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TITLE INFLUENCE OF ION IRRADIATED $SrTiO_3$ ON THE PROPERTIES OF THIN FILM OXIDE SUPERCONDUCTORS

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INFLUENCE OF ION IRRADIATED $SrTiO_3$ ON THE PROPERTIES OF THIN FILM OXIDE SUPERCONDUCTORS

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Summary

The quality of high temperature superconducting thin films is dependent on the structure of the substrate used. The present work examines the effects of radiation damaged $SrTiO_3$ substrates on the properties of $Y_1Ba_2Cu_3O_7$ thin film superconductors. Prior to film deposition, single crystal $SrTiO_3$ substrates were cooled to 77 K and irradiated with 400 keV Ne ions to doses of $1x10^{15}$ and $1x10^{16}$ ions/cm^2. Following deposition the film/substrate couples were annealed in "wet" oxygen at either 850 or 900 ^oC. Films on substrates irradiated at high doses showed an increase in transition width from 2 to 8 degrees and lowered transition temperature from 92 to 65 K relative to films on low dose and unirradiated substrates. These differences are discussed in terms of results obtained from high energy and Rutherford

backscattering (RBS) and channeling experiments, scanning electron microscopy (SEM) observations and X-ray diffraction data (XRD).

Introduction

It has been well documented that the quality of thin film high temperature superconductors (hTS) is critically dependent on crystallographic orientation. One of the most favorable materials for the epitaxial growth of good quality HTS films is <100> oriented $SrTiO_3$ substrates [1,2,3]. However, the lattice matching between (100) planes of $SrTiO_3$ and (001) planes of $YBa_2Cu_3O_7$ is not perfect and interface strain is anticipated to effect the ultimate epitaxy of the HTS film [3]. Based on these observations we have chosen to examine the effect of growing thin film $YBa_2Cu_3O_7$ superconductors on (100) $SrTiO_3$ substrates that have been heavily damaged or amorphized by ion irradiation. A recent study has shown that $SrTiO_3$ is amorphized by 540 keV Pb ions at a dose of 1×10^{15} ions/cm^2, and the amorphous layer regrows epitaxially with a relatively low temperature anneal (<500 ^{o}C).[4] In the present work we explore the effects of radiation damaged $SrTiO_3$ substrates on the fabrication of thin film oxide superconductors.

Experimental details

Single crystal <100> $SrTiO_3$ substrates were irradiated at 77 K with 400 keV Ne ions to doses of 1×10^{15} and 1×10^{16} ions/cm^2. The projected range of Ne at this energy was calculated with TRIM [5] to be 0.39 μm with the maximum damage at 0.368 μm. TRIM also indicated that the numbers of displaced target atoms per Ne ion (dpa) at the surface and the maximum were 0.195 dpa and 1.95 dpa for the low dose and 0.613 dpa and 6.13 dpa for the high dose.

The initial step in the production of superconducting thin films was the electron beam co-evaporation of Y, BaF_2 and Cu onto both irradiated and non-irradiated <100> $SrTiO_3$. The evaporation took place in a vacuum of $5x10^{-8}$ torr with the deposition rate of each component controlled by a separate quartz crystal monitor. The as-deposited stoichiometry was determined by Rutherford backscattering spectroscopy (RBS) measurements using 6 MeV alpha particles to be $Y_1Ba_{1.8}Cu_{3.06}$.

The film/substrate couples were then annealed at a maximum temperature of either 850 or 900 ^oC. In the 850 ^oC anneal, the films are heated in a dry oxygen flow at 750 ^oC for 1 hour, followed by 1 hour at 850 ^oC in flowing oxygen which had been bubbled through de-ionized water ("wet" oxygen anneal) and slowly cooled to room temperature in dry O_2. The 900 ^oC anneal consisted in heating and maintaining the film at 900 ^oC in "wet" oxygen for 45 minutes, followed by a slow cool to 25 ^oC in dry O_2.

The films were characterized by four-point resistivity, RBS, high energy backscattering [6], ion channeling, x-ray diffraction (XRD) using both a position sensitive detector spanning 4-124 ^{o} 2θ and a standard back reflection goniometer, and scanning electron microscopy (SEM). All results are compared to those obtained from reference samples which were produced on undamaged substrates.

Results and discussion

Channeling of low energy He ions in the <100> direction was used to measure the depth distribution of the disorder in the substrates produced by the irradiations. Figure 1 shows the channeling results obtained on $SrTiO_3$ using 2.2 MeV He particles. These data indicate a partial disorder following the low dose irradiation and the formation of a 5000 Å thick layer with complete dechanneling for the high dose irradiation. The $1x10^{15}$ Ne/cm^2 data compared to the total target displacements calculated with TRIM suggest that the minimum dpa necessary to heavily damage the $SrTiO_3$ ranges between 0.19 and 0.6. The channeling yield for the $1x10^{15}$ Ne/cm^2 data increases slowly in the first thousand Å of the substrate, reaches the random yield and then decreases. In the high dose implantation case the yield from the first 5000 Å is the same as the random yield which is consistent with the presence of an amorphous or heavily damaged layer on the surface.

