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A METHOD FOR ANNEALING ION-IMPLANTED-SILICON ON A VITREOUS CARBON STRIP HEATER

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ABSTRACT

A description is given of a simple method for the transient annealing of ion-implanted semiconductors on a vitreous carbon strip heater. Samples of Si implanted with doses of 1-5 x 10^{15} cm^{-2} As and Sb ions at 35 or 80 keV were annealed at temperatures in the range 650 - 1100°C and for times between 15 s and 2 min. Annealing was confirmed by Rutherford backscattering and electrical measurements. The details of these measurements are explained by taking into account the impurity solid solubility and the maximum as-implanted concentration. Supersaturated solutions of Sb in Si were found in all samples examined in this work. The production of supersaturation by strip heater annealing does not seem to have been reported elsewhere.

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ANNEALING; BACKSCATTERING; CARBON; DOPED MATERIALS; HEATERS; RUTHERFORD SCATTERING; SILICON; SOLID SOLUTIONS; SUPERSATURATION

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1. INTRODUCTION

Ion implantation is a well established technique for producing doped layers on semiconductors, especially the technologically important crystalline silicon. It is used, for example, to produce contacts on such devices as integrated circuits and radiation detectors. However, the damage caused to the lattice by the energetic implanted ions has to be removed. In many situations, this is so severe that the surface is amorphous after implantation. Furthermore, it is, in general, necessary to arrange that the implanted ion occupies a substitutional lattice site so that it is electrically active.

Traditionally, crystallinity and 'substitutionality' are obtained by furnace annealing in an inert atmosphere. However, because of the high temperatures ($\sim$ 1000°C) and long times ($\sim$ 30 min) involved, the implanted ion diffuses. This nullifies one of the main advantages of the implantation process, namely the controlled location and distribution of the implanted species. Furthermore, with such an annealing cycle the chances of contaminating the sample with fast diffusing, deep level impurities are quite high. Such impurities have deleterious effects on device operation.

Recently, new methods of annealing have been developed which allow the removal of damage in much shorter times [see, for example, Ferris et al. 1979; White and Peercy 1980; Gibbons et al. 1981; Appleton and Celler 1982], thus enabling diffusion and contamination effects to be reduced or effectively removed. Of these methods, Q-switched lasers and pulsed electron beams are exceptional, not only allowing annealing in a few tens of nanoseconds but also actually melting the surface. Annealing by these methods is essentially effected by liquid phase epitaxy. However, owing to segregation effects and high diffusion coefficients in the liquid, the implanted species is still redistributed.

There are also several techniques for annealing by solid phase epitaxy in the intermediate time range of 1 ms to 100 s [see, for example, Appleton and Celler 1982]. These involve the use of continuous wave lasers and electron beams (pulsed or scanned), incoherent light sources, and strip heaters. The simplest of these is probably the strip heater method which is suitable for annealing times from 10 to 100 s. Although this method has not been well reported in the literature, brief descriptions were given recently of the successful use of graphite strip heaters to anneal ion-implanted Si [Tsaur et

thickness. Each end of the heater is clamped between two pieces of graphite to provide low resistance contacts. The nominal heater resistance is 0.5 Ω at room temperature and 0.35 Ω at 1000°C. The heater is connected to a 10 V, 100 A a.c. power supply controlled manually by a mains Variac. The current passing through the heater is measured with an inductively-coupled, clip-on ammeter. The heater is mounted in a bell jar which allows annealing to be carried out either in vacuum or in a gaseous atmosphere. The sample is placed directly on the heater with the ion-implanted face down. This geometry gives the best thermal contact and allows tests for contamination effects.

2.2 Sample Temperature

Since sample temperature is a very important annealing parameter, considerable effort is made to measure it accurately. However, as with low temperature measurements far from ambient, it is difficult to do this with precision. At high temperatures ($\geq$ 950°C), the heater temperature can be measured to ± 20°C using an optical pyrometer. However, since the quality of the thermal contact between heater and sample in vacuum is an unknown parameter, the sample temperature is not known with such confidence. Furthermore, the optics of the pyrometer are such that it is not possible to focus solely on the sample. It is estimated that the sample temperature could be as much as 50 to 150°C lower than that of the filament when employing anneal times of a few tens of seconds. Nevertheless, some annealing experiments (on As ion-implanted Si) have been carried out under these conditions.

