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THE INFLUENCE OF THE PRIMARY RECOIL SPECTRUM
ON
RADIATION-INDUCED SEGREGATION IN NICKEL-SILICON

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by

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The Influence of the Primary Recoil Spectrum on Radiation-Induced Segregation in Nickel-Silicon *

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Abstract

Radiation induced segregation in Ni-12.7% Si has been examined for 1.5 MeV He, 2.0 MeV Li, and 2.75 MeV Kr irradiations. A method to simultaneously damage and analyze the specimens during light-ion irradiation is described. The amount of segregation was determined by using Rutherford backscattering spectrometry to measure the thickness of the γ' layer which develops at the surface. Substantially less segregation of Si to the surface is observed for the Kr irradiation than for the light-ion irradiations at 520°C.

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Introduction

Segregation of alloying elements during irradiation at elevated temperatures has been observed in many alloys.(1) This radiation induced segregation (RIS) has been studied extensively in recent years, particularly in binary alloys of Ni(Si). It has been shown, for example, that electron,(2) proton,(3) and Ni^{+}(4) irradiations of low concentration Ni(Si) alloys all induce precipitation of the γ' phase, Ni_3Si, at grain boundaries, dislocations, and external surfaces. The temperature range for which γ' has been observed is ~ 50°C to 650°C for electron irradiation(2) and ~ 400°C to 700°C for 3.5 MeV Ni^{+}.(5) These ranges vary somewhat with the displacement rate. Aside from this rudimentary comparison of RIS for electron and Ni irradiations, very little work has been done to investigate the effect of the primary recoil spectrum on RIS. We have initiated such a study.

One of the difficulties encountered in comparing RIS for different types of irradiation is establishing a quantitative measure of the degree of segregation. In the present study the thickness of the γ' layer which is induced at the irradiated surface is used as a measure of RIS. Various techniques are available to profile the concentration of alloy elements as a function of depth below a surface. Auger electron spectroscopy(6) and SIMS(7) in conjunction with sputtering have been used in the past for RIS studies. In the present work high resolution Rutherford backscattering spectrometry(8) (RBS) has been employed. We have found that by using RBS, the same ion beam can be employed to simultaneously irradiate and analyze a specimen. This procedure has several advantages compared to previous methods. One major advantage is that the growth of the γ' layer can be measured on one specimen. Aside from the economy of time in preparing, irradiating, and analyzing specimens, the use of one specimen eliminates errors associated with variations in the specimen microstructure, purity, and irradiation temperature. The technique is particularly useful at high temperatures, where fast thermal back diffusion competes with RIS. At these temperatures the segregated phase tends to redissolve into the bulk after the irradiation has terminated but before the specimen has cooled. Simultaneous analysis and irradiation eliminates this difficulty. In this paper we describe our technique and give results for He and Li ion irradiations of Ni-12.7 % Si. In addition, results for these light ion irradiatins are compared with preliminary results for 2.75 MeV Kr irradiations. A significant dependence of RIS on the primary recoil spectrum is observed.

Experimental Methods

Figure 1 illustrates a schematic backscattering spectrum for a Ni-12.7% Si alloy before and after formation of a γ' surface film. The backscattered yield, $H_{Ni}(E)$ results from incoming particles being scattered from Ni atoms; the steep decrease in the yield at the highest energy is designated the Ni "leading edge". The leading edge of the lighter Si atoms is superposed at a lower energy on the yield from Ni at some depth, as indicated in the figure. The composition of the unirradiated alloy can be determined from the relative yields H_{Ni} and H_{Si}. The ratio H_{Si}/H_{Ni} is approximately equal to the ratio of the scattering cross sections for Si and Ni times their relative atomic concentrations.(9) Thus, $H_{Si}/H_{Ni} \approx 0.04$ for a Ni-12.7% Si alloy. The increase in the Si concentration at the surface region due to segregation is reflected by the increase in the backscattered yield, ΔH_{Si} and the decrease ΔH_{Ni} at and behind the respective leading edges. One may note that ΔH_{Ni} is significantly greater in magnitude than ΔH_{Si}. This results because changes in the Si concentration are weighted in the backscattered yield by the ratio of the cross sections (0.25) at the Si leading edge, and by the ratio of the stopping powers (~ 0.8) at the Ni leading edge.$^{(9)}$

