Ratio between the energy-loss spectrum in coincidence with secondary electrons and the normal energy-loss spectrum for thin carbon films in the carbon K-edge region

Harald Müllejans* and Andrew L. Bleloch
Microstructural Physics Group, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, England
(Received 24 February 1992; revised manuscript received 26 May 1992)

In experiments similar to previous work [F. J. Pijper and P. Kruit, Phys. Rev. B **44**, 9192 (1991)] we have investigated the ratio between an energy-loss spectrum in coincidence with secondary electrons and a normal electron energy-loss spectrum in the energy-loss range 0–500 eV. We obtained similar results in the low-loss region, but in the high-loss region different results were obtained. The ratio of the coincident and normal energy-loss spectrum is the product of the probability of an energy-loss event emitting one secondary electron and its detection probability. The ratio increased with energy loss up to 200 eV and remained constant for higher-energy losses. No features were observed in the ratio at the carbon K edge. A plateau in the ratio at high-energy losses was attributed to an energy-loss-dependent escape depth. The absence of any structure at the K edge indicated that secondary electron emission is independent of momentum transfer from the primary electron to the specimen.

In a recent paper Pijper and Kruit[1] have reported coincidence experiments between secondary electrons and energy-loss events performed in a scanning transmission electron microscope. The emphasis in their work has been on the low-loss region, and energy losses larger than 100 eV were only investigated briefly. The results presented were the energy-loss spectrum in coincidence with a secondary electron, the normal electron energy-loss spectrum, and the ratio of the two spectra.

We performed similar experiments in our dedicated scanning transmission electron microscope (VG HB501) at 100 keV primary energy with an interest in the high-energy-loss region. A holey carbon film supplied as a specimen support film (Agar Scientific), was analyzed using a collection angle for the energy-loss spectrum of 32 mrad. The electronics to analyze the coincidence events[2] were very similar to the system used by Pijper and Kruit.[1] Secondary electrons were accepted without energy analysis. Time spectra were acquired for 5 s each for 128 different energy losses. An energy-loss spectrum and the secondary-electron count rate were recorded before and after each run of the experiment. All data were stored on the hard disk of a computer and analyzed off line after the experiment.

The time spectra showed a coincidence peak superimposed on a background of false coincidences. The number of true coincidences was taken as the area under the peak after subtraction of the background. The false coincidence count rate R_F in a channel of width τ, at a delay time t in the time spectrum, measured with a time-to-amplitude converter with effective dead time T_D, which is started by the energy-loss count rate R_{EELS} and stopped by the secondary-electron count rate R_{SE}, can be written as[3]

$$R_F = \frac{R_{\mathrm{EELS}}}{1+R_{\mathrm{EELS}}T_D} R_{\mathrm{SE}} \tau \exp(-R_{\mathrm{SE}} t) \ . \quad (1)$$

The factor $(1+R_{\mathrm{EELS}}T_D)^{-1}$ corrects for the dead time of the time-to-amplitude converter, and the factor $\exp(-R_{\mathrm{SE}}t)$ gives the probability that it has not been stopped after a time t. The dead time of the time-to-amplitude converter was obtained from a comparison between the start and valid start count rate and agreed with the expectation from the manual. The factor $\exp(-R_{\mathrm{SE}}t)$ was neglected as it is close to 1 for the count rates and the time ranges which were used. With the independently measured secondary-electron count rate R_{SE}, the count rate R_{EELS}, which would be observed in a normal energy-loss spectrum, was calculated from Eq. (1). The energy-loss spectrum in coincidence with a secondary electron was also corrected for the dead time of the time-to-amplitude converter.

