SHI irradiation induced nano scale surface micro-relief’s in the polar (010) cleavage of pure and doped TGS crystals

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The resulting image topology change as a function of irradiation is analyzed. The smooth surface of pure TGS shows pits and protrusions when irradiated with SHI beam. The height and dimensions of these micro-reliefs vary with ion beam fluence as well as with doping. The height of the pits changes from 20 nm to roughly 70 nm from pure TGS to 15% alanine doped TGS. Observed micro-relief is analyzed considering the lamellar domain structure of TGS. The domain movement induced by the internal bias field created due to irradiation results into piezoelectric compression and stretching forming these features on the surface. The results are used to calculate the internal field developed due to irradiation using the \( d_{33} \) and height of pits formed as reported earlier. The calculated values of internal fields are of the same order as that obtained from hysteresis measurements. This demonstrates that swift heavy ion beam irradiation could be used as a tool to modify the surface nano structures.

Triglycine sulphate belongs to one of the important family of room temperature ferroelectrics. Recently, nano scale writing on TGS surface has been demonstrated using surface microscopic probe\(^1\). Atomic force microscopy has emerged as a powerful tool to measure the nano-scale domain structures in ferroelectrics\(^2-4\). The atomically smooth polar (010) cleavage of pure TGS crystals and those doped with alanine were irradiated with 100 MeV O\(^{+7}\) ion beam with varying fluence. Irradiated surfaces were studied using atomic force microscopy in the non-contact mode.

The atomic force microscopy is one among dozens of scanned-proximity probe microscopes. The atomic force microscope (AFM) measures topography with a force probe. AFM operates by measuring attractive or repulsive forces between a tip and the sample\(^5\). In its repulsive "contact" mode, the instrument lightly touches a tip at the end of a leaf spring or "cantilever" to the sample. Thus, in contact mode the AFM measures hard-sphere repulsion forces between the tip and sample. In non contact mode, the AFM derives topographic images from measurements of attractive forces; the tip does not touch the sample\(^6\). AFM’s can achieve a resolution of 10 ppm, and unlike electron microscopess, can image samples in air and under liquids.

Triglycine sulphate has been intensively studied in recent years by the various scanning force microscopy (SFM) operation modes\(^7-16\). Different configurations of antiparallel domains are reportedly form in the ferroelectric phase in TGS, comprising the most common cylindrical shaped domains along the b-axis with lenticular cross section in the ac plane as well as plate like, lamellar and irregular shaped pattern\(^18\). In the dynamic non-contact operation mode in electrostatic force microscopy (EFM), high resolution imaging of domain walls has been achieved in ferroelectric single crystals of TGS, stemming from the pronounced electrostatic force gradient at domain boundaries\(^4,7-10\). Visualization of ferroelectric domains and domain walls has been also performed by friction force microscopy (FFM)\(^11-13\). Domain contrast observed in FFM has been shown to depend essentially on differences in the chemical composition and surface potential of antiparallel domains of the particular ferroelectric material under study\(^14\). Voltage modulated SFM, originally developed for nanoscale imaging of static charges on insulating surfaces\(^14\) has been fruitfully applied to determine the domain distribution on ferroelectric surfaces\(^15-22\) and to image polarization domain patterns in ferroelectric thin film studies\(^3,4,9\). The TGS domain structure is known to

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depend on several factors such as growth conditions and defect structure, thermal treatment and most importantly to exhibit a substantial temporal evolution.

Atomic force microscopy (AFM) has been used for the study of the surface topography and domain structure of TGS crystals. The images of various types of domains at the polar surfaces of as-cleaved crystals in contact and resonance mode are observed that revealed microstructure of domains on a nano scale. Tolstikhina et al. reported that the crystals grown old and those annealed and γ-irradiated show different surface relief. The domain parameters were also measured. Further, that the surface polarization undergo reversal after prolonged exposure. They have observed that structure vary widely depending upon the sample history. Micro-relief of islands and depth are observed. The application of DC field also leads to the generation and the motion of the domain walls having view of the lucent lines. Kolosov have reported that domain contrast observed in AFM images results from the piezoelectric stretching or compressing of domains of opposite sign in the internal field of the ferroelectric crystals, in the contact mode AFM, whereas Luthi et al. have opposite view and associate it due to scan direction dependence of contrast. The observation of holes and hillocks has been explained in terms of written domains, i.e., deposition of tip materials. The process has been observed by Mamin et al. and is found to be highly reproducible and applicable as storage medium. The erasure of deposited mounds of material is feasible by applying adequate voltages. Thus, in this interpretation, the observation of such micro-relief features needs further investigation.

