TRACK EVOLUTION OBSERVED IN NiO EXPOSED TO SWIFT HEAVY ION IRRADIATION

Danielle Douglas-Henry, Jacques O'Connell
CHRTEM, University Way, Summerstrand, Port Elizabeth, South-Africa
Danielle.Douglas-Henry@mandela.ac.za, jacques.oconnell@gmail.com

In this study, the track evolution in single crystal Nickel Oxide (NiO) exposed to Swift Heavy Ion (SHI) irradiation has been studied using electron microscopy techniques. Scanning Transmission Electron Microscopy (STEM) was utilized to interrogate the microstructure of the latent tracks formed in both low fluence (non-overlapping regime) and high fluence (overlapping regime) specimens. Ion energies used were 593 MeV and 1.6 GeV, while fluences ranged from $1.0{\cdot}10^{11}$ ions/cm² to $1.4{\cdot}10^{14}$ ions/cm². Electron Energy Loss Spectroscopy (EELS) was used to determine the chemical composition of the "tracks" seen in high fluence samples. Elevated levels of Oxygen suggest radiolytic decomposition of NiO into O_2 during SHI bombardment.

Keywords: SHI; Electron Microscopy; STEM; EELS; NiO.

Introduction

Exposure to swift heavy ion irradiation (SHI) is known to induce material specific changes in the microstructure. Various models are used to predict damage formation and explain such microstructural changes [1]. These changes can vary from the production of continuous cylinder-like amorphous "latent tracks" for susceptible materials, to no detectable modification for resistant materials.

Amorphous latent tracks have been seen in insulators irradiated with SHIs in the electronic slowing regime [2] whereas ionic crystals such as CaF_2 (that are typically radiolytic) have been seen to exhibit faceted voids along SHI tracks. In these voids Ca vacancy complexes filled with fluorine gas have been found [3]. Latent tracks have been thought to result due from the imperfect recrystallization of the molten volume along the SHI trajectory. It has been proposed that the efficiency of recrystallization is in-part related to the materials structural complexity, it's self-diffusion coefficients in the melt and it's interatomic potential [4-6]. Without electron microscopy investigations, nothing can be definitively said about the microstructural changes occurring in these materials, making it a powerful tool in investigating the structural effects of SHI.

Experimental

In this study, the microstructural changes in single crystal NiO(001), irradiated at 45° with 1.6 GeV to a fluence of $1.0{\cdot}10^{11}$ ions/cm² has been studied and compared to specimens irradiated with 593 MeV Au to a fluence of $1.4{\cdot}10^{14}$ ions/cm². Specimens were irradiated at GSI Helmholtzzentrum für Schwerionenforschung, Darmstad and the former ISL lab in Berlin, respectively. The respective energies yielded similar electronic stopping powers which allowed for the investigation of the progression of track formation from low to high fluences.

Standard Focused Ion Beam (FIB) lift-out procedure was used to prepare specimens investigated through Scanning Transmission Electron Microscopy (STEM). This was done using an FEI Helios 650 dual beam system. The lamellae were analyzed using a JEOL ARM200F analytical TEM operating at 200 kV. Electron Energy Loss Spectroscopy (EELS) was also performed using the JEOL JEM-ARM200F which is fitted with an advanced GIF (Quantum) electron spectrometer with dual EELS capabilities.

Results

In figure 1 a Dark Field (DF) STEM image of the low fluence specimen is seen.

In the low fluence specimens, the track morphology was observed to be typical of that in non-amorphizable materials. The latent tracks resembled discontinuous lines of small defect clusters with accompanying strain fields. Dislocations are seen to run

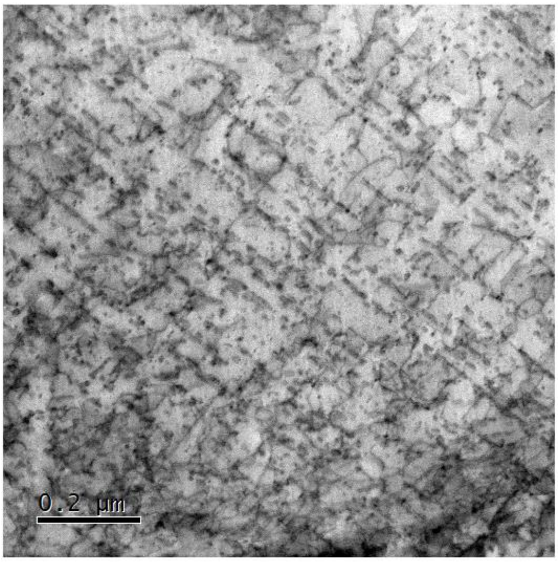

Fig. 1. DF STEM of specimen NiO(001) irradiated at +45° with 1.6 GeV Au to a fluence of $1 \cdot 10^{11}$ ions/cm^2. The tracks are oriented within the image plane. Irradiation direction was from the bottom right of the image following the <011> direction

