

ELECTRON IRRADIATION DAMAGE IN OXIDES

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Structural changes occurring at or near surfaces during irradiation in the electron microscope have been reported in a broad range of oxide systems, but only relatively recently have they been investigated primarily in terms of radiation damage. The present study seeks to categorize some recent results as well as results given in the literature by the type of structural modification observed in order to gain a better understanding of the damage mechanism, whether it be ballistic, electronic, or thermal in nature. A specific example is given comparing TiO_2 , a material known to undergo surface ionization damage in the form of desorption induced by electronic transitions (or DIET), and NiO , a material whose DIET characteristics are not well established. Electron irradiation damage is found to depend not only on the nature of the system, for example the valency of the cationic species, but also on the crystal orientation and surface preparation. The behavior of these materials indicates a complex radiation damage scheme which cannot be explained solely by electronic, thermal or ballistic damage considerations.

1. Introduction

It has long been recognized that some materials will undergo radiation damage when observed in the electron microscope. A number of mechanisms may be operative, ranging from simple ballistic damage to ionization damage initiated by electronic excitations. Non-metallic solids are particularly susceptible to ionization damage, either by radiolysis in the bulk or desorption induced by electronic transitions, or DIET, at the surface [1–6].

The study of surface radiation damage of oxides is relatively new to electron microscopy. Most of the previous work has been done at much lower energies using electron-stimulated desorption, low-energy electron diffraction, and Auger electron spectroscopy experiments [1,2] from which an understanding of the damage mechanisms has evolved. DIET processes initially require only the creation of an electronic excitation which subse-

quently leads to both an atomic desorption and a corresponding structural change. Whether the initial excitation is described as a core-loss phenomenon, such as the Knotek–Feibelman [3] mechanism for maximum valency oxides, or a valence excitation, such as the Menzel–Gomer–Redhead [4,5] and phonon-assisted recombination [6] mechanisms, structural rearrangement at or near the surface can readily occur.

Very early in the study of oxide surfaces using high resolution electron microscopy, it became apparent that in-situ DIET-related processes were occurring [7,8,37]. The intention of this note is to present results comparing two materials – TiO_2 , which is believed to undergo DIET via the Knotek–Feibelman mechanism [3], and NiO , where there is controversy concerning the role of the DIET process as a damage mechanism [9–11]. We find that the tendency for TiO_2 to lose oxygen is strong, in agreement with the Knotek–Feibelman mechanism, whereas there is no evidence for preferential oxygen loss in NiO unless the surface is contaminated with an amorphous carbon layer. Clean NiO suffers primarily from ballistic damage;

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however, it is also seen to oxidize to a Ni_3O_4 spinel phase at the surface. Sample preparation plays a critical role in beam damage of NiO ; however, crystal orientation does not. This is not the case for TiO_2 , where crystal orientation plays a major role in the type of beam damage observed. Beam damage in TiO_2 is also seen to be highly sensitive to encapsulating contamination layers. Results for TiO_2 are summarized for the $[001]$, $\langle 110 \rangle$, and $\langle 111 \rangle$ zones. Finally, a summary classification of damage characteristics in a number of oxides is given incorporating both the results of the present authors, which include MoO_3 , LiNbO_3 , Y_2O_3 , Cr_2O_3 , BaTiO_3 , CaTiO_3 , BaO , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{La}_2\text{SrCu}_2\text{O}_7$ and BaCuO_2 , and those in the literature.

2. Experimental method

Specimens were prepared by crushing high-purity bulk crystals, either dry or in methanol, and dispersing onto holey carbon films. All the TiO_2 samples were crushed in methanol. The NiO samples were also crushed in methanol except where preparation by ion-milling was specified [12]. Each sample grid was baked on a 150 W light bulb for approximately 15 min just prior to insertion into the microscope to drive off any absorbed gases or water vapor. The maximum temperature achieved during this procedure was $240 \pm 5^\circ\text{C}$.

Specimen profile surfaces were examined in a Hitachi H-9000 electron microscope operating between 100–300 kV in a vacuum of approximately 3×10^{-7} Torr. Optimum particle sizes ranged from 5 to 10 μm in diameter. During irradiation, the beam was typically focused to crossover and positioned at the profile edge. The electron flux could not be measured directly, but was qualitatively estimated using the exposure meter and the assumption that a typical dose for an electron micrograph is of the order of 10^5 – 10^6 electrons/ $\text{\AA}^2$. Two flux conditions, low and high, were utilized. In the low-flux condition, the condenser aperture was inserted, producing an electron flux of the order of 10^2 A/ cm^2 . In the high-flux condition, the condenser aperture was removed, producing an electron flux of the order of 50 times larger.

