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## **SrTiO<sub>3</sub> surface micro-structuring with swift heavy ions in grazing incidence geometry**

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### **Abstract :**

In this work, we present first experimental results on the micro-structuration of monocrystalline strontium titanate (100)-SrTiO<sub>3</sub>. A self-organized structure appears on its surface due to irradiation with 0.71 MeV/u <sup>129</sup>Xe<sup>23+</sup> and 0.55 MeV/u <sup>136</sup>Xe<sup>19+</sup> swift heavy ions at room temperature and under grazing incidence. The resulting wave-like structure appears normal to the direction of the ion beam. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses were undertaken to probe microstructural properties below the surface, revealing in particular surface amorphization at high fluences. Such amorphous surface layers, further irradiated at high fluences, may lead to an anisotropic plastic deformation (hammering) effect, inducing the observed self-organized structure due to the grazing angle configuration. This surface morphology was characterized by atomic force microscopy (AFM). A dependency of the periodicity as well as the width of the undulations on the irradiation angle was found as they evolve in the same way. As the ripple formation depends on the irradiation parameters, the characteristics of these patterns can be controlled and thus opens the possibilities for custom surface structuration.

**Keywords :**

SrTiO<sub>3</sub>, Ripples, Swift heavy ions, Grazing angle, micro-structuring

**1. Introduction**

1 During the irradiation of solid materials with charged ions, an energy transfer takes place  
2 from the projectile to the target material throughout its trajectory and following different  
3 interactions. Two main processes can describe this energy transfer from the projectile to the  
4 target. Elastic collisions linked to nuclear shock, i.e. the projectile interacts mainly with the  
5 nucleus of the target atom and thus the nuclear stopping power dominates for low projectile  
6 velocities. Inelastic collisions, which involve the electronic system of the target and induce an  
7 electronic stopping power, prevail for high projectile velocity i.e. an ion energy greater than  
8 0.1 MeV/u. Modifications of the target can thus result from these multiple interactions and  
9 energy exchanges, depending on the nature of the material and the energy of the projectile. In  
10 the current article, ions of energy higher than 0.1 MeV/u are used where projectiles are known  
11 as swift heavy ions (SHI). Irradiation in this energy range i.e. for ions with a kinetic energy in  
12 the MeV-GeV range and above has been the subject of various studies under different  
13 conditions and for different types of materials in the last years. These irradiations lead to  
14 permanent structural modifications such as defect formation or even amorphization. For  
15 individual ion impacts, nano-structures appear at the surface, in the form of nano-hillocks,  
16 craters as well as chains of nano-hillocks [1-4].

17 Several studies have been carried out to describe the process behind these structural  
18 modifications and the energy transfer that occurs. A relatively successful approach based on  
19 the heat transport equations has been used to explain the track formation in insulators, namely  
20 the thermal spike model [5-6] and then a generalization to other materials has been developed

1 [7-9]. In the two-temperature model [10], the energy of the projectile is initially locally  
2 deposited in the electronic subsystem and subsequently transferred to the atoms by electron-  
3 atom interactions. Until now, this model explains fairly well the track formation in the bulk.  
4 However, irradiations with swift heavy ions with a grazing incident angle geometry create  
5 different modifications, as the aforementioned chains of nano-hillocks [11-12]. Due to the  
6 missing radial symmetry along the ion path and the implication of the electronic structure in  
7 the creation of these chains, the standard thermal spike model has been modified, taking into  
8 account the non-homogeneous nature of the electron density [2].

9 These material modifications at the surface as well as in the bulk are important because of  
10 their technological relevance, and depend strongly on the materials. In many solids, and with  
11 a certain stopping power threshold, which differs from one material to another, the energy  
12 deposited by the SHI around its trajectory can generate an amorphous cylinder, more  
13 commonly called an ion track or latent track. As in the case of the strontium titanate ( $\text{SrTiO}_3$ )  
14 where for an irradiation at low fluences, i.e. in the individual ion impact regime, for a normal  
15 incidence angle, each ion induces the formation of hillock like structure on the surface and an  
16 amorphous track surrounded by a disordered crystalline area in the bulk. By changing the  
17 angle of irradiation towards grazing angles, a chain of nano-hillocks is obtained on the  
18 surface, and a relatively straight track in the bulk. However, in the multiple ion impact  
19 regime, i.e. for fluences high enough to have an overlapping of the ion tracks, a surface  
20 amorphization is induced for an irradiation at normal angle of incidence with the appearance  
21 of an amorphous layer having a thickness of a few micrometers [13]. The main goal of the  
22 present contribution is to explore the response of the surface of  $\text{SrTiO}_3$  to irradiation with SHI  
23 by combining high fluence and grazing angle of incidence.