For the energy range 0–500 eV, the energy resolution of the energy-loss spectrometer was set to approximately 4 eV and the step size between time spectra was 4 eV. The coincidence and normal energy-loss spectrum are shown in Fig. 1. Their ratio (Fig. 2) increases monotonically with energy loss up to 200 eV except for a peak at low energies (<20 eV). At the K-shell ionization energy (284 eV), no features are observed. This was confirmed by investigating the K-edge region (235–365 eV), with ap-

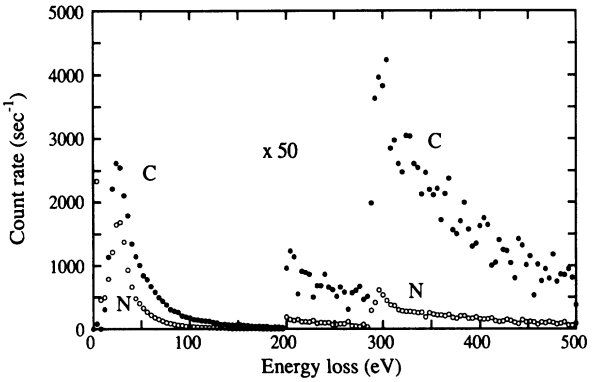

FIG. 1. Coincident (C) and normal (N) energy-loss spectra in the energy range 0–500 eV. The normal energy-loss spectrum is shown on a 100 times reduced scale. A gain change of 50× is introduced at 200 eV in the display.

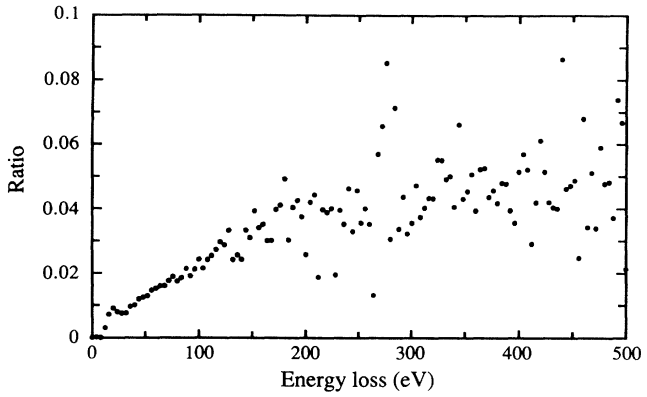

FIG. 2. Ratio of the two spectra in Fig. 1 showing the product of the probabilities of a certain energy-loss event emitting a secondary electron from the specimen and its detection.

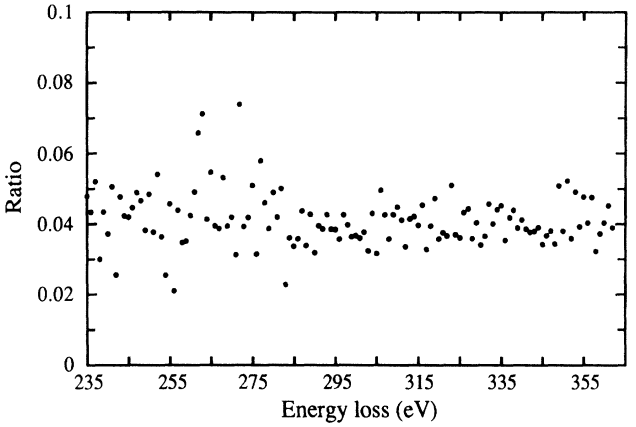

FIG. 4. Ratio of the two spectra in Fig. 3 showing the product of the probabilities of a certain energy-loss event emitting a secondary electron from the specimen and its detection. No special features are observed at the carbon K edge (284 eV).

proximately double the beam current and 1-eV step size (Fig. 3). In the ratio (Fig. 4) the counting statistics improve above the K edge, but no features are observed.

