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VACANCY SUPERSATURATIONS PRODUCED BY HIGH-ENERGY ION IMPLANTATION

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ABSTRACT

A new technique for detecting the vacancy clusters produced by high-energy ion implantation into silicon is proposed and tested. This technique takes advantage of the fact that metal impurities, such as Au, are gettered near one-half of the projected range (½R_p) of MeV implants (1). The vacancy-clustered region produced by a 2 MeV Si^+ implant into silicon has been labeled with Au diffused in from the front surface. The trapped Au was detected by Rutherford backscattering spectrometry (RBS) to profile the vacancy clusters. Cross-section transmission electron microscopy (XTEM) analysis shows that the Au in the region of vacancy clusters is in the form of precipitates. By annealing MeV-implanted samples prior to introduction of the Au, changes in the defect concentration within the vacancy-clustered region were monitored as a function of annealing conditions.

INTRODUCTION

There is currently a great deal of interest in the use of high-energy (MeV) ion implantation for silicon device processing (2), as it has the potential to offer many advantages. For instance MeV implantation can place dopants deep into silicon eliminating the long thermal drive-ins necessary for deep well formation. Another important application of MeV implantation into silicon is to create buried gettering layers beyond the device region for trapping of impurities. As MeV ion implantation becomes more widely used in silicon device processing a more complete understanding of the defects generated by high-energy ions is essential.

MeV Si^+ implantation into silicon has been shown to produce a net point-defect imbalance which consists of excess interstitials and interstitial clusters near the ion's projected range (R_p) and excess vacancies and vacancy clusters in the region near half of the ion's projected range ($\frac{1}{2}R_p$) (3), (4). Holland, et al., have verified the existence of the vacancy clusters produced by high-energy, high-dose Si^+ and O^+ implantation into silicon using positron annihilation spectroscopy (PAS) (4). Also, recent experiments suggest that the excess vacancies in lower dose MeV Si^+ implants can drive enhanced diffusion of Sb and annihilate interstitial clusters such as {311}'s and extrinsic dislocation loops (5), (6). However, because the vacancy clusters are difficult to detect, at least relative to their interstitial counterparts, there is comparatively little direct data regarding the vacancy defects formed from ion implantation. Experiments that measure enhanced Sb diffusion and interstitial cluster shrinkage as a result of MeV Si^+ implantation are sensitive only to the free vacancies and not the total number of vacancies that exist in clusters. This situation is in contrast to equivalent studies of interstitials, where interstitial clusters ({311} defects and extrinsic dislocation loops) have been directly observed in TEM and characterized and correlated with enhanced diffusion of interstitialcy diffusers such as B (7). In this work we propose a new technique, which is based on metal impurity gettering, for labeling the vacancy clusters to make them sensitive to detection by a conventional depth profiling technique, such as RBS.

Impurity gettering has been observed at $\frac{1}{2}R_p$ of a MeV implant into silicon in a number of studies. Agarwal, et al. (8), as well as Tamura (9), have shown that oxygen getters to $\frac{1}{2}R_p$ of a 2 MeV Si^+ or a 3 MeV As^+ implant into silicon, respectively. Metal impurities, such as Fe and Cu, have also been observed to getter at this region for a similar MeV implant (1). In those experiments, the researchers attributed the observed $\frac{1}{2}R_p$ gettering to the excess vacancies from the MeV implant. As a result, metal impurity gettering offers an opportunity as a method for detecting vacancy clusters produced by MeV implantation into silicon, and for tracking their evolution. However, gettering of Fe and Cu is difficult to relate quantitatively to the concentration of vacancy-type defects.

Au is known to diffuse by the kick-out mechanism in silicon (10), (11), whereby an interstitial Au atom "kicks" a substitutional silicon atom off of its lattice site and becomes a substitutional Au atom. As a result, a silicon interstitial is produced every time a Au atom becomes substitutional. Because of this, there will be an enhanced conversion of interstitial Au to substitutional Au in the presence of an interstitial sink. The pile-up of Au at surfaces and at dislocations has been observed previously (12). Vacancy clusters produced by MeV implantation provide sinks for interstitials, and so Au should be trapped in the region containing vacancy clusters. Since every self-interstitial created by a kick-out reaction will correspond to the conversion of one Au atom from interstitial to substitutional Au, it is reasonable to expect that the pile up of Au at the MeV induced vacancy clusters may be used quantitatively to measure concentrations of vacancies in clusters.

