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Implanted boron depth profiles in the AZ111 photoresist

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The isotope ^{10}B has been implanted into the photoresist AZ111 in the 30–150 keV energy range. The corresponding depth profiles have been analyzed using the $^{10}\mathrm{B}(n,\alpha)^{7}\mathrm{Li}$ reaction. At 60 keV, the profile changes from a regular shape to one with an additional tail directed towards the surface. Despite the nonregular shape of the ion distributions, it is possible to extract the characteristic range parameters such as projected range R_p, most probable range $\hat{R}$, and full width at half-maximum. Good agreement is found between the experimental results and the calculations by Ziegler, Biersack, and Littmark (ZBL). It is also shown that the tail distribution follows closely the ZBL calculated ionization profiles. A tentative explanation of this behavior is given.

INTRODUCTION

In recent years there has been a growing interest in ion irradiation and/or implantation of polymers, essentially for the application in advanced microelectronic technology. Thin photoresist films are required in order to limit the area of microelectronic devices in which dopants are implanted. Projected ranges (R_p) and range stragglings (ΔR_p) of the implanted ions must be known in order to determine precisely the thickness of the photoresist mask. Further, ion implantation has gained much attention since it was discovered that organic semiconductors might be created by ion beam doping of polymers.

Two of the least studied aspects of ion-implanted and irradiated polymers are the depth distributions of the ions and their energy transfer. The high implantation doses ($\phi > 5\times10^{14}$ atoms/cm^2) needed for the usual detection techniques (SIMS, RBS, and AES) can significantly alter the physical and chemical properties of the polymers, and consequently render the polymer useless for range determination purposes. This limitation accounts for the paucity of experimental data on range parameters of ions in photoresists. Nevertheless, in the last years several measurements of ion ranges in polymers have been done. Adesida and Karapiperis[1] determined the profiles for various light ions in polymethylmethacrylate (PMMA) using the technique of ion beam lithography (IBL). In this technique the polymer is bombarded with ions and subsequently developed in a suitable solvent. The saturated developed depth is interpreted as the mean path length of the implanted ion. In another work Tennant *et al.*[2] reported measurements of boron ranges in photoresists using the SIMS technique in an alternative way. They implanted B ions at a fixed energy through a series of polymer thicknesses, measuring the SIMS depth profiles in the underlying Si substrate. In both cases the indirect nature of the used techniques was a limiting factor in the accuracy of the range measurements, and prevented the precise reconstruction of the implanted ion concentration profiles. This detail is important since in a recent work Fink *et al.*[3] have shown that light ions (^{6}Li and ^{10}B) after implantation into epoxy resist and photoresist AZ111 distribute according to a nonregular shape. As a consequence, further experimental investigations on boron-implantation profiles in photoresist are needed.

In the present work, we have determined the depth distribution of ion-implanted ^{10}B in AZ111 photoresist in the 30–150 keV energy range. We used the nuclear reaction analysis (NRA) technique with thermal neutrons,[4] as it is highly sensitive for ^{10}B ions and gives direct information on the depth distributions, while producing negligible radiation damage in the sample.

EXPERIMENTAL PROCEDURE AND RESULTS

Clean silicon wafers were spin coated with AZ111 photoresist of 1 μm thickness and baked for 1 h at 150 °C. Small pieces of the wafers (≈ 2 cm^2) were implanted with fluences of 10^{14} atoms/cm^2 at energies of 30, 60, 90, 120, and 150 keV. The implantation was performed at room temperature with low beam current densities (≈ 50 nA/cm^2) in order to avoid excessive heating of the samples.

Depth profiles were obtained through the $^{10}\mathrm{B}(n,\alpha)^{7}\mathrm{Li}$ reaction with thermal neutrons at the high flux reactor of the Institute Laue-Langevin, Grenoble, France. The α particles were detected by an ORTEC silicon surface barrier detector with energy resolution of 14-keV FWHM. For the energy to depth transformation the stopping powers after ZBL were used.[5] All other experimental details can be found in Ref. 4.

