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AN ATTEMPT TO DETECT ELECTROCHEMICAL DOPING OF SILICON WITH ARSENIC BY RUTHERFORD BACKSCATTERING ANALYSIS

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ABSTRACT

Rutherford backscattering analysis with 2.0 MeV $^4He^+$ ions failed to detect doping of silicon substrates with arsenic following cathodic electroplating. This is in contrast with the claims of J. Antula [J. Appl. Phys., 48:2581, 1977] that electromigration leads to the formation of n-type, arsenic-doped, near-surface layers in silicon. Arsenic was detected only in the surface oxide layer formed during plating. Complementary thermoprobe measurements also showed no doping effects in the silicon substrates.

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ARSENIC; ARSENIC ADDITIONS; BACKSCATTERING; DOPED MATERIALS; ELECTRODEPOSITED COATINGS; ELECTROPLATING; RADIATION SCATTERING ANALYSIS; RUTHERFORD SCATTERING; SILICON

CONTENTS

1. INTRODUCTION 1

2. EXPERIMENTAL 2

3. RESULTS 3

3.1 Rutherford Backscattering Analysis 3

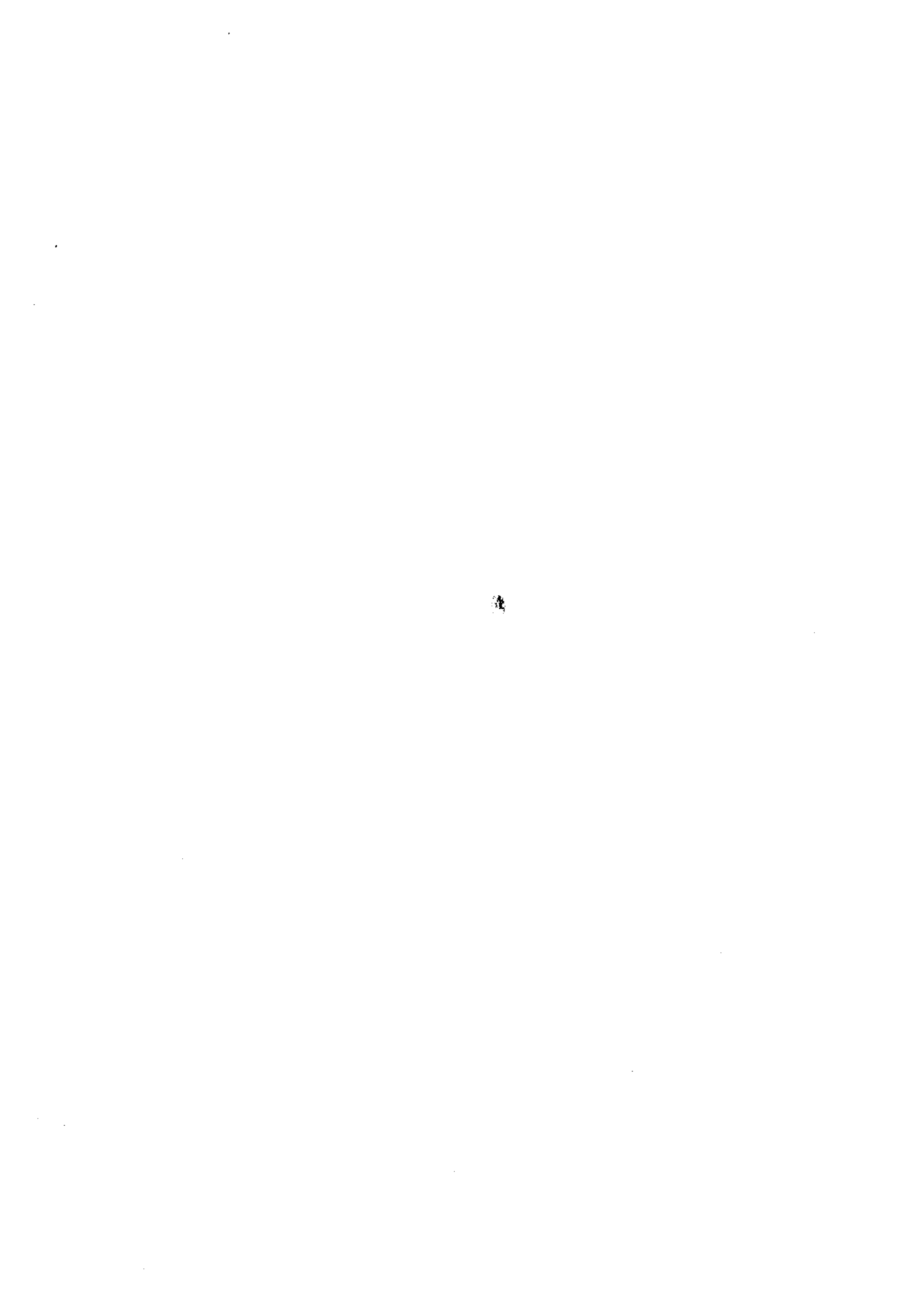
3.2 Thermoprobe Measurements 4

4. DISCUSSION 4

5. REFERENCES 5

Figure 1 Rutherford backscatter spectra from 2.0 MeV $^4He^+$ channelled ions on arsenic-electroplated, <111> oriented silicon (170° detector). Arsenic is seen only in the as-plated, oxide-coated sample; no arsenic is seen in the oxide-free sample. 7

Figure 2 Rutherford backscatter spectra from 2.0 MeV $^4He^+$ ions at random incidence on arsenic-electroplated silicon (100° detector). Arsenic is seen only in the as-plated, oxide-coated sample; no arsenic is seen in the oxide-free sample. 8



CONTENTS

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3.2 Thermoprobe Measurements 4

4. DISCUSSION 4

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1. INTRODUCTION

It has been claimed by Antula [1977] that it is possible to dope near-surface layers (∿ 10 nm thick) in silicon n-type by field-assisted migration of arsenic ions during cathodic electroplating from a solution of 1 per cent arsenic trioxide in concentrated hydrochloric acid (platinum anode). It was also suggested that this method could provide an alternative technique to ion implantation or thermal diffusion as a means of introducing dopant impurities into semiconductors. A simple mathematical model was proposed to support the experimental measurements of arsenic concentration, where the depth was determined by secondary ion mass spectroscopy. Surface concentrations were further quantified by measurements of n^+-p junction depth after the 'drive-in' of arsenic by thermal diffusion following plating on boron-doped substrates.

