Effect of Chemical Polishing on the Electron Field Emission of Niobium Samples and Cavities

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In several experiments on high purity niobium samples and on a 1.5 GHz niobium cavity of the same material the dependence of the electron field emission behaviour on incremental material removal was studied. For the dc field emission measurements and the evaluation of the rf cavity performance the final cleaning step in the surface preparation was a high pressure ultrapure water rinsing followed by a rinsing with electronic grade methanol in a class 100 clean room. The dc experiments showed no systematic dependence of field emission on the amount of material removal, but a significant reduction on surface contamination. For the first time no sites were detected at 100 MV/m on a non heat treated broad area niobium cathode. The rf tests also showed no "depth profile" of field emitting sites. In seven subsequent experiments no field emission loading was encountered and the high field performance of the cavity was always limited by a thermomagnetic breakdown.

1. Introduction

In a series of experiments with single cell 1.5 GHz niobium cavities the benefits of high pressure ultrapure water rinsing as a final cleaning step after chemical surface treatment was recently evaluated. The experiments showed that it was possible to consistently and reproducibly improve the cavity performance to reach peak surface electric fields $E_p \approx 50$ MV/m without field emission loading [1].These measurements indicated that using this advanced cleaning technique surface contamination could efficiently be removed and avoided during subsequent handling. The cavity examined in this particular test series had undergone a post purification heat treatment (T = 1400°C, 4 h) as well as large amounts of material removal (> 200 μm) by both chemical polishing and electropolishing.This is usually not the case for production cavities e.g. at CEBAF, where only approximately 60 μm are taken off the surface. It seemed to be of particular interest to find out whether the favourable field emission behaviour of this cavity was a result of the excessive surface treatments.
Investigations of dc field emission on Nb cathodes seemed to indicate that emission sites usually were connected with surface contaminations, mainly particles of micrometer size. Only after heat treatments "intrinsic" emitter caused by impurity segregation were detected [2, 3]. To our knowledge no experiments had been performed to investigate whether there exists a "depth profile" of field emission sites in commercially available niobium, i.e. if there are weak spots within the surface damage layer of sheet Nb. The results of the high pressure water rinsing rf tests have made such experiments possible because they had shown that with this technique one could eliminate field emission from artificial contamination below $E_p \approx 50$ MV/m. Therefore, in this study a series of 3 different experiments were carried out:

1. A set of niobium samples with different amounts of material removed from the surface by buffered chemical polishing were analyzed by x-ray diffraction to obtain a depth profile of the surface damage layer.
2. The performance of a single cell 1.5 GHz cavity fabricated from the same Nb with RRR (Residual Resistivity Ratio) ≥ 250 has been studied. Different amounts of material were successively removed followed by a high pressure water rinsing. In rf tests the surface resistance, peak surface electric/magnetic field, and field emission behaviour were investigated.
3. DC field emission behaviour was measured on 6 niobium samples which had undergone similar surface processing treatments as the cavity. In the dc tests the density of sites, threshold fields, and Fowler–Nordheim characteristics were measured. In the following chapters the results of these investigations are reported.

2. X-ray diffraction measurements

Ten samples of rolled, polycrystalline high purity niobium sheet of dimensions 25.4 mm * 25.4 mm * 3.2 mm were chemically treated resulting in a surface layer removal between 7 μm and 130 μm. The measurements [4] to assess the structure of the material after incremental material removal were carried out on a θ:2θ–diffractometer using Zr–filtered Mo radiation of 17.4 keV. This configuration allowed only for grains to diffract which are parallel to the specimen surface. All specimens were probed under identical conditions to a depth ranging between 5 μm and 10 μm.
The diffraction patterns produced from the different samples did not show a systematic relationship between the amount of material removal and the characteristics of the diffraction signals such as line width, line shift or variation in background. The diffraction patterns showed that all specimens were textured which had to be expected for a rolled sheet metall. The texture direction and the degree of texture varied randomly from sample to sample. The niobium sample with the smallest amount of material removal showed the largest signals indicative for grains with their 100 planes parallel to the surface.
From this set of measurements it can be concluded that already a material removal of about 5–10 μm from the surface of rolled sheet niobium eliminates the damage layer as far as crystal structure is concerned. Of course this method does not allow any conclusions about the depth profile of defects causing deteriorations of the superconducting properties of the material in rf fields.

