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Transmission electron microscopy study of an electron-beam-induced phase transformation of niobium nitride

Jonghan Won,[a,*] James A. Valdez,[a] Muneyuki Naito,[b] Manabu Ishimaru[b] and Kurt E. Sickafus[a]

[a]*Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[b]*Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan*

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Tetragonal γ-NbN_{1-x} was irradiated with 300 keV electrons at room temperature to fluences from 1.8×10^{24}–5.4×10^{26} e/m^2. The superlattice structure in γ-NbN_{1-x} was observed using transmission electron microscopy and found to disappear at a fluence of 5.4×10^{26} e/m^2. During this process, displaced nitrogen atoms occupy vacant sites on the nitrogen sublattice. The final structure is a δ-phase (B1) structure. A randomized arrangement of N vacancies is responsible for the observed $\gamma \rightarrow \delta$ transformation.
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Niobium nitride, NbN_{1-x} exhibits attractive physical properties such as exceptional hardness [1,2] and superconducting behavior in the case of stoichiometric NbN (critical temperature $T_c = 17$ K) [3,4]. In nitrogen (N) deficient NbN_{1-x}, it is known that N vacancies as well as large variations in the hypostoichiometric composition variable (x) lead to a variety of crystal structures: β-phase (hexagonal: $0.51 < x < 0.55$), γ-phase (tetragonal: $0.15 < x < 0.25$), δ-phase (cubic: $0.02 < x < 0.16$), and ε-phase (hexagonal: $0 < x < 0.08$). Due to the variety of crystallographic phases in this binary Nb–N system, researchers have performed detailed structure/property investigations on Nb–N compounds [5–9]. However, the most of these studies were performed using traditional methods such as high temperature annealing or cooling under vacuum or N_2 atmosphere. Another possibility is to use energetic particle irradiation to induce structural changes, including order-to-disorder (O–D) and crystal-to-amorphous (C–A) phase transformations [10–13]. In the case of the Nb–N system, Skelton et al. [14] reported that phase transformations, such as hexagonal β-Nb_2N to cubic δ-NbN_{1-x} and cubic δ-NbN_{1-x} to hexagonal ε-NbN phase changes, occurred under irradiation with a variety of ions. Traditionally, energetic electron irradiation and concomitant, in-situ transmission electron microscopy (TEM) observation have been shown to be useful methods for studying structural evolution under irradiation [15,16]. In this study, we performed 300 keV electron beam irradiations of γ-phase NbN_{1-x} and found a phase transformation to another crystalline NbN_{1-x} phase, an irradiation-induced transformation not previously observed. In this report, we describe the atomistic structure of this metastable phase and discuss its formation processes.

A commercial niobium nitride (NbN_{1-x}) sputtering target (Kurt J. Lesker Company) with a purity of 99.5% was used as a pristine sample. Grazing incidence X-ray diffraction (GIXRD, Bruker AXS D8 advanced X-ray diffractometer) measurements (results not shown) indicated that the pristine NbN_{1-x} sample is isostructural with γ-$NbN_{0.75}$ with tetragonal lattice parameters $a = 0.439$ and $c = 0.867$ nm. γ-$NbN_{0.75}$ (γ-Nb_4N_3) possesses a crystal structure that is a derivative of the cubic rock salt (B1) structure, but with a tetragonal super unit cell due to ordering of N vacancies along the c-axis (space group I4/*mmm*). According to the previous studies [17–19], the c parameter depends on the N content of the γ-NbN_{1-x} phase, ranging from 0.863 nm for $x = 0.25$ to 0.867 nm for $x = 0.15$. This suggests that the pristine γ-NbN_{1-x} sample used in this study is a sub-stoichimetric composition, but is relatively N-rich with x closer to 0.15 than to 0.25.

* Corresponding author. Tel.: +1 505 903 1033; e-mail: jhwon@lanl.gov

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For the electron beam irradiation study, a TEM specimen was prepared in plan-view geometry. This plan-view sample was examined at room temperature in a JEOL JEM 3000F TEM instrument operating at 300 kV. Electron irradiation experiments were carried out by focusing the electron beam onto small regions of electron transparent material (a typical irradiated region was ~100 nm diameter). During these electron beam irradiation experiments, the incident electron flux, measured using a faraday cup, was approximately 1.8×10^{24} e/m^2 s. Irradiations were performed over a range of fluences from 1.8×10^{24}–5.4×10^{26} e/m^2. Irradiations were performed with the electron beam aligned along both low- and high-index crystallographic directions. No crystal-orientation dependences of the structural changes described in this report were observed. Both high-resolution TEM (HRTEM) images and electron diffraction patterns (EDPs) were recorded on imaging plates. These were typically obtained along low-index crystallographic directions. Simulations of EDPs were carried out with SingleCrystal software (CrystalMaker software Ltd.).

To examine irradiation-induced structural changes of γ-NbN_{1-x}, we performed 300 keV electron beam irradiations on this material. Figure 1(a) shows an HRTEM image of the unirradiated specimen, along with its fast Fourier transformation (FFT) diffractogram. Diffraction analysis revealed that the FFT pattern shown in Figure 1(a) is consistent with the tetragonal γ-$NbN_{0.75}$ structure, viewed along a [1 1 0] orientation. The HRTEM image shown in Figure 1(a) shows a doubly-redundant periodicity along the [0 0 1] direction. An HRTEM image obtained after electron beam irradiation to the maximum electron fluence used in this study (5.4×10^{26} e/m^2) is shown in Figure 1(b). It is apparent that the double periodicity fades and disappears after irradiation. Consequently, the first-order reflections in the FFT diagram of Figure 1(b) are significantly diminished in intensity. These results suggest that γ-NbN_{1-x} transforms to another crystalline phase. These results also led us to conclude that the irradiation-induced structure is cubic because the symmetry of the FFT pattern in Figure 1(b) looks remarkably similar to that of a face-centered cubic (fcc) Bravais lattice, viewed along a <1 1 0> direction.