Figures 1(a)–1(c) show the ^{10}B depth distributions after 30, 60, and 150 keV implantation, respectively. Figure 1 shows clearly that between 30 and 60 keV a transition occurs from a regular ion-implantation profile to another one with an additional tail directed towards the surface. This feature is more clearly observed in the depth profile corresponding to 150-keV energy implantation. Then the usual data analysis based on the determination of the four characteristic moments of the particle distribution (projected range R_p, range straggling ΔR_p, skewness γ, and kurtosis β) should be done with restrictions. This is due to the nonregu-

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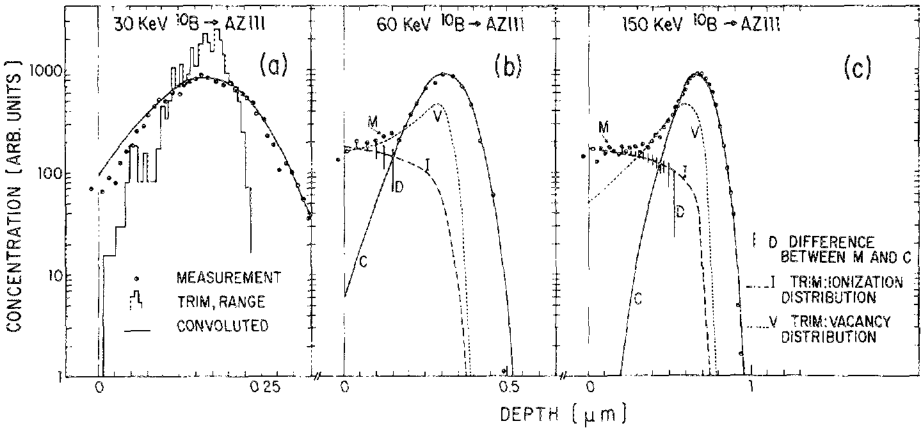

FIG. 1. (a) Experimental depth distribution of ^{10}B implanted at 30 keV into the AZ111 photoresist (full points). The histogram represents the TRIM calculated particle distribution, and the line the TRIM results convoluted with the detector resolution. (b) 60-keV ^{10}B implanted into AZ111. The full points (M) represent the experimental results, the full curve (C) shows the TRIM-convoluted particle distribution, the dotted line (V) the predicted vacancy distribution, and the dashed line (I) the calculated ionization profile. The vertical bars (D) indicate the difference between the experimental results and the TRIM calculated particle distribution. (c) 150-keV ^{10}B implanted into AZ111. The symbols have the same meaning as in (b).

lar character of the ion-implanted profiles. In particular, it is useless to try to determine the higher moments of the particle distributions (ΔR_p, γ, and β), since comparison with the theory would be meaningless. For evaluation of R_p we subtracted the tail distribution from each measured spectrum. This procedure is justified since even in the most extreme case, the tail is only 10% of the peak height. In addition, we determine directly the position of the most probable range $\hat{R}$ (i.e., the maximum of the distribution). Both values R_p and $\hat{R}$ are quoted in Table I as a function of the energy. As was mentioned above, for the particle distributions corresponding to energy higher than 60 keV, determination of the second moment would be meaningless. Therefore, we have characterized the distributions by the full width at half-maxima (FWHM) which are quoted in Table I.

In order to compare the present results with the latest theoretical predictions, we have used the Monte Carlo code TRIM[6] with the universal potential developed by Ziegler, Biersack, and Littmark (ZBL)[5] and an improved electronic stopping power due to Brandt and Kitagawa[7] as inputs. After convoluting the TRIM results with the detector resolution and the straggling of the ^{4}He particles we have obtained for each implantation energy the corresponding R_p, $\hat{R}$, and FWHM which are quoted in Table I and displayed in Fig. 2, together with the results of the present and previous experiment.[1]

Table I and Fig. 2 show that there is an overall good agreement (within 10%) between the present experimental results and the theoretical predictions. Figure 2 also shows that the results of Ref. 1 for B implanted into PMMA (which has a composition very similar to the AZ111 photoresist) are larger than the present ones and consequently than the TRIM predictions. As was mentioned before, those differences might be attributed to the indirect character of the IBL measuring technique used in Ref. 1 and therefore to the lack of precision in the determination of the ion distribution parameters of the implanted boron. The experimental results of Ref. 2 are not included in the figure since they refer to photoresists with different compositions and densities.

Figure 1(a) shows in addition to the experimental results the calculated and convoluted TRIM particle distributions. The calculated profile follows quite well the experimental points indicating that at 30 keV the ^{10}B particle distribution is regular. This is not the situation for higher energies. To get some insight into the origin of the nonregularity of the ion distributions we have plotted in Figs. 1(b) and 1(c) the TRIM convoluted particle (full line), vacancy (dotted line), and ionization (dashed line) distributions. They were arbitrarily normalized to the experimental results. Figure 1(c) suggests that the tail follows the ionization profile as calculated by the TRIM. For further clarification we subtracted the corresponding convoluted particle distribution (as predicted by TRIM) from each experimental profile. The results are depicted by vertical bars, the lengths indicating the uncertainty introduced by this operation. It is clearly seen in both figures that the bars (which are identical to the points where there is no TRIM particle contribution) follow very closely the TRIM calculated ionization profile.

