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Applied Surface Science 231–232 (2004) 874–877

applied surface science
www.elsevier.com/locate/apsusc

QSA influences on isotopic ratio measurements

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Abstract

The quasi-simultaneous arrival (QSA) effect has been tested with the Cameca NanoSIMS 50. The capability of obtaining rather large values of K (ratio of secondary ions ejected per primary ions) has been used to follow the evolution of QSA over a large range of K value by changing the collection efficiency. The amplitude of the effect associated with QSA has been determined and compared to the theoretical value by using silicon and sulfur isotopic ratio measurements. QSA influence on pulse height distribution (PHD) has also been demonstrated.

Keywords: SIMS; Isotopes; Electron multiplier; Sulfur; Silicon

1. Introduction

The Cameca NanoSIMS 50 mass spectrometer achieves double focusing and high mass resolution at all positions along the focal plane. It includes seven detectors: four moveable miniature electron multipliers (EM), two EMs at fixed positions and one moveable Faraday cup (FC) [1,2].

Weak ion signals are conveniently detected with EMs working in the counting mode, nonetheless quasi-simultaneous arrivals (QSA) may induce a specific type of bias.

Secondary ions are often considered to be only a small fraction of the bunch of sputtered particles resulting from the impact of a single primary ion. However, the average number K of secondary ions ejected per primary ion may reach values as high as 20% for some elements. In such conditions, the probability of more than one secondary ion per primary impact is not negligible and those ions may arrive at nearly the same time on the conversion dynode of the electron multiplier. QSA are registered as single pulses so that the registered number of counts is slightly lower than the actual number of incoming ions.

Assuming a Poisson statistics, the correction factor is given in a first-order approximation [3] by

$$N_{\mathrm{cor}} = N_{\mathrm{exp}}(1 + \tfrac{1}{2}K) \qquad (1)$$

where N_{cor} is the real number of ions reaching the first dynode and N_{exp} the number of pulses counted with a given threshold (strictly speaking N_{exp} in Eq. (1) is the number of ions after a correction made to account for the quantum detection efficiency).

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doi:10.1016/j.apsusc.2004.03.155

2. Characterization of QSA effects on isotopic ratio measurements

2.1. Sulfur measurements

In order to show the effect of QSA on isotopic ratio measurements, the ratio $^{34}\mathrm{S}/^{32}\mathrm{S}$ has been measured for different K. As K for $^{34}\mathrm{S}$ is roughly 22 times lower than for $^{32}\mathrm{S}$, the effect of QSA can be neglected. Thus the experimental sulfur isotopic ratio R_{exp} must vary with K according to

$$R_{\mathrm{exp}} = R_{\mathrm{cor}}\left(1 + \tfrac{1}{2}K\right) \tag{2}$$

R_{cor} being the isotopic ratio determined at low K (<0.01).

The experimental data have been obtained on Balmate pyrite[1] by using two EMs in multicollection mode—$^{32}\mathrm{S}$ and $^{34}\mathrm{S}$ were collected simultaneously. To avoid effects linked to the use of a particular pair of EMs, different sets of two EMs have been used through the four moveable identical EMs available on the NanoSIMS 50. These EMs are numbered from 1 to 4, 4 being the one located on the high radius side (Table 1, raw EMs no.).

To vary K different aperture and energy slit widths have been used while the entrance slit width was kept constant. K has been varied from 0.023 to 0.208 without changing the primary ion beam intensity (Cs^+) set at 0.96 pA.

As K has to be determined experimentally and as the real number of ions reaching the EM is unknown one has to apply a correction to K_{exp}, the experimental ratio of secondary intensity over primary intensity [3]:

$$K_{\mathrm{cor}} = \frac{K_{\mathrm{exp}}}{(1 - K_{\mathrm{exp}}/2)}$$

K_{cor} being the corrected ratio that must be considered.