The state of the substrate had a strong influence on the superconducting properties of the film produced on it. This is illustrated by the four-point probe measurements shown in Fig. 2. These data show very little difference in the transport properties between the reference and $1x10^{15}$ $ions/cm^2$ samples for both anneals. The samples exhibit a narrow transition (1 K width) and zero-resistivity at about 92 K for the 850 ^{o}C anneals. The transition temperature for the 900 ^{o}C anneals was 87 K. The substrates irradiated at

$1x10^{16}$ Ne/cm^2 display a deterioration in their superconducting transport properties indicated by a broadened transition (8 K) and a decreased T_c (60 - 65 K). With the exception of the $1x10^{15}$ Ne/cm^2 damaged substrate annealed at 850 ^{o}C, the room temperature resistivity is observed to increase with the dose and the annealing temperature.

The x-ray diffraction data provide information on the structural disorder in the samples resulting from the substrate irradiation. In both anneals, the films evaporated on unirradiated substrates show the presence of the $YBa_2Cu_3O_7$ (123) phase, with some mixing of other phases including $Y_2Ba_4Cu_8O_{16}$ (248), and possibly $Y_2Ba_4Cu_7O_{14}$ (247) or Y_2BaCuO_5 (211). This is shown in Fig. 3 for 2θ from 4.4^o to 17^o when the incident x-ray beam is fixed at $\theta=3.8^o$, the Bragg angle for the 123(001) diffraction line. The broad features centered around $2\theta=7^o$ and 9.7^o indicate disorder in the films, which might be originating in transition regions between the differing material phases. The presence of the 123(001) line at $2\theta=7.5^o$ and the 248(002) line at $2\theta=6.4^o$, with the absence of others indicates a preferred growth orientation with the c-axis along the $SrTiO_3$ [100] direction. Following substrate irradiation by $1x10^{15}$ $ions/cm^2$, some film degradation is observed because the relative intensities of the 123(001) or 248(002) lines are diminished with respect to the broad disorder features for both anneals, and the 123(011) line is present in the complete data of the 850 ^{o}C anneal. However, the observed effects are minimal.

A much more pronounced effect is seen in films evaporated on substrates irradiated at $1x10^{16}$ ions/cm^2. The broad disorder features are now negligible and the diffraction patterns indicate principally c-axis aligned material, but the high intensity of the 123(002) and 248(004) lines at $2\theta=15.1^o$ and 13^o respectively show that angular deviation of the c-axis in the film from the $SrTiO_3$ [100] direction is now quite large. The lack of general (hkl) lines in the $\theta=3.8^o$ incidence data, which are present when θ is scanned between 3 and 50^o, indicate that the film orientation is not random but remains preferentially aligned with regard to the superconducting phases c-axes. A possible explanation of this result could be that the crystallization does not proceed epitaxially during the anneals in the high dose irradiation case, but rather grows locally with the c-axis (and possibly the $SrTiO_3$ within the damaged region) varying in some angular range from the underlying $SrTiO_3$ <100> substrate. This is considered in the x-ray pole figure analysis.

X-ray diffraction pole figures were measured in a standard back-reflection goniometer. For each sample, five figure poles were measured: (001), (002), (003), (102)/(012) and (110)/(103). The (003) pole figure overlaps with the (100) pole figure of the $SrTiO_3$ substrate and the (110)/(103) pole figure overlaps with (110) pole figure. Fig. 4 shows the (001) pole figure for the substrate irradiated at $1x10^{16}$ Ne/cm^2 and annealed at 900 ^oC. It has been corrected for defocussing and normalized. It shows a strong maximum at the center and broad maxima at either side at a tilt of approximately 45°. The pole figures of all the specimens showed essentially the same qualitative result, i.e. that the superconductor is highly oriented with the c-axis normal to the film. The (110)/(103) pole figures also show that the superconductor film is also aligned in the plane with the substrate although no distinction is apparent between the a and b axes. The quantitative results show that the degree of alignment is high in the unirradiated and low dose samples but decreases markedly in the high dose samples. In terms of the intensity of the (001) reflection at the central maximum, the 850 °C samples show 50 times random unirradiated, 120 times random at low dose but only 3 times random at high dose. The 900 °C samples showed 200 times random unirradiated, 220 times random at low dose but only 10 times at high dose (If there were no preferred orientation i.e. if the sample was randomly oriented, the intensity would be 1 time random everywhere in the pole figure). This loss of intensity of the central maximum appears to occur by a randomization of the orientation of the superconductor because no other definite preferred orientations appear in the pole figures.

High energy channeling experiments using 8.8 MeV alpha particles have been performed with the beam aligned along the [100] axis of the $SrTiO_3$. Results are presented for the 900 °C anneal in Fig. 5. Both the high energy and low energy portion of the data show no significant difference between the Ba, Y, Cu, and O signals from the reference film and the film grown on the substrate irradiated with $1x10^{15}$ Ne/cm^2. This was also true in the samples annealed at

850 °C. However, dechanneling can be observed at the front edge of the substrate Sr and O signal for both irradiated substrates. In the case of the $1x10^{16}$ Ne/cm^2 irradiation, the channeled spectrum reaches the random one in the film and in the $SrTiO_3$ for both anneals suggesting that the film and a small depth of the $SrTiO_3$ are not aligned with the underlying substrate, consistent with the x-ray diffraction data.

SEM results presented in Fig. 7 show that the samples annealed at 850 °C have a needles and pebbles structure while the 900 °C samples display fewer needles and some small holes on a smoothed background. The lower density of needles observed following the 900 °C anneal suggests a higher density of c-axis orientation. At both temperatures, no large differences between the reference and the $1x10^{15}$ ions/cm^2 samples were observed. However, in the case of the high dose implanted samples, for both anneals, cracks parallel to the needles were present suggesting that the films on the highly irradiated $SrTiO_3$ were under tension during the annealing process.