However, it was pointed out by Northrop [1979] that such field-assisted doping of silicon was extremely unlikely since arsenic is immobile in device structures operating at very high electric fields; in fact, should doping occur, a non-uniform field would result, invalidating the theory of Antula. Northrop suggested that a more likely explanation would be that the arsenic was located in the thin oxide layer formed on the surface of the silicon substrate during plating. In rebuttal, Antula [1979] stated that it was difficult to conceive of the existence of sufficiently high arsenic concentrations in such oxide films for substrate doping.

Recently, Martinez and Ruiz [1982] reported results of C-V measurements on metal-oxide-semiconductor (MOS)/n-p junction structures supposedly formed by the electrochemical diffusion of arsenic in silicon through thermally grown, thin SiO_2 films on silicon. Evidence was presented from $1/C^2$ vs V plots in the 'turn off' to 'accumulation' regions that doping could be occurring which was also dependent on the plating current-time product.

In view of the controversy and uncertainty surrounding the proposed technique of 'electrochemical doping', and because of its potential as a low-temperature method for doping semiconductor materials for such applications as solid state nuclear radiation detector construction, we have applied Rutherford backscattering (RBS) analysis in an attempt to detect arsenic that may have been introduced by electromigration into silicon. Antula [1977] suggested an exponential profile for the arsenic with a concentration of 2 x 10^{21} atoms cm^{-3} at the surface and a characteristic length (1/e) of 2.7 nm. This is equivalent to a concentration of 5.4 x 10^{14} As atoms cm^{-2}. Such a

concentration can readily be detected in silicon by RBS [Chu et al. 1978]; the sensitivity for arsenic in silicon is $\approx 1.8 \times 10^{13}$ As atoms cm^{-2} for random orientation and less than this when channelled.

2. EXPERIMENTAL

Boron-doped, <111> oriented, 20 Ω-cm p-type silicon was used for the cathode and platinum for the anode respectively. Silicon slices 22 mm dia. x 1 mm thick were prepared in a standard manner with an electrolessly nickel-plated ohmic contact on one face and a polish-etched finish on the other (15 minutes' etching in 4 HNO_3 (70%) + 1 HF (40%), with the nickel-plated face masked). The electrodes were set up in a plating cell with a solution of 1 wt % As_2O_3 in HCl (32%) acid. The ohmic contact was appropriately masked against attack by the acid electrolyte.