Annealing cycles were also carried out in vacuum at lower temperatures, at which the pyrometer is not useful. Tests using a low thermal mass Chromel-Alumel thermocouple were basically unsuccessful, significant temperature discrepancies being found with the thermocouple contacting either sample or heater. The magnitude of the discrepancy decreased considerably in a gas atmosphere, presumably because the gas allowed much better thermal contact between sample and heater. The Sb implanted samples were annealed in a flowing helium atmosphere. Helium was considered very suitable, being inert and having a high thermal conductivity.

The true sample temperature was estimated from the measured thermocouple temperature as follows. The difference between two temperatures was first obtained at a high temperature with the optical pyrometer. The thermal contact was so good that there was no difference between heater and sample

temperatures. The difference was then assumed to decrease linearly with temperature to become zero at room temperature. Figure 1 shows a graph of the true temperature as a function of the thermocouple temperature based on this assumption, and was used to estimate the sample temperature in the region below the optical pyrometer range.

The characteristics of the thermal pulse experienced by the sample were assumed from the shape of the current pulse, which had a risetime of $\sim$ 5 s in vacuum and $\sim$ 15 s in helium. The falltime was exponential, with a time constant similar to the risetime. Thermocouple temperature measurements of the thermal pulse gave very similar values.

2.3 Silicon Samples

A number of <100> oriented p-type Si samples, implanted with As or Sb ions (1 to 5 x 10^{15} cm^{-2}, at 35 or 80 keV), were annealed on the VC strip heater. To make electrical measurements, the implanted layer conductivity type must be opposite to that of the substrate. Details of the base material and the implant parameters are provided in Table 2. It should be noted that those samples implanted with As were annealed in vacuum at high temperatures for short times, whereas the material implanted with Sb was annealed in a flowing He atmosphere. More confidence is attached to the temperatures estimated for the gas environment. However, no real attempt was made to look for differences in the annealing characteristics of Si implanted with either Sb or As, nor were effects due to the environment sought.

Separate samples were used for the two types of analysis to ensure that electrical measurements were not made on samples which had been exposed to, and possibly damaged by, the RBS analysing beam. Samples, 5 mm by 5 mm, were quite adequate for RBS analysis, where the beam diameter was only 1 mm, but samples at least 7 mm by 7 mm were required for the electrical measurements.

3. ANALYSES AND RESULTS

Samples annealed on the VC strip heaters were examined by RBS and by electrical (sheet Hall and resistivity) measurements. The RBS analysis allowed both annealing parameters (crystallinity and substitutionality) to be examined, and the electrical measurements provided an estimate of the electrical quality of the annealed contacts.

3.1 Rutherford Backscattering

Samples were examined on the RBS spectrometer attached to the 3 MV Van de Graaff accelerator at Lucas Heights. The analysing beam was 2.0 MeV He^+ and current was typically 30 nA. Spectra were collected from Si surface barrier detectors set at 170 and 100° with respect to the beam. Spectra from the backward detector were used to determine the minimum yield (χ_{min}) - a measure of the crystal quality - and the substitutional fraction (f_s) of the implanted ion. Spectra from the other detector provided better depth resolution, thus allowing changes in the profile of the implanted ions to be monitored. The results of the RBS analyses are given in Table 2. From the low values of χ_{min} and high values of f_s it is obvious that, in general, annealing had taken place. A furnace-annealed sample is included for comparison. Figure 2 shows an RBS spectrum from a silicon sample annealed at 1000°C for 40 s. Rutherford backscattering is a sensitive technique for detecting trace impurities heavier than the substrate; no evidence was found for impurities heavier than Si.

3.2 Electrical Measurements

Sheet Hall and resistivity measurements were made at room temperature on samples annealed on the VC heaters, using the method suggested by Van der Pauw [1958]. A measurement of the sheet Hall coefficient allows the calculation of N_s, the carrier concentration per unit area. This is then compared with the known concentration of implanted ions. The sheet resistivity (ρ_s) is combined with N_s to allow the effective mobility μ_{eff} to be determined; μ_{eff} and N_s are measures of the quality of the contact.

