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ION BEAM INDUCED DIFFUSION AND CRYSTALLIZATION IN HIGH DOSE Er IMPLANTED Si

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ABSTRACT

High doses (1×10^{16} - 1×10^{17}/cm^2) of 145 keV and 175 keV Er+ ions were implanted into single-crystal Si using implantation temperatures (T_i) between room temperature and 500°C. Implanted samples were subsequently annealed using thermal annealing at 800°C under vacuum as well as a 1 MeV As+ ion beam assisted annealing (IBAA) at 300°C. During Er+ implantation, we find evidence for ion beam induced mobility for T_i as low as 300°C. A measurable redistribution of the implanted Er also occurs during the IBAA for Er doses greater than 5×10^{16}/cm^2. During Er+ implantation at T_i >300°C a polycrystalline $ErSi_2$ phase is formed. For T_i >400°C the coherent precipitation of $ErSi_2$ phase occurs within the crystalline Si matrix. During subsequent thermal annealing of samples implanted at T_i >400°C, the Er distribution narrows due to Ostwald ripening, and preferential allignement occurs to form a discontinuous buried layer of a single crystalline Er silicide.

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INTRODUCTION

Metal silicides have been widely used in VLSI technology to form uniform and thermally stable contacts, interconnects and low-resistivity gates for high speed applications [1,2 and ref.therein]. Recently the rare-earth silicides have attracted considerable attention because they form the lowest known Schottky barrier hights on n-type Si [3,4] and appear to be potentially attractive as low contact resistance materials for high integration density device structures. Silicides of Tb, Ho, Er, Tm, Yb, Lu and Y have been shown to grow by solid phase epitaxy [5,6], while silicides of Tm, Yb, Lu, Gd and Dy can be formed epitaxially in liquid phase reaction using electron beam melting [5]. Ultra-high vacuum co-deposition of Er and Si, followed by an appropriate thermal annealing has also been successfuly used to form single crystal Er silicide layers [1,2]. Although a variety of buried silicides has been formed using ion beam synthesis [7 and ref.therein], only a few results concerning implantation of rare earth elements have been reported so far [8]. One of the potential difficulties related to the ion beam synthesis of these compounds is a relatively high theoretical value of the sputtering yield Y (Y=5.6 for 145 keV Er+) which may act as a dose-limiting factor. However, a substantial decrease of Y values has been observed for implantations performed at elevated temperatures [9]. The physical mechanism responsible is believed to be a combination of thermally activated (or radiation-enhanced) diffusion and compound formation leading to an increase in

the effective surface binding energy. During formation of erbium di-silicide by interaction of deposited metallic thin films with single crystal Si, the silicon atoms are the dominant diffusing species and the metal atoms do not acquire any significant mobility up to temperatures of 700-800°C [10], a temperature which is considerably in excess of the silicide formation temperatures [6]. One might therefore expect the implanted Er distributions to be stable for the T_i range used in this work. We have systematically investigated implanted Er distributions for a variety of the T_i values to determine whether beam induced or chemical effects are significant in the case of Er implantation into single crystal Si.

EXPERIMENTAL

Er ions for implantation were produced in a sputter ion source. Various doses were implanted at 145 keV or 170 keV into single crystal (111) and (100) oriented Si samples. Careful precautions were taken in order to minimize channeling effects during implantation. The substrate temperature T_i was regulated within the range $RT<T_i<520^{\circ}C$ using a heater located within the sample holder. For most of the implants ion beam current density was below 10 $\mu A/cm^2$ in order to minimize beam heating effects. Implanted samples were subsequently annealed at 800°C for 1 hour in a vacuum of 8×10^{-7} Torr. Ion beam assisted annealing (IBAA) was carried out using 1.02 MeV As ions. The beam current density was close to 8 $\mu A/cm^2$. The substrate temperature

was monitored during the implantation and maintained close to 300°C. RBS-ion channeling analysis (using 1.2 MeV He ions) and cross-sectional transmision electron microscopy (XTEM) were used to characterize the implanted and annealed samples. X-ray diffraction patterns were measured using a Huber 651/652 Guinier thin film diffractometer. Selected samples were analysed using secondary ion mass spectrometry (SIMS).

RESULTS AND DISCUSSION.

