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ABSTRACT

A project has been initiated at the Lucas Heights Research Laboratories to investigate simple but effective ion implantation and pulsed annealing techniques for the fabrication of high efficiency silicon solar cells. In particular, the method aims to eliminate the mass analyser and associated components from the implanter. A solid feed source is used in a clean ultra high vacuum environment to minimise impurities.

This work, commenced in the AAEC's Applied Physics Division with the support of the National Energy Research, Development and Demonstration Council, was transferred to the CSIRO's Chemical Physics Division in September 1981.

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ANNEALING; ION IMPLANTATION; ION SOURCES; SILICON SOLAR CELLS

CONTENTS

1. INTRODUCTION

The development of thin layer devices and modified surface and subsurface regions of materials is becoming increasingly important in modern technology; concurrently, the study and application of ion beams has become a significant factor in this development. Of particular importance is the use of ion implantation to modify materials properties.

High current (mA) ion implantation systems have been developed to speed the production of semiconductor materials. Wegmann [1981] recently reviewed developments in high current implanters. In addition to their most common application, semiconductor doping, these devices permit either the rapid implantation of large areas or a host matrix to be doped with up to several atoms per cent of foreign atoms. Since any ion species can be implanted into any host material, many unusual combinations can be studied in this way; the results of such studies contribute significantly to knowledge of oxidation and corrosion properties, wear and friction, catalysis and other fields. Ion implantation techniques are now having an impact on general industrial practice.

This report describes a project initiated to explore the simplest, and hence the cheapest, techniques for ion implantation in such applications as the production of photovoltaic material and materials modification.

2. ION IMPLANTATION

A schematic diagram of a typical ion implantation system is shown in Figure 1. The ion source includes an oven, operating at temperatures up to 800°C, which can be used to vaporise solid materials. This enables the production of ion beams from 80 per cent of the elements and many compounds. For the remaining elements, special ion sources must be used. The ion beam is usually extracted at an energy of 20 to 40 keV and then mass-analysed to remove unwanted components. The analysed beam is then accelerated to a selected energy up to a maximum of 200 keV (400 keV in some systems). At these energies, the ion range in a sample is less than 1 μm. The beam is focused and swept across the sample surface by electrostatic deflection or, alternatively, the sample is moved through the beam to obtain the required coverage. The use of a mass analyser (usually magnetic) ensures that only one ion species and charge state is implanted into the sample. At the same time, it increases the complexity (and cost) of the ion implanter and places restrictions on the beam area which can be used. Typical performance figures of some commercial implant systems are given in Table 1.

Some of the advantages and disadvantages of the ion implantation techniques are described below.

Advantages

(a) Ambient temperature process.	Samples are implanted at room temperature. At high beam currents, beam heating can become significant and scanning is then used to limit the temperature rise during implantation.
(b) Precision control.	The number of foreign atoms can be controlled accurately and, by selection of appropriate beam energy and angle of incidence, a choice of depth distributions can be obtained.
(c) Any element or isotope.	Complete freedom of choice of foreign atoms is available, bypassing normal solubility rules and providing great versatility in application.
(d) Any substrate.	Any type of sample can be implanted provided that it can be mounted in the vacuum system. Crystals, polycrystals or amorphous materials can be doped by ion implantation.
(e) Benign environment.	Doping takes place in a clean environment and maintains original dimensional tolerances.
(f) Speed.	Implantation can be much faster than diffusion for the introduction of foreign atoms.

Disadvantages

(a) Shallow penetration.	The normal limit is less than 1 μm although higher energy accelerators can be used to achieve greater penetration.
(b) Line-of-sight.	Every part of the surface to be implanted must be placed at a suitable angle to the beam. It may therefore be difficult or impossible to treat samples having complex or re-entrant shapes.
(c) High technology.	Expensive equipment and skilled operation are usually needed.
(d) Competing processes.	Ion implantation is accompanied by sputtering and radiation damage which may limit some applications, particularly at high doses.

2.1 Semiconductors

The main dopants used in silicon semiconductor technology are boron, phosphorus and arsenic. Established ion source techniques permit the production of ion beams from these materials using either pure elemental or compound feed materials. The level of dopants required is of the order of 10^{14}-10^{16} ions cm^{-2}. A 1 mA beam contains 6 x 10^{15} ions s^{-1}; this enables small areas to be implanted in a very short time interval and larger areas to be implanted in minutes by scanning. The depth required for semiconductor doping is in the range 0.05 - 0.2 μm. This depth range is obtained for ion energies between 50 and 200 keV; well established techniques can be used to obtain ion beams at these energies.