In this investigation the micro-relief of TGS crystals irradiated with swift heavy ions have been studied and found that the surface topology changes with irradiation and is different in crystals which are doped before irradiation.

### Experimental Procedure

All AFM figures were obtained at room temperature using Digital Instruments Nanoscope at Inter University Accelerator Centre, New Delhi. The scan rate varied in each sample and is given along with the figure and average of 256 scans was taken. Roughness analysis of the surface image is made that reveal the surface height variation and sectional analysis gives dimensions of protrusions and pits observed. These data are shown in Table 1.

### Results and Discussion

The flatten figure representing height of crystal surface in as-cleaved TGS irradiated with \(10^{11}\) ions/cm\(^2\) influence of 100 MeV O\(^{8+}\) ion beam is shown in Fig. 1a with the scan size of 10µm and in Fig. 1b the surface morphology on XZ plan is depicted. The surface is flat with average roughness of 70 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Data scale (Maximum surface height), nm</th>
<th>Roughness of the surface 10 m size (nm)</th>
<th>Roughness in 2μ section (nm)</th>
<th>Dimensions of protrusions and pits</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS 10(^{11}) ions/cm(^2)</td>
<td>500</td>
<td>70.2</td>
<td>15.81</td>
<td>2.5 µ × 21 nm</td>
</tr>
<tr>
<td>TGS 5×10(^{11}) ions/cm(^2)</td>
<td>400</td>
<td>299.2</td>
<td>66.49</td>
<td>2.109 µ × 7.9 nm</td>
</tr>
<tr>
<td>LATGS11 10(^{11}) ions/cm(^2)</td>
<td>300</td>
<td>233</td>
<td>50.0</td>
<td>116 nm × 4.2 nm</td>
</tr>
<tr>
<td>LATGS11 5×10(^{11}) ions/cm(^2)</td>
<td>200</td>
<td>68.7</td>
<td>39.2</td>
<td>101.36nm×3.96 nm</td>
</tr>
<tr>
<td>LATGS15 10(^{11}) ions/cm(^2)</td>
<td>150</td>
<td>45.72</td>
<td>47</td>
<td>164.26×2.86nm</td>
</tr>
<tr>
<td>LATGS15 5×10(^{11}) ions/cm(^2)</td>
<td>150</td>
<td>4.3</td>
<td></td>
<td>125×4.0nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>507.81×286nm</td>
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<td></td>
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<td></td>
<td>468.75×12 nm</td>
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<td>335.93×0.25 nm</td>
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<td></td>
<td></td>
<td></td>
<td>250×1.3 nm</td>
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<td></td>
<td></td>
<td>117.19×0.44 nm</td>
</tr>
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<td></td>
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<td>78.19×0.718nm</td>
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</tbody>
</table>
When the energy fluence is increased to $5 \times 10^{11}$ ions/cm$^2$, the rounded homogeneously distributed mounds are observed as shown in Fig. 2a. The sectional analysis of these mounds is shown in Fig. 2b. The same surface is scan in 2 µm scan size where these protrusions are very clear. The observed domains size is typically 2.5 m and vertical heights of 21 nm, whereas the homogeneously distributed mounds size on 2 µm surface scan is 116 × 4 nm. Oriented domains with some evenly distributed protrusions having a height ~15 nm are visible on the surface. The XZ scan in 2 µm shows the surface morphology more clearly.

In LATGS11, the surface micro-relief feature are similar to TGS, except that the surface folding is observed at fluence of $10^{11}$ ions/cm$^2$ and the surface roughness is 233 nm as shown in Fig. 3a, highly folded surface is observed in this case as shown in Fig. 3b. Protrusions observed are also not very symmetric, however are of larger dimensions than pure TGS. The folding of surface and growth of protrusions is more clear in 2 µm scan size. At $5 \times 10^{11}$ fluence, the surface in LATGS crystals becomes flatter with rounded micro-relief of size (287×12.9nm) as shown in Figs 4 (a) and (b) in 10:10 scan size.

