

Sputtering during Ion Implantation into Gallium Arsenide

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Abstract. The surface erosion caused by ion bombardment of solids and its effect on the number of ions retained in the solid was studied experimentally for a variety of ions implanted into GaAs with various fluences and energies. Experimental methods were interferometry and semi quantitative X-ray analysis by means of an electron microprobe. By an easy-to-use computer calculation the change in the implantation profiles was determined and the number of retained ions were related to the surface shift caused by sputtering. Comparison of this shift with the real erosion found before and after annealing was made. From the results, we conclude that the collapse of the crystal lattice contributes to the sinking of the bombarded surface. Sputtering data necessary to estimate the technical consequences of sputtering, range data of 100 keV Fe ions, and data indicating the sensitivity of X-ray analysis are presented.

Index Headings: Sputtering-Ion implantation

It is well known that during ion bombardment of solids, a number of target atoms and ions initially absorbed are removed by sputtering. This effect changes the ion distribution profile, sets an upper limit on the ion concentration, and is, therefore, important for many applications of ion implantation as well as for the application of sputtering in surface analysis. In the field of ion implantation, sputtering has to be taken into account when high fluences are used to deposit impurities for diffusion, to produce chemical compounds, or to improve contacts. In the field of surface analysis by ion bombardment, it is important to know the fluence at which the equilibrium concentration of sorbed bombarding ions is reached. Therefore, the effect of sputtering on ion concentration and distribution has been treated analytically by several authors using the model of implantation through a receding surface [1—3]. An experimental study of bismuth implantation into GaAs using helium backscattering for the determination of the number of retained Bi ions was published by Tinsley *et al.* [4]. Kräutle and Kalbitzer [5] have made similar studies for a variety of ions implanted into

silicon. These authors used secondary ion emission to measure the implantation profiles and deduced the sputter efficiency from the retained number of implanted ions but do not report on measurements of the surface erosion. Generally, available sputtering data is insufficient to calculate the practical consequences of sputtering as an accompanying effect of ion implantation. Furthermore, the sputter efficiency is frequently deduced immediately from surface erosion [4] neglecting the expansion of the solid by the implanted ions and the contraction caused by collapse of the lattice. This can be justified if the penetration depth of the ions is less than the surface erosion depth as it is the case under conditions usually chosen for the technical application of sputtering. In the case of ion implantation a relatively high penetration depth is of interest and the changes in the lattice cannot generally be neglected in the evaluation of surface erosion.

It is the aim of this paper to present data on the sputtering of GaAs which offers sufficient information to estimate the influence of sputtering in the most important practical cases. The number of retained ions will be calculated from the surface erosion. The

result will be compared with direct measurements and the effects contributing to the migration of the surface will be separated. Furthermore, our paper demonstrates the feasibility of electron microprobe measurements for the investigation of implanted materials.

Experimental Technique

Ions were implanted into single crystalline (111)-oriented GaAs wafers at fluences usually in the range from 2×10^{15} to 4×10^{16} ions/cm² and at energies between 10 and 120 keV. The crystal axis was tilted by 7° to the beam axis. A focussed swept beam was used and the average current densities according to the sweep area were 0.4–1.6 μ A/cm².

By means of a metal mask the implantation was restricted to an area of some mm². The step from the unimplanted to the implanted part of the surface was measured in the as implanted state using an interference microscope. In the case of 70 keV tellurium implantations and for some other implantations a second measurement was made after annealing at 630° C for 20 min in forming gas. Before annealing, the wafers were covered with a 190 nm Si₃N₄ layer produced by reactive sputtering.

In the case of 70 keV Te and 100 keV Fe implantations the number of ions retained in the target was determined by X-ray analysis by means of a scanning beam electron microscope using a wavelength dispersive spectrometer with gas flow proportional counter. The experimental conditions are listed in Table 1. Three spots on every sample were investigated by three countings on each. Presented data are the average of these 9 countings, background radiation being subtracted. The line to background ratio is discussed in section "X-ray measurements".