1. Ion beam induced diffusion and segregation.

For 145 KeV Er+ ions the theoretical value of the retention R (defined as the fraction of the implanted dose retained in spite of the sputtering erosion) calculated using the Profile code [11] varies from 100% at a dose of $1x10^{16}/cm^2$ to 51% at a dose of $1x10^{17}/cm^2$. The dose of $1x10^{16}/cm^2$ was therefore used for a systematic investigation of the Rp values for a variety of implantation temperatures T_i. The results are summarised in the Fig.1 where the average experimental Rp(ex) values, normalised to the theoretical value of Rp(th)=569 Å [11], are plotted as a function of T_i. As shown in Fig.1 at low temperatures the ratio of Rp(ex)/Rp(th) is approximately 1. For T_i close to 300°C, values determined for Rp are not reproducible because they depend strongly on the ion beam current density and dwell time. For T_i >350°C, the ratio Rp(ex)/Rp(th) is quite reproducible and is reduced to 85%. The corresponding

channeling spectra for the Si substrate (not shown) suggest that the observed decrease in Rp(ex) for $T_i > 350^{\circ}C$ is related to the dynamic annealing process which occurs during implantation and is strongly dependent on T_i. Consequently the observed mobility of Er atoms for $T_i > 300^{\circ}C$ might be interpreted as resulting from a defect mediated diffusion mechanism. This temperature is at least $400^{\circ}C$ below the minimum temperature required for the thermaly activated Er diffusion to become observable [10].

In order to get more insight into the ion beam induced diffusion effects the samples implanted with 145 keV Er+ ions at $RT < T_i < 200^{\circ}C$ were exposed to the thermal annealing as well as to the IBAA at the temperature of approximately $300^{\circ}C$. For the Er doses used in this work thermal annealing at $300^{\circ}C$ does not modify the implanted Er distributions. At the same temperature of $300^{\circ}C$ the IBAA does not lead to any measurable modification of the Er distribution for the Er dose of $1 \times 10^{16}/cm^2$. However, a significant Er redistribution occurs during IBAA for an Er dose of $8 \times 10^{16}/cm^2$. The IBAA was carried out in two steps, each step corresponding to a dose of 5×10^{15} As ions/cm^2. The resulting solid phase recrystallization and the Er segregation towards the surface are shown in Fig.2. The observed average growth rate corresponding to the first IBAA step is about 45 nm per 5×10^{15} ions/cm^2, a value which is about a factor 6 higher than that reported for (111) Si recrystallized using 600 keV Kr++ at $350^{\circ}C$ [12]. The growth rate slows considerably during the second IBAA step and no regrowth is observed during further

irradiation. This suggests that interface breakdown has occured due to Er concentration reaching a limiting value [13]. The results shown on Fig.2 indicate that the redistribution of Er atoms occuring during the IBAA affects the totality of the Er profile in a manner which is not related to sputtering. The redistribution is also not related to the position of the recrystallization front. The mechanism of the observed concentration dependent, ion beam induced segregation of unbound Er atoms is not understood at the moment. It is believed however that both radiation induced phenomena described above may be responsible for the observed decrease in Rp(ex) at temperatures of 300°C or higher.

2. Formation of the polycrystalline phase.

Contact reactions between Si substrate and deposited Er metal have been shown to occur in a narrow temperature range around 390°C for (100) Si and 480°C for (111) Si [6], leading to the formation of a polycrystalline di-silicide as a first and apparently last phase [14]. Fig.3 shows the X-ray diffraction patterns for the (111) Si substrate implanted with the Er+ ions at the temperatures RT<T_i<350°C. The two principal lines corresponding to the diffraction angles of Θ_1=13.6° and Θ_2=17.5° have been identified as corresponding to the $ErSi_2$ phase [15]. Both lines become observable for T_i>250°C. With the increasing T_i the relative intensity of the two lines vary as the Θ_2 line becomes predominant, indicating that the growth is

orientation dependent.

Assuming that formation of the di-silicide phase leads to an increase of the surface binding energy and to a decrease of the sputtering coefficient [9] one would expect the retention R of Er to be strongly dependent on T_i. This effect is clearly seen on the Fig.4. The Er distributions in the "as implanted" state were measured in the center (a) and at the edge (b) of the same (111) Si sample pre-heated up to 325°C and implanted ($1x10^{17}/cm^2$, 145 keV Er+) using beam current density of 46 $\mu A/cm^2$. From the comparaison between the corresponding X-ray diffraction patterns (Fig.5) and those shown on the Fig.3 one may estimate the difference of temperature between a and b resulting from the beam heating to be close to 50°C. The corresponding difference in the R values is about 30%. The best-fitting values for the sputtering coefficient (calculated using the Profile code [11]) are Y(a)=3.82 and Y(b)=5.2. We note that the theoretical value of Y corresponding to this experiment is Y=5.6 [11].