3. Cavity measurements

For this investigation a single cell 1.5 GHz cavity of the Cornell/CEBAF shape was fabricated from high purity niobium with RRR ≥ 250. This series of experiments consisted of the measurements of Q_o at T = 2 K as a function of peak surface electric fields on the cavity surface after material had been successively removed by buffered chemical polishing. A solution of equal parts of hydrofluoric (49%), nitric (69%), and phosphoric (85%) acids was always used. In a last preparation step the cavity was rinsed for ≈ 30 min. with high pressure (≈ 85 bar) ultrapure water (resistivity > 18 MΩcm). A final rinsing was performed in a class 100 clean room with electronic grade methanol.
The results of these measurements are shown in figures 1 to 3 and can be summarized as follows. In seven experiments with incremental material removals between 4 μm and 190 μm no field emission was observed except for the last experiment when slight emission occured at $E_p \geq 45$ MV/m (figure1). The cavity was always limited by a thermomagnetic

breakdown. With increasing material removal the field level at which the breakdown occured increased monotonically (figure2). Except for the last experiment the residual surface resistance decreased monotonically with increasing material removal (figure3). The removal of only a very thin surface layer (4 μm) caused "strong heating" of the superconducting surface, i.e. a strong Q_0 degradation with increasing field level.
From these experimental observations one can draw the following conclusions. Up to peak surface fields of $E_p = 45$ MV/m no "intrinsic" field emitter were encountered. The achievement of higher electrical fields at the niobium surface was prevented by the fact that the cavity field was always limited by thermomagnetic breakdown. Areas of weak superconductivity such as niobium suboxides have been identified in the past as being responsible for quenching a cavity. Suboxides could then also act as emission sites because of a lowered work function. At least it has been found on copper electrodes that copper oxide strongly emits electrons [5]. Therefore, it was unexpected that defects which are responsible for thermal instabilities in the cavity surfaces do not promote electron field emission. The model of a "layered material" with a decreasing number and size of defects after increasing material removal seems to be confirmed by both the decrease in residual surface resistance and the increase in quench field levels.

4. DC field emission studies

The experimental technique and measurement procedure which have been developed for the investigation of dc field emission studies on broad area electrodes have been reported in detail elsewhere [6]. In addition, a review talk on dc field emission issues has been given by one of the authors (E.M.) at this workshop [2]. Therefore, here we focus on a short description of the experimental facts of this test series.
Six samples from polycrystalline, high purity (RRR $\geq$ 250) niobium were machined to 16 mm diameter disks with rounded ($r \approx 1$ mm) top edges. These disks were fitted into special niobium holders that are needed for the transfer of the samples into the field emission apparatus. We removed between 4 μm and 84 μm from the surfaces of the "as received" material by buffered chemical polishing as in the case of the cavity surface treatment. Subsequently the samples were rinsed with a high pressure jet of ultrapure water, rinsed in a class 100 clean room with electronic grade methanol, and assembled to a standard sample transport system developed at the University of Wuppertal to prevent a dust contamination. The samples were prepared at CEBAF and measured in the field emission scanning microscope at Wuppertal.
The results of successive FE scans between 40 MV/m and 100 MV/m on the high pressure water rinsed samples are summarized in table 1 and figure 4. No systematic dependence between emitter density and material removal up to 84 μm was observed. For 44 localized sites the threshold value of field emission (E_{onset}) scattered with one exception between 25 MV/m and 72 MV/m. Measuring the I–V characteristic of the various emission sites the field enhancement factors ranged from 49 to 239. On average, these β's are larger than on samples after standard surface treatments. The emitting areas S were extracted from Fowler–Nordheim plots. With a few exceptions S ranged between 10^{-10} and 10^{-16} cm^2. These values are markedly lower than those of standard samples and escpecially cathodes after high temperature (200°C–1400°C) heat treatments [2].
After the broad area scans all FE sites were individually localized with microtip anodes. The obtained SEM images at each site gave a surprising result. A very significant difference between these samples and samples not being exposed to high pressure water rinsing was the absence of emission caused by particles sticking on the surface. The emission always