2.2 Annealing

When crystalline materials such as silicon are implanted, the crystal structure is damaged down to the depth reached by the dopant ions. To obtain full electrical activity, this damage must be removed by annealing. The traditional method of thermal annealing has a number of disadvantages including high cost, slowness, formation of precipitates, surface contamination and the inability to localise the effects of the junction region of a semiconductor. Recent experiments reviewed by Brown [1981] have shown that the use of pulsed or scanned laser or electron beams can give very rapid annealing of the near surface region of a semiconductor and produce fully restored electrical activity and a more damage-free surface than can be achieved by thermal annealing. The success of pulsed annealing further enhances the usefulness of ion implantation for semiconductor doping. Experiments have also shown that both pulsed laser and pulsed electron annealing can give comparable results. However, for the very high throughputs required in solar cell production, it would appear that pulsed electron beams may be useful. Recent work has shown that incoherent light [Harrison 1981] or pulsed ion beams [Baglin et al. 1981] can also be used to produce rapid annealing.

3. SOLAR CELLS

Photovoltaic cells prepared from single crystal silicon and other semiconductor materials have doping requirements similar to those for microelectronic devices. Ion implantation therefore merits strong consideration as a potential production technique for solar cells. The special features are a need for large area production rather than the treatment of microscopic regions, and a shallow junction depth. Also, variations in dose uniformity of 20 per cent or more and the presence of small quantities of impurities may reduce the efficiency of a solar cell by only a small amount.

Because of these special features, the optimum requirements for ion implantation of photovoltaic materials differ from those for microelectronics manufacture. A low voltage, large area beam - possibly without the use of mass analysis - should be all that is necessary to reduce costs and simplify operation. Ion implantation is only one step in the production of solar cells; the ultimate objective is the development of integrated machines which will carry out implantation, annealing, application of contacts and encapsulation. The market for such machines has been estimated to be up to ten times that for semiconductor implanters (A. Wittkower, cited in Wegmann [1981]). This shows very clearly the potential opportunities for implantation; however, there is a risk that this potential may be eliminated by the development of alternative techniques.

Research and development programs in the USA, UK, France and other countries aim to achieve reduction in the cost of manufacturing solar cells by at least an order of magnitude over the next three to four years. Major progress has already been made with the development of production technology for the silicon cells used in the various space programs and for remote area usage. Improvements have been made in each of the three main areas: silicon production, crystal growth and preparation, and cell manufacture and encapsulation. It has been estimated that compared with diffusion doping, the use of ion implantation/pulsed annealing techniques will achieve a 10 per cent reduction in total cost. More important is the fact that the energy 'pay-back time' could be much reduced by the use of ion implantation/pulsed annealing methods.

3.1 Ion Implantation Developments

Solar cells have been manufactured by ion implantation in many laboratories (these include Spire Corporation, Oak Ridge National Laboratory (ORNL), Royal Melbourne Institute of Technology (RMIT), Motorola and Strasbourg-Cedex). Much of this work has involved production of a small number of cells - usually with areas of a few cm^2 and efficiencies of up to 17 per cent AM1 (air mass 1, the solar spectrum at the Earth's surface) have been achieved [Minucci and Kirkpatrick 1979; Kirkpatrick et al. 1980]. Some work has involved the production of hundreds of cells with diameters up to 7.5 cm; the efficiencies achieved are usually around 15 per cent.

One of the first industrial implanters for solar cell production was developed at Ion Physics Inc. in 1965; it required no mass analysis of the ion beam. Two recent projects have explored the possibilities of simplified ion implantation. At Motorola Inc., Coleman et al. [1980] have investigated factors affecting the cost of solar cell ion implantation and have tested the effects of using an unanalysed ion beam to obtain high currents and large beam diameters. They simulated cell production without mass analysis by sweeping the field of the analyser magnet to allow all beam components to reach the silicon sample. Cells made with phosphine (PH_3), arsine (AsH_3) and boron trifluoride showed open circuit voltages greater than 600 mV - comparable with those produced using implantation with an analysed beam. Coleman et al. also produced a batch of cells from an ion milling machine using an unanalysed beam, and observed open circuit voltages of 500-600 mV for 7.5 cm diameter wafers.

Muller and Siffert [1981] prepared a number of cells using a simple glow discharge tube to implant phosphorus into silicon at 10-50 keV without mass analysis. Laser annealing was used to restore electrical activity. Efficiencies of 11.4 per cent were achieved (with anti-reflective coating) compared to 12.1 per cent for thermal diffusion doped cells. This suggests that a simple implantation system may be as effective as more complex equipment but it is necessary to show that cells with at least 15 per cent efficiency can be produced in routine large scale production.