The thickness of the γ' layer is obtained from the spectrum by using the expression$^{(9)}$

$$\Delta E = E_2 - E_3 = \frac{K_A}{|\cos\theta_1|} \left.\frac{dE}{dX}\right|_{in} + \frac{1}{|\cos\theta_2|} \left.\frac{dE}{dX}\right|_{out} \cdot \Delta X \; . \qquad (3)$$

Here, ΔE is the energy difference between particles scattered from the front and back edges of the layer; $\theta_1 (\theta_2)$ is the angle between the incident (backscattered) particle direction and the surface normal; $\left.\frac{dE}{dX}\right|_{in}$ $(\left.\frac{dE}{dX}\right|_{out})$ is the average stopping power of the particle at the incident (backscattered) energy; K_A, the kinematic factor, is the fraction of energy retained by the incident particle upon backscattering through the angle $[360-(\theta_1+\theta_2)]$ from target atom A; and ΔX is the thickness of the film. It is evident that for fixed energy resolution of the particle detection system, the depth resolution can be enhanced by appropriate choices of θ_1 and θ_2. In the present experiment $\theta_1 = 150$ and $\theta_2 = 75^{\circ}$; this geometry enhances the depth resolution by a factor of ~ 3 compared to a normal incidence and backscattering geometry $(\theta_1 = 180^{\circ}, \theta_2 = 0^{\circ})$.

Simultaneous RBS analysis and defect production requires that the dose necessary to acquire a RBS spectrum be much smaller than that necessary to cause appreciable segregation. For the present experimental conditions, a 1.5 MeV He beam, 1.0 mm in diameter, backscattering at 135° into a solid angle of 2.5×10^{-4} steradians with $\theta = 150^{\circ}$ and $\theta_2 = 75^{\circ}$, a multichannel energy width of 1.5 keV/channel, the count rate was 1.8×10^{4}/channel-dpa or 4 x

10^3/ Å -dpa. Suitable spectra could therefore be acquired every few tenths of dpa. The ratio of count rate to displacement rate, or counting efficiency, λ, can be improved by various methods. Geometric means of increasing λ are increasing the solid angle of the detector, using additional detectors, and irradiating a larger area. These methods, however, have limitations, increasing the solid angle impairs the depth resolution, increasing the size of the beam increases beam heating; and adding detectors adds expense. Another way of increasing λ is to reduce the projectile energy since the scattering cross section varies as $1/E^2$ whereas the displacement cross section varies as 1/E. Moreover, the lower projectile energy reduces beam heating, as a result, the beam size can be made larger, further increasing λ. The lower limit on energy is generally determined by the required mass resolution since mass resolution is proportional to the projectile energy. For the present case it is undesireable to have the Ni_3Si surface layer overlap the Si leading edge. Energy straggling of the beam and accumulation of implanted ions also limit the lowest useable energy.

Particles other than He can be used for RBS. Many factors are involved in evaluating their applicability; however, a few general remarks can be made. For Rutherford scattering, the cross section varies as ${Z_1}^2$ and the displacement cross section varies as $M_1{Z_1}^2$ where M_1 and Z_1 are the mass and atomic number of the projectile. Thus λ is the largest for the lightest particles. The mass resolution, however, is the worst for the lightest particles. Moreover as the displacement rate varies as ${Z_1}^2$, the displacement rate per particle is lowest for light particles and high displacement rates are difficult to achieve. Finally the stopping power of the particle should also be considered. The stopping power increases with increasing Z_1 for light projectile so that better depth resolution, as seen in eq. (3), can be obtained using heavier particles. Unfortunately, values of stopping powers in most materials have been determined accurately only for H and He.