Before electroplating the arsenic, the silicon electrodes were soaked in HNO_3 (70%) acid for 30 minutes to produce a 'standard' oxide on the surface. Following electroplating, the silicon electrodes were rinsed in water then in HNO_3 (70%) acid to remove excess arsenic and finally in water again. The electrodes were carefully sectioned so that an RBS comparison could be made of 'as-plated' material and material from which the residual oxide had been stripped (after plating) by soaking in HF (40%) acid.

Rutherford backscattering spectroscopy [Chu et al. 1978] was performed using a 2.0 MeV $^{4}He^{+}$ beam with a diameter $\sim$ 1 mm. Silicon solid state detectors with energy resolutions $\sim$ 15 keV were placed at 170° (to give good mass resolution) and at 100° (to give good depth resolution) with respect to the incident beam. The samples were mounted on a goniometer which could be adjusted outside the vacuum target chamber, thus permitting both random and channelled spectra to be collected. The 170° detector incorporated pile-up rejection circuitry to reduce the number of unwanted counts above the silicon backscatter edge.

3. RESULTS

3.1 Rutherford Backscattering Analysis

Data were obtained from one sample with the oxide layer and another from which the oxide layer had been stripped by dissolution in HF (40%) acid. The samples had been plated for a current-time product of 4 A h m^{-2} at a cell potential of 46 V. Channelled spectra obtained from the 170° detector for the two samples are shown in Figure 1. Channelling reduced the count rate by ≈ 30, with a corresponding reduction in pile-up events. The 170° detector was chosen to provide a better sensitivity for element (mass) detection.

There is clear evidence of arsenic in the oxide-coated (as-plated) sample but not in the oxide-stripped sample. The arsenic concentration for the oxide-coated sample was 3.7×10^{13} atoms cm^{-2} and the upper limit for the oxide-stripped sample was $\lesssim 2 \times 10^{12}$ atoms cm^{-2}. Evidence for iron and other heavy elements can also be seen in the spectra from the oxide-coated sample, but not in those from the oxide-stripped sample; these elements most likely are present as impurities in the acid electrolyte.

Although this evidence seemed conclusive, the random backscatter spectra were also examined since it was just possible that all of the arsenic might have taken up substitutional sites in the silicon following electromigration. In this situation, no arsenic would be seen in a channelled orientation. Unfortunately, the severity of pulse pile-up from the 170° detector masked possible arsenic scattering events.

In spite of an increase in the value of the Rutherford cross-section with decreasing scattering angle, the 100° detector experienced a lower count rate owing to its significantly smaller solid angle. Pulse pile-up was much less of a problem in the random spectra from the detector. Figure 2 shows random spectra taken from samples with and without the oxide layer. An arsenic concentration of 4.5×10^{13} atoms cm^{-2} was obtained in the oxide-coated sample and an upper limit $\lesssim 3.4 \times 10^{13}$ atoms cm^{-2} was achieved in the oxide-stripped sample. It is emphasised that, in the case of the spectrum from the oxide-stripped sample, no statistically significant peak is seen, the background being in the form of a monotonic decreasing distribution due to pile-up. So again, there is no evidence for the presence of arsenic in the oxide-stripped sample but arsenic and other elements are seen in the spectrum from the oxide-coated sample.

3.2 Thermoprobe Measurements

Thermoprobe measurements were made both on as-plated samples and on those stripped of oxide for a range of current-time products. Results from the first class of samples were variable, usually giving a low thermoelectric output which could be related to the presence of an oxide film. The oxide-free samples invariably gave outputs identical to the base material and no n-type doping effect was detected for any sample, thus confirming the RBS results.

4. DISCUSSION

The work reported here confirms the proposition by Northrop [1979] that the arsenic is present only in the surface oxide layer of the cathodically electroplated silicon substrate and that the substrate is not penetrated. It is apparent that the source of arsenic for the thermal diffusion drive-in performed by Antula [1977] was the surface oxide film and not a sub-surface, electrochemically implanted layer.

