Effect of excessive-trapping operation of sequential mass spectrometers shown for collision cross-section data of BCl_3

Z. A. Hafidh and H. L. Hartnagel

Department of Electrical and Electronic Engineering, University of Newcastle Upon Tyne, The Merz Laboratories, Newcastle Upon Tyne, NE1 7RU, U. K.

(Received 31 March 1975; in final form 20 June 1975)

The transients of ion trapping were studied in sequential mass spectrometers. The optimization criteria of the trap are very complex and are dependent on such parameters as the mass of the trapped ions. A new calibration scheme was developed for the measurement of the collision cross section of unknown gases and was applied to BCl_3, which is commonly used for boron-ion implantation into silicon.

PACS numbers: 34.90., 07.75., 35.10.H, 34.70.D, 52.25.K

A sequential mass spectrometer[1–3] is employed for the measurement of collision cross-section data for higher-order ions and electrons. It uses an electron beam to produce the singly charged ions and to trap them by its space-charge depression. The trapped primary ions can then be further ionized by either the same electron beam or, in a more sophisticated system, by an additional axial beam whose energy can then be different from that of the primary beam. In the latter case, the primary beam can conveniently be of tubular shape. The trapped ions are extracted via a conveniently placed aperture with a suitable value of negative bias voltage. The ions are analyzed according to their charge-to-mass ratios by a subsequent mass analyzer.

Sequential mass spectrometers have demonstrated their importance for collision cross-section measurements of higher-order ions,[1,4] where no other method is easily available. First experimental investigations on ion-trapping phenomena have, however, clearly shown[2] that the ion densities are critically dependent on secondary-electron production and on opportunities for their immediate trapping by any positive ion-potential trap which temporarily occurs during the ion-filling transients. Further systematic experiments with the same system as described previously[2] have shown that substantial changes in primary ion densities occur with varying pencil-beam densities.

Figure 1 shows an approximately 10% increase in trapped, singly charged, ion-density N_i^+ for an increase in the axial pencil-beam density N_e by a factor of 2, as obtained by increasing the anode potential with respect to the space-charge-limited cathode of the constant-perveance gun. By increasing the pencil-beam energy further (and thus further increasing N_e), a sharp decrease in N_i^+ is observed which is only partly accounted for by the onset of the production of doubly charged ions by the axial beam.

Because of the influence of the ionic-mass-dependent flow rate through the extraction aperture during the transient on the steady-state ion density, N_i^+ was found to be dependent on the mass of the relevant trapped ion species (see Fig. 2). Correspondingly, the filling rate of the trap (t_n) was also found to be mass de-

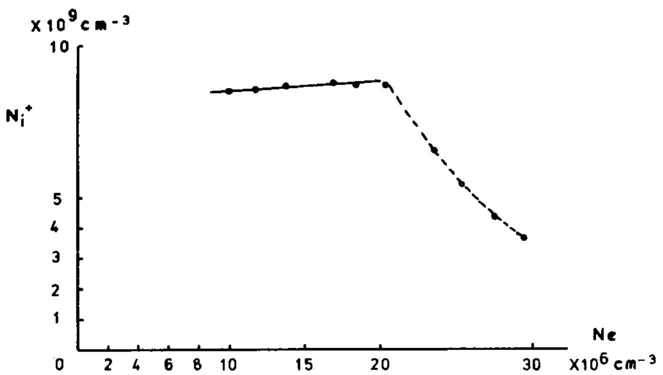

FIG. 1. Primary ion density N_i^+ vs the electron density N_e of the pencil beam, with the energy of the tubular beam set at the first ionization potential. The dotted line indicates the case where the pencil-beam cathode is above the third-order ionization potential of the gas in the collision chamber.