These results clearly show that the quality of the superconducting film is dependent on the crystalline quality of the substrate. In the case of the $1x10^{15}$ ions/cm^2 Ne irradiated $SrTiO_3$, the partial disorder created by the implantation was partially cured at 850 and 900 °C by recrystallization of the damaged area. The film evaporated on top did not show any change in T_c but did show a factor of 2 improvement in epitaxy relative to unirradiated substrates based on x-ray pole figures. However, in the case of the

$1x10^{16}$ ions/cm^2 Ne implanted substrates, a deterioration of the superconductivity is observed in terms of a lower T_c. The presence of the cracks in the films at both anneals might be related to the origin of this degradation. It is possible, as suggested by the XRD data, that crystallization occurs on top of the damaged $SrTiO_3$ but with the film's crystal axes tilted with respect to the underlying substrate. Under this assumption, channeling could not be achieved in the first few microns of the sample. Presently, experiments are being carried out with O implantation to determine if the non crystallization of the amorphous layer is due to a chemical or a crystalline effect. In addition, experiments are being performed in the low dose range to further examine the substrate dose dependence on the epitaxial growth of $YBa_2Cu_3O_7$ films .

Conclusion

Studies have been carried out on $Y_1Ba_2Cu_3O_7$ films evaporated on Ne implanted $SrTiO_3$ at 400 keV and doses of $1x10^{15}$ and $1x10^{16}$ ions/cm^2. Normal thin film superconductors can be produced on the low dose irradiated substrates by annealing at either 850 or 900 ^oC. X-ray pole figure analysis shows a marked improvement in the epitaxial quality of these films relative to films on unirradiated substrates. For the high dose substrates the damaged layer does not grow back epitaxially and the thin film superconductors have lowered Tc and degraded morphology.

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Figures

Fig. 1. Ion channeling results in implanted and virgin $SrTiO_3$.

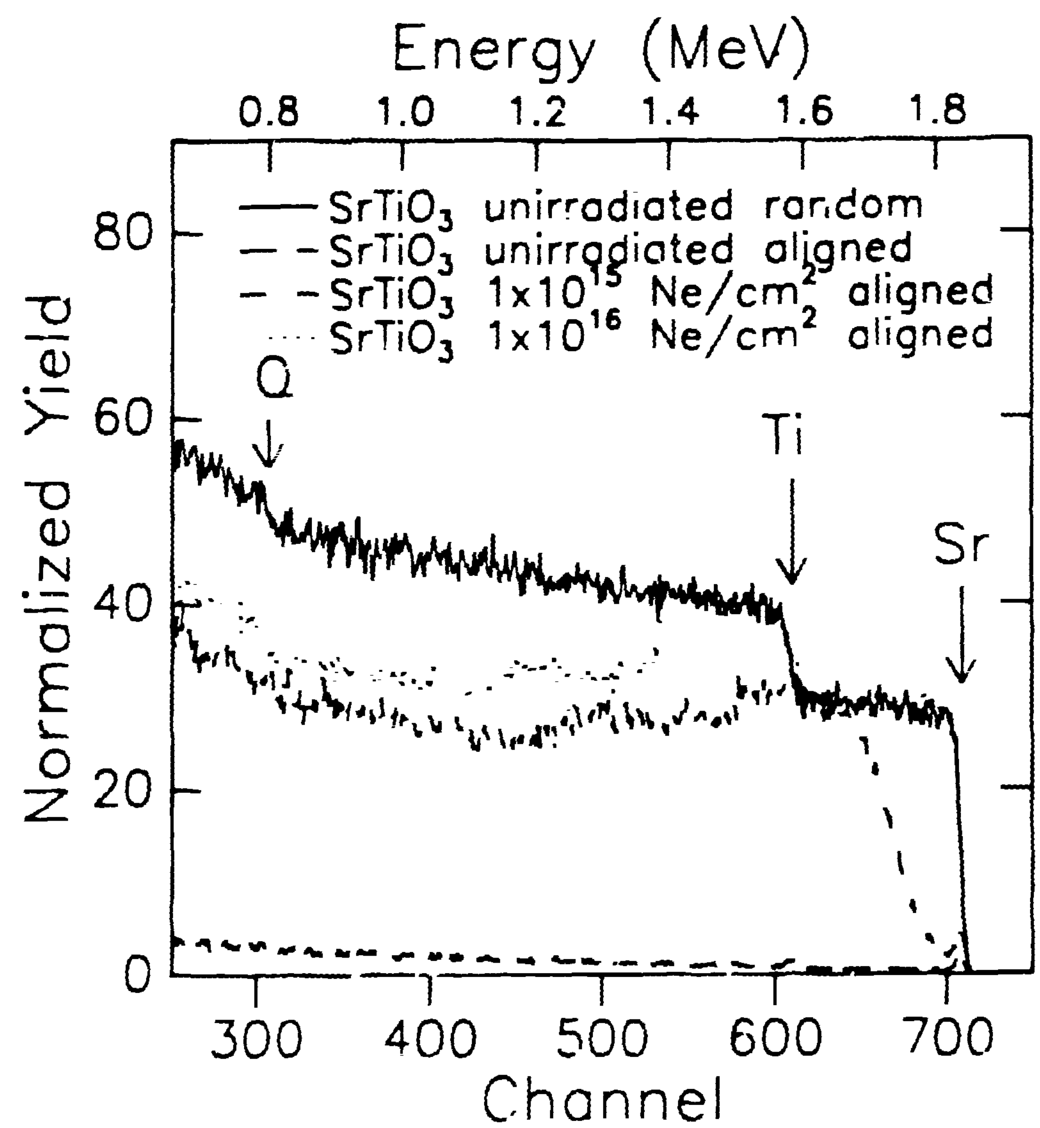
Fig. 2. Resistance versus temperature of $Y_1Ba_2Cu_3O_7$ films for the 850 and 900 ^oC anneals on unirradiated and $1x10^{15}$ Ne/cm^2 implanted $SrTiO_3$ (a) and on $1x10^{16}$ Ne/cm^2 implanted $SrTiO_3$.