3. Formation of the single crystal di-silicide phase.

The single crystal $ErSi_2$ phase can be formed by implantation at T_i>400°C, followed by thermal annealing. The RBS/channeling spectra as well as the XTEM micrographs corresponding to the sample implanted at T_i=500°C with $6x10^{16}/cm^2$ of 170 keV Er+ and subsequently annealed at 800°C in vacuum are shown on Figs.6-7. It may be seen from the Fig.7a that the implantation process leads to formation of

precipitates of various sizes, correlated to the implanted Er distribution. From a preliminary analysis of TEM diffraction patterns (not shown) the precipitates are found to be small coherent precipitates of single crystalline $ErSi_2$ phase. The corresponding RBS/channeling data show that in the "as implanted" state only a small fraction of precipitates are oriented along the [111] Si surface normal.

During thermal annealing at 800°C the Er distribution narrows due to Ostwald ripening [16] and separated islands of the buried single-crystalline $ErSi_2$, approximately 250 Å thick, are formed (Fig.7b). The crystalline $ErSi_2$ is now preferentielly oriented with its [0001] direction parallel to the [111] surface normal. However, large undissolved ErSi precipitates remain on both sides of the buried layer. A temperature of 800°C appears to be the optimum annealing temperature because higher temperatures lead to an increase in the dechanneling yield and broadening of the Er distribution.

CONCLUSIONS

1. Implantation of Er+ ions into single crystal (111) Si at $T_i > 280$°C results in formation of the polycrystalline $ErSi_2$ phase. For $T_i > 400$°C the $ErSi_2$ crystallizes as coherent precipitates within a crystalline Si matrix.

2. Formation of the di-silicide phase results in an increase in the surface binding energy, causing a 30% decrease of the sputtering coefficient and a similar increase in the

retention of Er.

3. During thermal annealing the morphology of the implanted system dramaticaly changes and a discontinuous buried layer of the single crystalline ErSi is formed.

4. At implantation temperatures $T_i > 300^{\circ}C$, ion beam induced, defect mediated diffusion of the Er atoms strongly influences implanted Er distribution, causing a significant decrease in measured Rp values.

5. During ion beam assisted annealing at $300^{\circ}C$, a concentration dependent surface segregation of the unbound Er atoms is observed.

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FIGURE CAPTIONS:

FIG.1: Normalized ratio Rp(ex)/Rp(th) for 145 keV Er in Si plotted as a function of the implantation temperature (T_i).

FIG.2: RBS/channeling spectra for the <111> Si implanted with 145 keV Er+ at RT<Ti<200^{0}C and subsequently exposed to IBAA at 300^{0}C using the doses of 5×10^{15}/cm^{2} and 1×10^{16}/cm^{2} of 1.02 MeV As ions. The "beam off" spectra correspond to the thermal annealing at 300^{0}C.

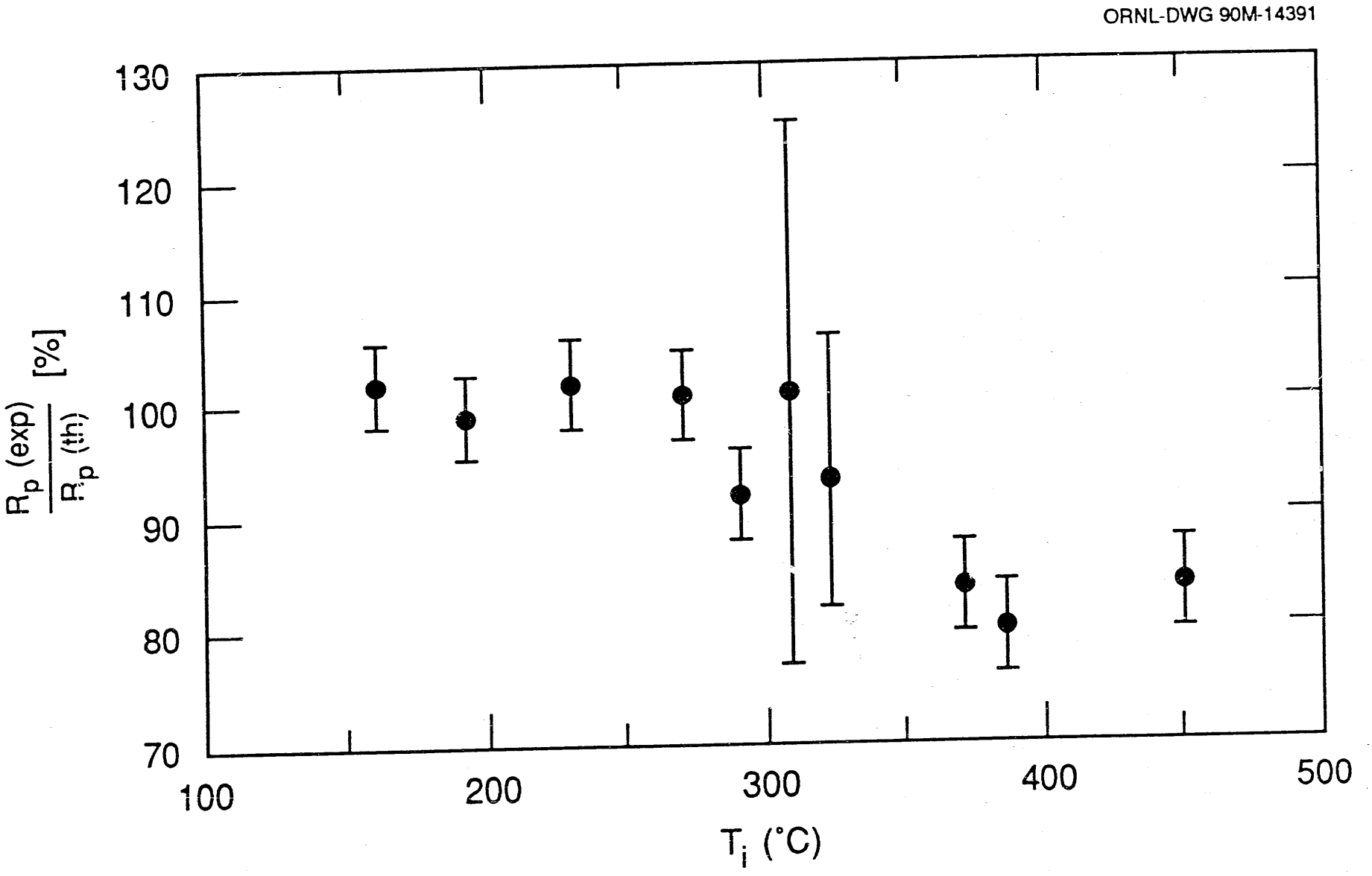
FIG.3: X-ray diffraction patterns for Er implanted <111> Si for RT<Ti<350^{0}C.