24 Surface nano- and micro-patterning is important and gaining popularity, especially in the  
25 fabrication of periodic patterns like waves with controllable characteristics, which is useful in

1 modeling and adapting a material for different technological purposes. The first observation  
2 of periodic structures was made by Navez *et al* in 1962 after ion bombardment of a glass  
3 sample at low energy [14]. At large incident angles close to the surface normal direction,  
4 ripple patterns with ridges oriented perpendicular to the beam direction are created. The  
5 distance between these periodic patterns decreases as the angle of incidence increases toward  
6 the normal to the surface.

7 Studies have intensified in the following years, focusing mainly on the creation of these  
8 periodic waves by irradiation with low energy ions, i.e. an energy below 10 keV/u, on  
9 different types of materials such as metals [15], insulators, or semiconductors [16-18].  
10 Considering nuclear collisions and sputtering as the main processes inducing modifications at  
11 low energy, the formation of these periodic structures on the surface results directly from a  
12 combination of the roughening effect due to removal of surface material and smoothing  
13 (which may be due to ion induced diffusion or viscous flow for amorphous surfaces). Studies  
14 at high and medium energy are less numerous. The first observation of dimensional changes  
15 induced by SHI irradiation was reported by Klaumünzer *et al* [19-20] for metallic glasses,  
16 where an anisotropic growth of the sample was observed, appearing as a swelling in the  
17 dimensions perpendicular to the ion beam and a contraction in the dimension parallel to it,  
18 such effect increases with the electronic energy loss. Several studies have followed with other  
19 amorphous metallic and non-metallic alloys and all have shown the same behavior, with the  
20 production of disorder and defects followed by an anisotropic deformation of the sample  
21 dimensions. This so-called “hammering effect” was explained [21] by the shear stress  
22 generated by the thermal expansion of the cylindrical thermal spike around the ion trajectory,  
23 followed by the relaxation of this stress within the molten phase, and then the freezing-in of  
24 the associated strain increment during the subsequent cooling-down process. The “hammering  
25 effect” was also invoked to explain the development of periodic nano-patterns and lamella

1 structures observed under SHI for off-normal irradiations in the case of oxide thin film  
2 systems, like NiO deposited on SiO<sub>2</sub> [22] and on other different substrates [23], where they  
3 appear at the beginning of the irradiation in the form of cracks perpendicular to the ion beam  
4 direction. Then by increasing the fluence, these cracks form periodic patterns whose width  
5 decreases with an increase in the periodicity as the fluence is increased, forming thus the  
6 pattern known as ripples. Different halide thin films were also investigated like LiF and BaF<sub>2</sub>  
7 deposited onto glass substrates and maintained at the temperature of liquid nitrogen during the  
8 irradiation. Different fluences were used at an angle of incidence of less than 15° with respect  
9 to the sample surface and where SHI induced surface reorganization into lamella structures  
10 was observed, but not for those irradiated at room temperature [24]. The different  
11 technological applications offered by this ion-induced surface nano-structuring are becoming  
12 more and more interesting. An application of these ripples is considered in the case of thin  
13 film deposition, or for the manufacture of micro and optoelectronic devices. [25-26].

14 The aim of this paper is to present first experimental results on the modification, structural  
15 and morphological evolution of the surface of strontium titanate single crystals irradiated by  
16 swift heavy ions at various grazing angles of incidence. Although our samples are not thin  
17 layers deposited on substrates of different natures, and thus the irradiation conditions differ  
18 from the previous reported studies, we find that periodic patterns like ripples also develop at  
19 the surface of our single crystals. The different experimental parameters like the incident  
20 angle of the projectile and the ion fluence appear to control the characteristics of this surface  
21 micro-patterning and can therefore be tuned according to the application needs. An attempt to  
22 understand the mechanism is also suggested.

## 23 **2. Experimental**

1 For our experiments, single-crystal samples of (100)- SrTiO<sub>3</sub> from Crystec company (Berlin),  
2 were irradiated at room temperature under vacuum on atomically clean surfaces.

3 The swift heavy ion irradiation experiments were performed at the GANIL (Grand  
4 Accélérateur National d'Ions Lourds – France, Caen) facility, at the IRRSUD beam line with  
5 92 MeV <sup>129</sup>Xe<sup>23+</sup> and 75 MeV <sup>136</sup>Xe<sup>19+</sup>. It corresponds mainly to an electronic energy loss at  
6 the surface (calculated with the SRIM code [27] with the density of 5.117 g/cm<sup>-3</sup>) of 21  
7 keV/nm and 19 keV/nm respectively, well above the stopping power threshold needed for  
8 track formation of 12 keV/nm [13]. On the contrary, the nuclear energy loss is very small at  
9 the surface, being around 0.18 keV/nm, and 0.22 respectively, and increases slightly inside  
10 the bulk up to a maximum at the projected range of ~ 8 μm. Different angles of incidence with  
11 respect to the surface were used, ranging from  $\theta = 0.5^\circ$  (grazing incidence) up to 90° (normal  
12 incidence). The fluences were chosen in such a way to have individual ion impact up multiple  
13 overlapping ion impact regions, by using ion fluxes low enough to avoid macroscopic sample  
14 heating.