TABLE I. Experimental and TRIM calculated range parameters for ^{10}B implanted into the AZ111 polymer at various energies. Typical errors around 4%.

	Experimental			TRIM predictions			
Energy (keV)	$\hat{R}$ (nm)	R_p (nm)	FWHM (nm)	$\hat{R}$ (nm)	R_p (nm)	FWHM (nm)	FWHM convoluted (nm)
30	162	154	155	160	153	60	165
60	275	270	165	300	290	85	170
90	378	390	175	430	415	85	170
120	552	520	210	565	528	140	195
150	670	610	240	690	622	170	240

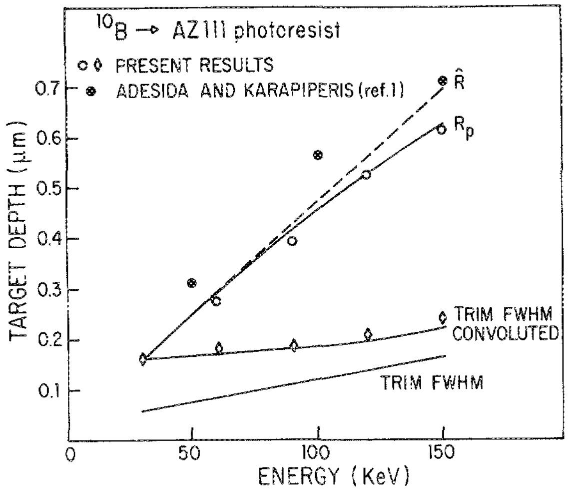

FIG. 2. Experimental and theoretical range profile parameters as a function of the energy for ^{10}B implanted into the photoresist AZ111. The lines represent the TRIM theoretical predictions for $\hat{R}$ (dashed line), R_p (upper full line), and FWHM (lower full lines). ○ and ◇ = results of the present work, ● = results of Adesida and Karapiperis. Note that at 30 keV, the R_p and the FWHM are identical.

This feature is also observed for the 90 and 120 keV cases which are not displayed in Fig. 1.

DISCUSSION AND CONCLUSION

From the results of the present work several conclusions can be drawn. First, at about 60 keV the boron-implantation profile suffers a change to a nonregular shape. At this energy around 10% of the implanted ions distribute according to the ionization profile. In addition, there are indications that with increasing implantation energy this number increases, reaching a value of about 15% at 150 keV. This number is in agreement with the recent findings of Fink *et al.*[8] By implanting ^{10}B at a fixed energy (200 keV) in different kinds of polymers the authors of Ref. 8 found that in all cases typically 90% of the implanted ions follow the regular profile as predicted by the TRIM, while the remaining 10% follow the ionization profile.

It should be also pointed out that the change in shape observed in the present work for the B profile occurs at an energy where the electronic stopping power S_e is higher by a factor of 5 than the nuclear one S_n, i.e., $S_e \approx 5S_n$. This should be compared to a previous result for fluorine also implanted in the AZ111 photoresist[9] where the profile changes from a nearly regular shape to a nonregular one at an implantation energy for which $S_e \approx 2S_n$.

In order to explain the transition from the regular range distribution towards the ionization profile, one has to assume a certain mobility of the implanted light ions. The diffusing ions may be trapped by free radicals which are created by electronic energy transfer processes efficiently enough only for $S_e \geqslant S_n$, so that the ion depth distribution approaches the shape of the ionization distribution. Since this is still a very tentative explanation, more experimental work should be done.

Second, it should be pointed out that despite the nonregularity of the implanted-ion distributions one can still characterize them by some range parameters like R_p, $\hat{R}$, and FWHM. The TRIM predictions with the ZBL stopping power reproduce quite well the above parameters, and therefore at least for B in AZ111 photoresist they can be regarded as reliable.

Finally, it should be stressed that a direct technique like NRA with thermal neutrons used in the present work, yields more information about the profiles of implanted ions than the indirect techniques of Refs. 1 and 2. In fact, in previous works there were no hints about the nonregularity of the implanted boron profiles in polymers while in the present work this feature clearly shows up.

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