A simple model of secondary-electron emission predicts that it is proportional to the energy dissipated by the primary beam in an escape depth (stopping power). The escape depth is assumed to be the same for all energy losses. According to this model, the ratio should be a linear function of energy loss. The mean free path for electrons inside the specimen increases, however, for larger energies. Furthermore, such electrons can even escape after they have undergone inelastic scattering. Therefore high-energy losses have a larger effective escape depth. This suggests that they contribute more strongly to the emission of secondary electrons than the low-energy losses. On the other hand, the energy of the emitted secondary electrons after a high-energy-loss event can be higher, and therefore fewer secondary electrons per eV of energy loss are produced. This reduces the contribution of high-energy losses to secondary-electron emission. For specimens much thicker than the escape depth, these two influences might be expected to cancel each other out, and experimentally, for a thicker specimen (0.4λ), the ratio was found to increase monotonically up to 1000 eV energy loss (not shown here). For thin specimens the first of the two factors, the increased escape depth of secondary electrons, is not effective. The probability of detecting a secondary electron from a high-energy-loss event would therefore appear to be lower than expected from the stopping power. This may explain why the ratio reaches a plateau (Figs. 2 and 4). From a separately recorded energy-loss spectrum, the thickness of our specimen was estimated[4] to be about 0.1λ, where λ is the mean free path for inelastic scattering. This yields a thickness of about 10 nm, which agrees with the expected thickness.

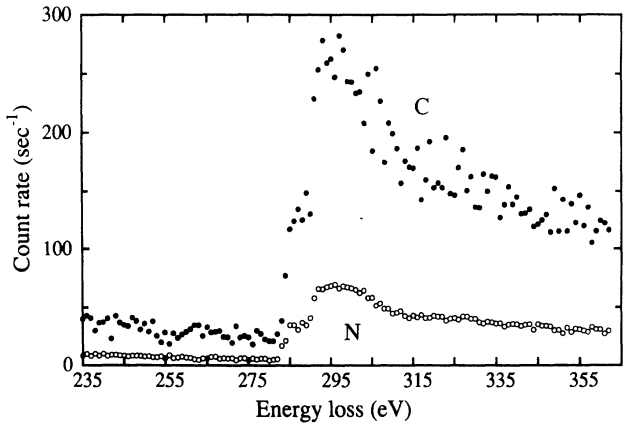

FIG. 3. Coincident (C) and normal (N) energy-loss spectra in the energy range 235–365 eV. The normal energy-loss spectrum is shown on a 100 times reduced scale. The jump ratio in the normal electron energy-loss spectrum is greater than 10.

Over the energy range 0–500 eV, Pijper and Kruit[1] have found this ratio to increase up to 125 eV, and then to decrease and to increase again at the carbon K edge (284 eV). In our experiments the secondary electrons emitted from the primary-beam exit surface were detected, whereas Pijper and Kruit[1] investigated the entrance-surface emission. The explanation for the maximum in the ratio proposed by Pijper and Kruit[1] was that the faster secondary electrons travel more forwardly inside the specimen. Here the ratio was found to be smooth across the K edge. Below the threshold for K-shell ionization, only single-electron scattering occurs, which produces one fast electron in the specimen. A K-shell excitation produces two excited electrons, one slow electron (from the K shell) and a fast ($\approx$270 eV) Auger electron. The Auger electron emission is isotropic, whereas the single-electron scattering is forward peaked. The secondary-electron emission probability from the exit surface should be higher below the K edge, where only single-electron scattering occurs, than above, where mainly Auger electron processes occur. The opposite applies to the entrance surface, and the ratio should in this case increase at the K edge. The results found here, namely, that the ratio is smooth across the K edge, suggest that there is no effect due to forward scattering. This argument supports

the statement that, although the momentum transfer is forward peaked, the short mean free path for elastic scattering ensures that the directions are randomized quickly.[5] Therefore similar results are expected, irrespective of whether the primary-beam entrance or exit surface of the specimen is investigated.