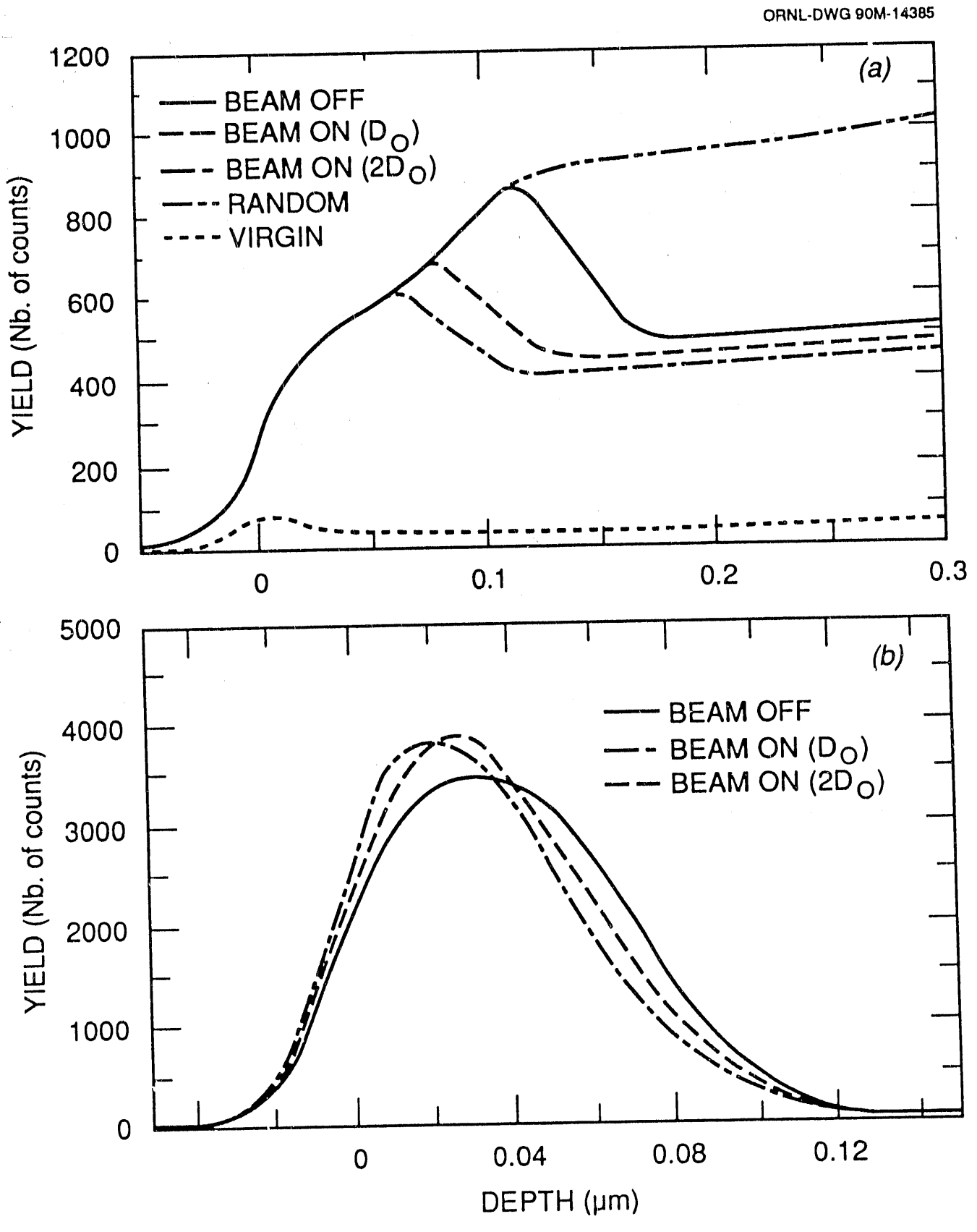
FIG.4: The effect of $ErSi_2$ phase formation during implantation of Er (145 keV, 1×10^{17}/cm^{2}) on the retention R of the implanted Er. The sample pre-heated up to Ti=325^{0}C was exposed to the beam heating. The resulting difference between the surface temperatures in the sample center (a) and edge (b) may be close to 50^{0}C. The corresponding R values are 86% and 54%. The RBS spectrum for 1×10^{16} Er/cm^{2} (R=100%) is shown for comparison.