Fig. 3. X-ray diffraction patterns of $Y_1Ba_2Cu_3O_7$ on $SrTiO_3$ following the 850 ^oC and 900 ^oC anneals on unirradiated (a), implanted at $1x10^{15}$ Ne/cm^2 (b), implanted at $1x10^{16}$ Ne/cm^2 (c) substrates.

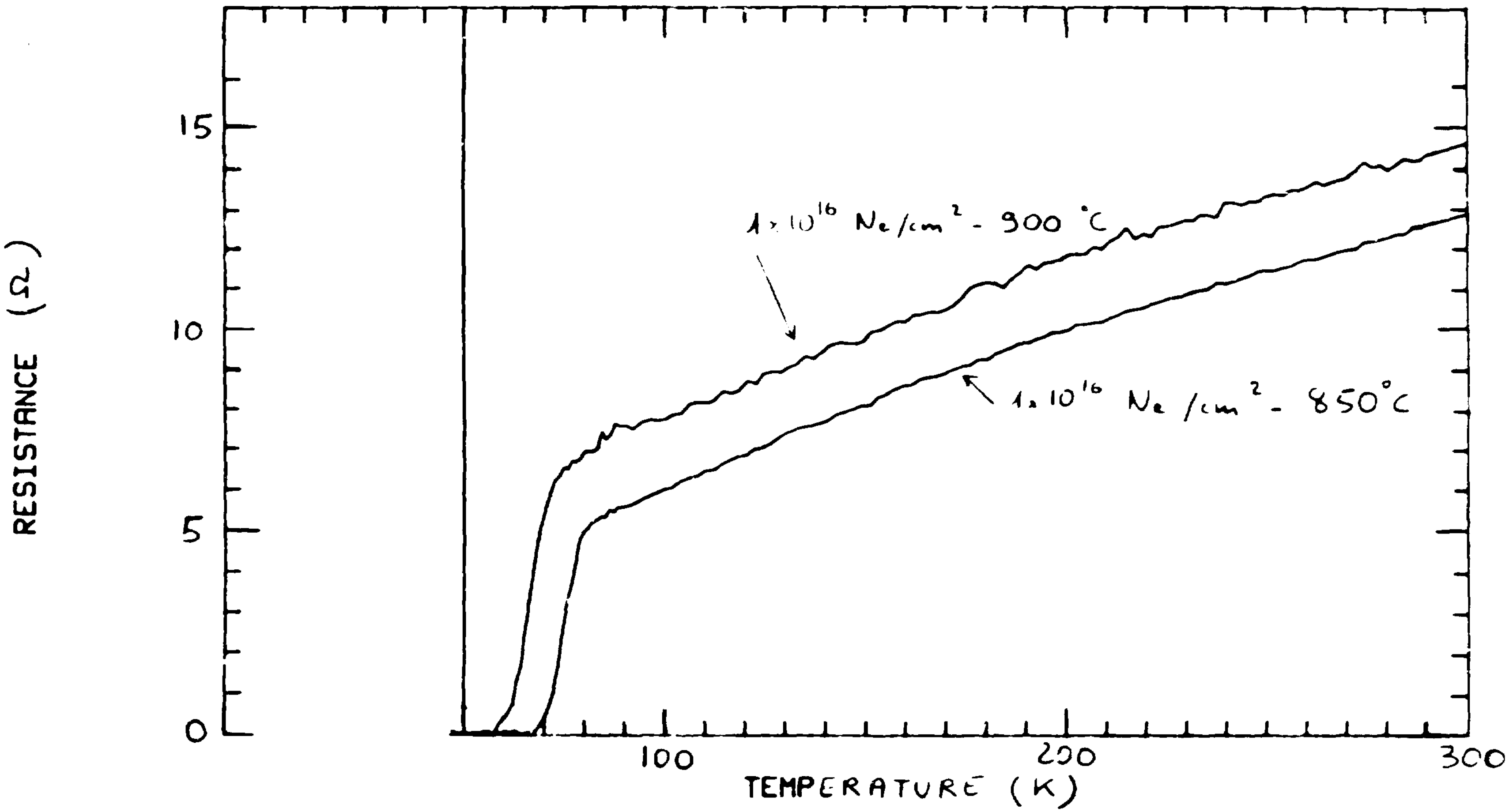
Fig. 4. (001) x-ray pole figure for the $Y_1Ba_2Cu_3O_7$ film deposited on the substrate irradiated at $1x10^{16}$ Ne/cm^2 and annealed at 900 ^oC (the scale of grey indicates the number of times random intensity).