Qualitative estimates of the temperature rise in TiO_2 under these conditions were made using the theoretical treatment of Fisher [13]. The calculated temperature rise was negligible for the low-flux case. For the high-flux case, the calculated temperature rise was less than 300 K. A slight (< 20 $\text{\AA}$) carbon contamination layer on the surface could usually be etched away by flooding the area with the beam at low magnification for a few minutes (for further details, see ref. [14]).

The resulting structural transformations were monitored on videotape and identified by selected-area diffraction, optical diffraction, and comparison with computer image calculations. These calculations were carried out on an Apollo workstation using the NUMIS programs written at Northwestern University. In some cases, experimental images were acquired directly into the computer via a bus-interfaced framestore.

3. Results

3.1. TiO_2

Electron beam damage of the rutile (tetragonal) phase of TiO_2 resulted in extensive structural changes and showed a strong dependence on sample orientation. The observed changes were also not found to vary significantly with incident electron energy between 100 and 300 keV. The results are summarized in table 1.

Along the $[001]$ orientation, a continuous phase transition was seen to initiate at the profile surface and extend into the bulk along the following reaction pathway.

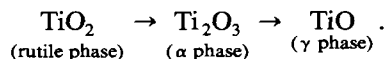


Fig. 1 shows the irradiated area after 55 min. The phase transformations had progressed to a depth of approximately 100 nm and may well have extended further with increased exposure times. Irradiation of the $\langle 101 \rangle$ and $\langle 110 \rangle$ zones under similar conditions resulted in void formation. As seen in fig. 2, the $\langle 101 \rangle$ zone also showed extensive near-surface damage, whereas the $\langle 110 \rangle$ zone did not. The $\langle 100 \rangle$ zone (fig. 3) showed extensive

Table 1
Anisotropic damage in TiO_2 at 300 kV

Irradiation direction	Defects at the profile surface	Bulk structure
[001]	Phase change to TiO via collapse of {200} planes	Phase change to TiO via collapse of {200} planes
$\langle 101 \rangle$	Defective surface layer forms and grows with time	Void formation, growth, and coalescence
$\langle 100 \rangle$	Defective surface layer forms and grows with time	Three-fold fringe structure along $\langle 101 \rangle$ planes, prismatic dislocations
$\langle 110 \rangle$	Surface roughening	Void formation
$\langle 111 \rangle$	Surface phase transformation to $\alpha\text{-Ti}_2\text{O}_3$	Moiré fringes with $\alpha\text{-Ti}_2\text{O}_3$

near-surface damage in addition to the appearance of a three-fold superstructure which was more strongly evident away from the profile edge. There

was no evidence of a surface phase at the profile edge. These observations lead us to believe that the 3d periodicity is a true superstructure and not