Table 1
Evolution of sulfur isotopic ratios versus K

K_{exp}	K_{cor}	$\delta_{34\mathrm{exp}}$	$\delta_{34\mathrm{cor}}$	EMs no.
0.023	0.024	−29.5	−45.9	2 and 3
0.033	0.034	−17.3	−40.8	1 and 2
0.042	0.043	−4.82	−34.7	3 and 4
0.049	0.050	−1.09	−35.9	2 and 3
0.074	0.077	28.2	−25.4	1 and 2
0.095	0.100	39.0	−30.3	2 and 3
0.096	0.100	33.3	−36.1	2 and 3
0.099	0.105	38.3	−34.2	2 and 3
0.113	0.119	46.6	−36.0	2 and 3
0.142	0.154	70.5	−35.4	2 and 3
0.152	0.165	73.1	−40.7	3 and 4
0.189	0.208	104.4	−39.0	2 and 3

Let $\delta_{34\mathrm{exp}}$ be the relative deviation of $^{34}\mathrm{S}/^{32}\mathrm{S}$ ratios normalized to the Canyon Diablo Troilite well known standard and expressed in per mil. It can be seen in Fig. 1 that $\delta_{34\mathrm{exp}}$ exhibits a rather linear relationship with respect to K_{cor}, which is certainly related to the QSA effect. If $\langle\delta_{34\mathrm{cor}}\rangle$ represents the corrected relative deviation of $^{34}\mathrm{S}/^{32}\mathrm{S}$ ratio, the linear relation (Fig. 1) becomes

$$\delta_{34\mathrm{exp}} = \langle\delta_{34\mathrm{cor}}\rangle + 0.69K_{\mathrm{cor}} \times 1000$$

This experimental coefficient, 0.69 instead of being 0.5, is obviously different from the value given by relationship (2) obtained from Poisson statistics. It might be due to the inadequacy of Poisson statistics to describe the phenomenon or to other effects such as fractionations due to differences in ion selection generated by the change of K. Further investigation needs to be done with measurements coupling Faraday cup and EM and on different elements.

2.2. Silicon measurements

The following data have been obtained on a silicon wafer by using one Faraday cup for $^{28}\mathrm{Si}$ and one EM

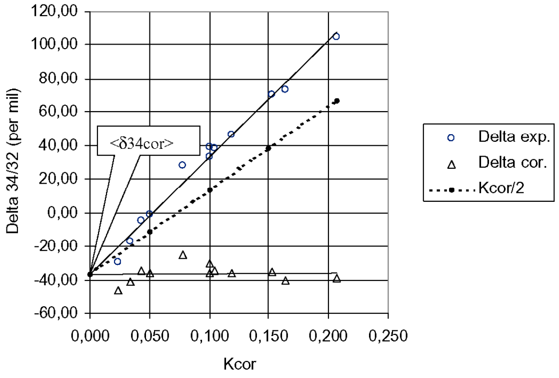

Fig. 1. Theoretical and experimental variation law of δ_{34} versus K_{cor}.

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[1] Thanks to E. Hauri for supplying the Balmate pyrite, Carnegie Institution of Washington, Washington, DC 20015, USA.

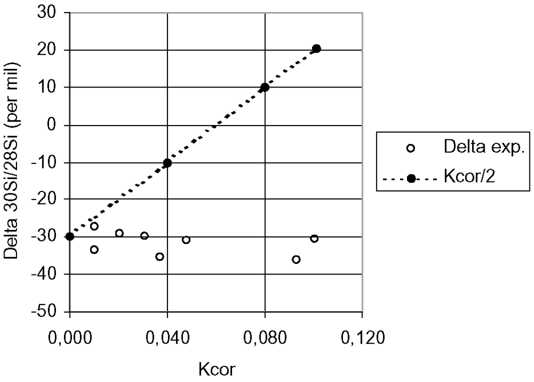

Fig. 2. Variation of $^{30}Si/^{28}Si$ versus K_{cor}.

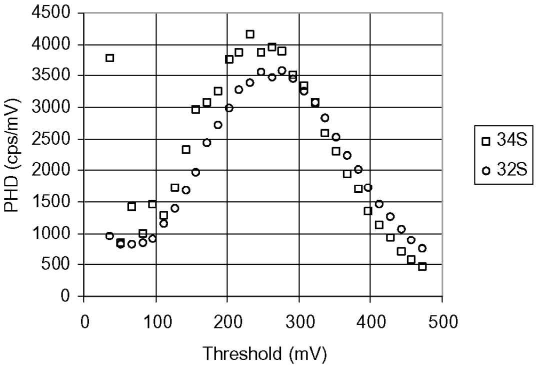

Fig. 3. ^{32}S and ^{34}S experimental PHDs.

for ^{30}Si in multicollection mode: ^{28}Si and ^{30}Si were collected simultaneously.

