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SIMS STUDIES ON ANOMALOUS BEHAVIOR OF PHORPHORUS
AND OTHER IMPLANTS IN SILICON

BY

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A phosphorus implant in p-type silicon was analyzed by SIMS, and both the implant profile and the matrix signal were observed to exhibit some anomalous behavior. Further studies revealed the same behavior in other implants. This phenomenon was observed when an n-type dopant was implanted into a p-type matrix, or vice versa. However, some exceptions arose, making the interpretation difficult. The use of matrix signal normalization was adopted and found to improve the results.

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SIMS STUDIES ON ANOMALOUS BEHAVIOR OF PHOSPHORUS AND OTHER IMPLANTS IN SILICON

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1. INTRODUCTION

Ion implantation has rapidly become a common and important doping technique for semiconductor materials because it offers advantages over conventional diffusion methods. Since the electrical properties depend on the concentration and location of the implanted species, ion implant distributions have been studied by both theoretical and empirical methods.[1-7] Of all the experimental techniques presently available, secondary ion mass spectrometry (SIMS) is one of the most widely used because it offers exceptional depth resolution and sensitivity.

We recently examined several phosphorus implants in silicon and found, for the case of p-type silicon, that the phosphorus implant profile was not the symmetrical Gaussian distribution predicted by the LSS theory[5]. In addition, the intensity of the silicon matrix signal did not remain constant throughout the depth profile. This discovery prompted further investigation with a series of implants. While some exceptions were noted, this work led to the general conclusion that polarity differences between the implanted species and the bulk matrix doping species would significantly alter the results of SIMS analysis of ion implanted silicon.

2. EXPERIMENTAL

Sample Preparation.

The p-type silicon and n-type silicon were purchased commercially and supplier polished. The samples were cut and mounted on aluminum discs with conductive silver paint for ion implantation and SIMS analysis.

Ion Implantation.

Ion implantation was performed on an Accelerators Inc. 300R ion implanter employing a hot filament ion source. Prior to implantation, each sample was cleaned with acetone and methanol. The focused ion beam was rastered over an area of about 27 cm^2 with the dose rate kept below 0.5 Amp/cm^2 to insure room temperature implantation. The implantation parameters for each sample are listed in Table 1.

SIMS Measurements.

SIMS analyses were done using a CAMECA IMS-300 ion microscope[8]. An oxygen primary beam ($O_2^+/O^+ = 10$), accelerated at 14.5 KeV and impinging at 57^o incidence for negative secondary ions, and at 5.5 KeV and 33^o for positive secondary ions was used. A primary current of 200nA was rastered over an area of 500x500 μm^2 yielding a flat crater bottom. All analyses were performed at a residual pressure of 10^{-7} Torr, and with the electrostatic analyzer tuned to maximum sensitivity for a 4.5 KeV sample voltage. The CAMECA IMS-300 was interfaced to a Digital Equipment Corp. PDP 11/20 minicomputer for data acquisition and manipulation, and a GT-40 for display. The projected range, R_p, and the standard deviation of the assumed Gaussian distribution, σ, were calculated by the computer. The depth of the craters were measured by a Talystep stylus device with a resolution of 50-100 Å. Normalization was accomplished by the computer performing a point by point ratio of two profiles.

3. RESULTS AND DISCUSSION

A 200 KeV 2×10^{15} atoms/cm^2 phosphorus implant in p-type silicon (100) originally doped with boron at a level of 10^{15} atoms/cm^3 was analyzed by SIMS using negative secondary ion detection. As shown in Figure 1, the phosphorus profile was found to be asymmetrical with the trailing edge falling off much more rapidly than the leading edge. In addition, the silicon matrix signal, which would be expected to be flat, exhibited an anomalous depression just after the peak of the implant. However, a phosphorus implant in n-type Si (100) gave the expected symmetrical Gaussian P^- profile and constant Si^- signal.

Since the effect was observed when phosphorus, an n-type dopant, was implanted into a bulk p-type doped silicon matrix, boron, a p-type dopant, was implanted into a bulk n-type doped silicon matrix to check if a similar effect would result. Figure 2 gives the result showing again the distortion of the expected Gaussian. Once again, boron implanted into p-type silicon did not show this anomaly.