Au has also been observed to trap in cavities formed in silicon by H or He implantation (13), (14), (15). Those experiments showed that Au is trapped by the internal surfaces of such cavities. In many of those experiments, the concentration of Au trapped was sufficiently high to be detected by RBS. Since the vacancy clusters produced by MeV implantation can essentially be viewed as micro-cavities, we expect Au may also be trapped by the vacancy clusters in a similar fashion. Unlike the cavities formed by hydrogen or Helium implantation, the vacancy clusters are known to be metastable, releasing vacancies as a function of annealing (5), (6). By labeling the vacancy clusters with Au, the evolution of the vacancy clusters could be tracked by the observed changes in the Au peak in the $\frac{1}{2}R_p$ region using RBS.

In this paper we describe experiments in which Au is used to label the defects in the $\frac{1}{2}R_p$ region of a MeV implant. This implant is shown to contain vacancy-type defects by PAS. The Au concentration in the $\frac{1}{2}R_p$ region was shown to saturate in less than 2 hours at 750°C. XTEM showed the presence of Au precipitates. Also, we demonstrate that changes in the $\frac{1}{2}R_p$ vacancy clusters can be tracked by pre-annealing MeV-implanted samples prior to the introduction of Au.

EXPERIMENT

Float-zone (FZ) silicon wafers of (100) orientation were implanted with 2 MeV Si^+ ions ($R_p \sim 1.9$ μm) to a dose of $1\times10^{16}/cm^2$ at a temperature of 300°C. Si^+ implants were performed at an elevated temperature to promote local recombination of damage and prevent amorphization. Samples were subjected to rapid thermal annealing (RTA) at 950°C for times ranging from 10 s to 10 min. After RTA annealing, samples were then implanted with 68 keV Au^- ions to a dose of $8\times10^{14}/cm^2$ at room temperature. Au drive-in was accomplished by annealing the samples at 750°C for 2 hrs in a quartz-tube furnace. All implants were done using a 1.7 MV tandem accelerator with a negative ion source and an electrostatic raster. Samples were analyzed by RBS/ion channeling with a 3 MeV He^{++} beam from the 1.7 MV tandem accelerator.

XTEM was also used to characterize the samples after Au drive-in. Cross-section samples were prepared by mechanical thinning and Ar^+ ion milling. Precipitates were imaged in bright field using the (400) reflection. High-resolution cross-section imaging was performed on a Topcon 200 keV electron microscope along the [100] direction.

RESULTS/ DISCUSSION

Figure I is an RBS profile of a FZ-Si(100) substrate implanted with 2 MeV Si^+ to a dose of $1\times10^{16}/cm^2$, annealed at 750°C for 10 min and then implanted with 68 keV Au^- to a dose of $8\times10^{14}/cm^2$ and annealed at 750°C for 2 hrs. The purpose of the post-MeV anneal was to eliminate any vacancy or interstitial clusters that are unstable at the Au drive-in temperature prior to the introduction of Au. It is clear in Fig. I that Au is collecting in a region approximately one micron wide, centered around 0.7 microns, which is approximately one half of the projected range of the 2 MeV Si^+ implant. The peak near the surface corresponds to the position of the 68 keV Au implant that provides the drive-in source.

Figure II is an overlay of the Au RBS data from Fig. I onto PAS data from the same 2 MeV, $1\times10^{16}/cm^2$ Si^+ implant into FZ-Si(100) following annealing at 750°C for 20 min. The S-parameter obtained from PAS spectra is a measure of the density of open-volume defects (3), (16). The S-parameter in Fig. II has been normalized by the value for a virgin sample and plotted vs. positron range (annihilation depth). A normalized S-parameter greater than 1 indicates the presence of open volume defects. From Fig. II, we see that the depth of the Au peak centered on 0.7 μm corresponds to the depth region with a large S-parameter. The Au profile From this data, we conclude that Au is collecting in the region of vacancy clusters produced by the MeV Si^+ implant.