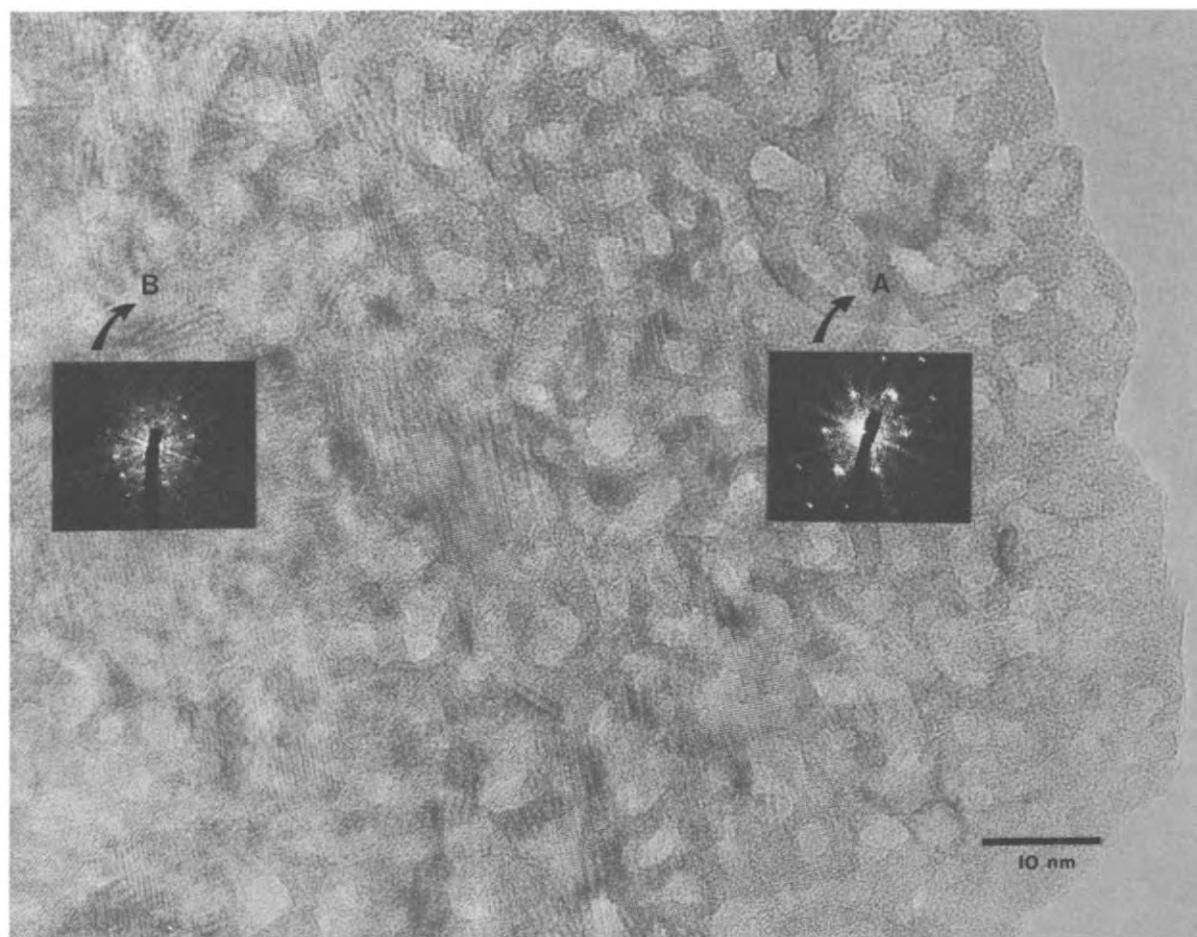


Fig. 1. TiO_2 (rutile) irradiated under high flux conditions along the $\langle 001 \rangle$ zone. The letter A marks a region of $\gamma\text{-TiO}$. The letter B marks a region of $\alpha\text{-Ti}_2\text{O}_3$. Optical diffraction patterns are inset.