Fig. 5. Ion channeling results in the $Y_1Ba_2Cu_3O_7$ film deposited on virgin and implanted $SrtiO_3$ for the 900 ^oC anneal.

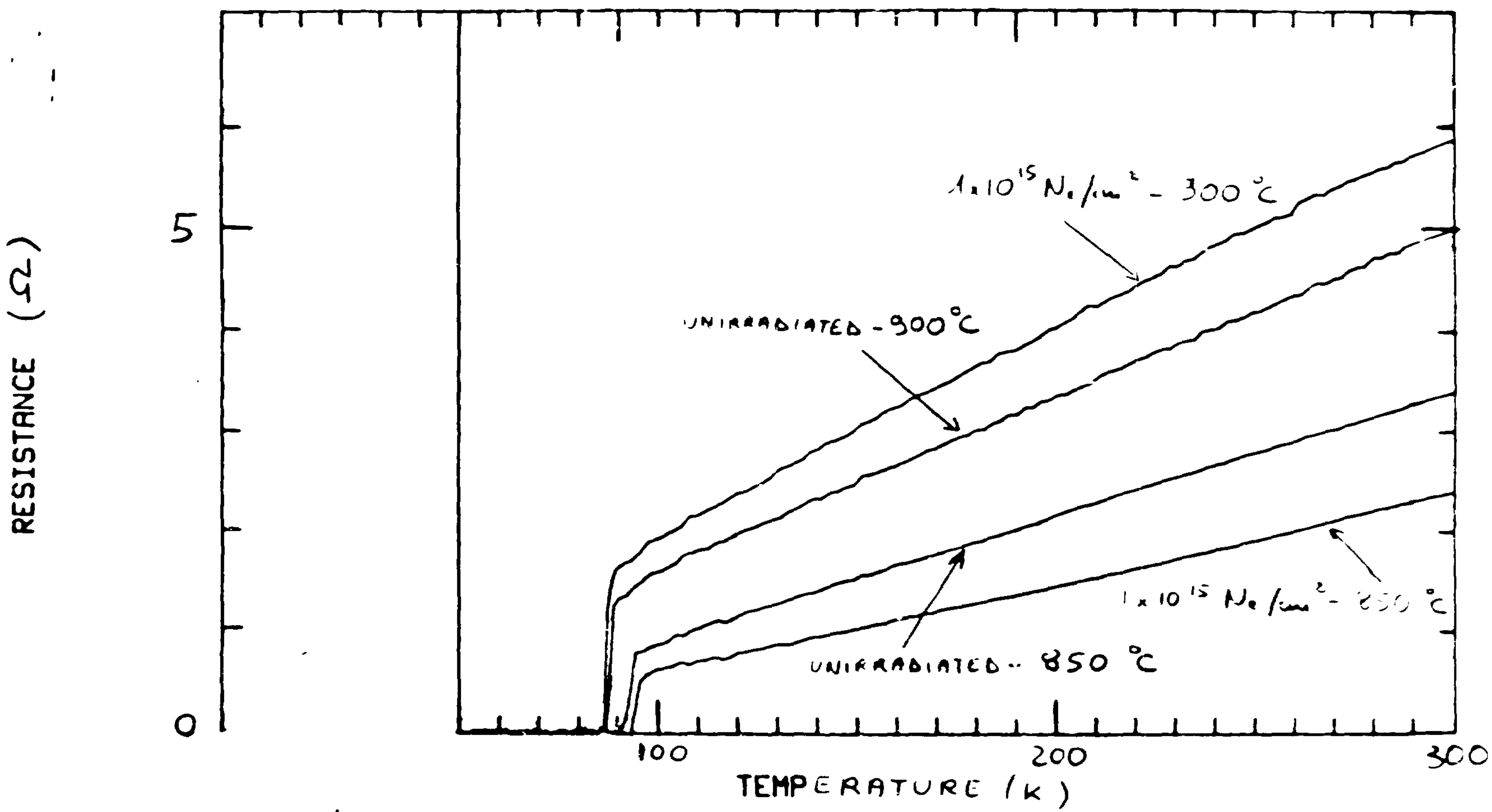
Fig. 6. SEM micrographs of the film evaporated on the virgin and implanted $SrTiO_3$ for the 850 and 900 ^oC anneals.