Fig. 2 shows the variation of δ_{30} versus K_{cor}. The behavior is obviously completely different from the measurements made on sulfur with two EMs. There is no increase of δ_{30} with K. We do notice a slight decrease of δ which could be due to mass fractionation effects at the aperture slit as it was used to vary K.

3. QSA effects on pulse height distribution (PHD)

In order to demonstrate the effect of QSA, two different PHDs have been recorded on a pyrite sample using ^{32}S and ^{34}S ions, while K_{cor} was kept constant at 0.195. These PHDs normalized to the same secondary ion intensity (10^6 counts/s) are shown in Fig. 3.

Simulations with a semi-empirical model can provide us with an approximate estimation of the general behavior of our EMs [3]. This algorithm has been used to obtain the PHD corresponding to ^{34}S by using the following parameters: Np = 10.7 (ion/electron yield on the first dynode), Ne = 3 (electron/electron yields on other dynodes). At our level of precision no QSA effect had to be considered as K for ^{34}S is lower than 0.01.

A reasonably good agreement between this semi-empirical model and the experimental data for ^{34}S is shown in Fig. 4. Dispersion of data points of this PHD is mainly due to the weak intensity of ^{34}S beam (4×10^4 cps) as we have chosen to record ^{34}S PHD with the same experimental conditions we used to record ^{32}S PHD.

The effect of QSA upon ^{32}S PHD has been determined as following: (i) K being known the probabilities were calculated with a Poisson law to obtain a single event made of 2, 3 or 4 ions reaching the first dynode simultaneously. The number of ions in one event has been limited to 4 as the total probability of getting more than four ions is less than 1.25×10^{-5} for $K = 0.2$. (ii) PHDs corresponding to Np = 11, 22, 33 and 44 are added, properly weighted by the above probabilities.

A comparison between the ^{32}S experimental PHD and two calculated PHDs is presented in Fig. 5. Two different K have been introduced in the model: $K = 0.01$ and 0.195, this last value corresponds to the experimental value of K. Ne and Np have been

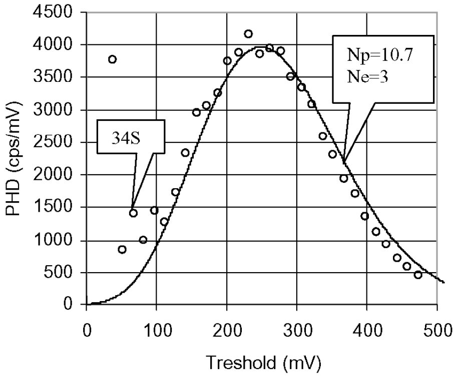

Fig. 4. Comparison between experimental and theoretical ^{34}S PHDs.

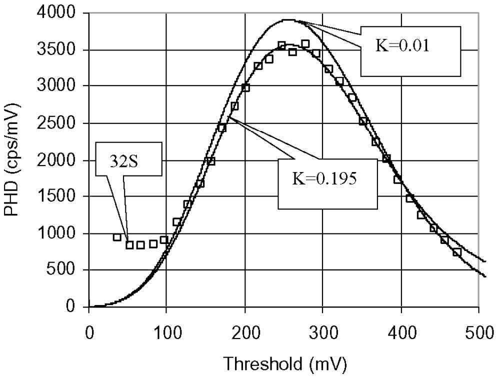

Fig. 5. Comparison between experimental and theoretical ^{32}S PHDs.

respectively set to 3 and 11. The variation of Np values between ^{32}S (Np = 11) and ^{34}S (Np = 10.7) has been computed according to the general semi-empirical law claiming that ion electron yields are proportional to the speed of the incoming ion, at least for isotopes of a given element. The agreement with the model using $K = 0.195$ is rather good especially for threshold values less than 400 mV. It shows clearly how QSA effects can influence the PHDs.

4. Conclusions

The experimental exploration over a large range of K values has shown that QSA effects have a clear influence upon measured isotopic ratios and on PHDs. However, the comparison with calculated values using sulfur isotopic ratio measurements exhibits differences that must be examined carefully before being able to use calculated values in correction procedures. Nonetheless, the observation of the general trends predicted by the calculations based upon Poisson statistics, reinforce the likelihood of the QSA effect.

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