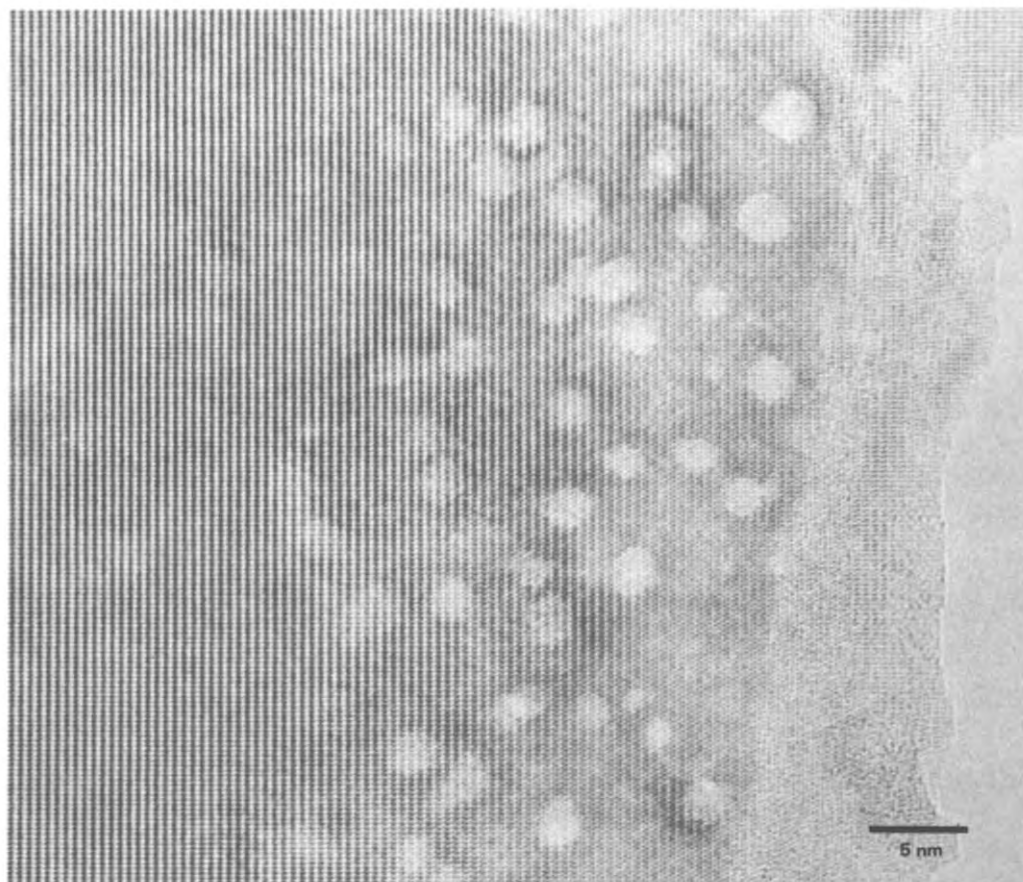


Fig. 2. TiO_2 irradiated under high flux conditions along along the $\langle 101 \rangle$ zone. Beam damage resulted in a defective surface layer and void formation.

a moiré effect, although identification of this structure is not yet conclusive. It appears that our observations of a three-fold periodicity are similar to those produced by ion-beam milling of specimens [15]. Lastly, as seen in fig. 4, the $\langle 111 \rangle$ zone showed the formation of $\alpha\text{-Ti}_2\text{O}_3$ at the profile surface, with evidence that top and bottom surfaces were also undergoing this phase transformation.

An encapsulating contamination layer significantly reduced the extent and rate of beam damage, indicating the importance of the surface-initiated processes and the lesser role played by ballistic processes. For zones other than the [001], no beam damage was observed during two hours of in-situ observation. Along the [001] zone bulk damage was evident by the slow appearance of

strain contrast, but neither the reduction of the material to lower oxides nor void formation were observed, possibly due to the inability of oxygen to escape from the surface [16].

Addressing the question of thermal effects, it is clear that point defect migration is playing a major role in the propagation of the damaged layer inward from the profile surface. It, however, is not clear that this is a thermal (temperature rise) rather than a radiation-enhanced (point defect creation) effect. We are inclined to believe that the latter is occurring for the following reasons: Calculated diffusion distances for both Ti and O are considerably smaller than the observed damaged layer widths. The series of phase transformations we observe in many cases are not