originated from material irregularities at the surface, usually microscopic and macroscopic scratches. The average emitter density was significantly lower on these samples than on cathodes prepared by standard chemical polishing at Wuppertal. From earlier investigations [6] it is well known that the observed FE sites can be switched off after a high temperature heat treatment at T ≥ 1200°C. Therefore, this type of field emitter are not expected as a serious limit for high gradients in superconducting rf structures.
Now we want to focus on two samples with special properties. Only one emitter at 100 MV/m was found on sample # 10. Despite that excellent result this site was one of the strongest (E_{onset} = 14 MV/m, β = 218) we ever found in our apparatus. On sample # 4 ($\approx$ 23 μm damage layer removal) no sites were detected at 100 MV/m for the first time on a non heat treated broad area cathode (figure 4). In subsequent scans (figure 5) at higher fields no emission site was found at 105 MV/m. The first electron emission was detected close to 120 MV/m. At a field level of 165 MV/m only 9 active FE sites were observed. One of these sites increased its FE activity due to the high field measurements and was active afterwards at 85 MV/m. A selected area (5.0 * 5.0 mm) of this sample surface was emission free even at 140 MV/m (figure 6). Increasing the field up to 215 MV/m switched on 14 new sites. Fowler–Nordheim analysis of these weak sites showed that the field enhancement factor β scattered (with two exceptions) between 18 and 45. In a "reproduction" scan at 140 MV/m it was found that three sites lowered their threshold field after the high field measurements. After careful localization of each site again no particles were visible in the SEM. Because of the poor surface finish of the sample the emitter positions could not be distinguished from the non emitting surface areas.

5. Conclusion

High pressure ultrapure water rinsing followed by rinsing with electronic grade methanol resulted in favourable rf field emission behaviour and the absence of emission caused by particles. A 1.5 GHz high purity niobium cavity was always limited by a thermomagnetic breakdown. The model of a "layered Nb material" with a decreasing number and size of defects after increasing material removal seems to be confirmed by both the decrease in residual surface resistance and the increase in quench field levels. No systematic dependence between emitter density and material removal up to 84 μm was observed in the dc field emission tests at 40–100 MV/m. In contrast to earlier investigations the electron emission always originated from material irregularities without the presence of microscopic particles sticking on the surface. Therefore, no "intrinsic" field emitter were found if surface imperfections are not counted in this category. We believe that a combination of surface smoothening by e.g. electropolishing or electron beam melting and high pressure ultra pure water rinsing might result in a further reduction of electron emission at even higher surface fields.

6. References

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7. Figure captions

Figure 1. Effect of successive material removal on the cavity performance.

Figure 2. Effect of material removal on the peak surface electric field E_{peak}.