Four ohmic contacts were produced at the corners of each sample. Initially, these were produced by simply placing small pads of clean bright In foil on the required spots; however, it was found that readings were unstable and results from any sample gave a large variation in the values of N_s. Much better data were obtained by evaporating Al (through a mica mask) to provide the ohmic contacts. Small pads of In foil were then placed on top of the evaporated spots to make the contacts more robust. The samples were placed in a non-magnetic holder and electrical contact made by four phosphor-bronze springs. The sheet Hall measurements were made in the 2.7 kG field of a permanent magnet.

Table 3 presents values of N_s, ρ_s, and μ_{eff} for samples annealed on a VC strip heater; it is immediately clear that annealing has taken place.

Sensible data could not be obtained from samples prior to being annealed on the VC strip heaters owing to implant damage effects

4. DISCUSSION

From Table 2, it can be seen that there is an obvious and significant reduction in the value of χ_{min} on annealing at high temperatures for short times. A value of 3 per cent is usually accepted as typical of a good undamaged crystal. It appears that if the time or temperature is reduced, annealing is not quite so good. Similar comments can be made about the substitutional fraction f_s, which generally is high ($\sim$ 90 per cent) but tends to decrease when time or temperature is decreased, leading to less effective annealing. Table 2 also indicates that longer periods ($\sim$ 2 min) at low temperatures ($\sim$ 650°C) can provide excellent annealing. However, if the time is increased to 10 min, annealing is less effective; in particular the value of f_s is significantly reduced. A furnace anneal at this temperature produced similar data.

The electrical measurements are more difficult to interpret. The Si(As) sample annealed at 1000°C for 20 s gave a carrier concentration N_s which is the same as that implanted. As was expected, the corresponding RBS measurements gave a high value of f_s. However, the Si(Sb) sample annealed at 910°C for 15 s gave a concentration which is too low by a factor of eight. This seems to contradict the RBS measurements which indicated a high f_s (85 per cent), although it should be pointed out that the comparison is for different values of N_{max}, the maximum as-implanted volume concentration. This apparent disagreement will be discussed later. If annealing is done at a lower temperature (670°C for 2 min) the disagreement lessens, giving a concentration which is only a factor of two lower than expected. However, if the anneal time at this temperature is increased, the comparison becomes worse - as was found with RBS. A furnace-annealed sample gave a carrier concentration which is also low by a factor of eight.

To understand the electrical measurements of N_s, the solubilities of As and Sb in Si must be considered. The maximum equilibrium solid solubilities for As and Sb, respectively, are 3×10^{20} cm^{-3} [Lietoila et al. 1980] and 7×10^{19} cm^{-3} [Trombore 1960]. Tables 2 and 3 include estimates (the values in square brackets) of the N_{max} of the implanted As and Sb before annealing. These have been calculated assuming a Gaussian distribution and using the

parameters given in the tables of Gibbons et al. [1975]. It should be pointed out that these values are independent of whether the implant is in solution. Indeed it can be seen that all are greater than the maximum equilibrium solubilities. If the electrically active concentration of the implanted species is determined by the equilibrium solubility, the measured N_s must be correspondingly lower. However, the expected value of N_s will be increased if there is a supersaturated solution.

Metastable supersaturated solutions can be obtained, provided that the diffusion length during the anneal cycle is negligible compared to the distance between impurities [Campisano et al. 1980]. The RBS measurements indicate (see Figure 2 for example) that no significant diffusion took place for either the high temperature (10 to 35 s) or low temperature (2 min) anneals. The corresponding values of f_s in Table 2 and N_s in Table 3 can now be semi-quantitatively understood. If, for example, we consider the sample implanted with 5×10^{15} cm^{-2} Sb at 35 keV, the value of N_s should be 3×10^{14} cm^{-2} which is a factor of two lower than that actually measured. If the solubility were supersaturated, at 1.7×10^{20} cm^{-3}, agreement would be obtained.

