 0.6eV at 64mR full angle referred to the specimen (x6 compression in objective lens), 0.45eV at 32mR, and 0.3eV at 12mR. All quoted angles are total angular spread.

R.F. Egerton: Will the filter be useful for energy losses above 100eV? If the zero loss beam hits the field plate, how large an instrumental background can be expected at higher energy loss?

R.D. Leapman: Is there any fundamental limit to the collection efficiency for detecting core loss excitations at energy losses in the range 100-1000eV?

Author: Presently the Scandium $L_{2,3}$ edge at 402eV is the highest energy loss that has been recorded. This required an integration time of about 2sec per point to obtain 5000 counts with a resolution of 0.5eV and a collection full angle of 20mR. The primary limitation seems to be a background intensity probably originating from field ionization of gas near the spectrometer electrode. This intensity is also accompanied by an unacceptable x-ray emission, and has been the main reason for limiting present operation to 80keV. The spectrometer electrode has been redesigned to eliminate this problem. The background in the Sc example due to this problem was comparable to the $L_{2,3}$ core intensity. I think the spectrometer will be useful below 1000eV.

R.D. Leapman: The high dispersion obtainable with the Wien Filter could be a significant advantage in recording the spectrum with a parallel detection device. How linear is the dispersion and what range of energy losses can be obtained in parallel?

Author: The linearity of the dispersion is limited by the velocity dispersive nature of all magnetic spectrometers. The error produced in identifying the fractional velocity change with the fractional energy change is roughly the energy loss divided by the analysis energy. So for a 200eV analysis energy, a 30eV energy window implies a 15% error in energy position near the edges. Thus the intensity positions would need to be mapped via a processor onto an accurate energy loss axis. To obtain a good energy resolution with a wide total energy range, it would probably be best to parallel record over a 20eV window with 500 points. If the spectrum were then

stepped one channel at a time, channel to channel response variations could be averaged, and the effective spectrum width could be as large as desired.

J.C.H. Spence: Unpublished work by D. Johnson indicates that the form of the trade-off between resolution improvement and noise amplification after deconvolution depends sensitively on the shape of the source energy distribution. A favorable trade-off results from numerical deconvolution (and reconvolution) if this contains large high order Fourier coefficients, i.e. if the distribution has some sharp edges, even though it may be broad. Is there anything which can be done toward this end to improve the effects of numerical deconvolution? (e.g. A one sided low pass filter could be applied to the gun.)

Author: This is a promising area to investigate. A quick analysis with the presently obtained field emission energy distribution indicates that 130meV deconvoluted resolution is possible with the room temperature field emission distribution that is nominally 220meV wide. Further, it may be possible to cool the emission tip to obtain a sharper high energy onset (e.g. see Figure 3.). This may allow even higher energy resolution. These ideas need to be tried.

J.C.H. Spence: Could the author provide a ray diagram showing how this device could be combined with a micro-diffraction screen. What would be the largest angular acceptance of the screen when using the smallest probe?

Author: The addition to Figure 1. is relatively minor. Immediately beyond the energy selecting slits, a single quadrupole lens would be situated. This lens would expand angles in the energy dispersion plane, and compress angles in the non-dispersive plane. At a point several cm. beyond the slit, there should be a real image of the specimen diffraction pattern. This operation should be possible due to the good optical properties of the Wien filter. However, it is fair to say that similar operation is possible in principle with an aberration corrected magnetic sector in conjunction with an axially symmetric final imaging lens. Obviously, the range of angles would be limited to those which can be accepted by the spectrometer. Probably a 100mR full angle of view with a 1eV resolution would be feasible.