These results suggest that an unanalysed large area, high current ion beam could be suitable for implantation of photovoltaic materials. However, more extensive investigations are needed to establish the performance capabilities and limitations of this method and to demonstrate fully that it is a practicable technology.

4. LUCAS HEIGHTS PROJECT

A project is under way at the Lucas Heights Research Laboratories to set up a simple implantation system to be used in conjunction with pulsed annealing for the manufacture of solar cells. This project uses a duoplasmatron ion source and an ultra-high vacuum system to permit the study of the role of secondary beam components and the effects of ion beam energy, uniformity and other parameters on the performance of solar cells prepared by simple implantation and pulsed annealing techniques.

4.1 Duoplasmatron System

A schematic layout of the duoplasmatron system is shown in Figure 2. The duoplasmatron (ORTEC model No.350) is mounted on an insulated platform so that the source and its power supplies can be operated at 5-70 keV above ground potential. Insulated control rods operate through a protective wire mesh cage which can be opened to allow access for maintenance. Protection is provided by microswitches which turn off the accelerating potential when the cage is opened, and a gravity operated shorting bar discharges the source voltage.

The source is mounted via an insulating vacuum section to a 15 cm diameter ultra high vacuum (UHV) cross to which is attached a turbomolecular pump with UHV gate valves and other accessories. The total system can be evacuated to 1 μPa before admission of gas to the ion source. A residual gas analyser is used to provide information on the amount and composition of gas present in the sample end of the system during implantation.

Samples for implantation are mounted in a second 15 cm 6-way UHV cross; beam profiling facilities are also available. Positioning or scanning is achieved by mechanical control using UHV components. Sample holders can accommodate up to four silicon wafers each of diameter 5 cm. This system is satisfactory for exploratory work but positioning and scanning control needs to be automated if large numbers of solar cells are to be processed.

Initially, the performance of the system was evaluated with nitrogen or argon gas being fed to the ion source. With no external focusing, the beam diameter is typically 15 mm (FWHM) at a distance of 65 cm from the extraction electrode. A typical beam profile in both horizontal and vertical directions is shown in Figure 3, and typical operating parameters are listed in Table 2. During operation of the source, a mass scan with the residual gas analyser, showed that no components other than the feed gas were present.

4.2 Rutherford Backscattering Results

The silicon surface structure can readily be studied using the Rutherford backscattering technique and channelled 2 MeV helium ions. Figure 4(a) shows an aligned backscattering spectrum for pure silicon in which only the silicon surface peak is seen. Figure 4(b) is a random spectrum of silicon implanted with 30 keV arsenic ions to a dose of 10^{14} ions cm^{-2}*; the arsenic peak stands out clearly. Figure 4(c) is an aligned spectrum of the same material; the arsenic peak is unchanged, indicating that the implanted ions are interstitial. The silicon peak shows that the structure has been damaged to a depth equal to the maximum range of the arsenic ions. Figure 4(d) shows the same material after annealing with a pulsed ruby laser; the arsenic peak has almost disappeared, indicating that >90 per cent of the arsenic is now substitutional and that the silicon peak is nearly identical to that for pure silicon, indicating that crystal structure has been restored.

4.3 Doping Times of Photovoltaic Materials

A problem that occurs with high current implantation is the amount of heating produced in the sample. In the case of silicon, if the heat dissipation is high it can melt, producing various effects. These can take the form of self-annealing which may be beneficial or can cause permanent crystal damage. Such effects have been described elsewhere [Beanland and Chivers 1978].

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* Normal implantation by Atomic Energy Research Establishment, Harwell, United Kingdom.

Since solar cells generally require low implant voltages and large beam areas, heating effects can be minimised. A 1 mA beam can implant a 1 cm^2 area in one second. For a 10 cm diameter wafer, the total implant time is of the order of 20 seconds, provided that suitable scanning is available. Under these circumstances, heating is not a significant problem, particularly if the beam energy is less than 25 keV. For laboratory-scale research this is an adequate implant time, but for commercial purposes, increase in throughput of several orders of magnitude would be required which would necessitate special precautions to reduce sample heating. In solar cell manufacture, dopant doses are not critical and variations in dose uniformity of up to 20 per cent may be tolerated; this can readily be achieved with the beam profiles shown in Figure 3.

4.4 Freeman Source

The duoplasmatron source has serious limitations for solar cell production. Unless significantly modified, it will not produce beams from solid materials, and even then it may require the presence of a carrier gas [Masic 1969]. Hence, the ion beam will contain various impurities which, in the absence of an analysing magnet, will be implanted into the sample, causing cell performance to deteriorate. It is therefore desirable to use a source capable of producing a high current beam from a solid element.