It is also suggested that Martinez and Ruiz [1982] may have misinterpreted their experimental results of C-V measurements on MOS/n-p junction structures thought to be formed after electrochemical diffusion. The C-V characteristics obtained by them could be explained equally well by lateral a.c. current flow generated in a charge inversion layer produced by arsenic ions in the surface oxide layer (no n-type doping of the silicon substrate required). Such effects have been analysed in detail by Nicollian and Goetzberger [1965] who showed that lateral current flow leads to considerably higher cut-off frequencies (tens of MHz). Thus, the choice of too low a measurement frequency ($\sim$ 1 MHz), although high enough in normal circumstances, may be insufficient to drive the MOS device beyond cut-off, leading to an incorrect assumption of conditions and interpretation of results [see Nicollian and Goetzberger 1965, Figure 6].

Finally, it is suggested that the plating technique described by Antula could offer an alternative method for providing an arsenic source for the diffusion-doping of silicon, although the co-plating from the electrolyte solution of other impurities (for example fast-diffusing iron) may present a problem.

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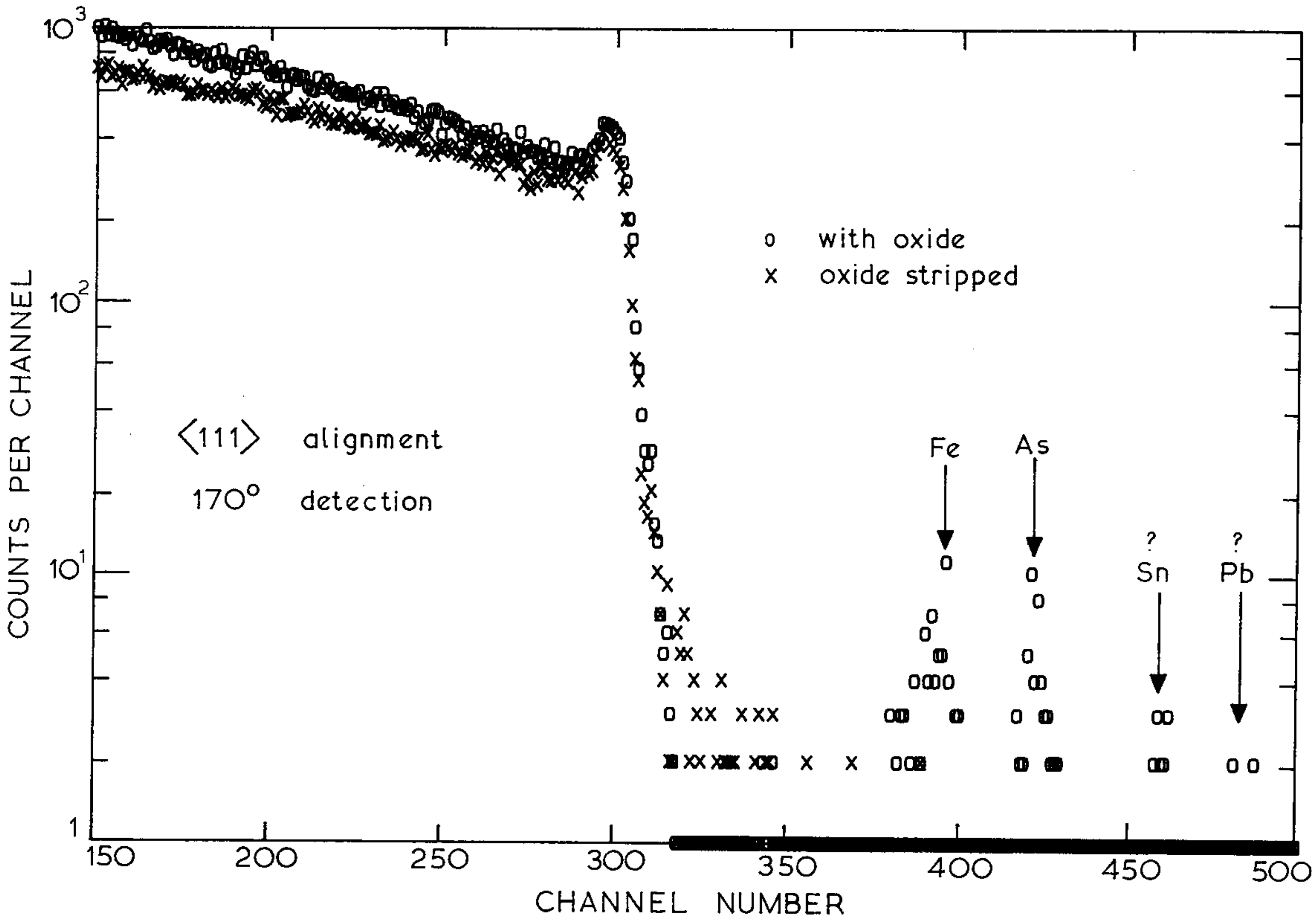