Fig. 1—(a) AFM Scan image of the surface showing XZ plan variation and (b) Roughness analysis of AFM image showing height of the crystal surface (Sample is TGS irradiated with $10^{11}$ ions/cm$^2$)
These micro-relief feature grow in height (12 nm) as well as in size with doping. A comparison of the surface morphology indicates that TGS crystals being soft, surface gets folded with smaller fluence. In pure crystals the ions seems to be diffusing in to the crystal making the surface folded, whereas in doped crystal the folded surface is observed at lower fluence and becomes flat at higher fluence. A closer look of these surfaces shows protrusions emerging on the surface with irradiation; these protrusions vary in dimension and distributions in various crystals. It seems that ions lose there energy and creates local heating which melt the material on the surrounding surface. The quenching that followed thus creates these protrusions for lower fluence the pure crystal being softer than the doped one shows etching type of behaviour with increasing fluence the surface gets strain and folded in doped crystals which are comparatively harder the heat distribution is less and therefore these folded surface is observed at lower fluence as can be seen in

Fig. 2— (a) Scan image of the same surface in 2m size. Mounds are clearly visible. Sample is TGS irradiated with $5 \times 10^{11}$ ions/cm$^2$ and (b) Sectional analysis of the mounds and pits seen of the surface.
LATGS11 at lower fluence. With increasing fluence, more and more number of ions heating the surface, redistributed the energy and coalescing of protrusions forms flatter surface. This is clearer in LATGS15 where initially such evenly distributed protrusions are observed at lower fluence (Fig. 5 (a,b)) and almost flat surface is observed at higher fluence (Fig. 6(a,b)).

More number of such micro relief emerges in doped crystals than in pure TGS may be associated with the fact that thermal diffusion in pure crystal is more than in doped crystals. In order to understand the mechanism of this micro-relief feature, we have shown the roughness analysis of the surface. One can clearly visualize the etched surface in TGS at fluence

Fig. 3—(a) Scan image of the same surface in 2 µm size. Folds created due to ion diffusion are clearly visible and (b) Sectional analyses of the mounds and pits seen of the surface of scan size 2 µm (sample is LATGS11 irradiated with $10^{11}$ ions/cm$^2$).
of $10^{11}$ and evenly distributed protrusions at $5\times10^{11}$ fluence. The roughness of the surface also decreases with increasing fluence (Table 1) the size of protrusions estimated using the sectional analysis shows the size and height of protrusions decreases with doping and fluence. One can visualized the orientation of domains/structures more clearly in doped crystals. Thus, the AFM image show stabilized oriented protrusions as a result of irradiation. AFM images show (protrusions) that are embedded in ordered crystals. This is possible if regions of non-polar materials are created. The observation of dielectric loss peaks in those crystals that are supposed to be mono-domain to a large extent before irradiation.
and not in those which were multi-domain implies that with SHI irradiation, could be explained as associated with regions of non-polar on the basis of AFM results as multi-domain crystals get stabilized and become mono-domain, whereas it induces the structural changes in mono-domain crystals making them multi-domain.

Conclusions

Atomic force microscopic images of irradiated samples of pure and alanine doped TGS crystals are analyzed. Oriented domains with some protrusions evenly distributed on the surface are observed which are seen as rounded homogeneously distributed mounds with increased energy fluence of irradiated
beam. In LATGS11, the surface micro-relief features are similar to TGS, except that the surface folding is observed. Protrusions observed are also not very symmetric however, are of larger dimensions than pure TGS. A $5 \times 10^{11}$ fluence, the surface in LATGS11 crystals becomes flatter with rounded micro-relief. These micro-relief features grow in height as well as in size. In pure crystals the ions seems to be diffusing in to the crystal making the surface folded, whereas in doped crystal the folded surface is observed at lower fluence and becomes flat at higher fluence. A closer look of these surfaces shows protrusions emerging on the surface with irradiation; these protrusions vary in dimension and distributions in various crystals. It
seems that ions lose their energy and create local heating which melt the material on the surrounding surface. The quenching that followed thus creates these protrusions. The roughness of the surface also decreases with increasing fluence (Table 1) and the size and height of protrusions decreases with doping and fluence. One can visualize the orientation of domains/structures more clearly in doped crystals. Thus the AFM image shows stabilized oriented protrusions as a result of irradiation. This supports the thermal spic mechanism being main energy loss in these crystals. This is clear from the formation of different micro-relief in different crystals and their coalescing with increased ion energy. AFM images show (protrusions) that are embedded in ordered crystals. This is possible if regions of non-polar materials are created.

Thus, AFM image analysis support the model used for dielectric response analysis where thermal diffusion and gradient formation is considered and used to explain the observed dielectric loss peak and dispersion.

References
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