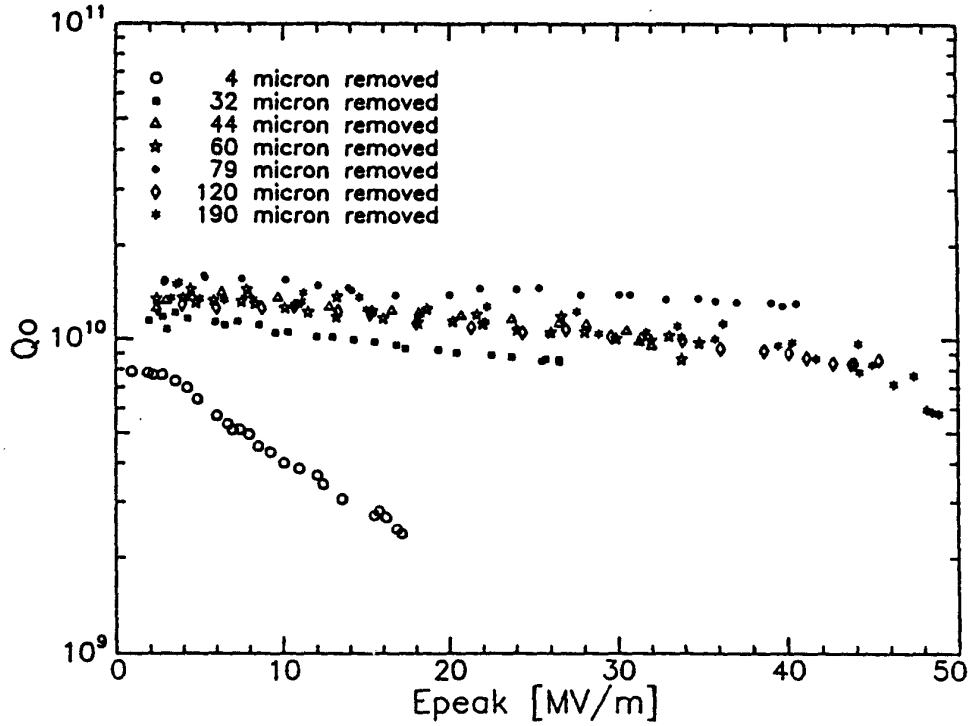
Figure 3. Effect of material removal on the residual surface resistance R_{res}.

Table 1. Field emission parameters of chemical polished and high pressure water rinsed niobium samples. The β and S values were extracted from Fowler–Nordheim analysis. E_{onset} was determined at I = 0.5 nA.

Figure 4. A selection of FE scans (Ø 13.5 mm) on chemical polished Nb samples (#1, #4, #8, #9, #10, #11) as a function of surface damage layer removal between 4 μm and 84 μm. The scans were made at 100 MV/m with a Ø 0.5 mm anode and a limiting current of 10 nA.

Figure 5. Subsequent field emission scans on sample #4 ($\approx$ 23 μm BCP) as a function of applied surface field. Scan parameter: Ø 10.0 mm scan area, Ø 0.5 mm anode, I $\leq$ 10 nA.

Figure 6. High field FE scans on a 5.0 * 5.0 mm area of sample #4 (see also Fig.5).



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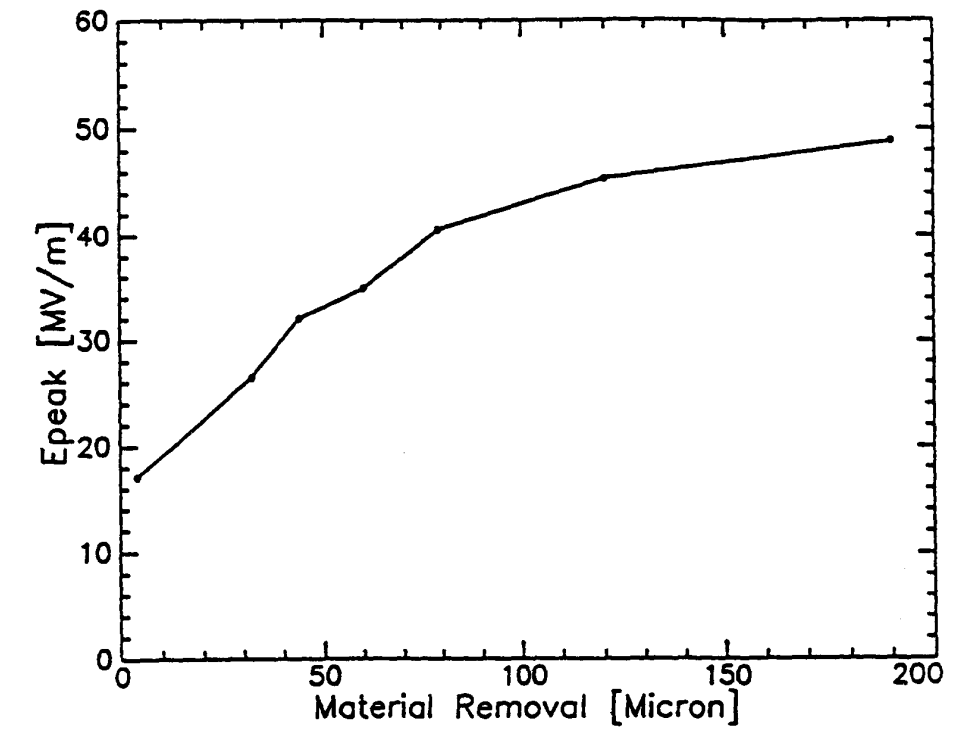