Freeman et al. [1977] have reviewed the different types of source, and shown that the source which most satisfactorily produces beams from phosphorus, arsenic and antimony is the 'Freeman' source developed at AERE, Harwell [Freeman 1963]. This source, shown schematically in Figure 5, comprises an arc discharge, a hot cathode and an external magnetic field. The ions are extracted in a direction normal to that of the magnetic field. The cathode is electrically isolated from the discharge tube and kept at a potential which is up to 200 V negative. The tantalum (or tungsten) ribbon cathode has a useful lifetime of 100 hours. It is necessary to have both high vacuum and high pumping speed in the region of the implant specimens. This can be achieved by using a pumping impedance between source and sample and a helium cryopump for the sample region. The latter has the advantage of a high pumping speed for all gases and also for water vapour, and can be operated for thousands of hours before needing to be warmed or purged to atmosphere. Vacuum components are all rated and designed to operate at 1.5 μPa (10^{-8}) mm.

A Freeman ion source, using either solid or gaseous feed, is to be installed at Lucas Heights together with a UHV system. Pulsed laser annealing and Rutherford backscattering facilities are already installed and will be used for a thorough investigation of the concept of ion implantation of solar cells with no mass analysis of the ion beam.

5. CONCLUSION

Ion implantation followed by pulsed annealing are established methods for use in all aspects of semiconductor technology including solar cells. They have considerable potential for use in the mass production of high quality solar cells. Preliminary evidence suggests that the use of an unanalysed ion beam could simplify the production process and reduce costs.

6. ACKNOWLEDGEMENTS

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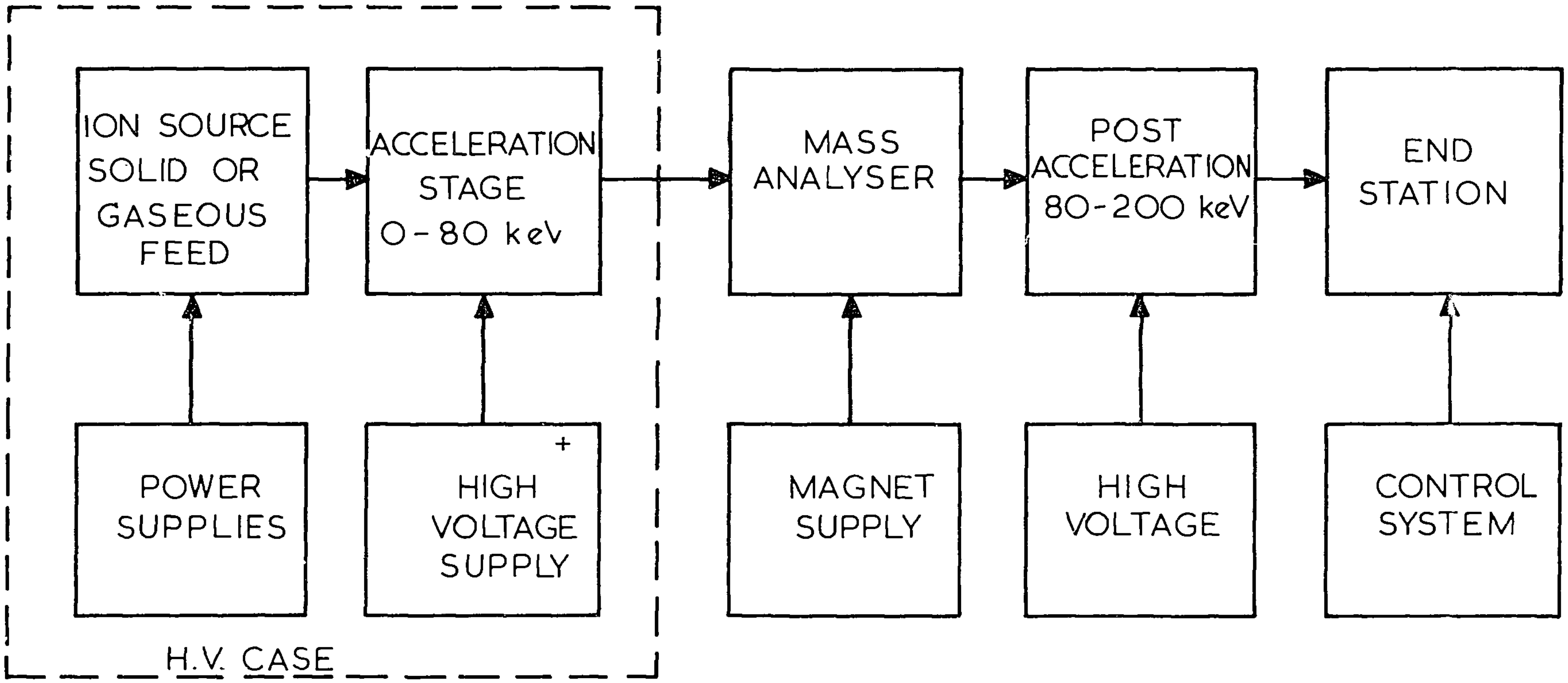
TABLE 1
PRINCIPAL FEATURES OF ION IMPLANTERS FOR SEMICONDUCTOR FABRICATION