Results

The RBS results for He irradiation of a Ni-12.7% Si specimen at 465°C are illustrated in Figure 2. Each spectrum was acquired over a 15 min. interval and thus each yields the time-average alloy concentration as a function of depth during the collection interval. The calculated displacement rate for this particular irrdiation was 3.7×10^{-4} sec^{-1}; the number of displacements per spectrum was accordingly 0.3 dpa. Analysis of the step height in yield between the surface layer and the bulk alloy, ΔH_{Ni}, indicates that the composition of the surface layer is ~ Ni_3Si, and is therefore consistent with precipitation of γ' at the surface. The smaller step height in the 0-15 min. spectrum reflects the fact that the spectrum is a time average of the composition and at $t = 0$, no γ' is present. The growth of the γ' layer with time is evident. The thickness of the layer after 87 min. was found, using eq. (1), to be 15.5 nm. An interesting feature in the kinetics of the segregation is revealed by this technique. Concomitant with the initial formation of γ' at the surface, is a strong depletion of Si in a narrow region contiguous with the γ'. The depleted zone is subsequently consumed by the advancing γ' layer. As the degree of Si depletion in the zone below the γ' diminishes during the advanced stages of segregation, the zone spreads to greater depths. A problem associated with the use of He irradiation is the accumulation of implanted gas atoms. It is unlikely that the He, which is trapped near to its end of range, ~ 1.5 μm, affects the segregation process which occurs within a few tens of nanometers of the surface; however the He does cause blistering at relatively low displacement levels, ≈ 2 dpa. This difficulty can be circumvented by using specimens which are thinner than the He range as was done by Janghorban and Ardell for proton irradiation.(3) In our work, however, higher dpa levels were attained by irradiating with 2.0 MeV Li beams. The displacement cross section for 2.0 MeV Li is ~ 3 times greater than that for 1.5 MeV He. Thus the number of implanted atoms per dpa are reduced for Li irradiation. Moreover it was of interest to evaluate the applicability of Li beams for performing simultaneous damage and analysis experiments.

Typical spectra for the Li irradiations are illustrated in Figure 3. The calculated displacement rate was 4 x 10^{-4} sec^{-1} and the specimen temperature was 520°C. Again the developement of the γ' layer is clearly visible. It may appear from comparing Figs. 2 and 3 that the γ' layer is much thicker for Li irradiation than for He irradiation. However, this is not the case. The larger values of ΔE for the Li irradiation result from the factor of ~ two greater stopping power of 2.0 MeV Li than 1.5 MeV He in Ni. The energy resolution of the detector for the Li ions however is degraded from that for the He ions. Thus the total spatial resolution is nearly the same for the He and Li irradiations. No evidence for a strong depleted region similar to that observed for the He irradiation at 465°C, is apparent in the Li spectra. Presumably the difference in the depletion layer is associated with the specimen temperature and not with the type irradiation since He irradiations at 520°C did not show a strongly depleted region either. Finally it is noted that a careful inspection of the Ni leading edge in the Li spectra reveals that the Si concentration at the surface is ~ 30%. This result indicates that a thin layer, richer in Si than is γ' formed on top of the γ' layer. Auger analysis of Ni irradiated Ni-Si alloys have also indicated additional Si enrichment in a layer on top of the Ni_3Si layer.$^{(10)}$