Fig. 2. Effect of material removal on the peak surface electric field E_{peak}.

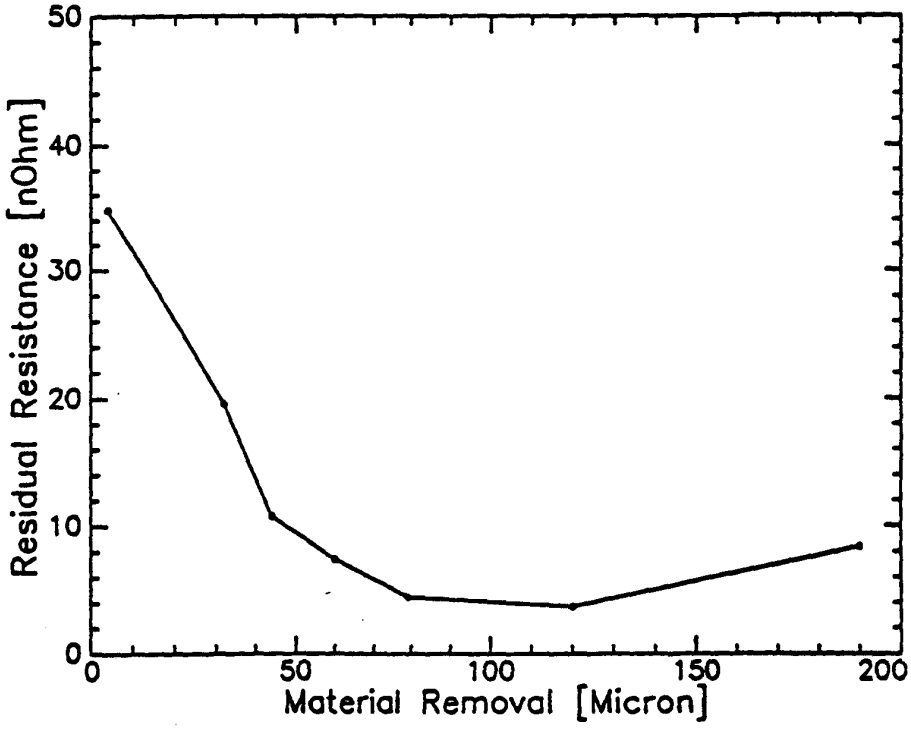

Fig. 3. Effect of material removal on the residual surface resistance R_{res}.

Sample	material removal [μm]	Number of sites	E_{onset} [MV/m]	β	S [cm^2]
# 1	≈ 4	15	25 – 69	56 – 239	10^{-13} – 10^{-16}
# 4	≈ 23	0	–	–	–
# 8	≈ 34	7	34 – 69	72 – 181	10^{-13} – 10^{-15}
# 9	≈ 49	11	35 – 72	60 – 179	10^{-10} – 10^{-15}
# 10	≈ 84	1	14	218	10^{-10}
# 11	≈ 67	10	39 – 72	49 – 154	10^{-11} – 10^{-15}