FIG.5: X-ray diffraction patterns corresponding to the RBS spectra shown on the Fig.4.

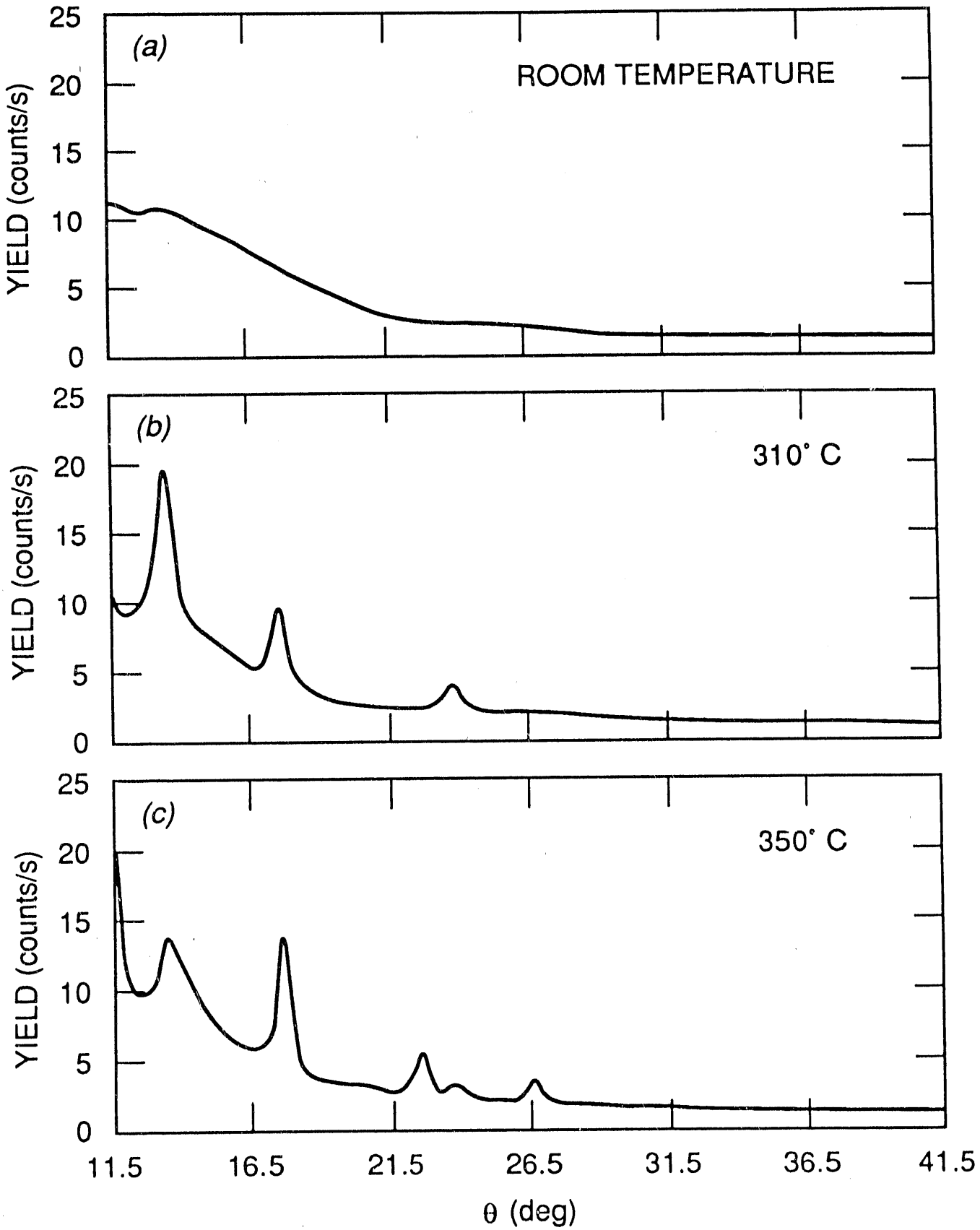
FIG.6: RBS/channeling spectra for Er (a) and Si substrate (b), corresponding to the "as implanted" and annealed <111> Si samples, implanted by Er (170 keV, 6×10^{16}/cm^{2}) at T_i=500^{0}C.