Manufacturer	Model	Voltage (kV)	Maximum Current (mA) B^+,P^+	Ion Source Type	Vacuum System	Sample Holder	Scanning	Throughput/hour for 10 cm wafer (2.5 x 10^{15} ions cm^{-2})
Nova Assoc.	NV-10	20-80	10.0	Freeman solid or gas	Diffusion/ cryopump	Spinning disk	Spinning disk Mechanical (Y)	200
Veeco/AI	210 MP	25-200	0.54	Hot filament penning or discharge	Cryopump	Cassette	Electrostatic (X and Y)	<100
Varian/ Extrion	80-10	10-80	10.0	Filament or vaporiser	Cryopump	Spinning disk	Magnetic (X) Mechanical (Y)	290
Applied Materials	120-IIIX	40-120	12.5	Freeman solid or gas	Diffusion/ cryopump	Carousel	Mechanical	300
Balzars	SCI 218	10-200	2.5	Rene Bernas	Diffusion	Carousel	Spinning disk Electrostatic	57
JLVAC	IM-200M	10-100	0.5	Filament vaporiser	Diffusion/ cryopump	Linear	Electrostatic	320
Wickham		10-120	3.0	Freeman solid or gas	Diffusion	Optional	Optional	

TABLE 2
TYPICAL DUOPLASMATRON OPERATING PARAMETERS (NITROGEN BEAM)

System Gas Pressure	0.2 mPa
Filament Current	27 A
Arc	0.5 A, 37 V
Source Magnet Current	0.7 A
Extractor Voltage	40 kV
Beam Current (2 cm^2 at 65 cm)	500 μA



Beam current: 10 μA - 10 mA

Beam species: Research accelerator: Almost any
Dedicated semiconductor: B^+, P^+, As^+

End station : Research: individual samples
Dedicated semiconductor: 300 10 cm dia. wafers per hour