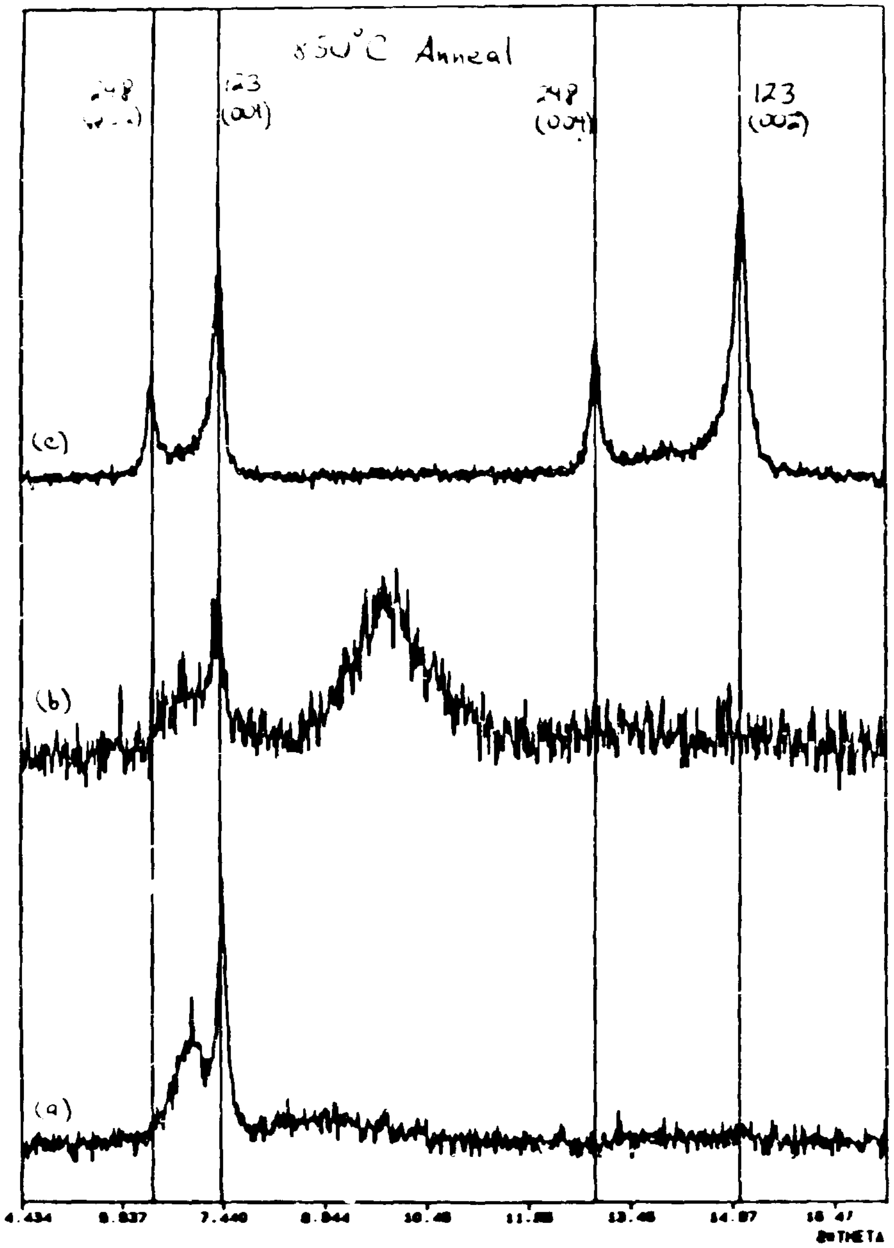
Energy (MeV)
0.8
1.0
1.2
1.4
1.6
1.8
SrTiO3 unirradiated random
SrTiO3 unirradiated aligned
SrTiO3 1x10^15 Ne/cm^2 aligned
SrTiO3 1x10^16 Ne/cm^2 aligned
O
Ti
Sr
Normalized Yield
80
60
40
20
0
300
400
500
600
700
Channel



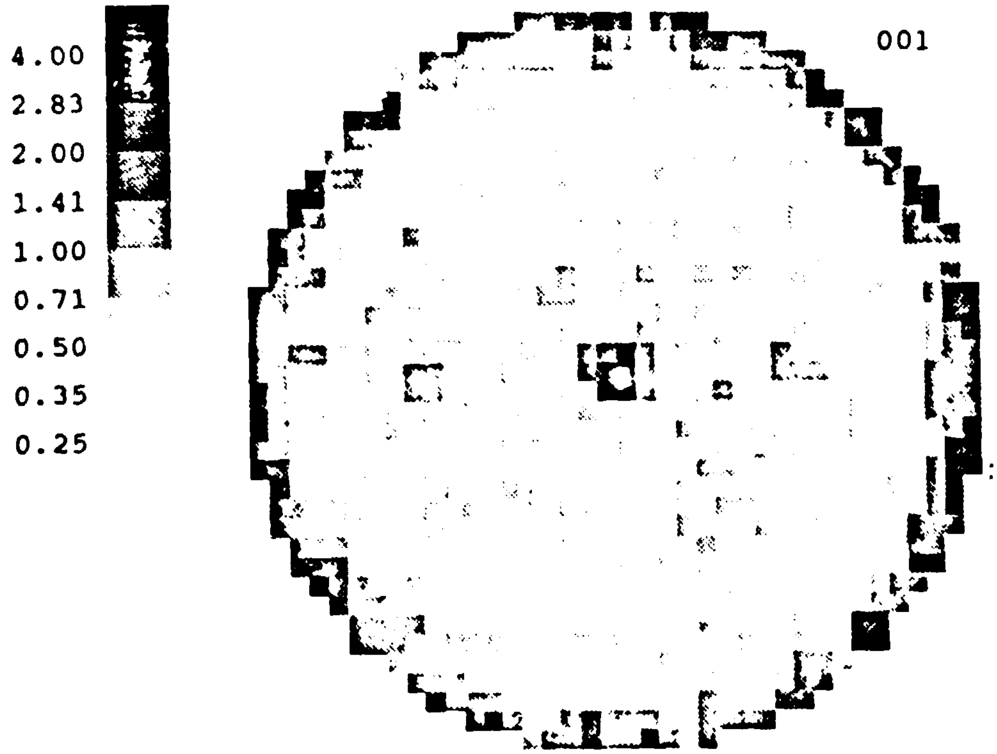
RESISTANCE (Ω)
15
10
5
0
100
200
300
TEMPERATURE (K)
1x10^16 Ne/cm^2 - 900 °C
1x10^16 Ne/cm^2 - 850°C