Surface Step Measurements

The surface step produced by implantation of 4×10^{16} ions/cm² is shown in Fig. 1 for Ge-, Kr-, and Sn-ions and in Fig. 2 for Fe- and Te-ions. Figure 3 shows the dependence of the step upon fluence for 70 keV Fe-implantations. The negative sign is chosen when the implanted surface was lower than the unimplanted surface. This was always the case for implantations into GaAs. For comparison the results of two argon implantations into silicon are shown in Fig. 1. Here, the surface step is positive and thus indicates a well pronounced expansion of the lattice. From the results of Eer Nisse [6] we can estimate a sputtered step of approximately -10 nm produced by our implantations

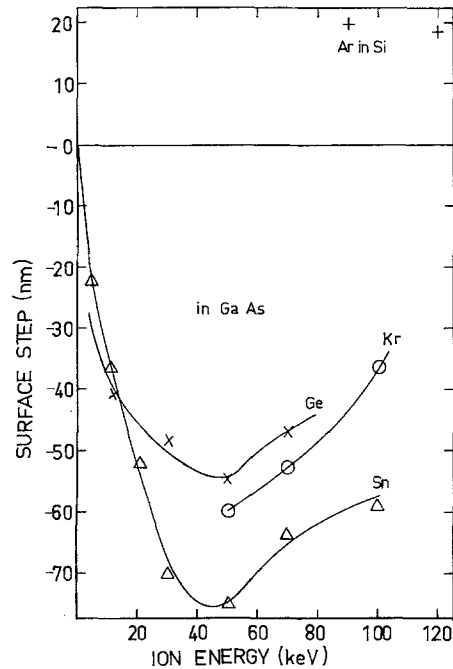


Fig. 1. Surface step produced by implantation of 4×10^{16} ions/cm² (not annealed)

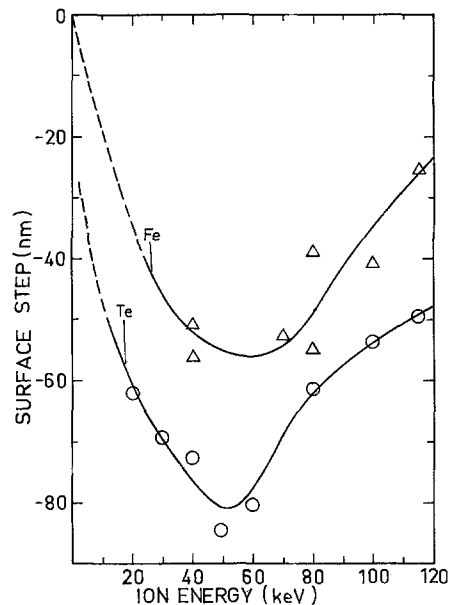


Fig. 2. Surface step produced by implantation of 4×10^{16} ions/cm² into GaAs (not annealed)

into silicon. By sputtered step we mean the step that would occur if there was no expansion or collapse of the lattice. It will be shown later that the surface step on a GaAs target is deeper than the sputtered step, thus indicating collapse of the lattice.

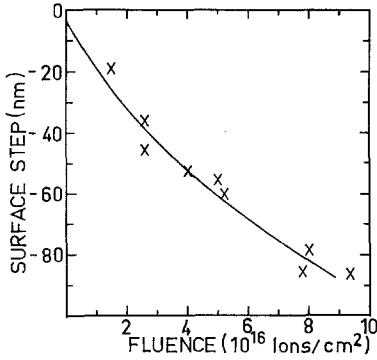


Fig. 3. Surface step produced by implantation of 70 keV Fe into GaAs (not annealed)

Calculation of Modified Implantation Profiles

If the sputtered step is high enough to remove a measurable part of the implanted ions it can be determined by calculation from range data and from the difference between implanted and retained number of ions. For this purpose we have calculated ion distributions as follows:

As suggested by Kräutle and Kalbitzer [5], deposition of ions and sputtering are alternately taken into account. However, corrections for the variation of the projected range are omitted, since in our experiments the sputter efficiency is high and consequently the ion concentrations are relatively low.