FIGURE 1. LAYOUT OF TYPICAL IMPLANTER SYSTEM

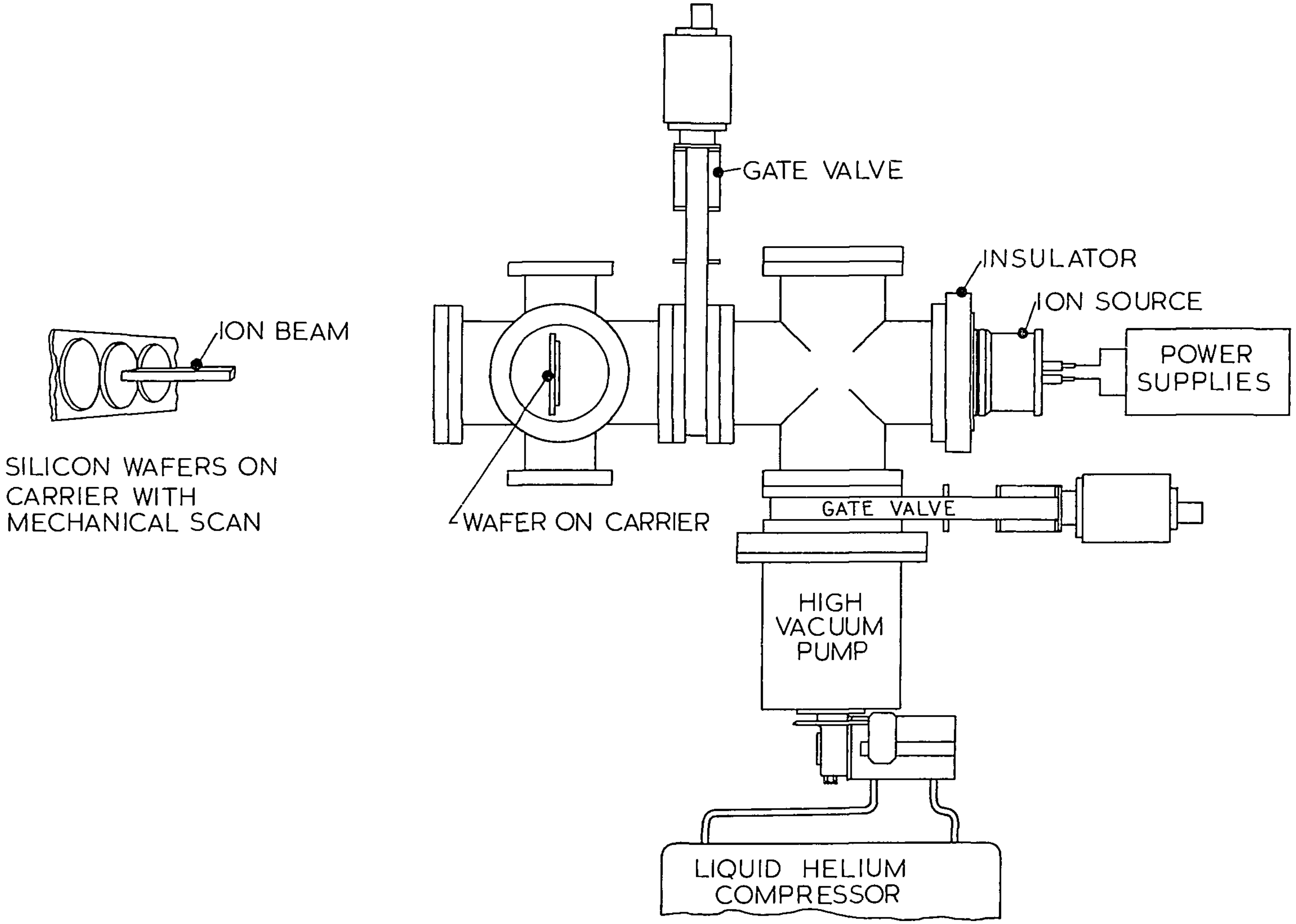


FIGURE 2. DUOPLASMATRON ION SOURCE AND IMPLANT SYSTEM WITH NO MASS ANALYSIS

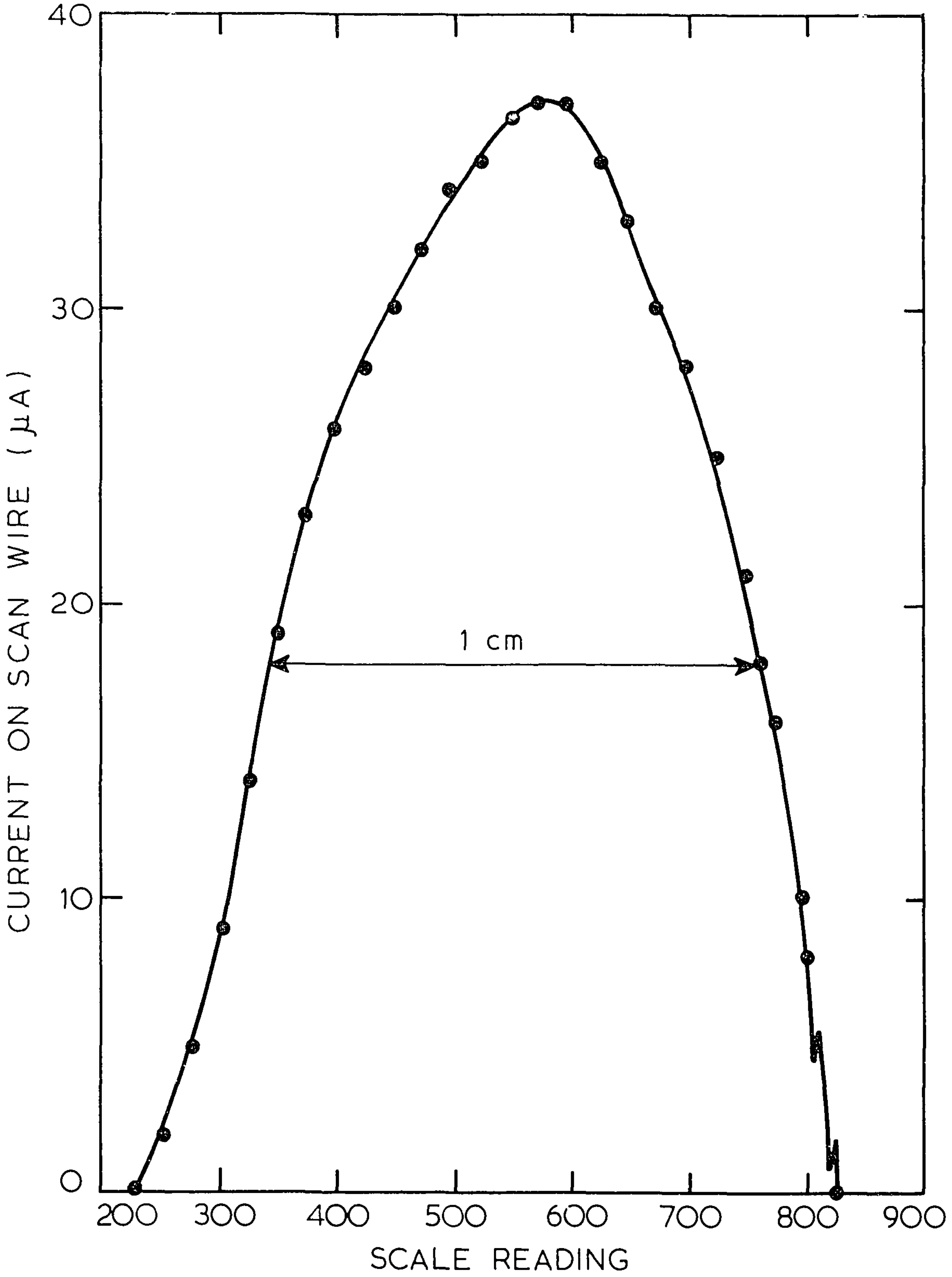


FIGURE 3. DUOPLASMATRON BEAM PROFILE