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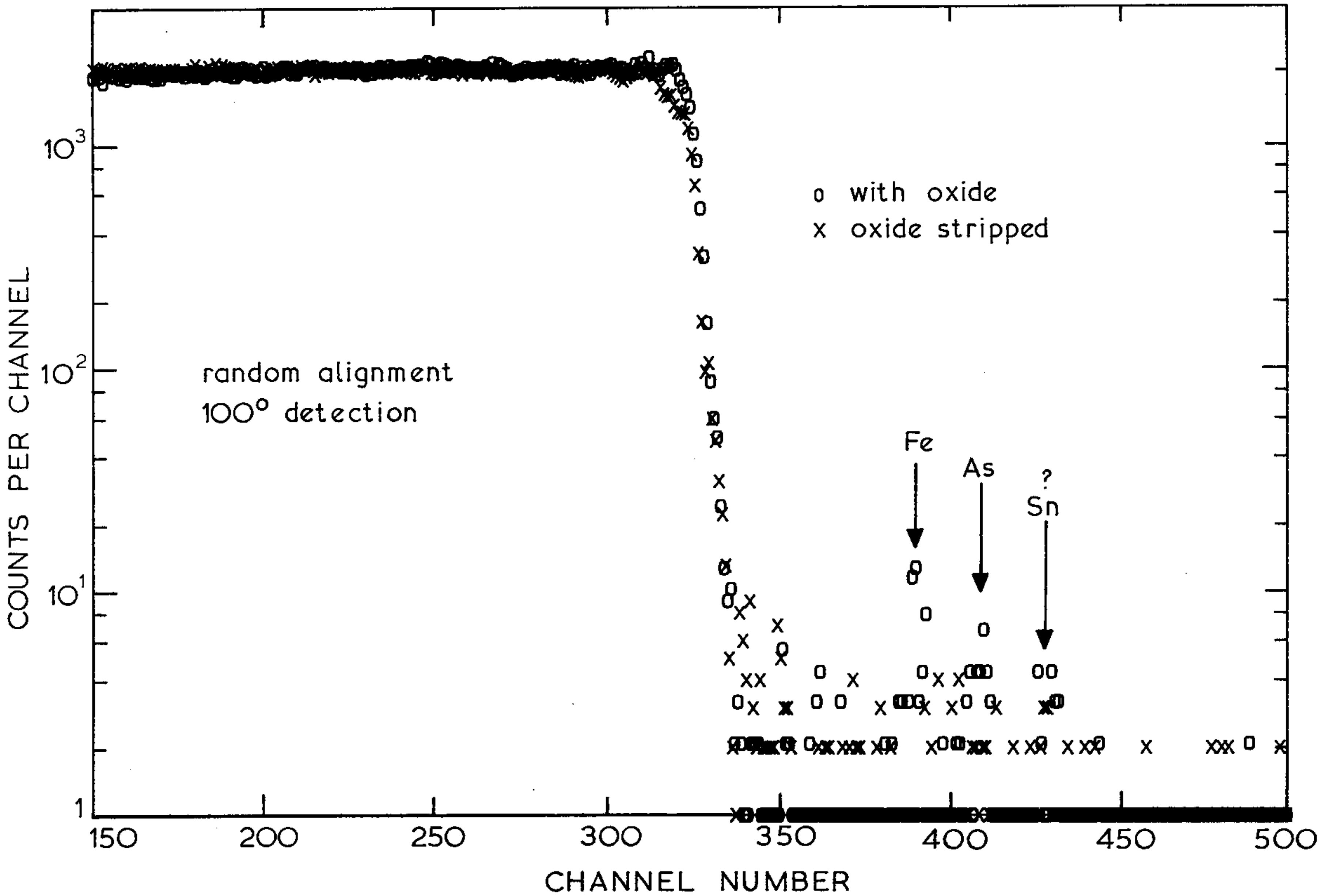

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