A comparison of these light ion irradiations has been made with 2.75 MeV Kr irradiations. For Kr, the film thicknesses were determined by post-irradiation He-backscattering at room temperature. The results for He, Li, and Kr irradiations at ~ 520°C are tabulated in Table 1. On the basis of calculated dpa, the Kr irradiations are considerably less effective in inducing segregation of Si at the surface than either the He or Li irradiation. The film thickness for Kr is less than half that for the light ions even though the calculated dose for the Kr was more than twice that for the light ions. The principal difference between the Kr and light-ion irradiations is their primary recoil spectra. Irradiation with Kr produces most of the defects in energetic displacement cascades, whereas the light-ion irradiations produce most of the defects by low-energy primary recoils. For example, only 10% of the defects produced by 2.75 MeV Kr result from recoils below 2 keV, whereas for 1.5 MeV He irradiation 50% of the defects are produced from recoils below 2 keV. It appears, therefore, that the predominance of large cascades in the Kr irradiations can significantly inhibit the formation of Ni_3Si films at the surface. This result is due to the high concentration of point defects in energetic displacement cascades. Segregation requires long-range migration of defects for the preferential transport of the segregating species. However, defects in cascades have an enhanced probability for annihilating with opposite defects or forming immobile defect clusters without undergoing long-range migration, as compared with defects produced by low-energy recoils. In addition, the immobile clusters are internal point-defect sinks, and therefore serve as solute segregation centers which can reduce the flow of solute to the specimen surface. Although the present experiments do not reveal the relative importance of recombination, clustering, and defect sink formation, they do show that the details of the defect production process can have a strong influence on RIS.

In conclusion we emphasize that the type of irradiation can have a significant influence on radiation induced segregation. This was shown by the large differences in the thickness of the γ' layer which develops at irradiated surfaces for light ion and Kr irradiations. It was also shown that it is possible to simultaneously analyze and irradiate a specimen by using Rutherford backscattering spectrometry. This combination is very useful for observing the kinetics of the segregation process.

Table 1: The effect of primary recoil spectrum on RIS in Ni-12.7% Si at 520°C

Projectile	Displacement Rate	Total Displacement	γ' Thickness
1.5 MeV ^{4}He	3.1×10^{-4} sec^{-1}	1.56 dpa	27.5 nm
2.0 MeV ^{7}Li	4×10^{-4} sec^{-1}	1.32 dpa	25-30 nm*
2.75 MeV ^{84}Kr	5×10^{-4} sec^{-1}	3.6 dpa	10.0 nm

*The uncertainty in γ' thickness reflects the uncertainty in the relative stopping power of 2.0 MeV Li to 1.5 MeV He.