15 After irradiation, the samples were analyzed ex-situ using atomic force microscopy (AFM)  
16 with a Park system Nx10 under ambient conditions in tapping and non-contact mode. The  
17 AFM images were processed with the Gwyddion software package [28]. X-Ray diffraction  
18 was carried out with a high-resolution Bruker D8 Discover diffractometer. A Cu X-ray  
19 source, a Göbel mirror and an asymmetric Ge monochromator are used as primary optics  
20 getting a wavelength  $\lambda_{\text{Cu}\alpha_1} = 0.154056$  nm, while a 1D LYNXEYE is used for the detection. A  
21 symmetric geometry was used to record  $2\theta$ - $\omega$  patterns implying a varying probed material  
22 depth as function of the diffraction angle of around  $8.14 \pm 0.0015$  μm for the (200) reflection  
23 recorded at 46.44°. Electron-transparent cross-sections were extracted using focused ion beam  
24 instrument Helios Nanolab 660 with Ga<sup>+</sup> ions accelerated at 30 keV (decreased gradually  
25 down to 1 keV for the final step). Transmission Electron Microscope (TEM) observations

1 were carried out with a JEOL F200 electron microscope operating at 200 kV equipped with a  
2 cold field emission gun.

### 3 **3. Results and discussion**

4 SrTiO<sub>3</sub> bulk is known to be an amorphizable material by swift heavy ion irradiation [29]. At  
5 low fluence and for a stopping power above a threshold of 12 keV/nm [13], each ion creates  
6 an individual amorphous cylindrical track along its trajectory in the bulk that partially extends  
7 to the surface. For grazing incidence irradiations, this modification gives rise to the formation  
8 of a chain of hillocks as often reported by AFM analysis [2]. These chains of nano-hillocks  
9 were also observed by electron microscopy as illustrated in Fig. 1a. To go further in the  
10 examination of these structures, TEM lamellae were prepared at the precise location of a  
11 chain of nano-hillocks using our SEM/FIB facility. The observations made by TEM show the  
12 ion tracks induced beneath the surface in the bulk by an irradiation at grazing angles. In Fig.  
13 1b a straight track is observed for an irradiation at 3.7° while a non-homogenous effect with a  
14 fragmented track is observed for an irradiation at 0.5° (Fig. 1c). This effect can be explained  
15 in a similar fashion as for the formation of the chains of nano-hillocks observed on the surface  
16 of SrTiO<sub>3</sub> irradiated at grazing incidence [2]. As the surface of a single crystal SrTiO<sub>3</sub>  
17 oriented along the (100) direction is considered, and due to its crystalline structure that  
18 alternates two different types of atomic planes (Ti-O and Sr-O layers distant from each other  
19 by 0.2 nm), irradiation with different grazing angles involves thus a different electron density  
20 depending on the traversed region of the crystal. During a SHI irradiation, the incident ion  
21 will cross along its trajectory the Ti-O crystalline plane containing the highest electron density  
22 inducing a greater energy loss every ~60 nm in the case of the nominal angle of 0.5° and  
23 every ~6 nm for the nominal angle of 3.7° with respect to the surface. As the deposited energy  
24 is directly related to the electron density, we therefore expect in the first case the formation of  
25 well-separated amorphous spheroids with a radius of the order of that obtained in the



1 cylindrical tracks, i.e.  $\sim 2,4$  nm, while in the second case these spheroids will join to create a  
2 quasi-continuous track. The morphology of these tracks or damaged area can thus differ from  
3 one angle to another. Moreover, a careful examination of the TEM image obtained in the case  
4 of the nominal irradiation at  $0.5^\circ$  (see Fig. 1c) gives an average spacing between spheroids of  
5 about 44 nm, indicating that the actual angle of incidence is  $\sim 0.35^\circ$  which is consistent with  
6 our estimated angular uncertainty of  $0.2^\circ$ .