Figure IIIa shows RBS profiles of a set of FZ-Si(100) substrates implanted with 2 MeV Si^+ of dose $1\times10^{16}/cm^2$ and 90 keV Au^- of dose of $8\times10^{14}/cm^2$ and subsequently annealed at 750°C for 2 and 8 hrs in order to evaluate the Au drive-in procedure. As in Fig. I, a broad Au peak is observed near the $\frac{1}{2}R_p$ region in Fig. IIIa. Figure IIIa also shows that the amount of Au that collects in the $\frac{1}{2}R_p$ region saturates after a 2 hr drive-in anneal at 750°C. While the 2 hr and 8 hr drive-ins gave the same distribution of trapped Au, there was less Au trapped after a 1 hr anneal. XTEM examination of a 4 hr annealed samples (Fig. IIIb) showed that the Au has formed precipitates on the order of 100 Å in diameter (high-resolution insert of Fig. IIIb). Au precipitates have been observed to form in H-induced cavities (15).

In the above experiments, Au was observed to getter at the ½ R_p region of a 2 MeV $1\times10^{16}/cm^2$ Si^+ implant in silicon. PAS also showed a large S-parameter in the same region, indicating the existence of vacancy-type defects. The trapping of Au in this region is consistent with the diffusion mechanism of Au, in that the vacancy clusters should act as interstitial sinks driving an enhanced conversion of mobile, interstitial Au to immobile, substitutional Au. Au trapping at $\frac{1}{2}R_p$ is also consistent with Au decoration of H- and He-induced cavities in silicon, inasmuch as the vacancy clusters at $\frac{1}{2}R_p$ may act as microcavities. TEM analysis showed the presence of Au precipitates in the $\frac{1}{2}R_p$ region, whereas prior TEM analysis had shown that there are no visible defects in the $\frac{1}{2}R_p$ region from MeV implantation into silicon (1), (6). Since vacancy clusters (voids) of comparable size to the precipitates would themselves be visible in XTEM, , the size of the Au precipitates does not reflect the size of the initial vacancy clusters. This indicates that the precipitates in Fig. IIIb have ripened, becoming large enough to be visible in XTEM. Based on the above observations, it should be possible to label the vacancy clusters and track their evolution with time by pre-annealing an MeV-implanted sample for different times at a fixed temperature and then introducing Au.

In order to demonstrate the feasibility of monitoring the evolution of the vacancy clusters during annealing, 2 MeV $1\times10^{16}/cm^2$ Si^+-implanted substrates were annealed at 950°C for times ranging from 10 s to 10 min prior to the introduction of Au. Figure IV shows the RBS profiles of Au in samples that have been post-MeV annealed at 950°C for 10 sec and 10 min, followed by the 750°C, 2 hr drive-in. A sample which received only a Au implant and the drive-in anneal is also included in the figure for reference. Figure V is a plot of the total amount of Au in the $\frac{1}{2}R_p$ peak vs. duration of the post-MeV anneal. The amount of Au in this region decreases as a function of the post-MeV anneal time. This experiment shows that it is possible to track the time evolution of the defects responsible for the Au trapping. Since these defects have a depth profile that is closely correlated to the PAS profile, the defects are thought to be vacancy related. Further experiments correlating the Au concentration with PAS are planned to establish the relationship between the number of Au atoms observed at $\frac{1}{2}R_p$ and the number of vacancies in clusters. It is not possible at this time to determine whether the time-evolution of the vacancy profile is controlled by the rate of release of vacancies from clusters or the rate of injection of interstitials from the surface because the mass transport of vacancies and interstitials is nearly identical at this temperature (17).