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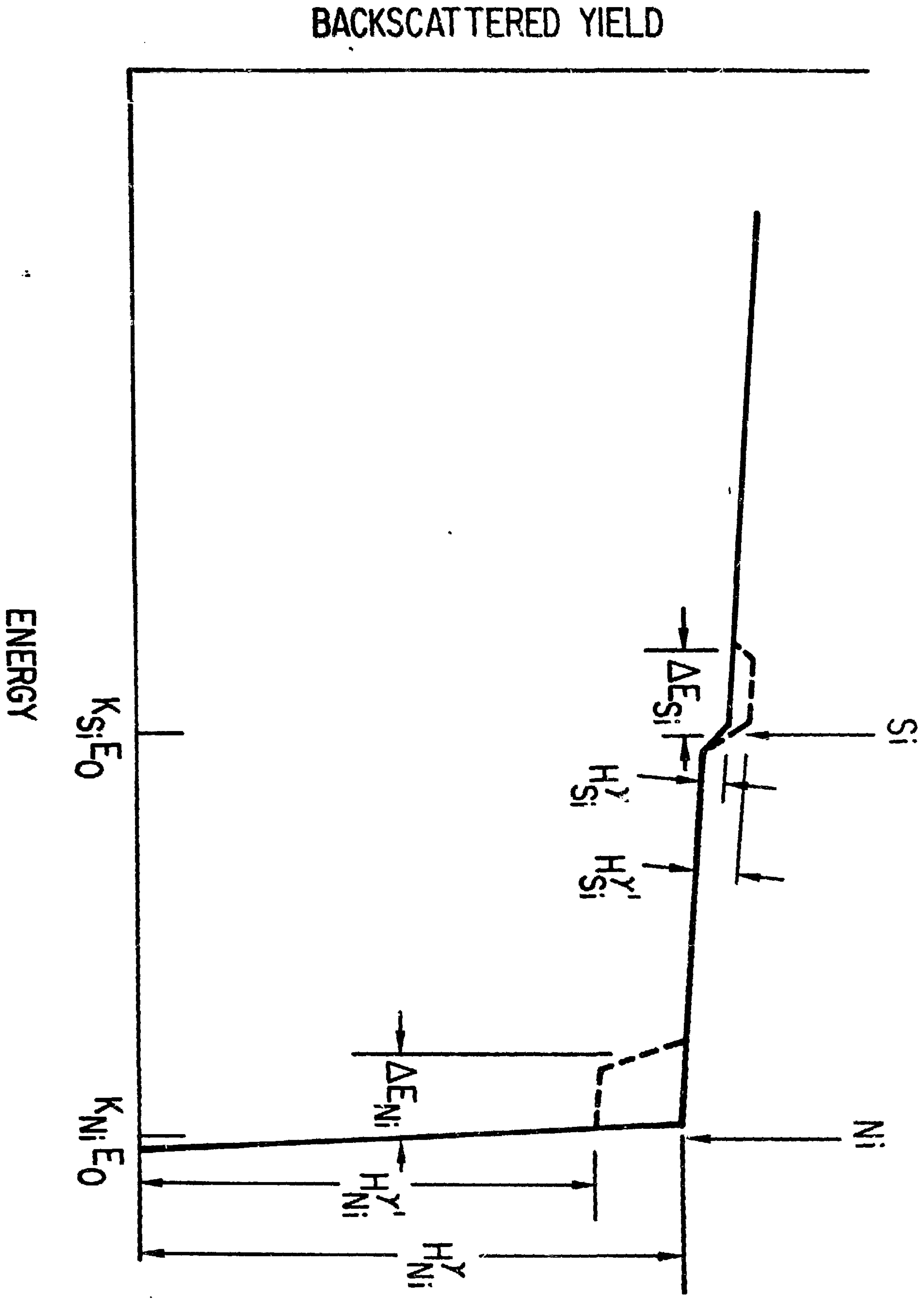
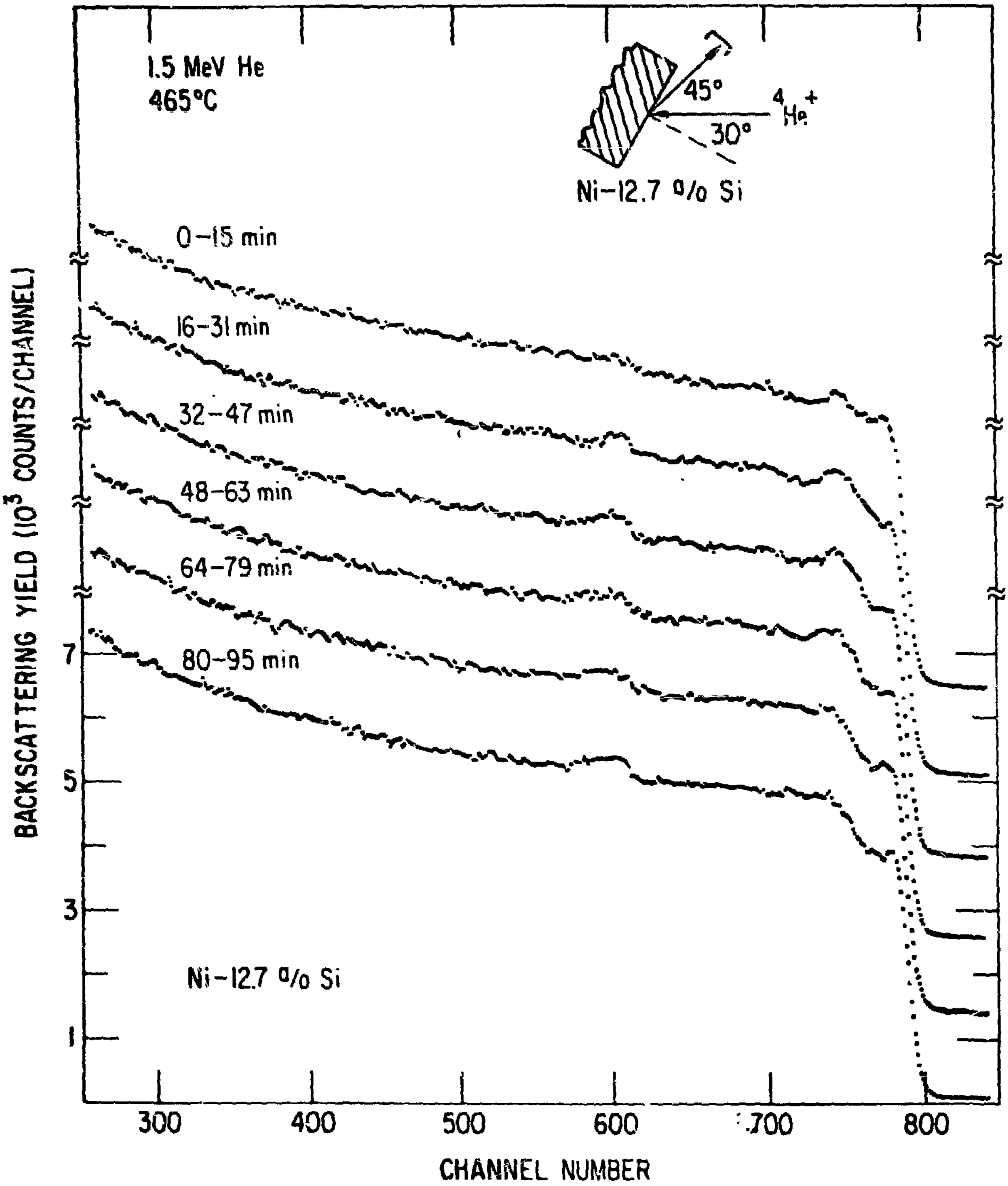
Figure Captions