7 On Fig 1b and 1c, density contrasts are also noticed around the tracks corresponding to  
8 deformation field in the crystalline matrix surrounding the tracks, reminding the observations  
9 done for SrTiO<sub>3</sub> irradiated at normal incidence [13, 29]. Considering the reported track radius  
10 of  $2.4 \pm 0.4$  nm, the amorphous tracks will overlap as the irradiation progresses giving then  
11 rise to a total amorphization of the sample surface for fluences higher than a few  $10^{13}$   
12 ions/cm<sup>2</sup>. In order to study the structural evolution of SrTiO<sub>3</sub> at high fluences but this time in  
13 grazing angle geometry, X-Ray diffraction pattern of (200) reflection of SrTiO<sub>3</sub> irradiated  
14 with 75 MeV Xe at  $6^\circ$  with  $8 \times 10^{13}$  ions/cm<sup>2</sup> is compared to a non-irradiated one in figure 2.  
15 For a probing depth of  $\sim 8$   $\mu\text{m}$ , thanks to the X-Ray diffraction geometry, corresponding to  
16 the irradiated material and well deeper into the non-irradiated material, the intensity of the  
17 diffracted signal of (200) reflection is decreased compared to the non-irradiated sample. This  
18 means that a loss of crystallinity of the initial perovskite structure occurs. It is due to crystal  
19 disordering induced by irradiation and surface amorphization. Furthermore, a large  
20 broadening on  $2\theta$  axis extended towards low diffraction angles is observed, which is due to  
21 an important tensile strain induced by irradiation [29]. To confirm the formation of an  
22 amorphous layer on the surface as in the case of an irradiation at  $90^\circ$  [13], TEM images of a  
23 cross section prepared by FIB on the same sample as the above analyzed by X-Ray diffraction  
24 is shown in Fig. 3. Different visible contrasts indicating different regions of the sample are  
25 observed. On the right, the selected area electron diffraction pattern (SAD) taken from the

1 first region along the ion path, i.e. near the surface, clearly indicates by the observation of  
2 only a diffuse ring the amorphization of the crystal by the incident ions. The thickness of this  
3 amorphous layer extending from the surface is around 1.0  $\mu\text{m}$ . Below this layer and deeper in  
4 the material, disorder and partial amorphization are observed, which are confirmed in the  
5 middle diffraction pattern by a diffuse ring with bright spots. At larger depth, a region where  
6 the material remains single crystalline is observed as shown by the last diffraction pattern.  
7 Although we tend to have the same structural changes at high fluences regardless of the  
8 irradiation geometry, at grazing angle the thickness of the amorphous layer is smaller than for  
9 an irradiation normal to the surface due to geometrical aspects. These results also confirm that  
10 strain in the defective crystalline layer localized beneath the amorphous layer also occurs at  
11 grazing angle incidence, as the one known at normal incidence. Taking into consideration the  
12 localized energy deposition of SHIs in the target and the thin amorphous layer developed on  
13 the surface, one can assume a resulting surface effect. This is why the main objective through  
14 this study is to investigate by means of AFM measurements the response of the  $\text{SrTiO}_3$   
15 surface to SHI irradiation. Variations of the grazing angles and the high fluence values are  
16 applied to explore the SHI induced surface structuring of a single crystalline insulator and to  
17 monitor the evolution of the microstructures formed on its surface.

18 Figure 4 shows AFM images of (100)- $\text{SrTiO}_3$  before and after irradiation where (a) represents  
19 a typical sample surface before irradiation with an inset showing a scan where the size was  
20 chosen to have a resolution where the atomic steps are visible indicating the good resolution  
21 of our AFM measurements. In addition, the root mean square (rms) value of the surface  
22 roughness is 0.4 nm, proving that the surface is indeed clean and flat without prior surface  
23 treatment. Fig.4 (b) represents a sample irradiated with  $1 \times 10^{14}$  ions/ $\text{cm}^2$  at an incident angle  
24  $\theta = 7^\circ$  with respect to the surface. Here a modification and reorganization of the surface can

1 be observed. This transformation appears in the form of quasi-periodic patterns like waves at  
2 the microscopic scale.

3 In order to investigate the formation process and the evolution of these micro-ripple patterns,  
4 several SHI irradiations were performed at various grazing angles of incidence on a series of  
5 samples by varying the fluences ranging from  $3 \times 10^{13}$  to  $4 \times 10^{14}$  ions/cm<sup>2</sup> and angles of  
6 incidence from 2° up to 45° with respect to the surface. Topography examinations of different  
7 irradiated samples were performed by means of AFM analysis. Figure 5(a) shows a (100)-  
8 SrTiO<sub>3</sub> sample irradiated at a fluence  $\phi = 9 \times 10^{13}$  ions/cm<sup>2</sup> and an angle  $\theta = 6^\circ$  with an inset  
9 showing the corresponding 2D Fourier transform of the whole image, allowing us to  
10 quantitatively obtain the ripple periodicity of the irradiated sample. Here the periodicity is  
11 considered as the peak-to-peak distance. As two separated spots are clearly observed in the  
12 Fourier transformation, a periodicity of the wave pattern can therefore be easily deduced. This  
13 periodicity was verified with the line scan taken from the same image and showing the surface  
14 profile shown below Fig. 5a. From Figure 5(b) to 5(e) 3D AFM images of (100)-SrTiO<sub>3</sub>  
15 surfaces irradiated with 92 MeV Xe are shown for fluences and angles as follow: (b)  $\phi = 7 \times$   
16  $10^{13}$  cm<sup>-2</sup> and  $\theta = 5^\circ$ , (c)  $\phi = 1 \times 10^{14}$  cm<sup>-2</sup> and  $\theta = 9^\circ$ , (d)  $\phi = 2 \times 10^{14}$  cm<sup>-2</sup> and  $\theta = 21^\circ$ , and (e)  
17  $\phi = 3 \times 10^{14}$  cm<sup>-2</sup> and  $\theta = 31^\circ$ .