An implantation with fluence F is assumed to be split into z steps of implantation with fluence F/z small enough to keep the sputtering negligible. The migration of the surface by a total distance D is taken into account by inserting $(z-1)$ steps of sputtering without deposition of ions, each step removing a layer of thickness $D/(z-1)$. We have assumed a Gaussian penetration probability, i.e. for a fixed surface the implantation profile is assumed to be

$$N(x) = \bar{F} (m \sqrt{2\pi})^{-1} \exp[-(x - R_p)^2 / 2m^2], \quad (1)$$

where N is the ion concentration, R_p the projected range, and m the standard deviation.

Then, for a migrating surface our approximation reads

$$N(x) = F z^{-1} (m \sqrt{2\pi})^{-1} \sum_{v=0}^{z-1} \exp\{-[x + vD(z-1)^{-1} - R_p]^2 / 2m^2\}. \quad (2)$$

To perceive the relation of this approximation to the exact solution one has merely to replace the argument of the exponential by ξ_v^2 and to extract the factor $\Delta \xi = (\xi_v - \xi_{v-1}) = D/(z-1)m\sqrt{2}$. Then, the sum can easily be converted into the well known integral [1—3] which, in the case of a Gaussian penetration probability, is equal to the difference of two error functions.

Our approximation has the following advantages:

It need not necessarily be based on a Gaussian penetration function. It can be handled by a pocket calculator if the number of steps of approximation is low.

It provides an easy understanding of the mechanism.

Fore instance, if the penetration probability has one maximum at R_p and is at least approximately symmetric it is plausible that a sufficiently tight superposition will exhibit a peak just in the middle between the peaks of the first and the last term of the sum. Hence, the peak is shifted from its initial position to the surface by $D/2$ and will disappear for $D \geq 2R_p$.

The highest index of the sum in (2) corresponds to the contribution of the first partial implantation to the number of retained ions. If $vD/(z-1)$ is smaller than $(R_p - m)$ most of the ions of the following implantations (lower index) will be retained. If $vD/(z-1)$ is greater than $(R_p + m)$ most of the ions of the foregoing implantations (higher index) will be lost. It follows that for $R_p/m \gg 1$ the partial implantations can be divided into such that have lost no ions and such that have lost all ions, regardless of the value of m . The condition that the loss of ions can be neglected is thus

$$D \leq R_p \quad \text{for } R_p/m \gg 1. \quad (3)$$

If m is very large, the concentration resulting from every partial implantation is approximately $0.4F/zm$ between the surface and the peak. The first step of sputtering removes the number $0.4FD/mz(z-1)$ per unit area stemming from the first implantation. The second step removes twice this amount stemming from two implantations and so on. Thus, the amount noted above is removed $1 + 2 + 3 + \dots = z(z-1)/2$ times and the ratio of removed ions to fluence is $0.4D/2m$. Hence, the condition that less than 10% of the implanted ions are lost is

$$D \leq 0.5m \quad \text{for } R_p/m \ll 1. \quad (4)$$

In all practical cases we have $2 < R_p/m < 10$ and neither of the conditions is correct, but an expression equivalent to (3) and compatible to (4) within the practical range of R_p/m is

$$D \leq R_p - 0.5m \quad (5)$$

which was found to approximately fit the critical value. For the calculation of the complete profil the number of steps of approximation should be 3 or 4 if only slight corrections for sputtering have to be made. Figure 4 shows the more critical case where D is close to R_p . Four steps can give a reasonable value of the surface concentration but result in an error of more than 10% in the peak height. After 10 steps the

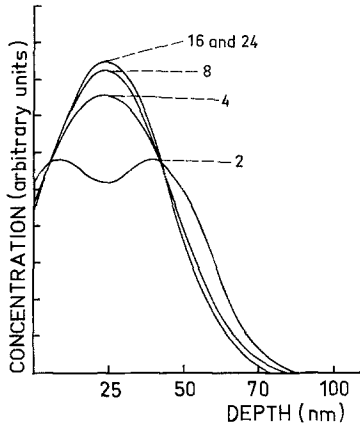


Fig. 4. Theoretical profile for $R_p = 41.7$, $m = 15.5$, $D = 37.0$. Parameter is the value of z in (2)