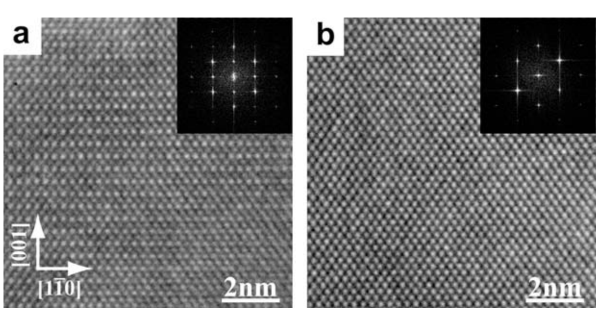

Figure 1. HRTEM images and corresponding FFT patterns (inset) obtained from pristine and electron irradiated NbN_{1-x}. (a) Pristine γ-NbN_{1-x} viewed along a $[110]_\gamma$ direction; (b) NbN_{1-x} following electron beam irradiation using 300 keV electrons to a fluence of 5.4×10^{26} e/m^2 at room temperature. The HRTEM image and the corresponding FFT pattern in (a) clearly show a double periodicity along the $[001]_\gamma$ direction. In the HRTEM image and corresponding FFT pattern in (b), the atomic superlattice and superlattice reflections are completely faded away.

In Figure 2, we compare and contrast experimental EDPs obtained in various low-index crystallographic orientations with simulated EDPs. The experimental EDPs before irradiation are shown in Figure 2(a, c and e) and after irradiation to the maximum electron fluence used in this study (5.4×10^{26} e/m^2) in Figure 2(b, d and f). The simulated EDPs for the pristine γ-phase structure are shown in Figure 2(a', c' and e'), while Figure 2(b', d' and f') show simulated EDPs assuming a cubic δ-phase structure forms upon irradiation (δ-NbN_{1-x} is a B1 rocksalt structure with an fcc Bravais lattice). Before irradiation, the experimental EDPs exhibit superlattice reflections in addition to strong fundamental reflections. During irradiation, the superlattice reflections were observed to gradually decrease in intensity and then vanish completely. For the electron flux conditions used here, the total irradiation time for the superlattice reflections to disappear completely was less than 5 min, corresponding to a fluence of ~5.4×10^{26} e/m^2. The simulated EDPs shown in Figure 2 are in very good qualitative agreement with the experimental EDPs. Thus, we conclude that a $\gamma \rightarrow \delta$ phase transformation was induced by the 300 keV electron beam irradiations.

To rationalize the $\gamma \rightarrow \delta$ transformation, consider kinetic energy transfer from incident electrons to target

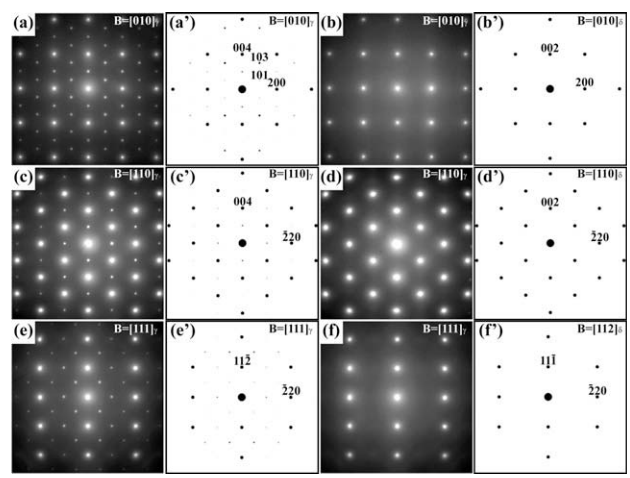

Figure 2. Electron diffraction patterns (EDPs), both experimental and simulated for pristine and irradiated NbN_{1-x}. Electron beam orientations are as follows: (a and b) $[010]_\gamma$, (c and d) $[110]_\gamma$, and (e and f) $[111]_\gamma$, where γ represents the tetragonal unit cell of the pristine γ-NbN_{1-x} phase. EDPs (a, c and e) were obtained prior to prolonged electron irradiation. EDPs (b, d and f) were obtained following 300 keV electron irradiation to a fluence of 5.4×10^{26} e/m^2 at room temperature. Superlattice reflections in (a, c and e) before irradiation are not apparent in (b, d and f) after electron irradiation. (a', c' and e') and (b', d' and f') show simulated EDPs. The incident beam directions in (a', c' and e') correspond to those in (a, c and e) (labeled γ for γ-phase NbN_{1-x}), while (b', d' and f') correspond to $[010]_\delta$, $[110]_\delta$, $[112]_\delta$, where δ represents the cubic unit cell of δ-NbN_{1-x}. Simulated EDPs in (a', c' and e') are based on a pristine, tetragonal γ-NbN_{1-x} structure with 85% N factional occupation in an ordered arrangement on the N sublattice. Simulated EDPs in (b', d' and f') are based on a cubic, δ-NbN_{1-x} with 85% N fractional occupation. The N atoms in the cubic δ-NbN_{1-x} model occupy randomly sites on a face-centered cubic (fcc) N sublattice.