CONCLUSIONS

In this work we have shown that the vacancy clusters formed at $\frac{1}{2}R_p$ from a MeV implant into silicon will getter and trap Au, consistent with the Au diffusion mechanism and previous observations of Au decoration of cavities. This labeling of the vacancy-clustered region by Au has the potential to provide a convenient detection and measurement tool for vacancy clusters, which are difficult to observe by most conventional techniques. We have shown that pre-annealing MeV-implanted samples prior to Au labeling leads to changes in the $\frac{1}{2}R_p$ trapping, indicating the evaporation of vacancy clusters. More work is underway to calibrate this technique to quantitatively relate the measured Au concentrations to vacancy cluster concentrations.

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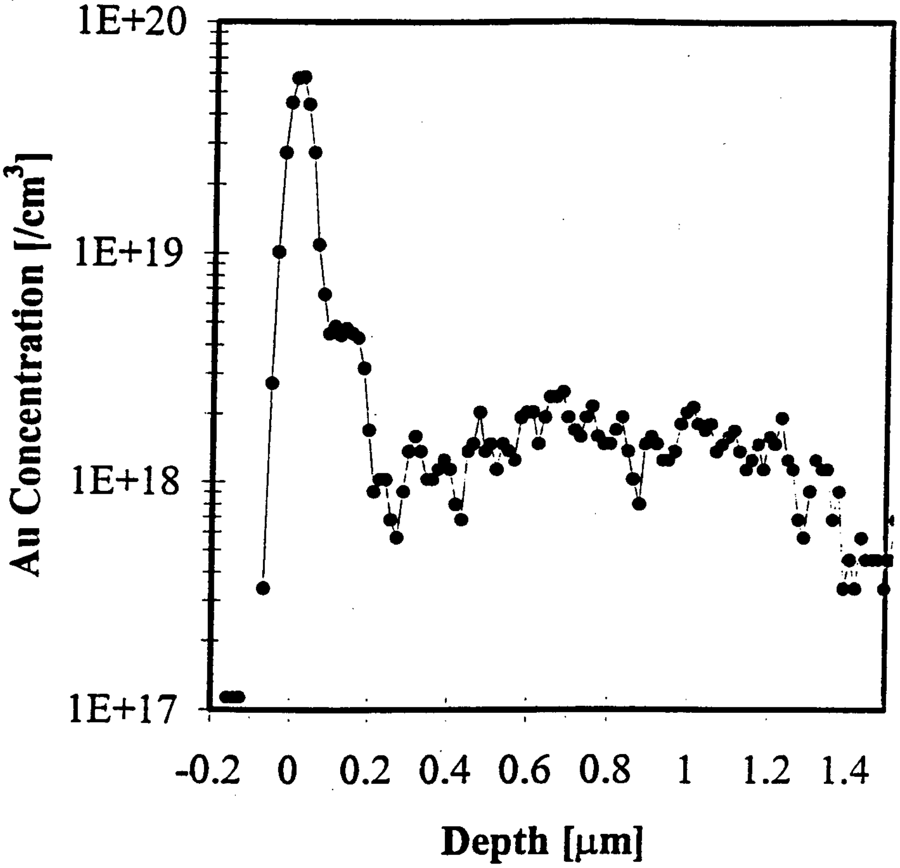


Figure I. RBS profile of a FZ-Si(100) substrate implanted with 2 MeV Si^+ ions to a dose of $1 \times 10^{16}/cm^2$ annealed at 750°C for 10 min, then implanted with 68 keV Au to a dose of $8 \times 10^{14}/cm^2$ and annealed at 750°C for 2 hrs.