There may also be supersaturated solutions in the Sb implanted samples annealed at low temperature (650 to 670°C) for 2 min. The existence of such solutions is, in fact, indicated by both the RBS and electrical measurements. The solubility estimated from the RBS data is 3.0×10^{20} cm^{-3}, which is well above the maximum equilibrium value. From the electrical measurements, another estimate can be obtained since a different value of N_{max} is involved. The solubility is calculated as 9×10^{20} cm^{-3}. This is probably a lower limit since, for high concentrations, not all impurities are ionised. The supersaturated solutions are metastable and the evidence shows that they are very sensitive to changes in the diffusion length. Increasing the time at 650°C from 2 to 10 min causes a significant reduction (a factor of $\sim$ 2) in the values of f_s and N_s. Supersaturated solutions produced by strip heater annealing have not been reported elsewhere.

5. CONCLUSIONS

The strip heater method for the transient annealing of ion-implanted semiconductors is simple and effective, and can probably be scaled up for complete wafer processing for use in such devices as solar cells. Vitreous

carbon is a very suitable heater material and has several advantages over the graphite used by other workers. No evidence was found to indicate that the VC strip heaters described here contaminated the samples.

Annealing has been demonstrated on Si implanted with As and Sb examined by RBS and electrical measurements. These preliminary measurements are discussed and apparent anomalies resolved by considering the solid solubilities and the as-implanted N_{max}. Metastable supersaturated solutions are shown to exist in some samples.

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TABLE 1
COMPARISON OF VITREOUS CARBON AND GRAPHITE

Feature	Vitreous Carbon	Graphite
Upper working temp. (°C) (vacuum or inert atmos.)	3000	3000
Porosity	low	high
Gas permeability	very low	high
Resistance to corrosive chemicals	high	low
Oxidation rate	low	high
Strength	high	low
Coeff. of thermal expansion per °C	$\sim 3 \times 10^{-6}$	$\sim 3 \times 10^{-6}$
Thermal conductivity	low	high
Thermal shock resistance	high	high
Electrical resistivity	high	low
Purity	good	good

TABLE 2
RUTHERFORD BACKSCATTERING

Sample Description	Anneal Atmosphere	Anneal Parameters (°C, time)	Silicon χ_{min} (%)	Impurity f_s (%)
1×10^{15} As cm^{-2}		not annealed	12.5	zero
35 keV	vacuum	1100, 25 s	2.7	89
<100> p- Si	vacuum	1000, 35 s	2.8	94
1 Ωcm	vacuum	1000, 25 s	3.0	93
[4.5×10^{20} cm^{-3}]*	vacuum	1050, 10 s	∿6	79
5×10^{15} Sb cm^{-2}		not annealed	12.5	zero
35 keV	He	670, 10 min	5.4	50
<100> p- Si				
4 Ωcm	furnace, N_2	650, 40 min	∿5	55
[3.1×10^{21} cm^{-3}]*				
1×10^{15} Sb cm^{-2}		not annealed	18.3	zero
80 keV				
<100> p- Si	He	910, 15 s	3.5	85
50 Ωcm				
[3.4×10^{20} cm^{-3}]*	He	650, 2 min	3.1	90

*N_{max}, the peak as-implanted impurity concentration

TABLE 3
ELECTRICAL RESULTS

Sample Description	Anneal Atmosphere	Anneal Parameters (°C, time)	ρ_s ($\Omega/\square$)	N_s (cm^{-2})	μ_{eff} ($cm^2\ V^{-1}\ s^{-1}$)
As 1×10^{15} cm^{-2} 35 keV [4.5×10^{20} cm^{-3}]*	vacuum	1000, 20 s	1.74×10^2	1.0×10^{15}	35.9
Sb	He	910, 15 s	2.10×10^2	5.9×10^{14}	50.3
5×10^{15} cm^{-2}	He	670, 2 min	1.40×10^2	2.2×10^{15}	20.6
35 keV	He	670, 10 min	1.98×10^2	1.0×10^{15}	30.6
[3.1×10^{21} cm^{-3}]*	furnace, N_2	650, 40 min	2.11×10^2	6.4×10^{14}	46.8