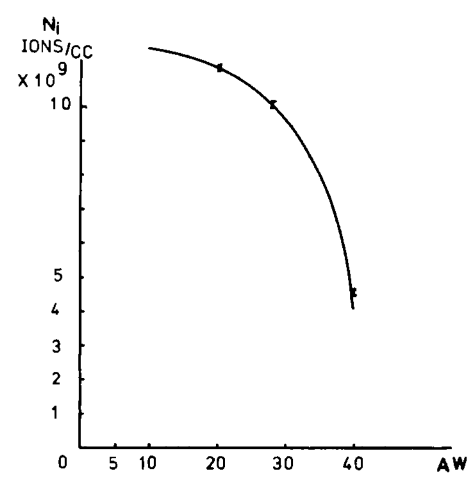

FIG. 2. Primary ion density (N_i^+) vs mass (amu). Data refers to Ne, N_2, and Ar measurements. The gas pressure is 0.5×10^{-6} Torr, the back pressure is 0.5×10^{-7} Torr.

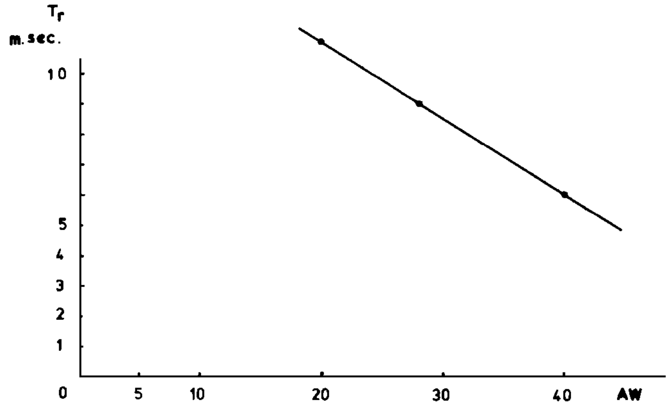

FIG. 3. Transient time (T_r) of filling the trap vs mass (amu). Data refers to Ne, N_2, and Ar; gas pressure is 0.5×10^{-6} Torr, back pressure is 0.5×10^{-7} Torr.

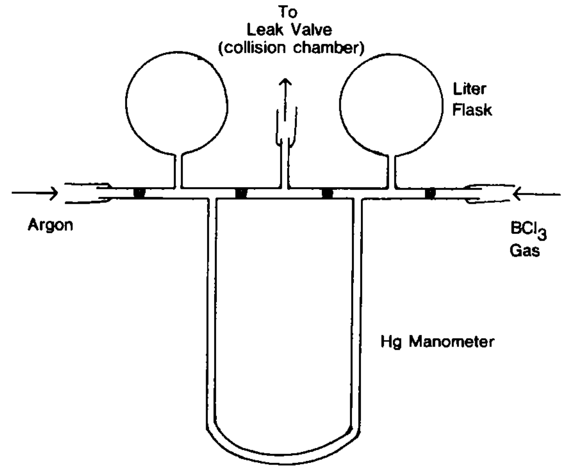

FIG. 6. Source of gas mixture.

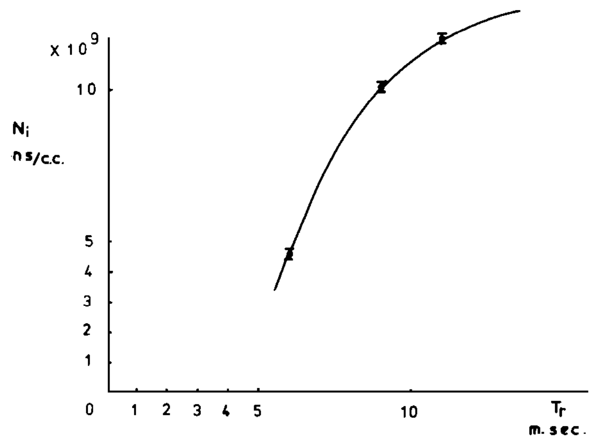

FIG. 4. Primary ion density (N_i^+) vs transient time (T_r). Data refers to Ne, N_2, and Ar; gas pressure is 0.5×10^{-5} Torr, back pressure is 0.5×10^{-7} Torr.