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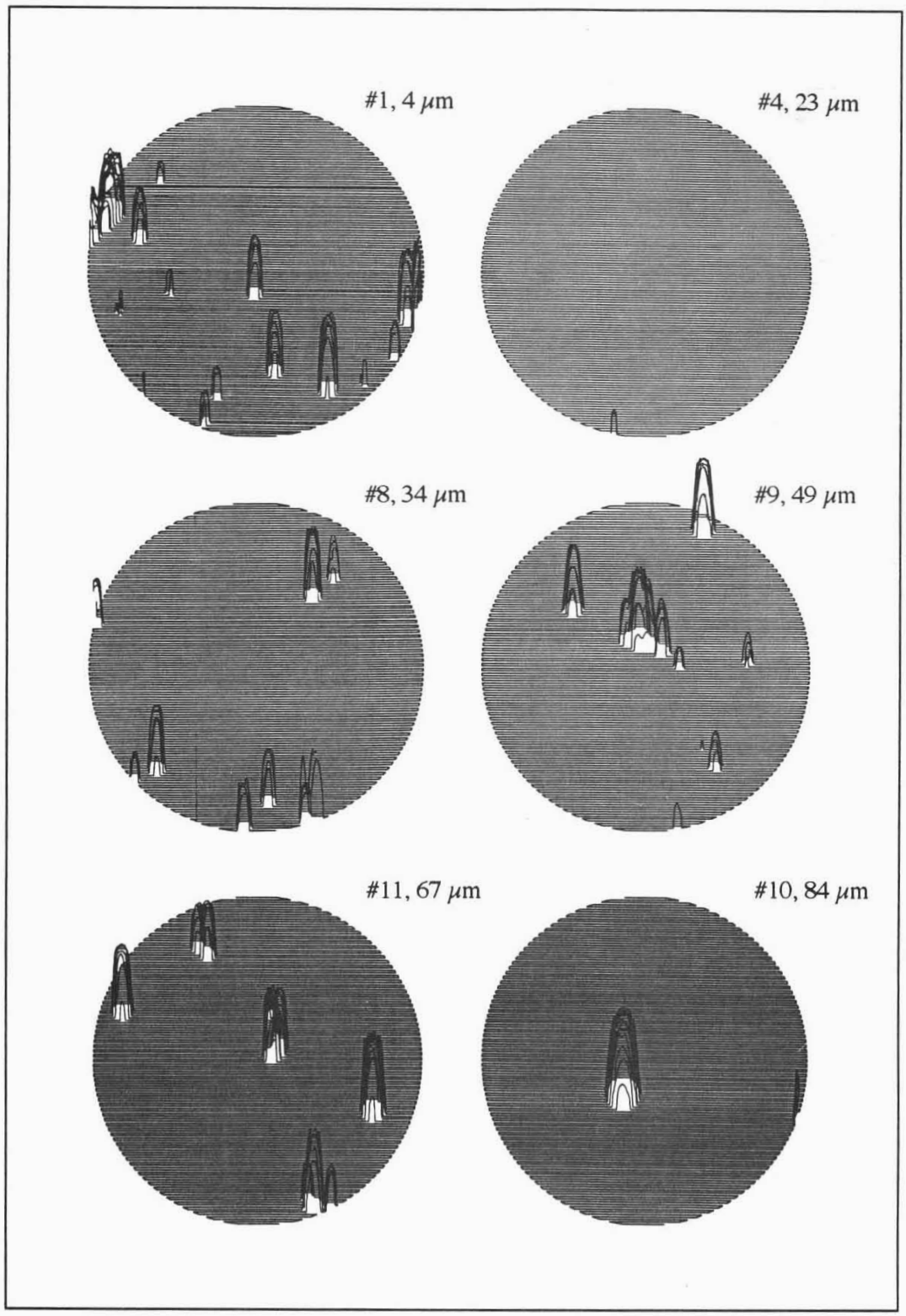