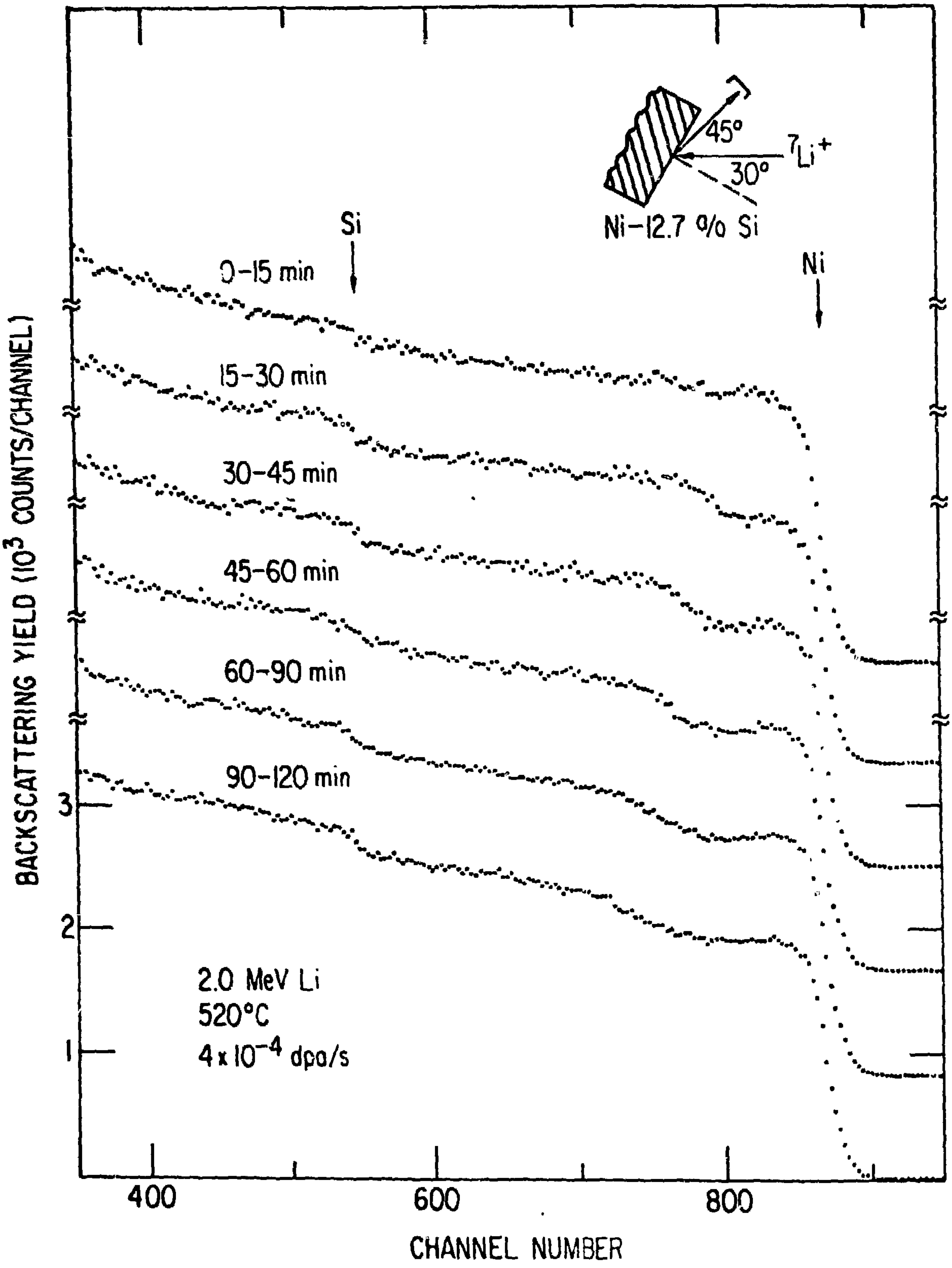
Figure 1. Schematic RBS spectrum for a thin surface layer of Ni_3Si on a Ni-12.7 % Si.