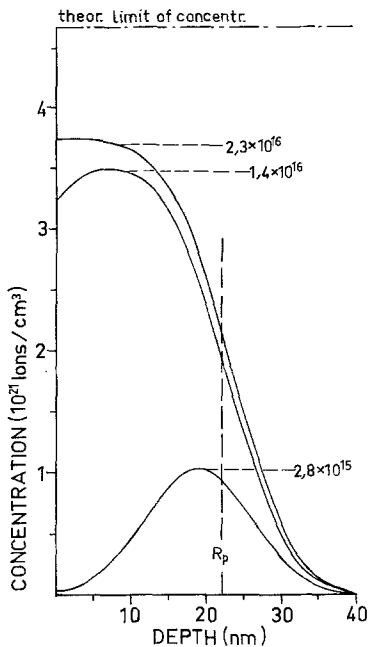


Fig. 5. Theoretical profile for 70 keV Te implanted into GaAs. Parameter is the fluence in ions/cm²

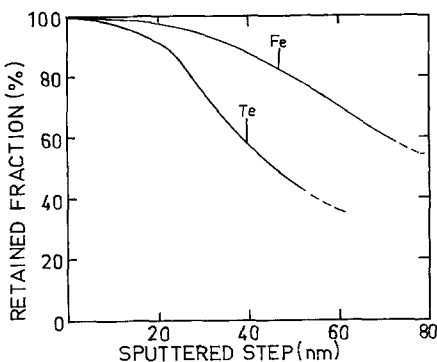


Fig. 6. Retained fraction of implanted ions vs. thickness of layer removed by sputtering (calculated curves)

accuracy will be better than that of usual profile measurements.

Figure 5 shows the theoretical profile for 70 keV Te into GaAs. The calculations are based on the following data: $R_p = 22.2$ nm, $m = 6.7$ nm, $D/F = 2.15 \times 10^{-15}$ nm/ions cm⁻². Range data are taken from the tables of Johnson and Gibbons [7], and D/F is calculated from own measurements after annealing described in the next section. If F/D equals the surface concentration the number of ions removed equals the number of ions implanted. This defines the limit of concentration.

By integration of curves like those of Fig. 5 the fraction of implanted ions which are retained in the target can be calculated as a function of the sputtered step. Examples are shown for 100 keV Fe and 70 keV Te in Fig. 6. By means of Fig. 6 the contribution of sputtering to the step at the boundary between implanted and unimplanted surface can be determined if the retained fraction is measured. This will be described in the next section.

X-Ray Measurements

The penetration depth of the electron beam producing the X-ray signal for microprobe analysis is normally much larger than the projected range of implanted ions. For the energies indicated in Table 1 the penetration depth of electrons in GaAs is about 1300 nm and 2500 nm respectively [8], while the projected range is 22.2 nm for 70 keV Te [7] and 47.7 nm for 100 keV Fe (interpolation between Ar and Zn, tables of Wilson and Brewer [9]). All implanted ions will therefore contribute equally to the X-ray signal. The average concentration of implanted ions obtained by the highest fluence used in our experiments is 6% for Te and 11% for Fe and all the ions are located inside a very thin surface layer such that corrections of the signal for X-ray absorption and atomic number of scattering particles are negligible. The probe current was found to be independent of ion fluence, but the change of current occurring when the beam scans the boundary of the implanted zone was found to depend upon annealing. This indicates that backscattering and secondary emission are influenced either by the radiation damage or by unequal removal of As and Ga during sputtering, whereas the influence of the implanted ions seems to be negligible. We shall report on this problem in a future publication. To summarize, we have sufficient reason to assume that the X-ray signal is proportional to the total number of implanted ions retained by the target.