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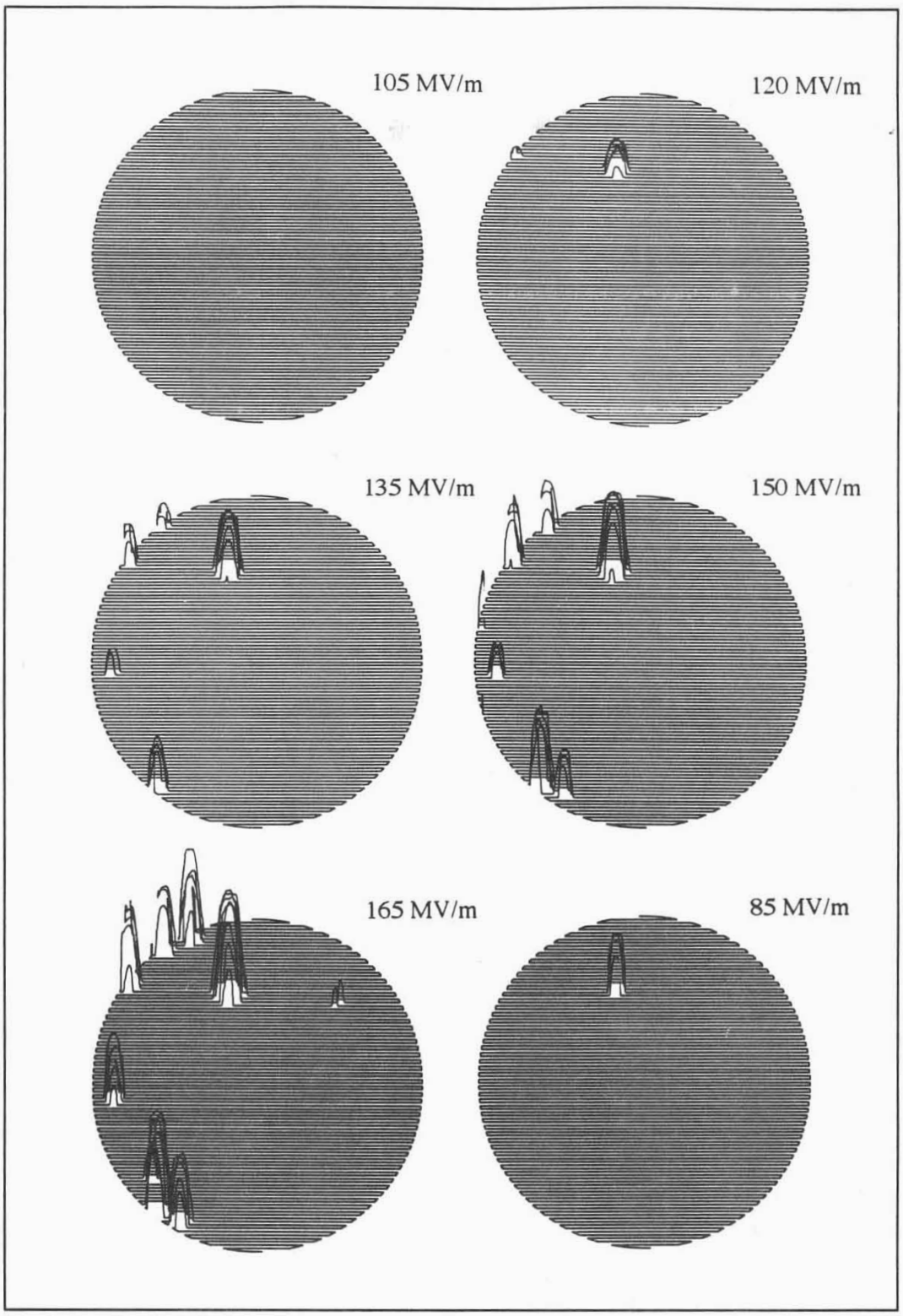