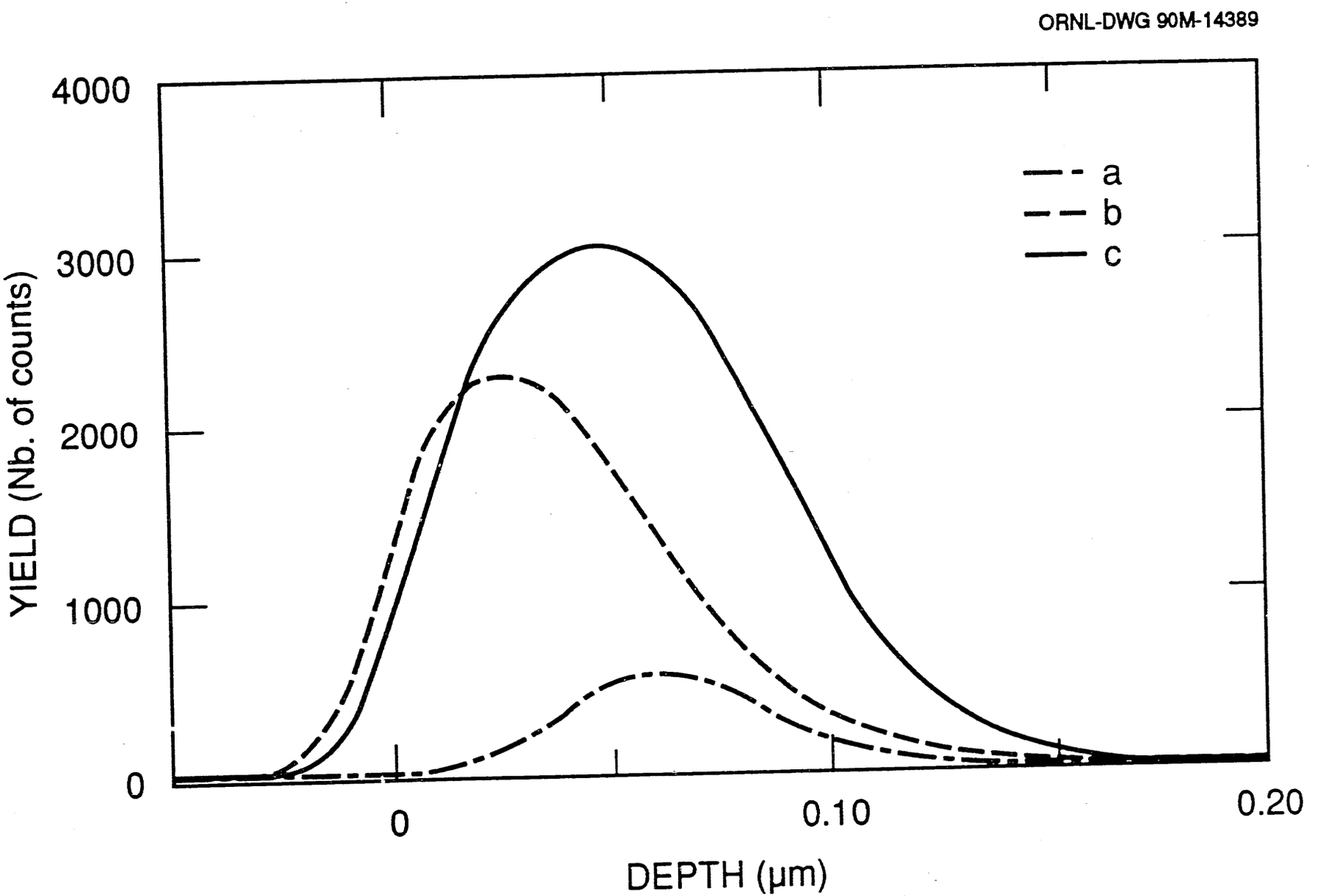
FIG.7: XTEM micrographs corresponding to the RBS spectra shown on the Fig.6: (a) coherent $ErSi_2$ precipitates in the as implanted state; (b) morphology of the system after annealing at 800°C in vacuum.