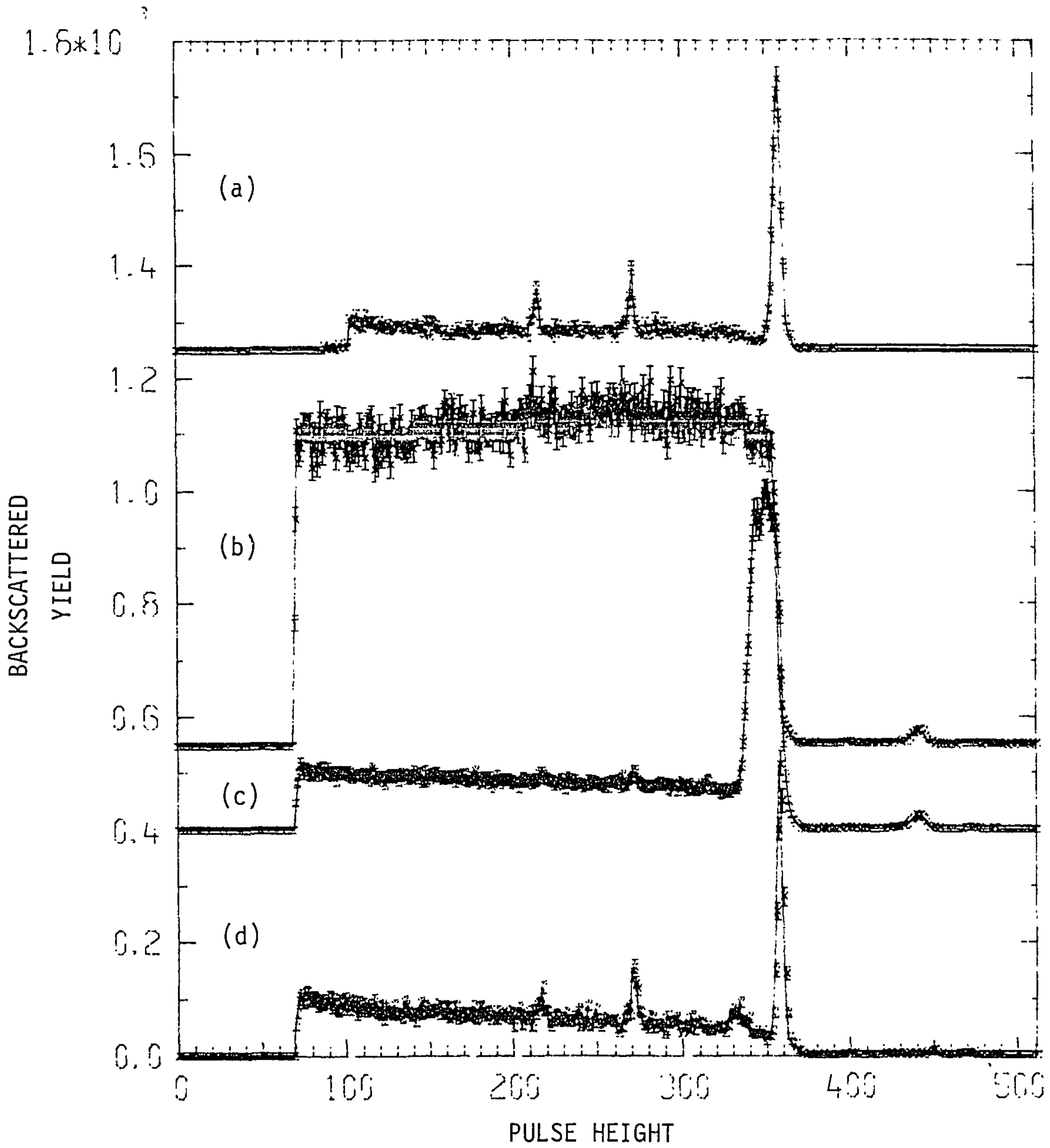


FIGURE 4. RUTHERFORD BACKSCATTERING AND CHANNELLING SPECTRA

(a) aligned spectrum for pure silicon;
(b) random spectrum, arsenic implanted in silicon;
(c) aligned spectrum, arsenic implanted in silicon;
(d) annealed spectrum from (c)