There have been a number of studies on the influence of implant induced damage and diffusion on implant distributions[9-16]. This phenomenon, however, seems to follow principally from the difference in polarity between the implanted element and the original bulk dopant. To further check this, a vapor epitaxial silicon layer deposited on an n-type Si(100) substrate was implanted with phosphorus. As shown in Figure 3, this implant did not show the anomaly.

It has been reported[17] that the use of an oxygen leak during SIMS analysis serves to amorphorize the crystalline or damaged region by forming an oxide layer. The same experiments mentioned previously were repeated under a 10^{-4} Torr oxygen backfill. No change in the results was observed. Moreover, there was further evidence that matrix damage was not responsible for this behavior. Those implants which gave anomalous results were annealed by heating under a slow nitrogen flow for 20 minutes at 800°C. Previous studies have shown that this is sufficient to anneal out implant damage without significantly altering the shape of the implant concentration profile. Annealing had no detectable corrective effect on the observed anomaly.

In an attempt to discover the degree of this polarity offset, a set of phosphorus implants in p-type silicon (100) were made to measure the effect of the implant dosage. The results revealed that the degree of asymmetry of the Gaussian implant profile and the amount of distortion from the ideal constant matrix signal were positively related to the implant fluences.

The study was then extended to include the remaining implants as shown in Table 1. In addition to phosphorus, five elements, nitrogen, arsenic, chlorine, bromine, and iodine showed this anomalous behavior in p-type silicon. Figure 4 gives the nitrogen profile (SiN^- was monitored for sensitivity) and Figure 5 shows the results of the bromine implant. (Chlorine gave results similar to nitrogen while iodine was much like bromine). Interestingly enough, fluorine did not exhibit any deviation from the expected Gaussian. Gallium and indium also gave symmetrical peaks with no Si signal variations.

These results, particularly the fluorine data, indicate that while a polarity difference between the implant ion and substrate is a necessary condition for this anomalous behavior, it is not a sufficient one. The issue is further clouded by the observation that, due to their strong electron affinities, the halogen elements are sometimes regarded as p-type dopants. Therefore, other factors are also contributing to this effect.

This phenomenon can have two origins, an intrinsic problem of the implant and substrate, or a SIMS phenomenon, or both. One common SIMS artifact is charging. To be sure that there was no charging effect at the implant produced n-p junction during ion bombardment, the surface of the implant sample was physically connected to the sample mount using conductive silver paint. The sample holder with attached sample was then coated with a thin, vapor deposited layer of gold to insure good electrical conduction. These samples showed no decrease in the severity of the observed anomaly. To further investigate if this anomaly was instrument dependent, a phosphorus implant in p-type silicon (100) was analyzed using a CAMECA-IMS-3f instrument,Similar effects were observed.

Although no definitive explanation of this effect could be deduced, it is still important from a practical viewpoint. In semiconductor device fabrication, the mean depth and degree of spreading of an ion implant are very important. These parameters can be predicted by the LSS Theory to within $\pm$ 20%. Using SIMS analysis, these values can be determined with a precision of 5% and 10% for the mean depth and standard deviation of the Gaussian, respectively. However, due to this anomalous behavior, the experimental values of these parameters are quite different from those predicted by the LSS Theory.

Further, owing to their inherent ability to inject an accurately known quantity of a given ion species into a selected host, implants also function as calibration standards for the quantification of many surface techniques including SIMS. There are two ways to calculate the concentration at the peak of an implant. The first [18] assumes the Gaussian profile as an ideal Gaussian distribution to calculate the peak concentration, given the standard deviation of the Gaussian and the implant fluence. The second method [19] ignores the actual experimental distribution and instead uses the construct of the hypothetical equivalence. While the distortion of the implant profile observed will have no effect on quantification based on the second method, it will lead to errors using the first method. Hence, for both quantitative and qualitative (i.e. mean depth, etc.) analyses, correction of this anomaly is important.

This can be accomplished quite well by normalizing the phosphorus implant profile to the matrix silicon profile point by point. Figure 6 shows the result of this procedure. The normalized phosphorus profile is given as well as the phosphorus implant profile as observed and the observed ^{28}Si profile. It is immediately apparent that the normalized profile agress much better with the symmetrical LSS Gaussian distribution. Table 2 lists the mean depths or ranges, Rp, and standard deviations, σ, calculated from both the original and normalized phosphorus profiles as well as the values predicted by the LSS Theory. It shows a significant improvement in the data. This improvement also carries over into quantitative analysis. For the observed phosphorus implant profile, the difference between the peak concentrations yielded by methods 1 and 2 is 11%. However, after applying the ratio correction method, this difference is reduced to 3.7%, indicative of the closer agreement to a Gaussian distribution required by quantitative method one.