Table 1

Element	Line	Crystal	Beam energy	Sample current	Counting time
Fe	$K_{\alpha 1/2}$	LiF	15 keV	16 nA	60 sec
Te	$L_{\alpha 1/2}$	PET	25 keV	10 nA	100 sec

The X-ray signals measured on two batches of implanted samples are shown in Fig. 7 as a function of ion fluence¹. For the Fe implantations, deviation from proportionality is low and indicates that for a fluence of 4×10^{16} ions/cm², 94% are retained. The accordingly sputtered step shown in Fig. 6 is 30.8 nm while the surface step shown in Fig. 2 is 34.5 nm for 100 keV Fe ions. This result is consistent with our assumption that the lattice collapses. The step produced by lattice collapse is approximately a tenth of the ion penetration depth. The curve for the Te implantations should be drawn, as indicated by the dashed line in Fig. 7. Tinsley *et al.* [4] have shown that for Bi implantations the number of retained ions actually reach the saturation value by oscillations. They explained this effect by the dependence of the sputtering yield upon the concentration of the implanted ions.

To simplify the calculations, we have assumed a monotone approach to saturation (solid line in Fig. 7) to deduce the sputtered step by means of Figs. 6 and 7.

The result is shown by the dashed line in Fig. 8. The solid line indicates the measured surface step. This curve can be complemented up to 4×10^{16} ions/cm² by the 70 keV value from Fig. 2 which ensures the nonlinearity. The triangles indicate measured values after annealing. Any single value is smaller than its corresponding value before annealing and thus closer to the calculated dashed line. Again this can be explained by lattice collapse during implantation and recovery of the lattice by annealing. For a fluence of 0.5×10^{16} ions/cm² the material should already be amorphous in the vicinity of the concentration peak. For this fluence the difference between the unannealed and the annealed step is 2 nm. Since the projected range is 22.2 nm, the ratio is again in the order of one tenth.

The accuracy of the X-ray measurements encouraged us to attempt the determination of an implantation profile. The following data confirms that our method is sufficiently sensitive. For 100 keV ions the X-ray signal is proportional to fluence up to some 10^{16}

¹ We are indebted to K. Wehner and G. Liebel, Laboratorium für Werkstoffuntersuchung GmbH (Kontron), Eching bei München for the X-ray analysis of the Fe-implanted samples.

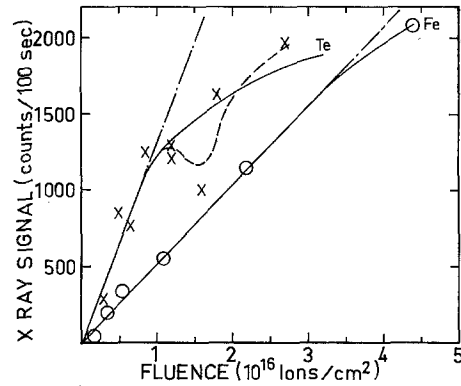


Fig. 7. X-ray signal from GaAs implanted with 70 keV Te or 100 keV Fe. Background signal was subtracted. (Dot-dashed: lines of proportionality)

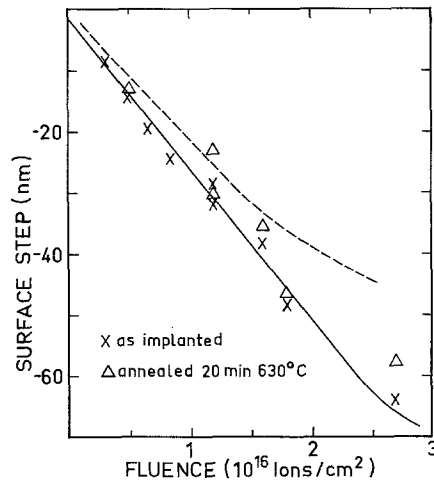


Fig. 8. Surface step vs fluence for 70 keV Te-implantations into GaAs. Dashed line is the calculated sputtered step