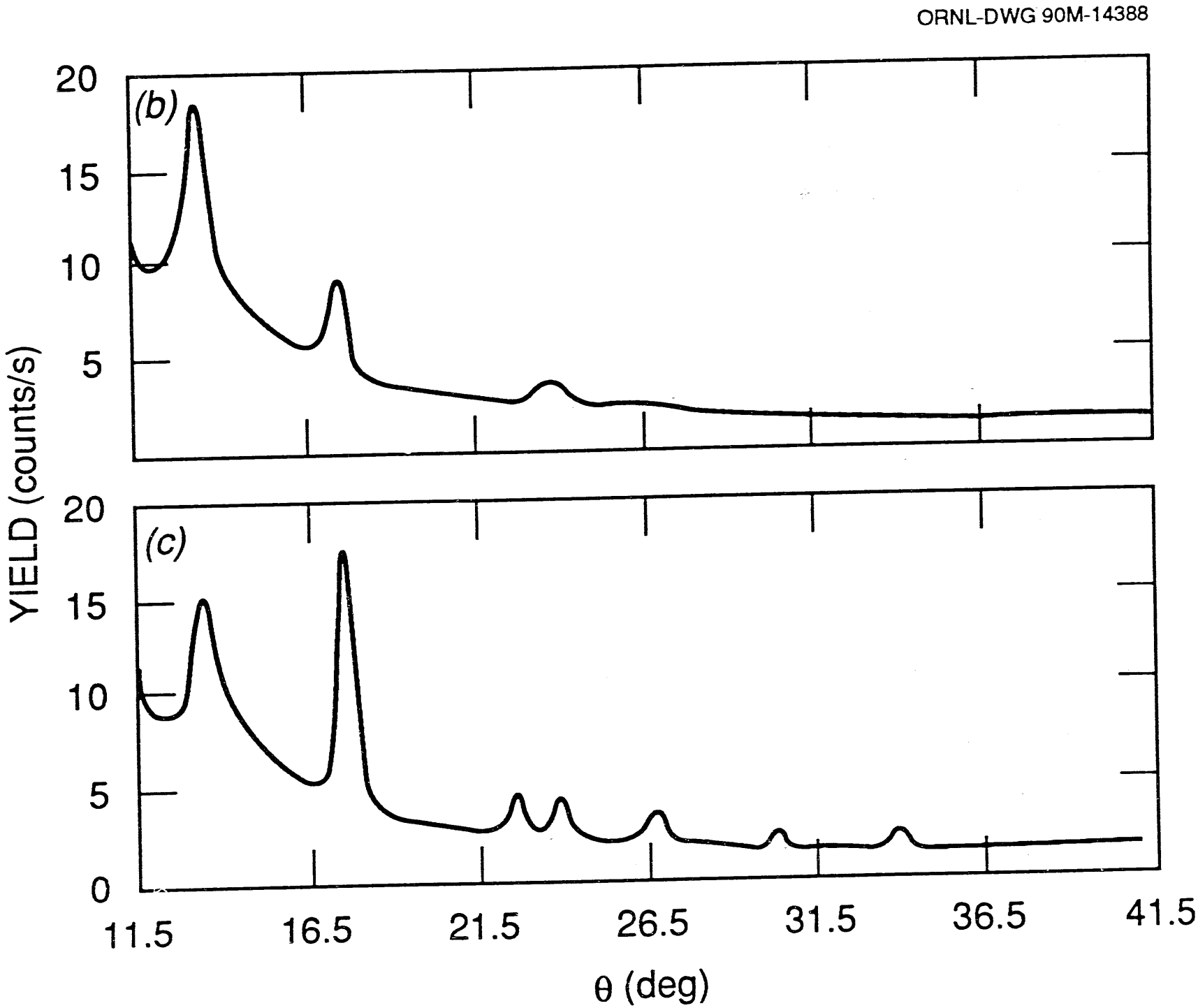

ORNL-DWG 90M-14391
130
120
110
100
90
80
70
100
200
300
400
500
T_i (°C)
$\frac{R_p\ (exp)}{R_p\ (th)}$ [%]