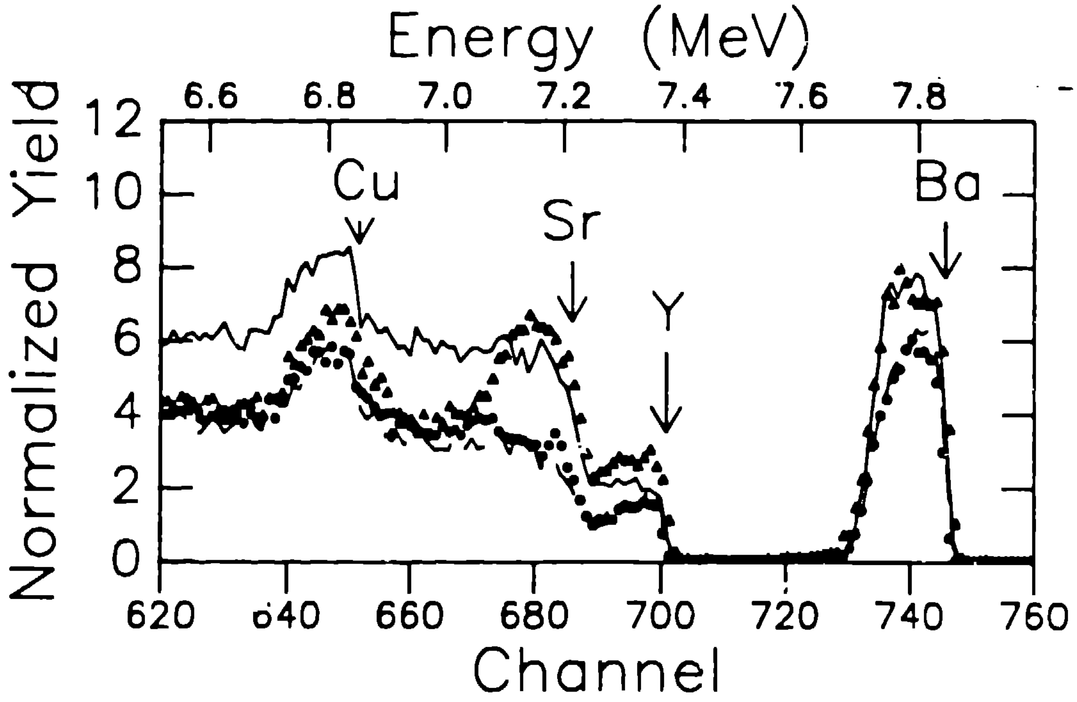


RESISTANCE (Ω)
5
0
100
200
300
TEMPERATURE (K)
1x10^15 Ne/cm^2 - 300 °C
UNIRRADIATED - 900 °C
UNIRRADIATED - 850 °C

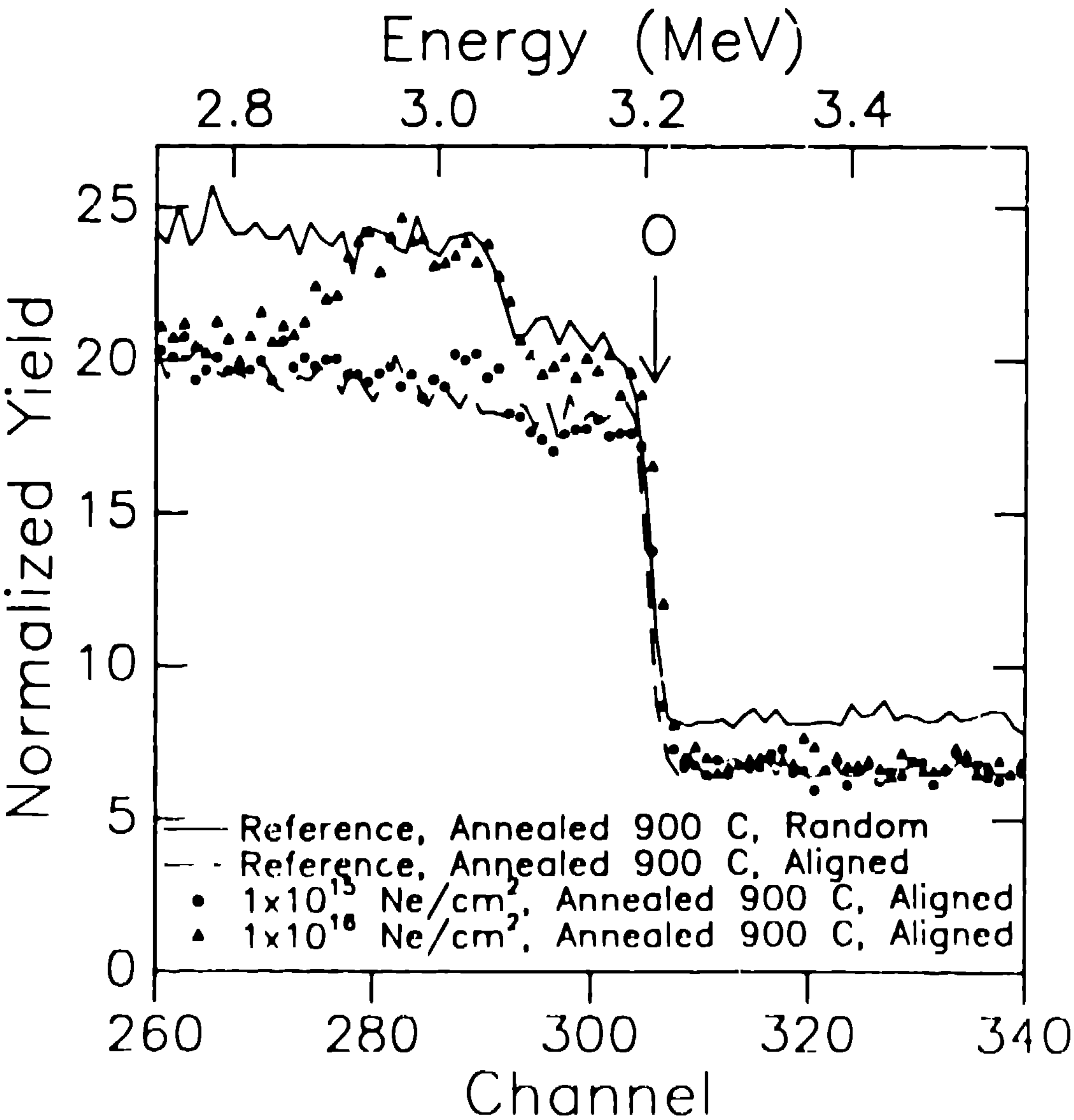

850°C Anneal
248
123
(001)
248
(004)
123
(002)
(c)
(b)
(a)
4.434
7.440
10.45
13.46
14.97
2θ THETA


(002)
123
(c)
(b)
4.440
7.488
10.45
11.87
13.46
14.98
2θ THETA


4.00
2.83
2.00
1.41
1.00
0.71
0.50
0.35
0.25
001

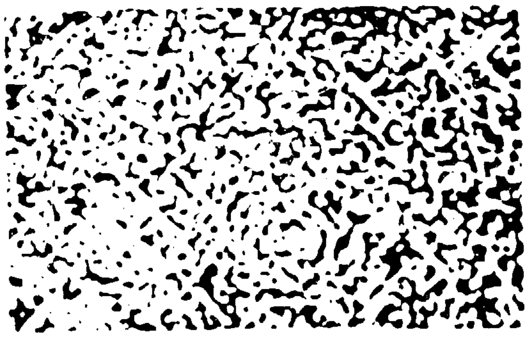


Energy (MeV)
6.6
6.8
7.0
7.2
7.4
7.6
7.8
Normalized Yield
12
10
8
6
4
2
0
Cu
Sr
Y
Ba
620