Thus, application of this correction method can improve both the external[19] and internal[20] calibration methods when this anomaly is encountered.

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Table 1: Implantation Parameters.

Implant Element	Matrix	Fluence	Energy	Source
^{11}B	n-Si,p-Si	$1.0x10^{15}$	100KV	BF_3 gas
^{14}N	n-Si,P-Si	$5.0x10^{15}$	200KV	N_2 gas
^{31}P	n-Si,p-Si	$2.0-4.0x10^{15}$	200KV	PF_5 gas
^{19}F	n-Si,p-Si	$2.0x10^{14}$	200KV	PF_5 gas
^{35}Cl	n-Si,p-Si	$2.0x10^{14}$	200KV	NaCl solid
^{81}Br	n-Si,p-Si	$2.0x10^{14}$	300KV	Br_2 gas
^{127}I	n-Si,p-Si	$5.0x10^{14}$	250KV	CsI solid
^{69}Ga	n-Si,p-Si	$2.0x10^{14}$	250KV	GaAs solid
^{75}As	n-Si,p-Si	$1.0x10^{15}$	250KV	GaAs solid
^{115}In	n-Si,P-Si	$5.0x10^{14}$	250KV	In solid

Table 2. σ and R_p values for the uncorrected, normalized and theoretical phosphorus profiles (values in parentheses are the % error calculated from the theoretical values).

	Uncorrected	Normalized	Theoretical
σ (Å)	566 (-27%)	692(-11%)	775
R_p (Å)	2337 (-8.0%)	2463(-2.3%)	2539

CAPTIONS

Figure 1 Depth profile of ^{31}P implanted Si, showing the anomalous asymmetry and matrix signal non-uniformity.

Figure 2 Depth profile of ^{11}B implanted Si showing asymmetry.

Figure 3 Depth profile of ^{31}P implanted into intrinsic Si. No anomalous behavior is seen.

Figure 4 Depth profile of ^{14}N implanted Si. Asymmetry is not apparent, but the matrix Si^- signal still exhibits the anomaly.

Figure 5 Depth profile of ^{79}Br implanted Si. Similar anomaly is observed.

Figure 6 Depth profile of ^{31}P implanted Si, with the P^-/Si^- ratio profile also shown. Normalized profile is more symmetrical.