* N_{max}, the peak as-implanted impurity concentration

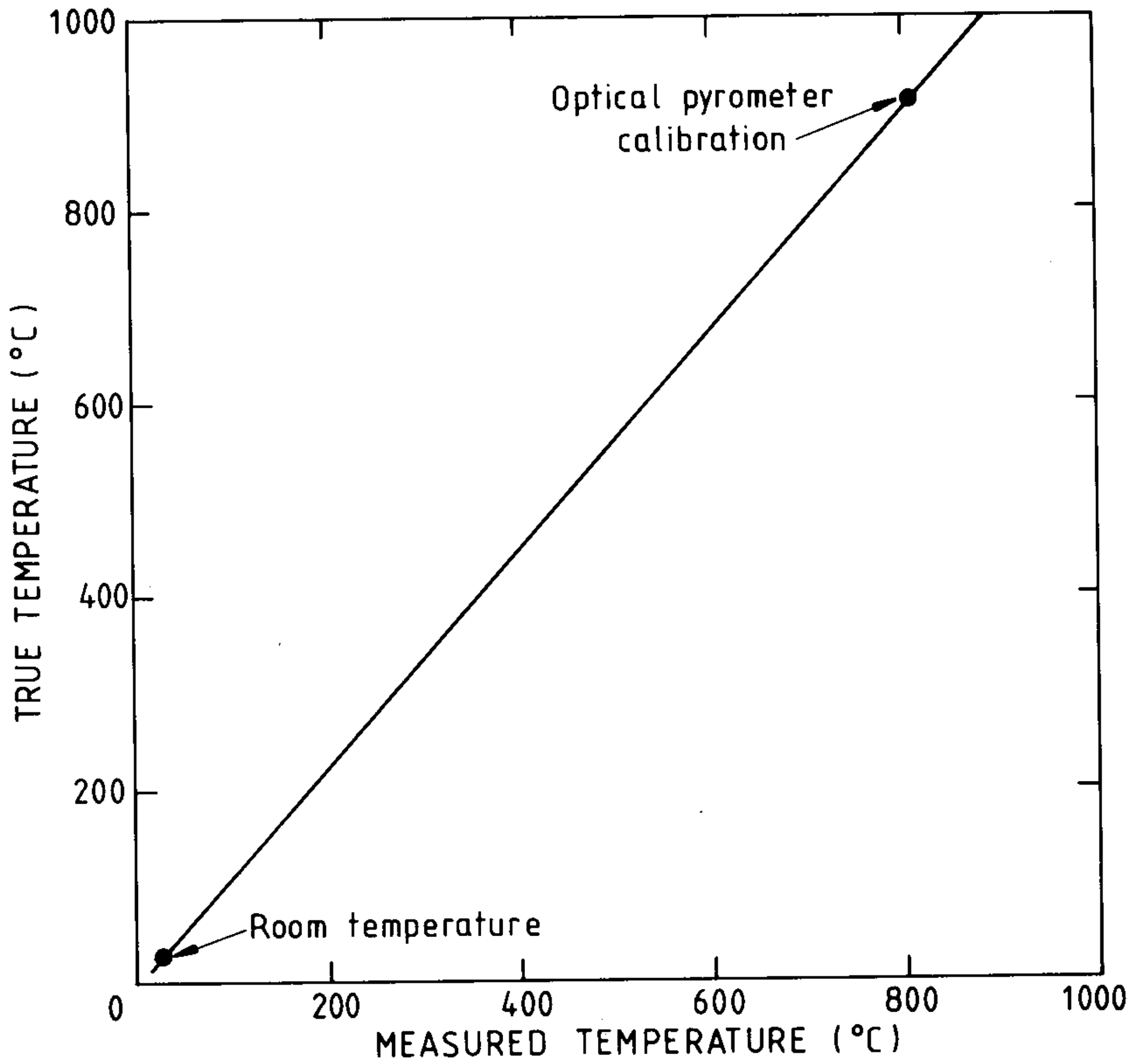

FIGURE 1. PLOT OF TRUE SAMPLE TEMPERATURE AGAINST