parallel and perpendicular to the projectile direction following the primary slip directions of NiO, namely <011>.

Figure 2 shows the respective latent tracks seen in the high fluence specimen. These “tracks” seen in figure 2 are notably different as they appeared to form a line of voids along the ion projectile. Upon a more detailed inspection as seen in figure 3, the dark contrast of the tracks in a dark field image suggested they were of lower density than the surrounding material.

This was further confirmed by Fresnel contrast in defocused Transmission Electron Microscopy (TEM) images. The voids were found to exhibit a faceted nature. This is attributed to the recrystallization following the cubic structure of the crystal.

These latent tracks were the result of damage accumulation from multiple track overlaps and are thus not due to individual ions.

Figure 4 shows a Bright Field STEM image with the tracks seen head on. This was used as the EELS site of interest.

EELS revealed a reduction in both Nickel and Oxygen concentration within the void area of the “tracks” due to the overall density reduction due to the void. However, a far

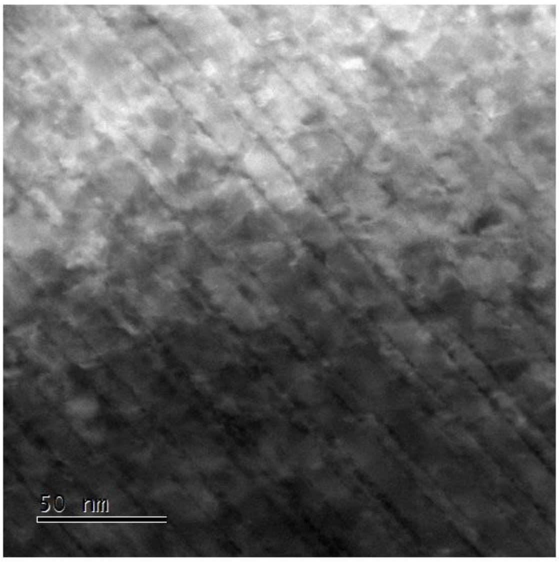

Fig. 2. DF STEM image of NiO(001) in cross section. Specimen irradiated at 45° with 593 MeV Au to a fluence of $1.4 \cdot 10^{14}$ ions/cm². Irradiation direction is from the bottom right of the image along the <011> direction

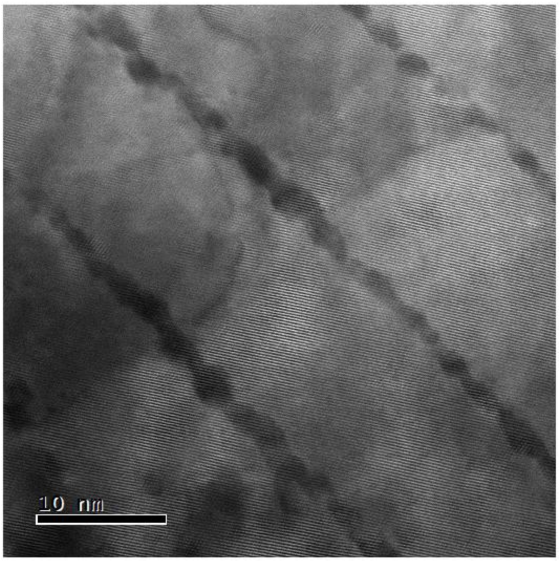

Fig. 3. Magnified DF STEM image in cross section of the high fluence “tracks”. The darker contrast withing the “tracks” are indicative of a lower density

more significant reduction was observed in the Nickel concentration.

Figure 5 shows the extracted Oxygen to Nickel ratio as measured across the highlighted track seen in figure 4.

Discussions

Areal density measurements done on specimens in the overlapping regimes found that the nearest neighbor distance remained similarly spaced despite the fluence increase.