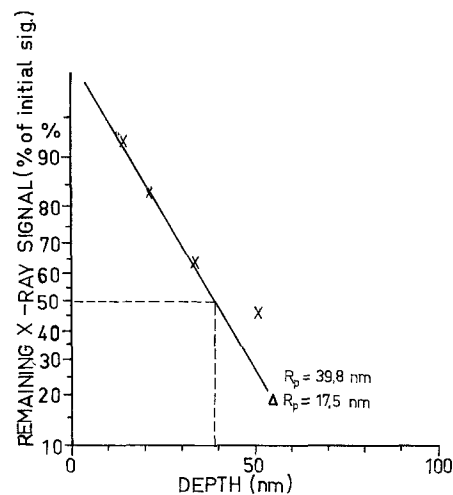


Fig. 9. Implantation profile of 100 keV, 5.5×10^{15} ions/cm² Fe into GaAs

ions/cm². From Fig. 7 we find 507 counts per 100 sec and per 10¹⁶ ions/cm². The background signal, which was already subtracted for this value, is 542 counts/100 sec. A signal is generally assumed to be amenable to evaluation if it is 3 times square root of the background above the background. Since we use the average of 3 × 3 countings, our accuracy is improved by a factor of 3. From these data we derive 23 counts per 100 sec above background as the minimum signal necessary to indicate the presence of Fe in GaAs. It corresponds to 4.5 × 10¹⁴ ions/cm². For Te the according calculation leads to a minimum fluence of 3.0 × 10¹⁴ ions/cm², but this value can be reduced to 1.3 × 10¹⁴ if an electron beam of 15 keV and 20 nA is used. According to the penetration depth of the electrons these values correspond to less than 0.01 atomic %. Ten times the minimum fluence would be sufficient to determine a profile and is still small enough to guarantee proportionality.

We implanted 5.5 × 10¹⁵ Fe ions/cm² at 100 keV. After measurement of the X-ray signal the target was thinned several times by krypton bombardment each bombardment being followed by a new measurement. Since the signal is proportional to the total number of ions, a probability plot of signal versus sputtered step should exhibit a straight line if the profile is Gaussian. Under this condition the depth of the 50% value corresponds to the projected range and the distance between the 50% and the 75% value divided by 0.674 corresponds to the standard deviation.

Our result is shown in Fig. 9. The measurements fit a Gaussian profile with a slight tail. The projected range obtained from the figure has to be corrected by the shift caused by sputtering. The correction is equal to half the surface step minus lattice collapse contribution. From Figs. 2 and 3 it is estimated to be 1.5 nm from which we deduce a projected range of 41.3 nm for 100 keV Fe into GaAs in very good agreement with 41.7 nm obtained by interpolation from the data of Wilson and Brewer [9]. No correction was calculated for the standard deviation, but the true value must be slightly smaller than the 17.5 nm obtained from Fig. 9. The interpolated value is 15.5 nm.

Discussion and Conclusions

For the X-ray measurements, our experimental problem was to find a range of fluence which contains the linear as well as the nonlinear part of the dependence of the X-ray signal upon fluence, and to set the lowest fluence at a value which yields a signal well above

background. For this reason an ion energy beyond the value of maximum sputtering efficiency was chosen. Thus, our measurements of the retained number of ions do not demonstrate the worst case. To get an impression of possible technical consequences of sputtering we will consider the situation at the peak of the curves of Fig. 2. For ions of moderate mass, for instance Fe⁵⁶ at 60 keV, the shift of the peak of the implantation profile towards the surface exceeds 10% of R_p at 4.3 × 10¹⁵ ions/cm² and our calculations showed that the retained dose falls below 90% of the fluence at 1.7 × 10¹⁶ ions/cm². For heavy ions such as Te¹³⁰ the corresponding fluence values are 1.8 × 10¹⁵ and 9.0 × 10¹⁵ ions/cm², respectively. These values show that deviations from LSS-range data can occur at rather usual fluences, while the difference between fluence and retained number of ions is large only at high fluences, yet may be important for the application of ion implantation in contact technology or formation of chemical compounds.

Our results can be summarized as follows:

Sputtering of GaAs reaches its maximum efficiency at ion energies between 30 and 70 keV. Collapse of the crystal lattice enhances the sinking of the surface by approximately one tenth of the projected range. The shift of the peak of ion distribution is equal to half the distance the surface recedes as a consequence of sputtering. More than 10% of the implanted ions are lost if this distance exceeds $R_p - 0.5 m$. Less than 4.5 × 10¹⁴ Fe ions/cm² and 1.3 × 10¹⁴ Te ions/cm² can be detected by X-ray analysis.

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