640
660
680
700
720
740
760
Channel

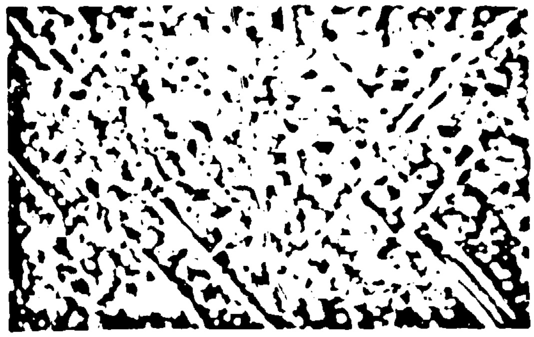


Energy (MeV)
2.8
3.0
3.2
3.4
Normalized Yield
25
20
15
10
5
0
O
Reference, Annealed 900 C, Random
Reference, Annealed 900 C, Aligned
1x10^15 Ne/cm^2, Annealed 900 C, Aligned
1x10^16 Ne/cm^2, Annealed 900 C, Aligned
260
280
300
320
340
Channel

AS-DEPOSITED PLUS ANNEAL

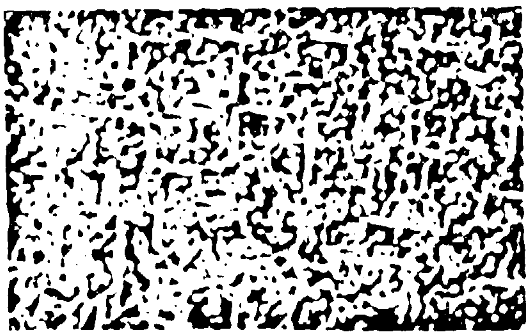


850°C

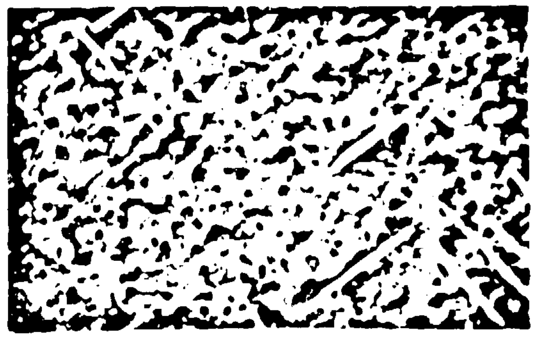


900°C

10^{15} Ne/cm^2 IN $SrTiO_3$



850°C



900°C

10^{16} Ne/cm^2 IN $SrTiO_3$

850°C

900°C

3 µm