pendent (see Fig. 3). This phenomenon can be explained by the thermal velocity (v_{th}) of the oscillations of the trapped ions, i.e.,

$$v_{th}\cong(2kT_i/m_pM)^{\frac{1}{2}},$$

where k is Boltzmann's constant, T_i is the temperature of the ions, m_p is the mass of the proton, and M is the atomic weight of the relevant gas. Consequently, the formation of the positive potential traps for the trapping of secondary electrons during this transient is ion-mass dependent, so that the ultimate trapped ion charge can be expected to be dependent on ionic mass in a very complex manner. Therefore, unfortunately, it is not possible to estimate the ion density of one species from the known density of another one. In order to establish without doubt that the ultimate ion density is a function of transient time (i.e., mass of ionic species), we measured this separately and present the experimental results in Fig. 4.

On the basis of this complexity of the trapping phenomena (i.e., the ion density is a function of the mass of the ionic species and the density and energy of the axial electron beam), experimental results can only be obtained by measuring N_i^+ for each pencil-beam current (I_p). We have, therefore, modified our experimental system (Fig. 5) by incorporating a new method of calibrating the collision cross sections of various gases. This is based on a source (see Fig. 6) which

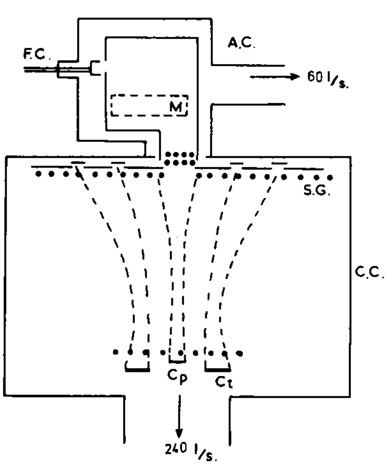

FIG. 5. Cross section of the collision chamber (C.C.) and analyzer chamber (A.C.); C_t—tubular cathode; C_p—pencil beam cathode; S.G.—suppressor grid with collector plate and probes; M—projected area of the pole of the magnet; and F.C.—Faraday cup.

TABLE I. Ionization potentials in volts of B, Cl, and Ar.

Ionization degree	B	Cl	Ar
I	8.29	13.01	15.7
II	25.15	23.8	27.6
III	37.92	39.9	40.9

TABLE II. Singly and doubly charged ion currents I_1 and I_2, respectively, of B, Cl, and Ar.

Element	$I_1\times10^{-12}$A	$I_2\times10^{-13}$A
B	3.8	1.8
Cl	3	2.45
Ar	2.9	2.6

TABLE III. Collision cross sections of B and Cl.

Collision cross section $\times10^{-17}$ cm^2	B	Cl	Energy (eV)
σ_{01}	6.486	5.120	22.5
σ_{12}	2.284	3.109	35

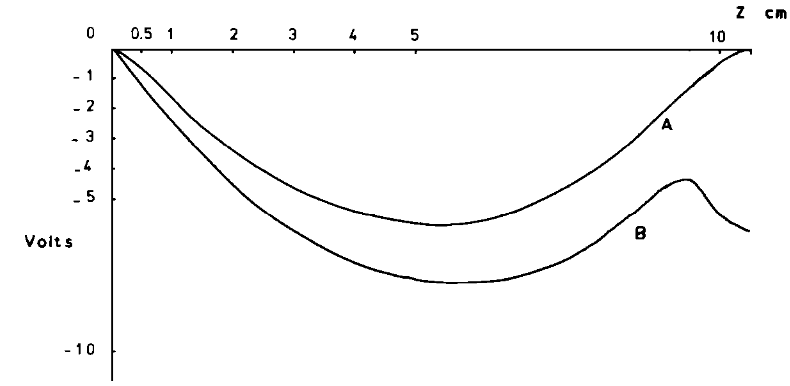

FIG. 7. Computed potential depth of the trap in collision chamber vs distance along the axis (Z). A—Closed system employing tubular beam only; B—open system employing tubular and pencil beams. Potential at the end is being lowered by the potential of the extraction electrode to maintain uniform flow of the trapped ions.