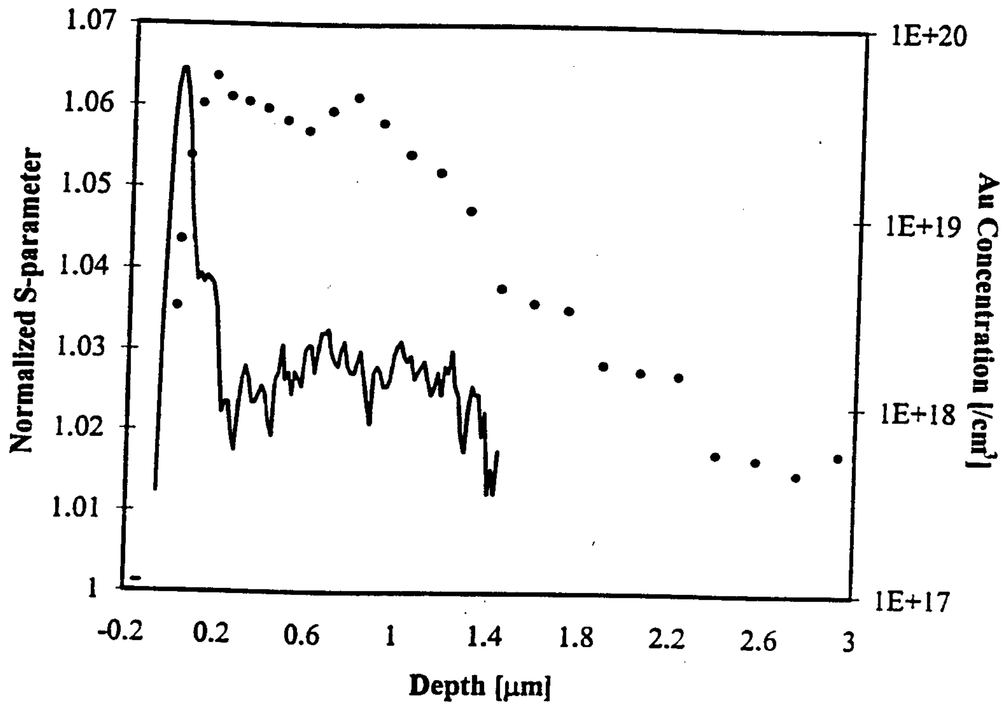
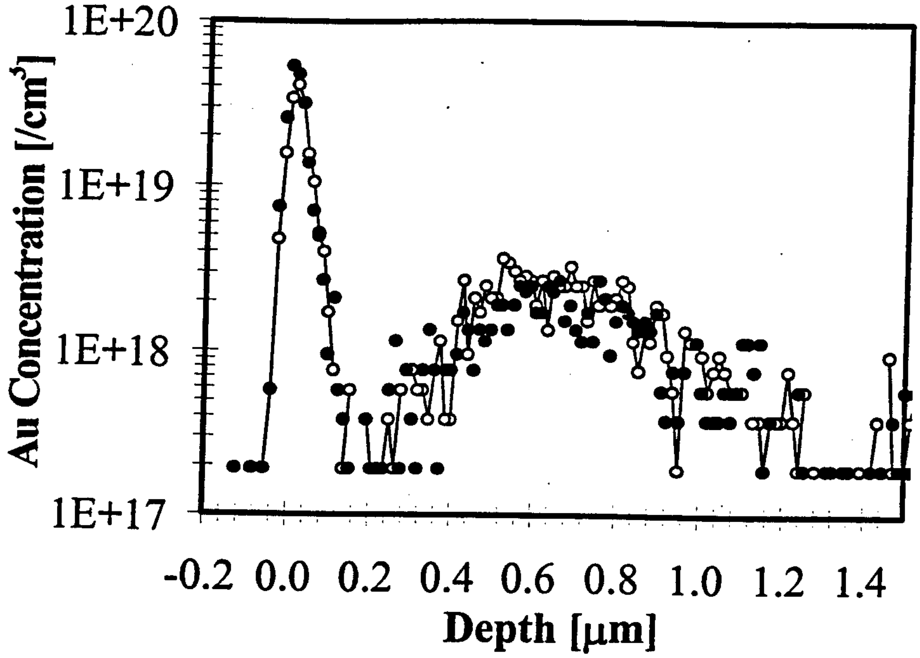


Figure II. Normalized S-parameter of a FZ-Si(100) substrate implanted with 2 MeV Si^{+} ions of dose of $1\times10^{16}/cm^{2}$ and annealed at 750°C for 10 min and Au RBS profile from figure 1.