FIGURE 1

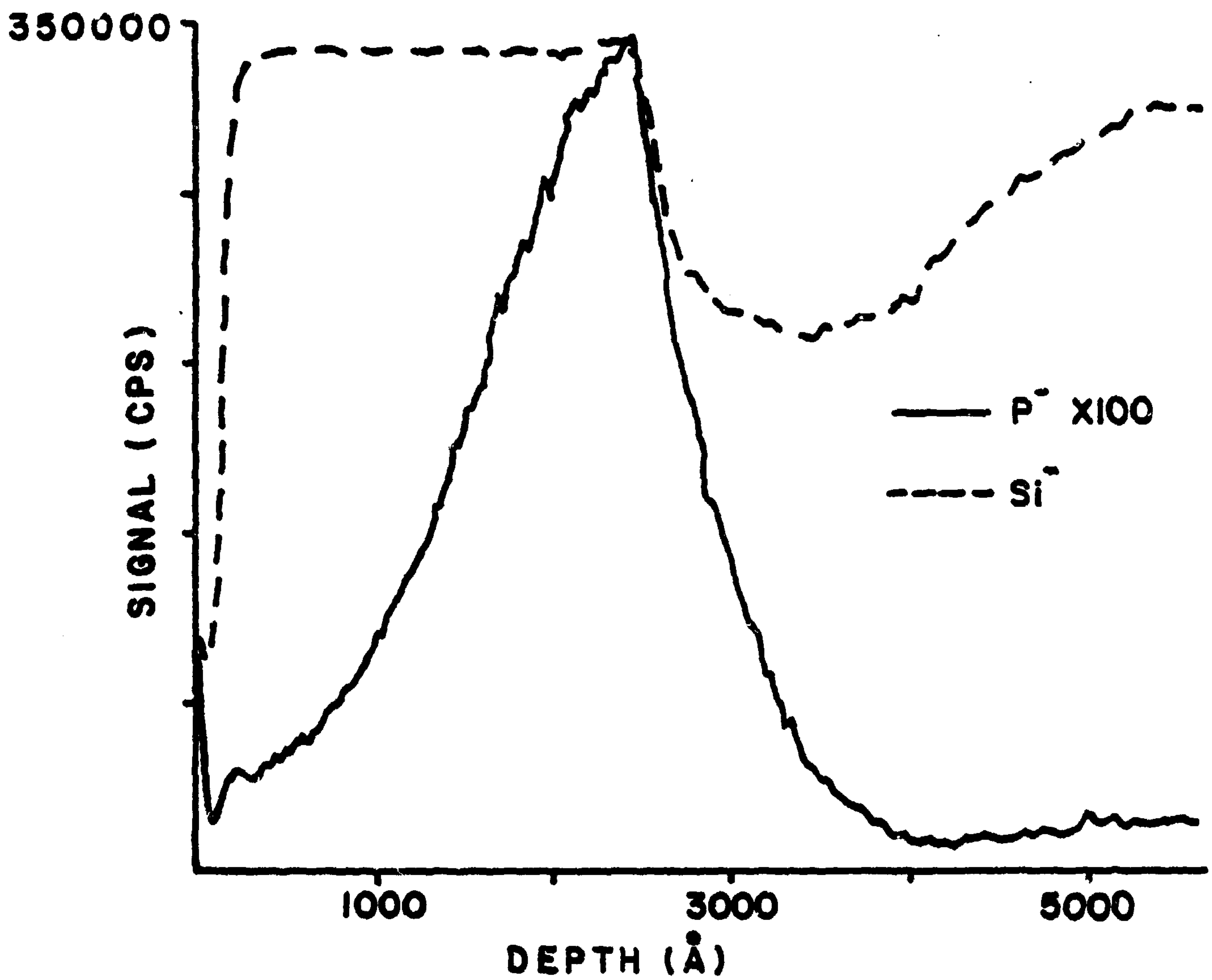


FIGURE 2