18 From these images, we can see that the formation of the wave-like structures is indeed  
19 reproducible and the ridges of the structures appear perpendicular to the direction of the ion  
20 beam onto the surface (indicated by the dark arrow on the images) for all the irradiation  
21 angles used in this study. It should be mentioned that the arrow does not represent the real  
22 value of the angle, but is there as an indication to allow a clear visualization of the direction of  
23 the beam and the distinction with an irradiation normal to the surface. Fig.5 (b) shows waves  
24 like structures with a periodicity around 3 μm, while in (c) for an irradiation at 9° a  
25 periodicity about 6 μm is obtained. By increasing the angle of incidence towards the normal

1 to the surface just as the fluence, the ridges of these quasi-periodic patterns tend to expand in  
2 the direction perpendicular to the ion beam. As can be seen in Fig.5 (d) and (e) for an  
3 irradiation at 21° and 31°, periodicities of 16 μm and 17 μm are observed, respectively. This  
4 means that the more the angle decreases towards the grazing direction, the more the  
5 periodicity decreases, giving then rise to a more important quantity of ripples on the surface  
6 for grazing angle than for large angles.

7 Figure 6 represents the angle-dependence of the periodicity. Four cases are depicted, in each  
8 case two samples have around the same fluence but different angles of incidence. For small  
9 angles of incidence with respect to the surface, the periodicity varies between 3 and 6 μm  
10 while for larger angles it increases and can reach 19 μm for an irradiation at 45° which is not  
11 illustrated in this figure. This means that the periodicity of these ripples can be controlled, as  
12 the ripple density on a given surface decreases with increasing the angle of irradiation towards  
13 the normal to the surface. Apart from the fact that the irradiation angle affects the ripple  
14 periodicity on the surface, in material depth it seems that it has a slight impact as shown by  
15 the XRD patterns in Figure 7, where two samples irradiated at 11° and 6° with respect to the  
16 surface with a fluence of  $9 \times 10^{13}$  ions/cm<sup>2</sup> are shown. The broadening along the 2θ axis  
17 synonymous of tensile elastic deformation is slightly different; it seems to be more  
18 pronounced at 11° than 6°, which may be due to a higher tensile strain in the defective  
19 crystalline layer caused by a thicker irradiated layer at 11°.

20 By performing the 2D Fourier transform on our SrTiO<sub>3</sub> surfaces irradiated at 90° in the  
21 fluence range of  $5 \times 10^{11}$  to  $5 \times 10^{14}$  ions/cm<sup>2</sup>, no periodic pattern was observed. Moreover,  
22 the irradiations were made up to an angle of 45°, and so far, there is no reorientation of the  
23 ripples (i.e. the ripples are still oriented perpendicular to the ion beam and have not become  
24 parallel to it) as observed in other reported studies for large angles [14]. In previous studies  
25 [24], the ripple width decreases as the periodicity between them increases. The width is

1 defined by the mean FWHM of the ripples determined from multiple cuts, and the periodicity  
2 is the peak-to-peak distance. In our case, the width of the ripples and their periodicity increase  
3 as the angle of irradiation increases towards the normal to the surface. It has also been noticed  
4 that the SHI fluences required for the appearance of these ripples is much lower than the  
5 fluences required in the experiments at low energies [18]. The analysis of our different  
6 samples irradiated at grazing angles shows that below  $4^\circ$  the ripples are not clearly visible on  
7 the AFM images. However, after performing the Fourier transform a periodicity with the  
8 appearance of two well-defined spots was observed. So for the incidence angles lower than  $4^\circ$   
9 the topological features are enough apparent. Effects as the ripple height could be enhanced  
10 by high fluences for instance, but we cannot affirm this, as our data are not sufficient to  
11 effectively discuss the impact of the fluence on the evolution of the periodic pattern heights.  
12 A more detailed analysis will be given in a later article, in particular on the impact of the  
13 fluence after complementary irradiations and analyses.