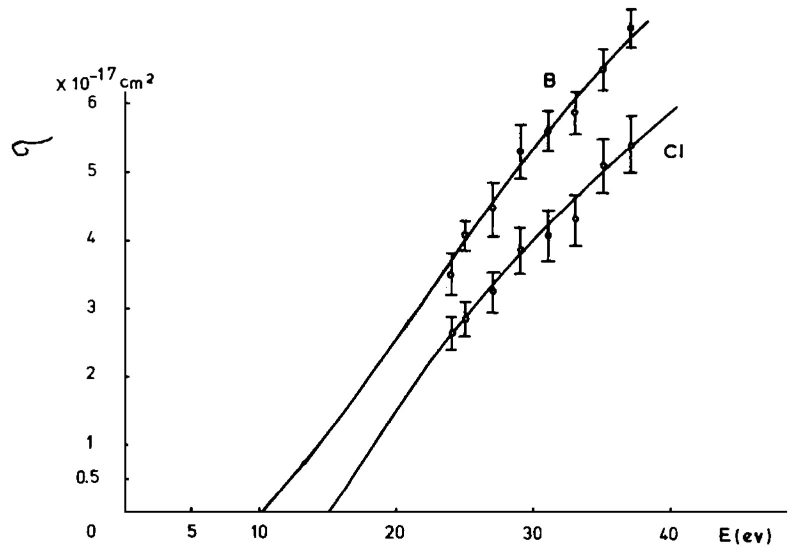

FIG. 8. Collision cross section (σ_{01}) of B and Cl vs energy of bombarding electrons, as obtained from BCl_3 gas.

maintains a mixture of an equal number of gas molecules of two different gases, where one gas represents known collision cross-section data and the other one has to be measured.

We employed argon and BCl_3 obtained from separate gas bottles. Equal volumes of each gas were mixed at constant pressure and temperature of diffusion over a period of 24 h, to ensure complete mixing before leaking the mixture into the collision chamber. The gas mixture was produced at a pressure of 200 Torr and was leaked into the collision chamber, which was at a pressure of about 10^{-7} Torr. The large difference in pressure ensured uniform flow of the mixture into the collision chamber, independent of the difference in atomic weights of both gases, as the flow in the low-pressure chamber is not affected by diffusion effects.

The voltages of the tubular (V_T) and pencil-beam (V_p) cathode were set to ionize the gas (Moore[5]) according to its ionization potentials, as shown in Table I, and to dissociate it into its fragments.[6,7]

The potential of the tubular cathode was set at 22.5 V (the tubular beam current $=2.17$ mA) to produce singly charged ions only of the gas mixture. The pencil-beam cathode was set at 35 V (the pencil-beam current $=0.21$ mA) to generate higher-order ions. The maximum potential depression along the tubular

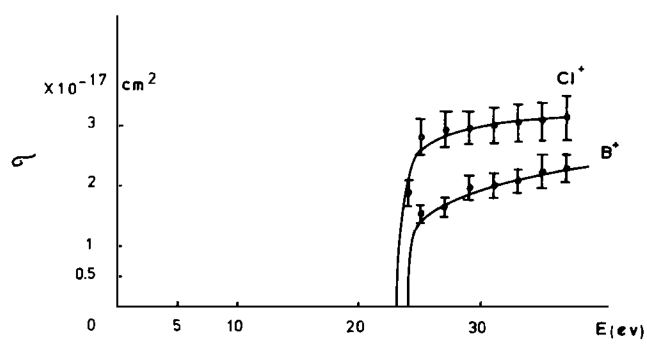

FIG. 9. Collision cross section of singly charged ions (σ_{12}) of B and Cl versus energy of bombarding electrons.