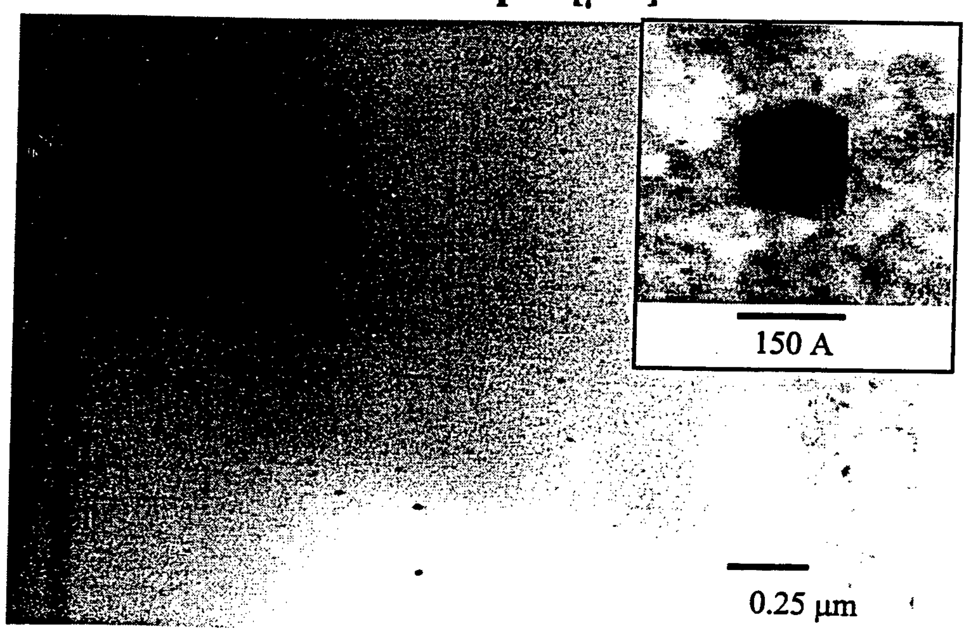


Figure III a. RBS profile of a FZ-Si(100) substrate implanted with 2 MeV Si^+ ions to a dose of $1x10^{16}/cm^2$ and 68 keV Au^- to a dose of $8x10^{14}/cm^2$ and annealed at 750°C for 2 hrs (●) and 8 hrs (-o-).
Figure III b. XTEM of above sample, with HRES insert.