14 Besides the 2D FFT analysis of the AFM images in order to quantify the repeatability of our  
15 ripples, another topological aspect of these microstructures can also be studied: to gain insight  
16 into the impact of the irradiation parameters, it is possible to characterize the degree of order  
17 of the surface patterns by quantifying the quality of the ripples [30]. As they form, different  
18 types of defects appear, either as a bifurcation, where a ripple splits into two, or a  
19 discontinuous ripple. To consider an application of these periodic patterns, the control of these  
20 topological defects or features is mandatory to have a short-range disorder. Figure 8 shows the  
21 steps used to determine the normalized density of pattern defects from a  $20 \times 20 \mu\text{m}^2$  AFM  
22 image (Fig. 8(a)) using Gwydion software [28]. We first did a 2D Fourier filtering (Fig. 8(b)),  
23 then a mask is created with Otsu's threshold [31], which behaves like a binary image (Fig.  
24 8(c)). Finally, the resulting images are thinned, consisting of ripples reduced to line traces  
25 with a thickness of one pixel (Fig. 8(d)). This procedure enabled us to count the total number

1 of defects in our image by considering each white pixel with more than two neighboring white  
2 pixels or with only one neighboring white pixel as a topological defect. Then the normalized  
3 density of defects is calculated using  $N_D = N \cdot \lambda^2 / A$  [30] where  $N$  is the raw number of defects,  
4  $\lambda$  the ripple wavelength, and  $A$  the scan area of our image. For a value of  $N_D = 0$ , the pattern is  
5 considered as perfect without any defect and when  $N_D = 1$  each ripple contains one defect per  
6 length. This was done for the various irradiated (100)-SrTiO<sub>3</sub> and was then represented as a  
7 function of the different angles of incidence in Figure 9. For the lowest grazing angles  
8 represented here, between 5° and 11°, and for fluences below  $1 \times 10^{14}$  ions/cm<sup>2</sup>, the  
9 normalized density evolves between 0.2 and 0.6. By increasing the angle,  $N_D$  increases up to a  
10 value that corresponds to a sample where the ripples were not well formed and with several  
11 defects. We assume that this can be due either to an insufficient fluence for the evolution of  
12 the patterns into a well-defined ripple structure or that a fluence threshold has been exceeded  
13 for this angle inducing thus the deformation of the ripples due to an accumulation of defects.  
14 For larger angles,  $N_D$  decreases again corresponding to ripples with few defects, giving then  
15 rise to well-formed quasi-periodic patterns as it can be seen in fig.5 (e) for an irradiation at  
16 31° with respect to the sample surface. This agrees well with what has been observed and  
17 demonstrated in previous studies, where the fluence does have an influence on the pattern  
18 quality evolution. As described by Keller *et al* [32] several processes occur during the  
19 formation and the evolution of ripples, as the fluence increases the ripple length grows,  
20 followed by different annealing processes inducing defect annihilation and therefore a  
21 decrease of the normalized defect density until a certain value. This is followed by the  
22 formation of a cluster of disorder implying an increase in the defect density for higher  
23 fluences [18] (which increases  $N_D$ ). To confirm the impact of the fluence on single crystalline  
24 SrTiO<sub>3</sub>, irradiations at intermediate fluences are planned during a future irradiation campaign

1 in order to determine the threshold fluence necessary for the formation of these ripples  
2 depending on the angle with a minimized amount of defects.

3 The surface topography of all the SrTiO<sub>3</sub> samples irradiated with SHI at grazing angles and  
4 high fluences shows the formation of quasi-periodic patterns on its surfaces, herein named  
5 ripples or waves, whose periodicity evolves and strongly depends on the angle of incidence of  
6 the ions. It is also worth remembering that the effect of the projectile velocity cannot be  
7 neglected, since SHI is used with an energy of a few MeV/u, the electronic regime is  
8 predominant over most of the ion beam path, giving rise to the formation of amorphous tracks  
9 for each ion impact. As the formation of these ripples strongly depends on the fluence, a  
10 regime where the tracks overlap is mandatory. As the fluence is increased, an amorphous  
11 layer finally forms on the surface with a certain thickness that varies according to the  
12 geometry of the irradiation. This could influence the height of the ripples. Moreover, the  
13 effect of the energy has not been demonstrated in our study given that we irradiated with two  
14 relatively close energies (72 MeV and 95 MeV) but it will be the subject of a future study  
15 with higher energy ions.

#### 16 **4. Mechanism**

17 In the following, the possible mechanism inducing the ripple formation on SrTiO<sub>3</sub> surface by  
18 SHI irradiation is discussed. As detailed a bit in the introduction section, when energetic ions  
19 pass through solid materials, a series of interactions and processes occur, depending on the  
20 energy of the projectile, and therefore the loss of energy in the material. Two main processes  
21 can occur, either elastic collisions with target atoms (nuclear regime) or inelastic collisions  
22 with target electrons (electronic regime). It gives rise to atomic displacements, displacement  
23 cascades, disorder, ionizations or electronic excitations, generating structural modifications up  
24 to amorphization at the surface and near the surface of the material and well in depth, along

1 the ion path, for high energy ions. In the latter case, the electronic energy loss is the dominant  
2 slowing down process and the trajectory of the projectile is at the beginning rather straight.  
3 The energy transferred to the electrons by the incident ion is quickly transmitted to the other  
4 electrons by electron-electron interactions and then to the atoms of the lattice by electron-  
5 phonon interactions. This will lead to a sudden increase in temperature within a cylinder of a  
6 few nanometers in diameter around the ion trajectory giving then rise to a possible melting of  
7 this cylinder. The latter will later undergo a cooling phase by dissipating its heat to the rest of  
8 the target by thermal conductivity. On the contrary, at the end of the projected ion range,  
9 nuclear collisions dominate giving then rise to displacement cascades.