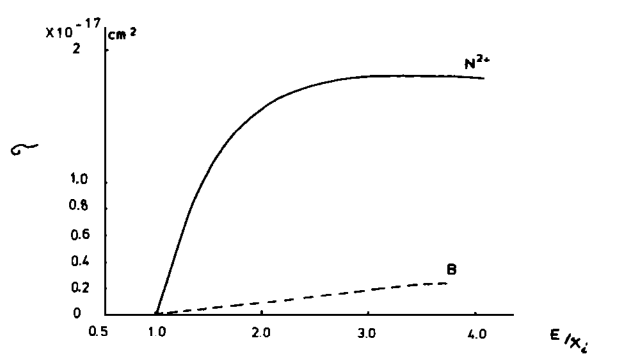

FIG. 10. Cross section (σ) vs electron energy (E)/threshold energy (X_i). The cross section for ionization of N^{2+} compared with the cross section for ionization of B.

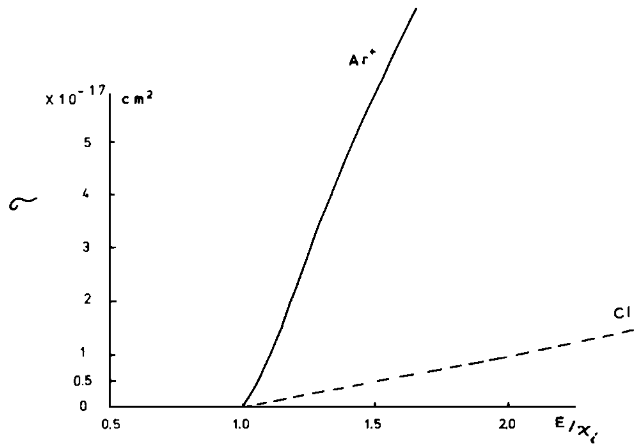

FIG. 11. Cross section (σ) vs electron energy (E)/threshold energy (X_i). The cross section for ionization of Ar^+ compared with the cross section for ionization of Cl.

beam was calculated to be -6.2 V, as compared to -6.7 V when the effect of the pencil beam and extraction potentials are included (see Fig. 7). This variation in the potential depression introduces an error of 7.5% in the calculation of the cross section. Argon was used for the calibration since it has known collision cross sections. The following atomic collision processes occur:

$$Ar+e \rightarrow Ar^{+}+2e,$$

where the collision cross section is

$$\sigma_{01}=5\times10^{-17}\ cm^2 \text{ at } 22.5\ eV$$

and

$$Ar^{+}+e \rightarrow Ar^{++}+2e,$$

with $\sigma_{12}=3.3\times10^{-17}$ cm² at 35 eV, as described by Hasted,[8] Hasted and Awad,[1] Latypov *et al.*,[3] and Awad.[9]

Boron was detected at an appearance potential of 22.5 eV (Marriott and Craggs[6]), which suggested the following reactions in the collision chamber due to electron bombardment:

$$BCl_3+e \rightarrow B^{+}+3\ Cl+2e;$$
$$Cl+e \rightarrow Cl^{+}+2e.$$

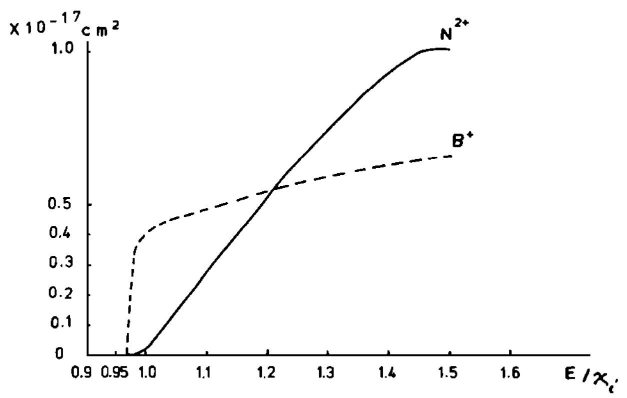

FIG. 12. Comparison of the cross section for ionization of N^{2+} with the cross section for ionization of B^+.