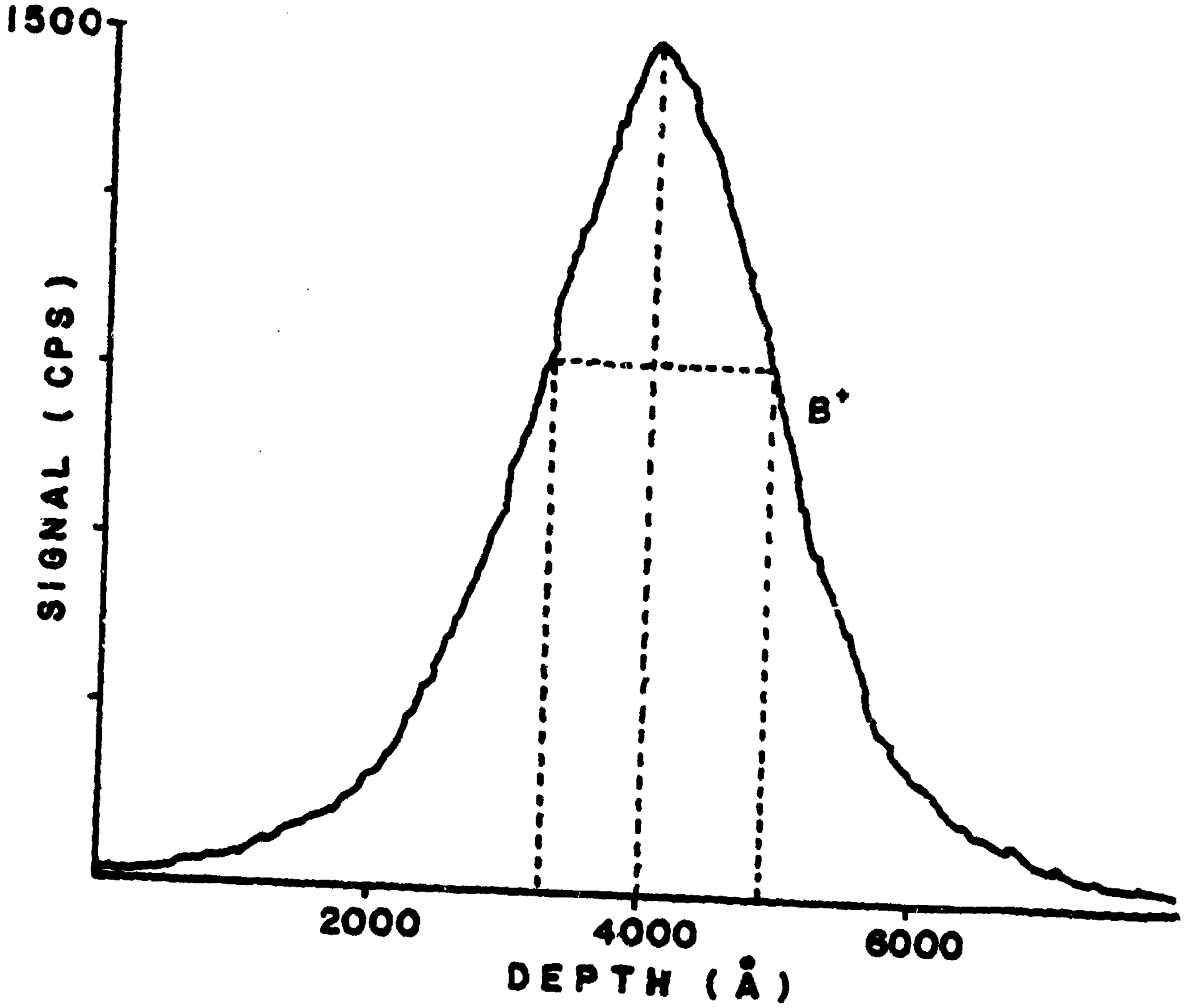


FIGURE 3

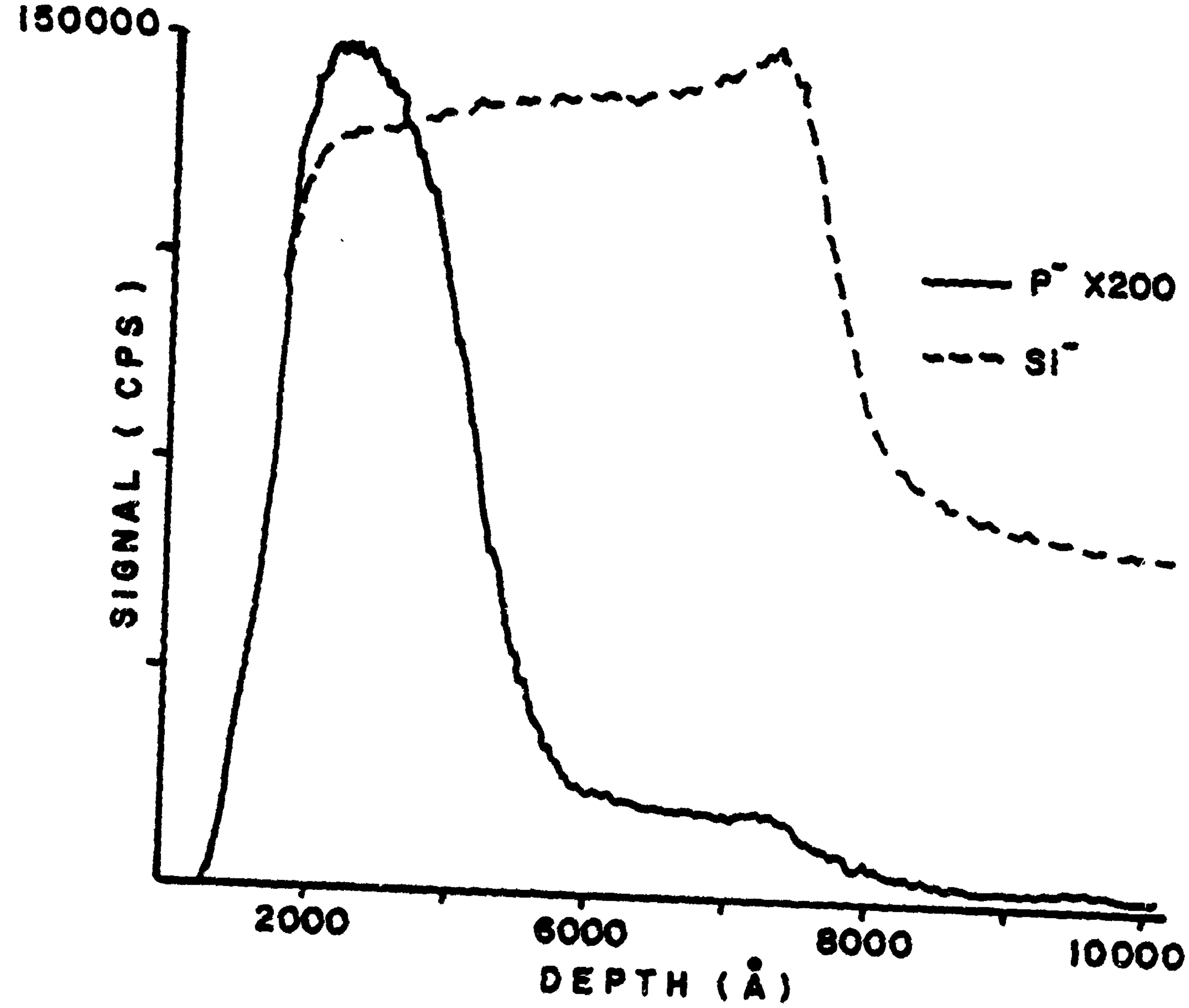