10 A particular attention is attached to understanding the mechanism behind the formation of the  
11 periodic structures observed at high energy and described above in the manuscript. In  
12 previous studies, for thin film systems especially metal oxides such as NiO [22-23], a  
13 combination of two complementary processes has been proposed. First, periodic cracking of  
14 the surface normal to the ion beam direction is created due to the Grinfeld's instability [33-  
15 34]. Subsequent melting and resolidification of the material within the cylindrical region  
16 create stress along the ion track [21] [35], which may induce surface instability in the  
17 deposited NiO layer. When this stress exceeds the resistance of the surface to fracture,  
18 periodic cracks can appear in the film. It is suggested that this step is later followed by an  
19 anisotropic plastic deformation (i.e., the hammering effect) [19-21] that explains the evolution  
20 of these cracks into lamellar structures.

21 It should however be emphasized that in our case the situation is different from that  
22 previously described because a single crystal is used with no thin layer deposited on the  
23 surface. Moreover, we did not notice any crack on the surface even after irradiation at high  
24 fluences, X-Ray diffraction even confirms that the material stays in an elastic strain regime.  
25 The question is therefore to understand how the extremely localized energy deposited by the



1 incident ions can induce the observed self-organization of the surface of a single crystal  
2 insulator such as SrTiO<sub>3</sub>. During SHI irradiation of SrTiO<sub>3</sub>, the individual amorphous tracks  
3 overlap as the fluence increases, this leads to the formation of an amorphous layer with a  
4 thickness of about one micrometer (owing to the grazing geometry), followed in depth by a  
5 disordered crystalline layer and very deeply by the non-irradiated crystalline matrix (see  
6 Fig.3). The density of amorphous materials is generally less than that of their crystalline  
7 counterparts. For instance, the reported values for amorphous and crystalline SrTiO<sub>3</sub> are  
8 4.2 g cm<sup>-3</sup> and 5.1 g cm<sup>-3</sup>, respectively [36]. For single crystals SrTiO<sub>3</sub> the mechanical  
9 properties like Young's modulus depend on the crystal directions. One can nevertheless define  
10 an average Young's modulus of 260-300 GPa. Regarding amorphous SrTiO<sub>3</sub>, recent results  
11 obtained by nanoindentation give a Young's modulus ranging between 190 and 210 GPa [37].  
12 This difference for the Young's modulus between the amorphous phase and the crystal is not  
13 surprising, since the former has a lower density and its structure can be considered less rigid  
14 than the crystalline phase (owing to the lack of long range order). From this and the results  
15 provided by our TEM observations, we are in a situation where we have an amorphous "soft"  
16 layer (about one micrometer thick) over a stiffer crystalline substrate. One can therefore  
17 expect an expansion of the amorphous layer with respect to the original dimensions (swelling)  
18 caused by the irradiation induced density change. However, as this amorphous layer is  
19 intimately bound to the crystalline substrate, only the dimension normal to the surface is free  
20 to expand. In contrast, along the two other dimensions, the amorphous layer is restrained and  
21 must adapt to the crystalline substrate. This may induce the formation of wrinkles at the  
22 surface in order to minimize the energy of the system. During subsequent irradiations, any  
23 protrusion at the sample surface (which is already amorphous) would be subject to anisotropic  
24 plastic deformation, which will decrease the dimension parallel to the direction of the beam  
25 and increase those perpendicular to it. This will cause the ripples perpendicular to the

1 direction of the beam to grow. Moreover, this effect can be more efficient on the top of the  
2 ripples than in the valleys due to the stopping power which decreases with the traversed  
3 depth.

#### 4 **5. Conclusion**

5 In summary, we have shown that wave-like structures can be created on the surface of SrTiO<sub>3</sub>  
6 single crystal material by irradiation with SHI. The formation of these periodic patterns, with  
7 the ridges oriented perpendicular to the ion beam direction, mainly depends on the irradiation  
8 parameters such as the angle of incidence. Periodic patterns are observed for irradiation in  
9 grazing geometry for angles up to 45°. The fluence is also important, as it must be in a regime  
10 of multiple impacts where amorphization occurs. The XRD and TEM analyzes confirm the  
11 amorphous nature of the surface layer on which the ripples are formed. Following AFM  
12 characterizations, we were able to extract some characteristics of these patterns like the  
13 periodicity and the width of the ripples. We noticed that they increase as the angle increases  
14 towards the normal to the surface, proving that the ripple density on a given area can be  
15 controlled and opens the routes for custom surface structuration. A mechanism involving the  
16 density change of the bombarded layer due to its amorphization followed by SHI induced  
17 anisotropic plastic deformation is proposed to explain the formation of these ripples. Further  
18 analyses are needed to conclude the interpretation of these processes and will be the subject of  
19 a future publication.