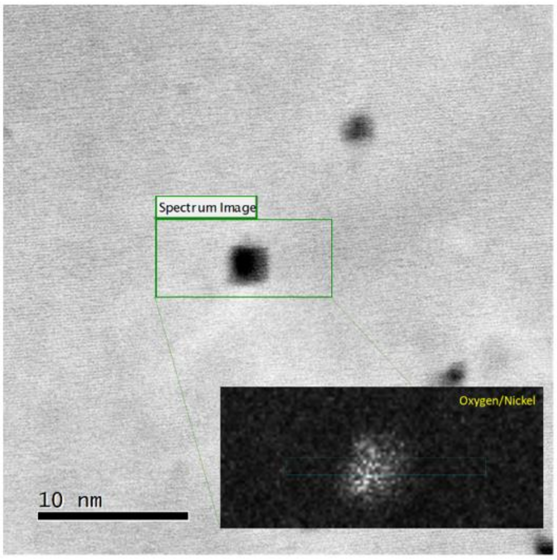

Fig. 4. A BF STEM image of the site of interest along with an inset of the ratio of Oxygen to Nickel as determined by EELS

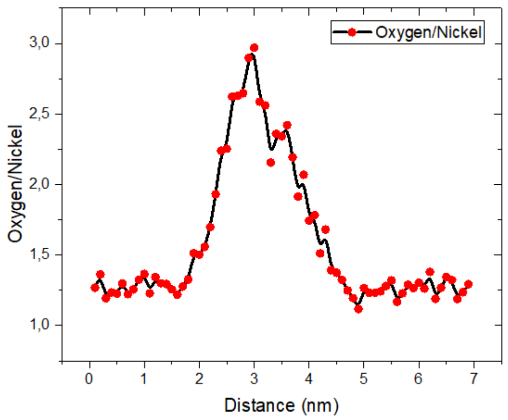

Fig. 5. The ratio of Oxygen to Nickel across the track

This further suggests the increased levels of Oxygen within the tracks.

The data suggested some saturation density of "tracks" which was far less that the irradiated fluence. An estimation of the "effective" ion track diameter yielded ~9.8 nm which was close to value of ~10 nm estimated in the low fluence specimen from diffraction contrast.

This supports the idea that the visible "tracks" are not simply due to individual ion impacts but the result of multiple impacts which. These tracks thus reached a steady state after some threshold fluence. From the EELS measurements of the high fluence "tracks" revealed an increased relative Oxygen signal within the void. This suggests that it possibly contains O_2 formed from O released during radiolytic decomposition of the NiO from SHI radiation.

Conclusions

Track evolution in single crystal Nickel Oxide (NiO) was successfully studied using electron microscopy techniques. STEM yielded visible differences in low fluence (non-overlapping regime) and high fluence (overlapping regime) specimens. Low fluence tracks resembled discontinuous lines while high fluence specimens revealed faceted voids along the ion projectile. EELS was used to determine the chemical composition of the "tracks" seen in high fluence samples. Elevated levels of Oxygen suggest radiolytic decomposition of NiO into O_2 during SHI bombardment.

Acknowledgements

The authors would like to acknowledge Siegfried Klaumünzer for the provision of the NiO specimens used in this study as well as all his valuable discussions.

References

1. Dufour C. and Toulemonde M. *Ion Beam Modification of Solids* 2016*;* 61: 63-104.
2. Fleischer R.L., Price B.P., and Walker R.M., *Nuclear Tracks in Solids*. University of California Press, 2011.
3. Karlušić M., *et al.* On the threshold for ion track formation in CaF2, *New J. Phys.* 2017; 19(2).
4. Rymzhanov R.A., Medvedev N., O'Connell J.H., A. Janse van Vuuren, Skuratov V.A., and Volkov A.E. Recrystallization as the governing mechanism of ion track formation. *Sci. Rep.* 2019*;* 9(1): 1-10.
5. O'Connell J.H., Skuratov V.A., A. Janse van Vuuren, and Rymzhanov R.A. Overview of SHI induced track morphology in crystalline non-metals from direct observation with TEM. *Acta Phys. Pol. A* 2019; 136(2): 233-236.
6. O'Connell J.H., Lee M.E., Skuratov V.A., and Rymzhanov R.A. SHI induced tetragonal tracks in natural zirconia. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* 2020. 473; 1-5.