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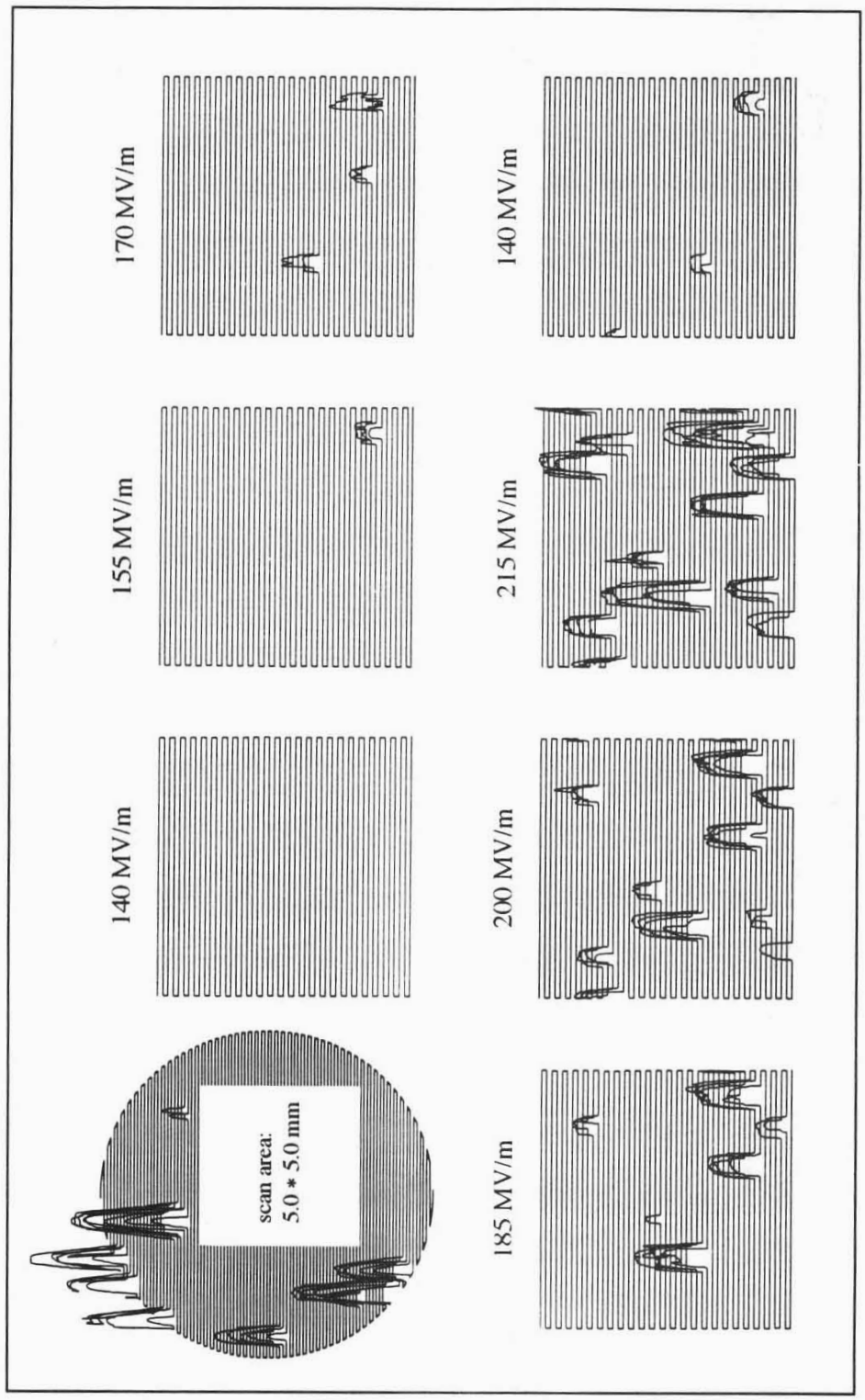

Fig. 6. High field FE scans on a 5.0 * 5.0 mm area of sample #4 (see also Fig. 5).