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1 **Figures Captions :**

2 **Figure 1:** (a) SEM/FEG image for (100)-SrTiO<sub>3</sub> irradiated with 92 MeV Xe ions at 3.7° with  
3  $\sim 5 \times 10^8$  ions/cm<sup>2</sup> in individual impact fluence regime. TEM cross-section images of an ion  
4 track observed for (100)-SrTiO<sub>3</sub> irradiated with 92 MeV Xe ions at (b) 3.7° (surface is marked  
5 with dotted line) or (c) 0.5° in individual impact fluence regime. The red and green arrows  
6 indicate the ion irradiation direction.

7 **Figure 2:** X-ray patterns for (100)-SrTiO<sub>3</sub> irradiated with 75 MeV <sup>136</sup>Xe<sup>19+</sup> ions at 6° with  
8  $8 \times 10^{13}$  ions/cm<sup>2</sup> compared to a non-irradiated sample with a probed depth of  $\sim 8 \mu\text{m}$  for the  
9 (200) reflection.

10 **Figure 3:** Left part: TEM image of a (100)-SrTiO<sub>3</sub> sample irradiated at 6° with  
11  $8 \times 13$  ions/cm<sup>2</sup>. The dark arrow indicates the ion beam direction (it is a guide for the eyes but  
12 it does not represent the real value of the incident angle). Right side images show selected  
13 area electron diffraction patterns (SAD) taken at different depths of the sample.

14 **Figure 4:**  $50 \times 50 \mu\text{m}$  AFM images: (a) a non-irradiated (100)-SrTiO<sub>3</sub> with an inset of an  
15 AFM image of  $5 \times 5 \mu\text{m}$  from the same surface; (b) a (100)-SrTiO<sub>3</sub> sample irradiated with 92  
16 MeV Xe ions at  $\theta = 7^\circ$  with  $\phi = 1 \times 10^{14}$  ions/cm<sup>2</sup> (the dark arrow indicates the ion beam  
17 direction along the x,z axis, it is a guide for the eyes but it does not represent the absolute  
18 value of the incident angle).

19 **Figure 5:** AFM images of ripples on (100)-SrTiO<sub>3</sub> surface irradiated with 92 MeV Xe ions.  
20 At  $\phi = 9 \times 10^{13} \text{ cm}^{-2}$  and  $\theta = 6^\circ$  (a) with the corresponding 2D Fourier transform of the entire  
21 image inset. The size of the image is  $20 \times 20 \mu\text{m}$ . A line profile of the surface is also shown  
22 below this figure (the dark arrow indicates the ion beam direction, it is a guide for the eyes but  
23 it does not represent the absolute value of the incident angle). At  $\phi = 7 \times 10^{13} \text{ cm}^{-2}$  and  $\theta = 5^\circ$



1 (b),  $\phi = 1 \times 10^{14} \text{ cm}^{-2}$  and  $\theta = 9^\circ$  (c),  $\phi = 2 \times 10^{14} \text{ cm}^{-2}$  and  $\theta = 21^\circ$  (d), and  $\phi = 3 \times 10^{14} \text{ cm}^{-2}$   
2 and  $\theta = 31^\circ$  (e).

3 **Figure 6:** Evolution of the ripple periodicity observed on (100)-SrTiO<sub>3</sub> surface irradiated with  
4 92 MeV Xe ions according to the angle of incidence for different fluences.

5 **Figure 7:** XRD patterns for the (200) reflection of (100)-SrTiO<sub>3</sub> samples irradiated with 92  
6 MeV Xe ions with  $\sim 9 \times 10^{13} \text{ ions/cm}^2$  at  $11^\circ$  (blue line) and  $6^\circ$  (red dotted line ).

7 **Figure 8:** (a) a  $20 \times 20 \text{ }\mu\text{m}^2$  AFM image of a (100)-SrTiO<sub>3</sub> sample irradiated with 92 MeV  
8 Xe ions at  $\theta = 6^\circ$  and  $\phi = 9 \times 10^{13} \text{ ions/cm}^2$ , (b) Fourier-filtering of (a), (c) application of the  
9 Otsu's threshold, and (d) thinning the ripples to lines.

10 **Figure 9:** Evolution of the normalized density of pattern defects  $N_D$  as function of the  
11 incident angle.