FIGURE 4

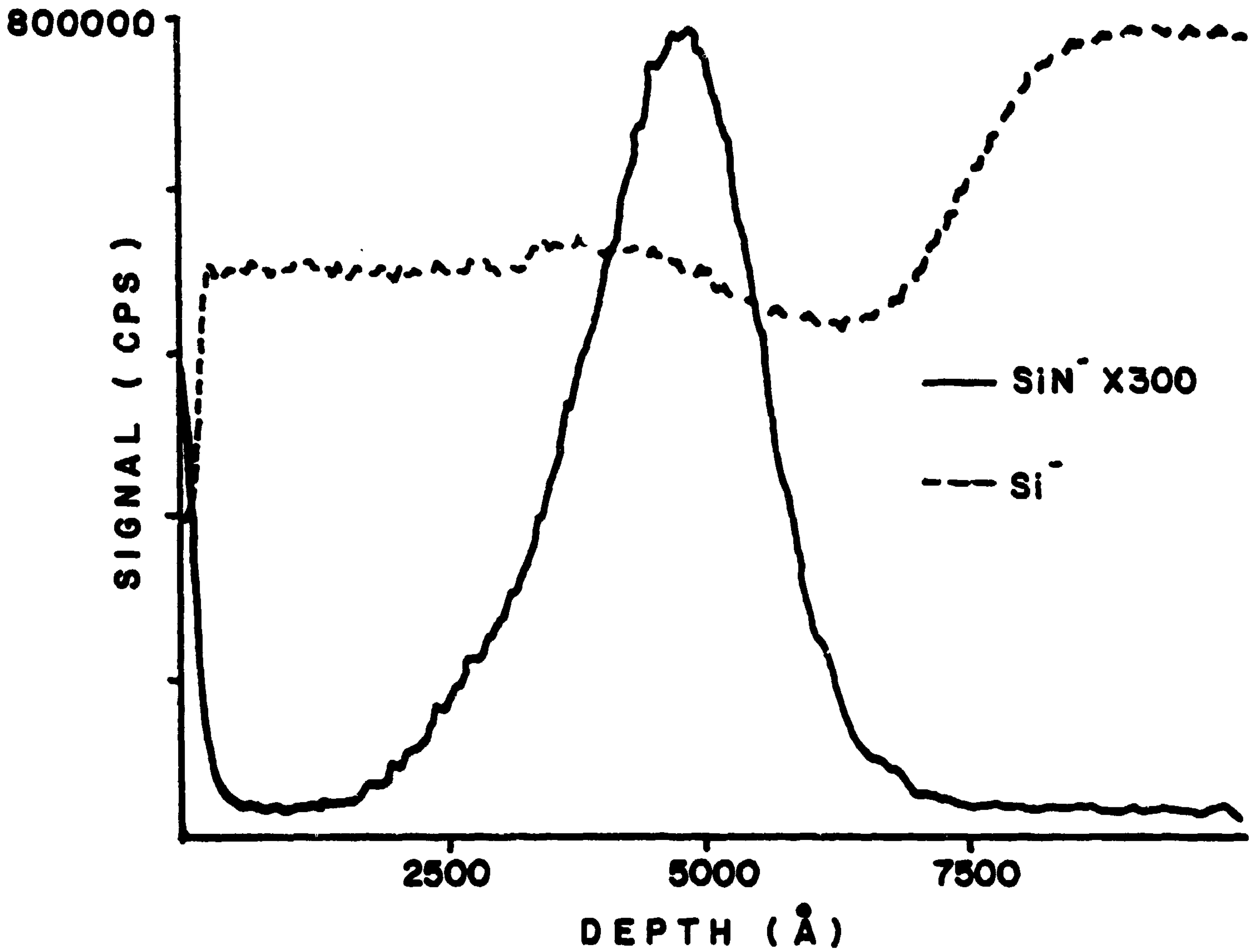


FIGURE 5