THE THERMOCOUPLE TEMPERATURE

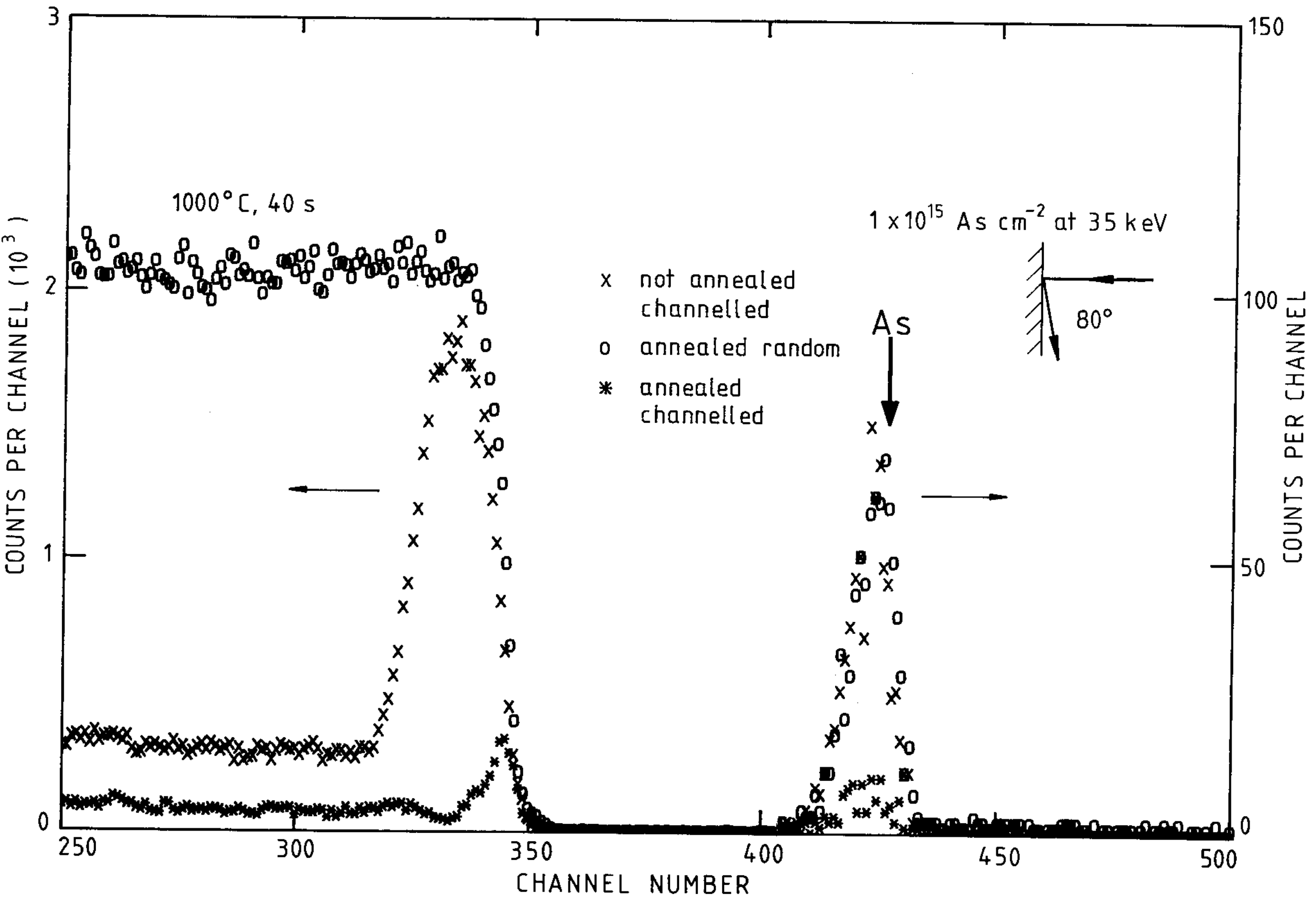

FIGURE 2. RBS SPECTRUM DEMONSTRATING THE ANNEALING OF ION-IMPLANTED Si