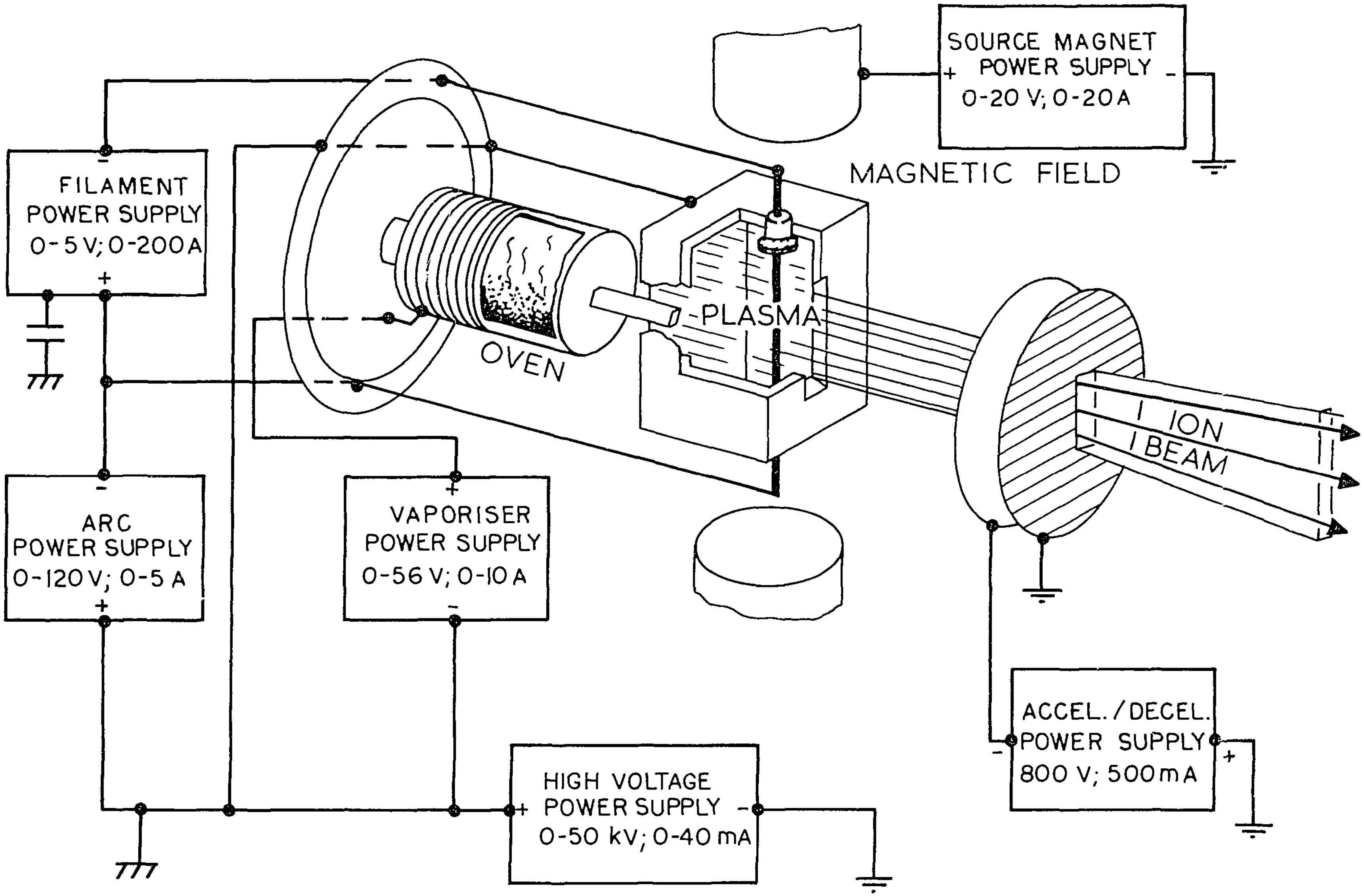


FIGURE 5. SCHEMATIC LAYOUT OF FREEMAN ION SOURCE