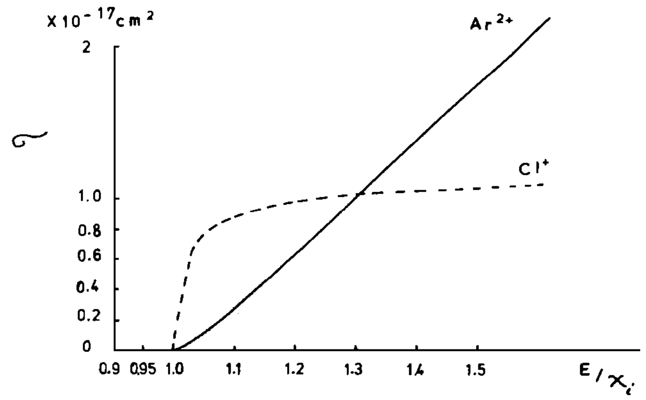

FIG. 13. Comparison of the cross section for ionization of Ar^{2+} with the cross section for ionization of Cl^+.

The ion density of the gas mixture in the collision chamber was 7.5×10^9 ions/cm³ as calculated from the relation $N_i^+=I_2/2I_p lk\sigma_{12}$ [see Eq. (4) of Ref. 2]. The detected current densities of the singly charged ions (I_1) and doubly charged ions (I_2) are given in Table II. The collision cross sections were calculated from this relation, and the results are listed in Table III. The measured value of the cross section for B atoms falls within the range of previous values (see Freeman *et al.*[10]).

The ionization potential of the two gases in the mixture shows a range of 6 V between the singly and doubly charged ions, and a range of about 8 V between the doubly and triply charged ions. This indicates that a plot of the collision cross section vs electron energy was not possible due to the small differences of electron energies between the various levels, including that of the Ar gas. However, this is not a basic limitation, as the collision experiment can subsequently be undertaken in the usual way with BCl_3 only, once the calibration has been undertaken by the gas mixture method. The measured collision cross section (σ_{01} and σ_{12}) of B and Cl were thus obtained and are plotted against the electron energy, as shown in Figs. 8 and 9.

The scalings (see McDaniel[11]) of the cross sections of B and Cl as compared with that of N and Ar (since both have $2p^q$ and $3p^q$ series, respectively, where q is the number of electrons in the outside shell) are shown in Figs. 10–13.

The scaling of the cross sections (σ_{01}) of B and Cl, as compared with those of N^{2+} and Ar^+, respectively, is poor, which could be caused by a higher compactness of the B and Cl atoms. The scaling of the cross sections (σ_{12}) of the singly charged B and Cl follow a comparable magnitude to that of N^{2+} and Ar^{2+}, respectively, which might be due to the effect of the coulomb interaction of the singly charged ions with bombarding electrons.

[1] J. B. Hasted and G. L. Awad, J. Phys. B **5**, 1719 (1972).
[2] H. Hartnagel and I. Herkman, J. Vac. Sci. Technol. **10**, 539 (1973).
[3] Z. Z. Latypov, S. E. Kupriyanov, and N. N. Tunitskii, Sov. Phys.-JETP **19**, 570 (1964).
[4] P. A. Redhead, Can. J. Phys. **45**, 1791 (1967).
[5] C. E. Moore, Natl. Bur. Standards Circ. 467, Vols I and II.
[6] J. Marriott and J. D. Craggs, J. Electron. Control **3**, 194 (1957).
[7] A. G. Gaydon, *Dissociation Energies and Spectra of Atomic Molecules* (Chapman and Hall, London, 1947) 2nd ed.
[8] J. B. Hasted, *Physics of Atomic Collisions* (Butterworths, London, 1972), 2nd ed.
[9] G. L. Awad, thesis (London University, 1972).
[10] J. H. Freeman, G. A. Gard, and W. Temple, A.E.R.E.-R6758.
[11] E. W. McDaniel, *Collision Phenomena in Ionized Gases* (Wiley, New York, 1964).