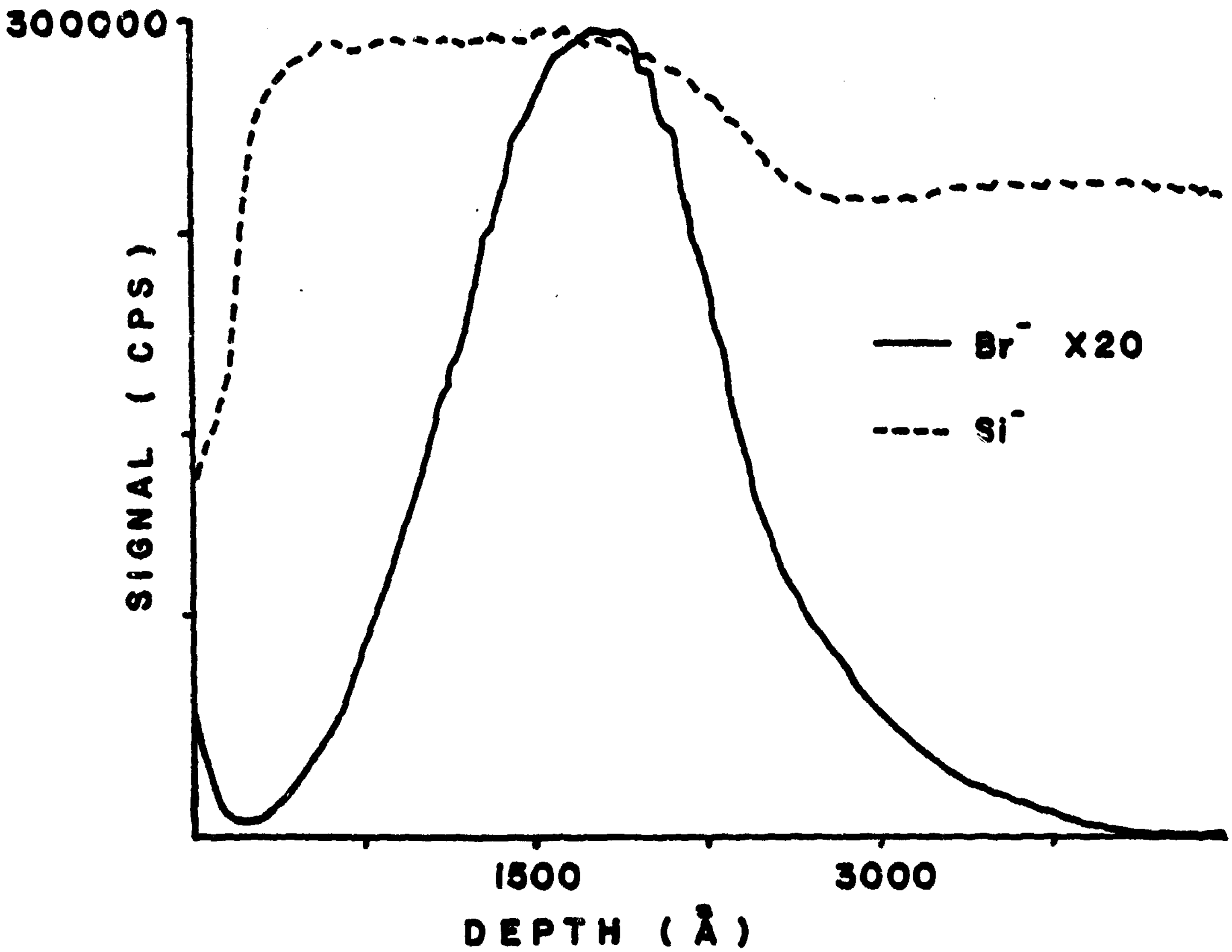
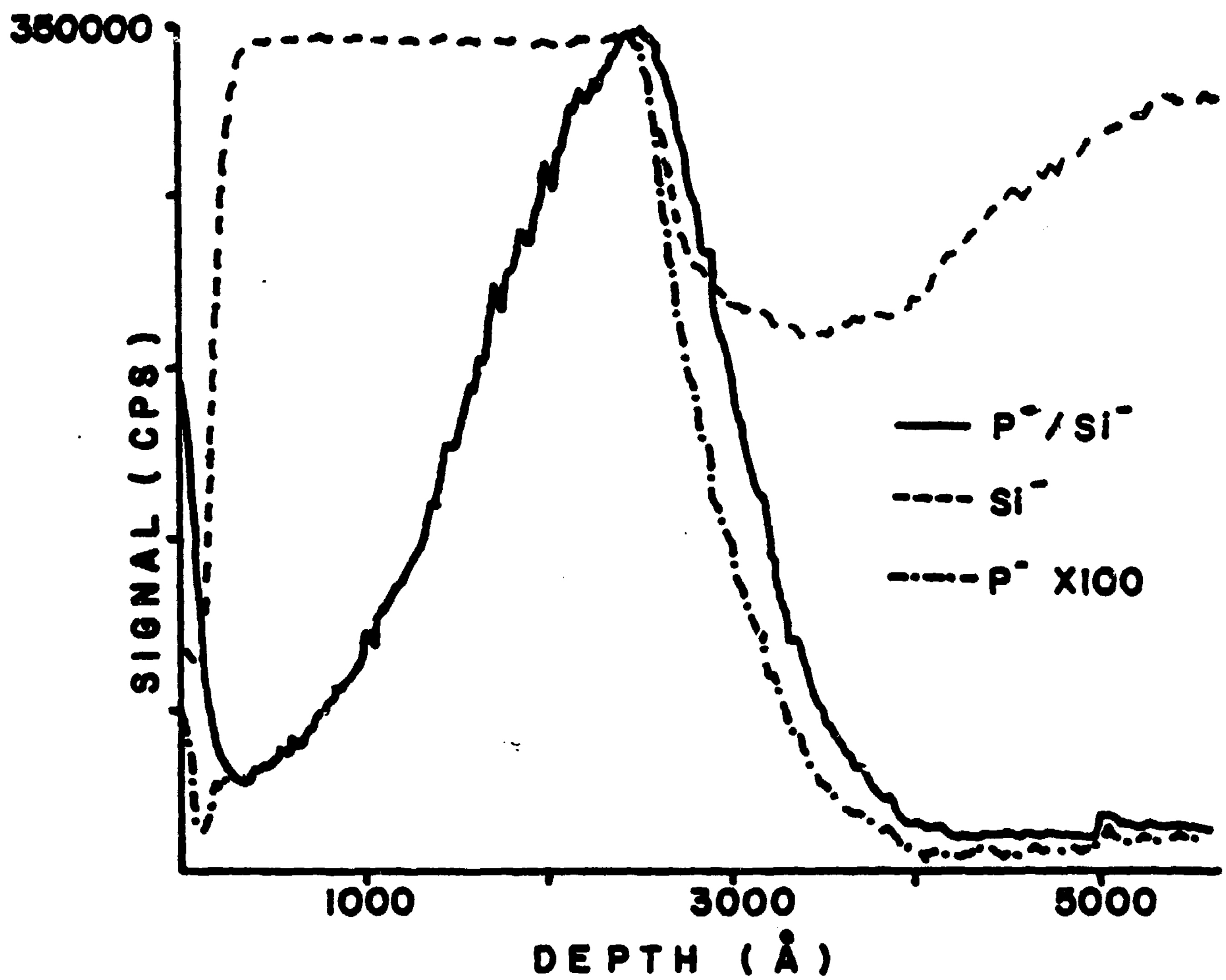


FIGURE 6



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