Figure 2. A series of RBS spectra acquired during 1.5 MeV He irradiation of a Ni-12.7 % Si specimen at 465°C.

Figure 3. A series of RBS spectra acquired during 2.0 MeV Li irradiation of a Ni-12.7 % Si specimen at 520°C.


BACKSCATTERED YIELD
ENERGY
$K_{Si}E_0$
$K_{Ni}E_0$
ΔE_{Si}
ΔE_{Ni}
Si
Ni
H^{γ}_{Si}
$H^{\gamma'}_{Si}$
$H^{\gamma'}_{Ni}$
H^{γ}_{Ni}


1.5 MeV He
465°C
45°
$^4He^+$
30°
Ni–12.7 a/o Si
0–15 min
16–31 min
32–47 min
48–63 min
64–79 min
80–95 min
Ni–12.7 a/o Si
BACKSCATTERING YIELD (10^3 COUNTS/CHANNEL)
7
5
3
1
300
400
500
600
700
800
CHANNEL NUMBER


BACKSCATTERING YIELD (10^3 COUNTS/CHANNEL)
CHANNEL NUMBER
400
600
800
1
2
3
Si
Ni
0-15 min
15-30 min
30-45 min
45-60 min
60-90 min
90-120 min
45°
30°
$^7Li^+$
Ni-12.7 a/o Si
2.0 MeV Li
520°C
4×10^{-4} dpa/s