ORNL-DWG 90M-14385
(a)
BEAM OFF
BEAM ON (D_O)
BEAM ON ($2D_O$)
RANDOM
VIRGIN
YIELD (Nb. of counts)
1200
1000
800
600
400
200
0
0
0.1
0.2
0.3
(b)
BEAM OFF
BEAM ON (D_O)
BEAM ON ($2D_O$)
YIELD (Nb. of counts)
5000
4000
3000
2000
1000
0
0
0.04
0.08
0.12
DEPTH (μm)

ORNL-DWG 90M-14390




ORNL-DWG 90M-14389
4000
3000
2000
1000
0
YIELD (Nb. of counts)
a
b
c
0
0.10
0.20
DEPTH (μm)


ORNL-DWG 90M-14388
(b)
(c)
20
15
10
5
0
YIELD (counts/s)
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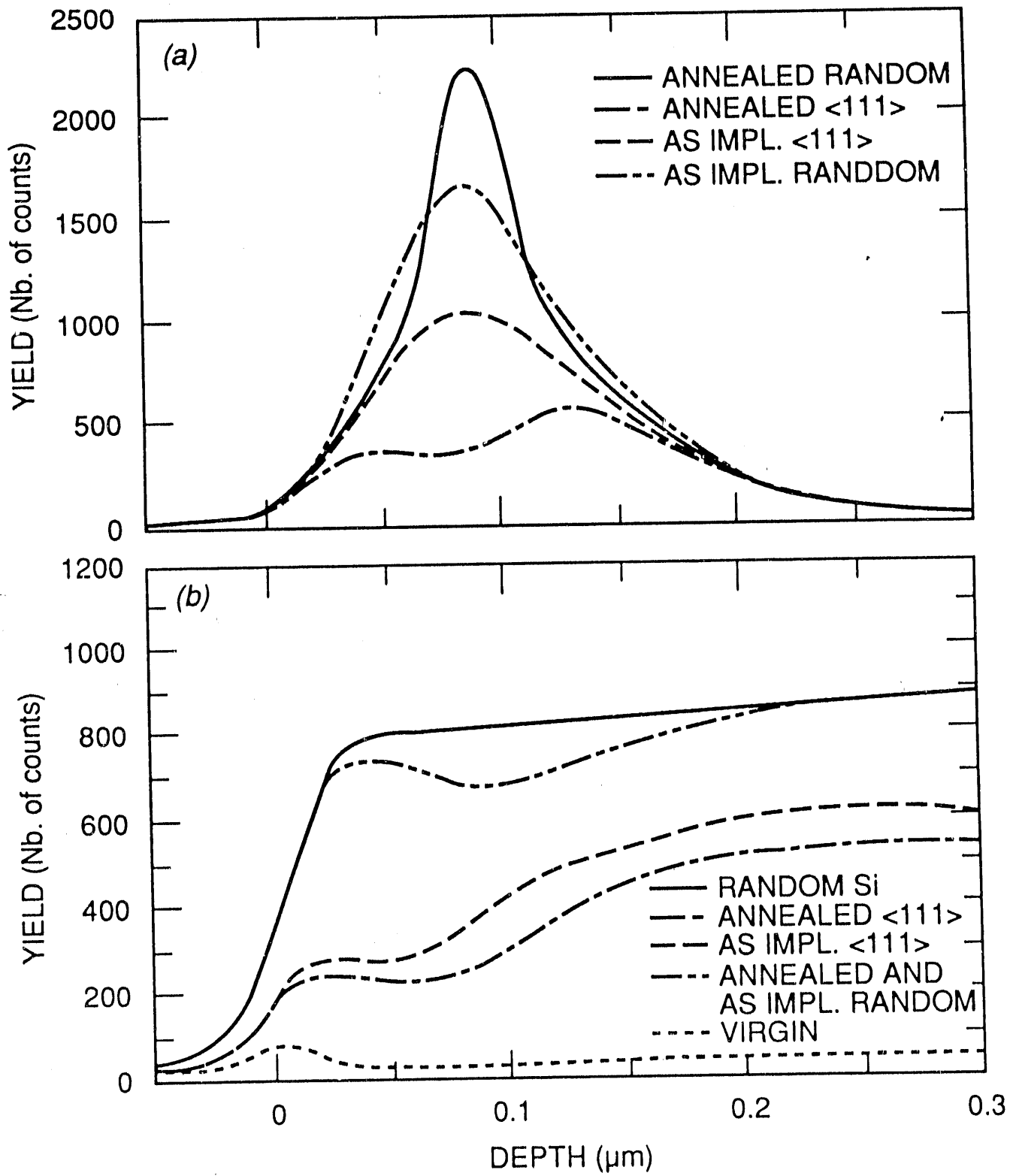
16.5
21.5
26.5
31.5
36.5
41.5
θ (deg)

ORNL-DWG 90M-14387



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