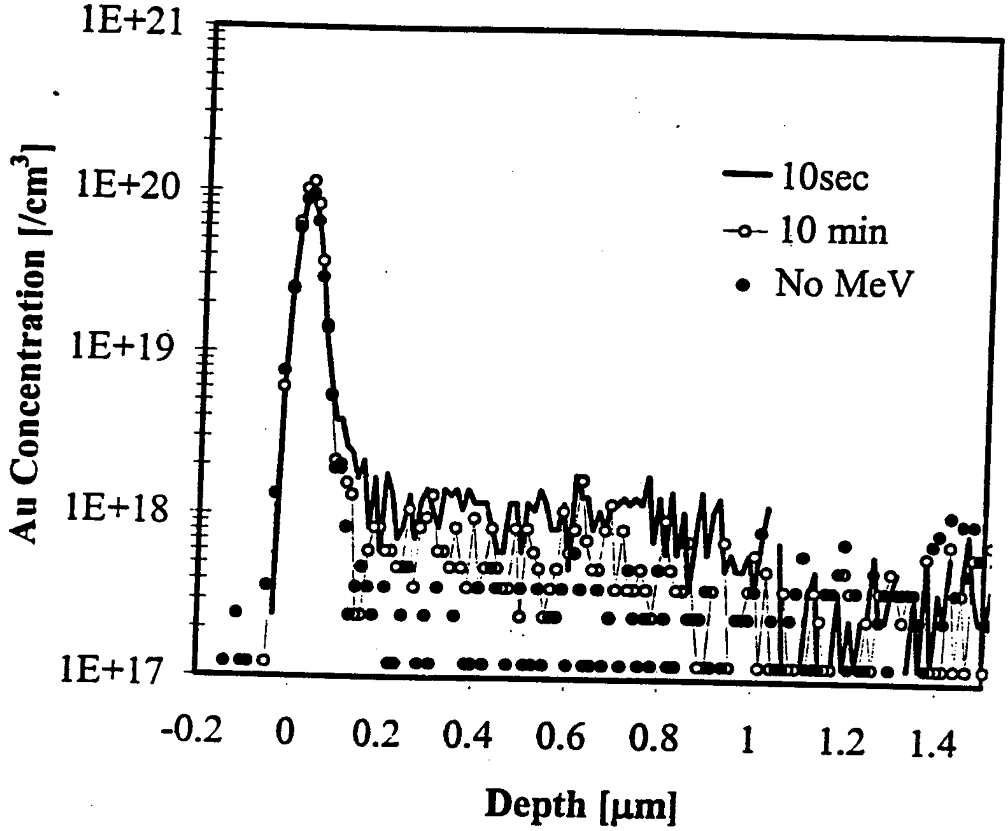


Figure IV. RBS profiles of a FZ-Si(100) substrates implanted with 2 MeV Si^+ to a dose of $1\times10^{16}/cm^2$ annealed at 950°C for 10 s and 10 min then implanted with 68 keV Au^- to a dose of $8 \times 10^{14}/cm^2$ and annealed at 750°C for 2 hrs. Also included is 68 keV $8 \times 10^{14}/cm^2$ Au^- implant into FZ and annealed at 750°C for 2 hrs

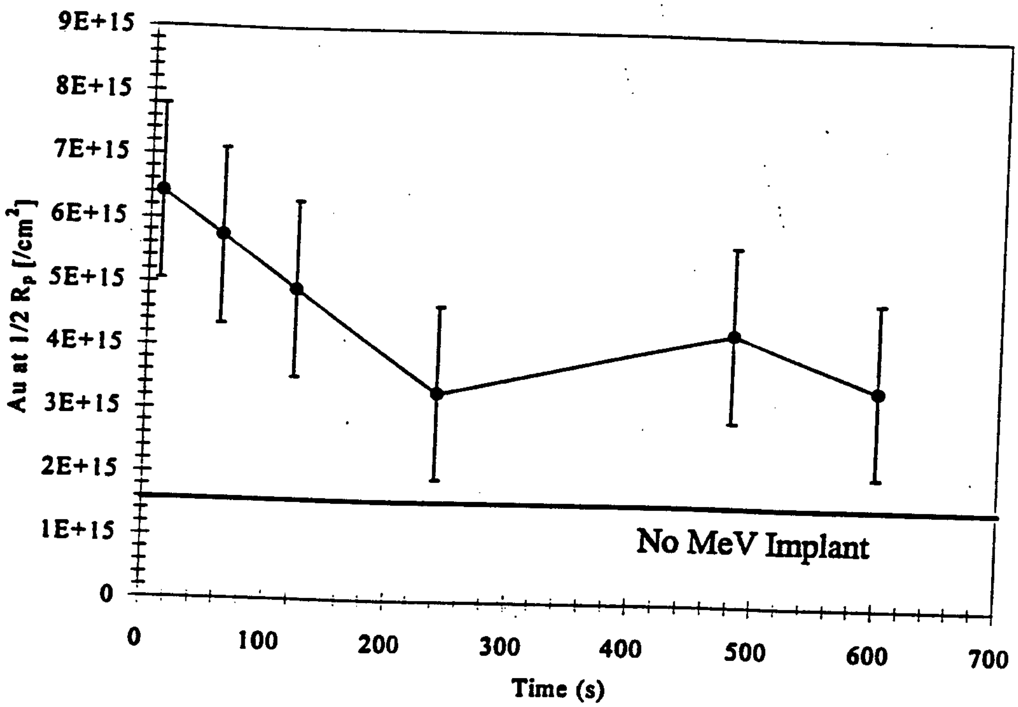


Figure V. Integral of Au peak at 1/2Rp vs post MeV annealing time (950°C). Line indicates the concentration in the 1/2Rp region of a sample implanted only with Au and annealed at 750°C for 2 hrs.

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