The difference between the ratio spectrum presented here and that of Pijper and Kruit[1] could be explained by an instrumental background in their energy-loss spectrum. Such a background would have the strongest effect on the ratio in the region just below the K edge, where the count rates are smallest. The significance of this background on the quality of data can be estimated by considering the jump ratio of the carbon K edge (intensity at the edge over intensity before the edge) in the energy-loss spectrum. The jump ratio is a good measure of spectrometer performance.[6] For our data it is larger than 10, as expected for thin carbon films,[7] and the instrumental background is therefore negligible. An instrumental background would not only produce a maximum in the ratio, but the peak position would also appear to be thickness dependent as the genuine background from single-electron scattering increases with thickness. In the ratio spectrum (Fig. 2), we found a smaller slope up to 100 eV energy loss than Pijper and Kruit.[1] This could be explained by dead-time effects in their time-to-amplitude converter which would reduce the coincidence count rate, and hence the ratio, in the low-loss region. The ratio of the coincidence to the normal energy-loss spectrum gives the probability that one secondary electron is detected. This is the product of the probability that it is emitted from the specimen following an energy-loss event and the detection efficiency of the secondary-electron detector. The detection efficiency of our secondary-electron detector is unknown, but was estimated to be up to 70% for secondary electrons with an energy up to 20 eV.[8] If the detection efficiency is known from an independent measurement, the ratio can be scaled to give the probability for secondary-electron emission per primary energy-loss event.

In our experiments no energy selection of secondary electrons was available, whereas in Pijper and Kruit[1] the maximum of the secondary-electron energy distribution was selected. The effects of secondary-electron energy selection in the low-energy-loss range (0–40 eV) has been shown by these authors.[1] For higher primary energy losses (as in the carbon K-edge region), it is expected that the energy distribution of the secondary electrons is largely independent of the energy-loss event due to the cascade effect.[9] Experiments should therefore yield similar results, independent of energy selection of the secondary electrons.

For high-energy-loss events, such as single-electron scattering near the K edge, bursts of secondary electrons can be generated. At the moment neither experimental setup analyzes such events, as only the secondary electron arriving first at the detector is considered. This is a serious limitation of the present experiments, and more complete information about the secondary-electron emission mechanism can only be expected if such events are taken into account.

The ratio between the coincidence and normal energy-loss spectrum was found to increase up to 200 eV energy loss and to be independent of it for larger energy losses. This was attributed to the larger effective escape depth of secondary electrons in this energy range, which becomes apparent for thin specimens. The results for the K edge showed the same secondary-electron emission probability, irrespective of whether single-electron scattering or Auger electron emission were the dominant process. The isotropy of the latter suggests that secondary-electron emission is independent of the momentum transfer from the primary electron to the specimen.

ACKNOWLEDGMENTS

This work was supported by an equipment grant from the Royal Society of the U.K. One of us (H.M.) thanks the SERC and the Studienstiftung des deutschen Volkes for financial assistance. The authors are grateful to Folbert Pijper and Pieter Kruit for their help and advice in setting up the experiments.

---

*Electronic address: muellejans@vaxww1.mpi-stuttgart.mpg.de. Present address: Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Seestrasse 92, D-W-7000 Stuttgart 1, Germany.

[1] F. J. Pijper and P. Kruit, Phys. Rev. B **44**, 9192 (1991).

[2] H. Müllejans, A. L. Bleloch, A. Howie, and D. McMullan, Beitr. Elektronenmikroskop. Direktabb. Oberfl. **24/1**, 93 (1991).

[3] H. Jeremie, Nucl. Instrum. Methods A **244**, 587 (1986).

[4] R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope* (Plenum, New York, 1986), p. 292.

[5] L. Reimer, *Scanning Electron Microscopy* (Springer, Berlin, 1985), p. 151.

[6] R. F. Egerton and J. Sevely, J. Microsc. (Oxford) **129**, RP1 (1983).

[7] J. Sevely, Y. Kihn, G. Zanchi, and B. Jouffrey, J. Phys. (Paris) Colloq. **45**, C2-441 (1984).

[8] C. A. Walsh, Ultramicroscopy (to be published).

[9] P. A. Wolff, Phys. Rev. **95**, 56 (1954).