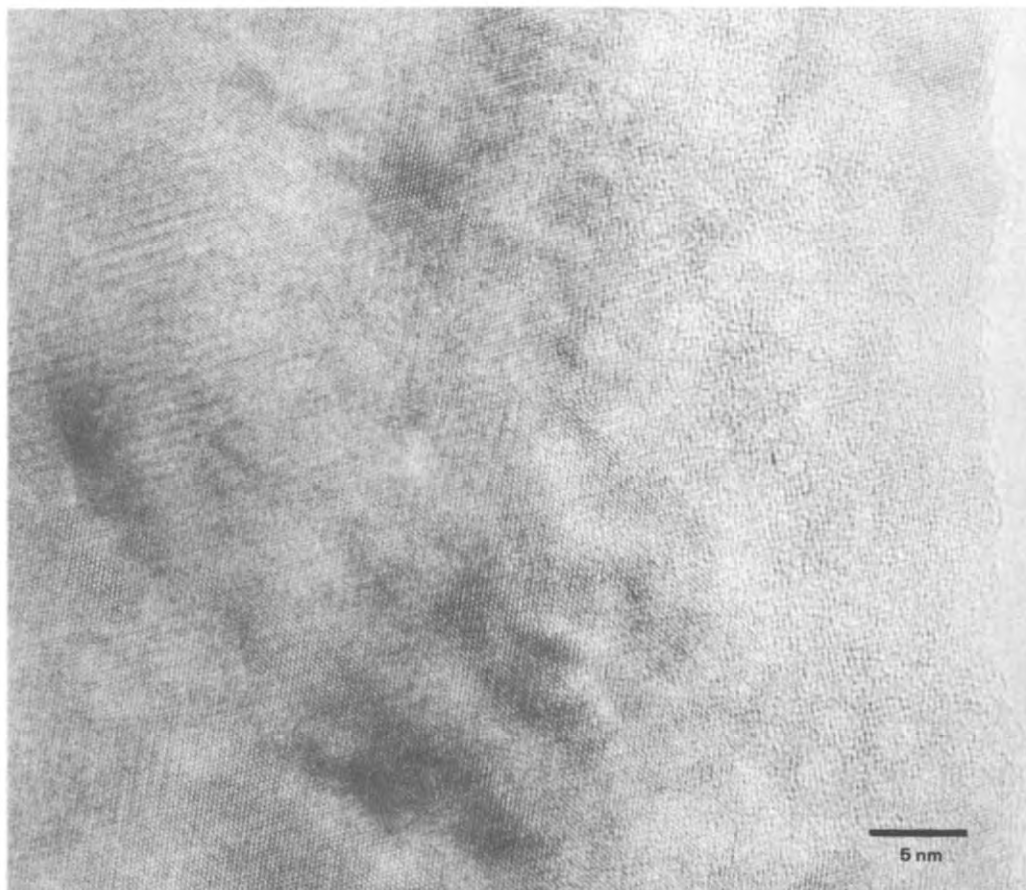


Fig. 3. TiO_2 (rutile) irradiated under high flux conditions along the $\langle 100 \rangle$ zone. Beam damage resulted in a defective surface layer, and the appearance of a three-fold periodicity.

predicted by equilibrium thermodynamics and seem to be governed by kinetics. For example, it is not expected that $\alpha\text{-Ti}_2\text{O}_3$, which is stable below 400°C [17], and $\gamma\text{-TiO}$ which is stable above 460°C [18], should form simultaneously as they do in the $[001]$ zone orientation. Ti metal planes appear to be undergoing only a minimal change, while approximately half of the oxygen atoms are being lost from the $\{200\}$ planes. $\{200\}$ planes can then collapse into a hexagonally packed (111) TiO plane with the $\alpha\text{-Ti}_2\text{O}_3$ being only a transitory phase along the damage path [14,19]. The rate-limiting step here seems to be the removal of the oxygen and the subsequent formation and diffusion of oxygen defects.

In summary, the beam damage in TiO_2 generally follows the DIET trend for maximum valency oxides. The surface-initiated damage was confirmed in many cases by repeating the experiments at an operating voltage to 100 kV, showing the lesser significance of ballistic processes. In no case could the behavior of the damage processes be described by a ballistic knock-on argument, unlike the NiO discussed in the next section. Perhaps what is most interesting is the strong orientation dependence. Similar observations have been made in other systems, such as the trigonal polymorph of the high-temperature superconductors as shown in table 2 [20]. These polymorphs were found to be fairly stable along the $[100]$ direction, but

Table 2
Classification of materials

Material	Final phase identification ^{a)}	Wetting	Epitaxy	Diffusion/segregation	Amorphous	Ref. ^{b)}	
Class 1							
V ₂ O ₅	~ VO _{0.9}	Yes	Yes	–	No	[29]	
WO ₃	~ WO	Yes	Yes	–	No	[29]	
WO ₃	~ W	Yes	Yes	–	No	[7,8]	
W(Nb)O _{2.933}	Met., lower oxides	Yes (?)	Yes	–	No	[37]	
TiO ₂ $\langle 111 \rangle$, $\langle 001 \rangle$, $\langle 100 \rangle$	~ TiO	?	?	–	Yes	[14,29]	
Nb ₂ O ₅	~ NbO	Yes	Yes	–	No	29	
MoO ₃	Met.?	Yes	Yes	–	No	PS	
(Mo, Ta) ₅ O ₁₄	Met.?	Yes (?)	Yes	–	No	[28]	
CuO	Cu ₄ O ₃ , Cu ₂ O, Cu	No (?)	?	?	?	[30]	
Ti ₂ Nb ₁₀ O ₂₉	Met.?	Yes	Yes	–	No	[31,37]	
VNb ₉ O ₂₅	Met.?	Yes	Yes	–	No	[28]	
MoO ₂	~ Mo	Yes	Yes	–	No	[27]	
NiO (dirty)	Ni	No	Yes	–	No	PS, [21,28]	
Bi _x WO ₃	Met.?	?	?	Yes	No	[28]	
Class 2							
NiO (clean)	Ni ₃ O ₄	Yes	Yes	?	No	PS, [22]	
CrVO ₄	Cr ₂ O ₄	No	No	Yes	?	[27]	
ZnCrFeO ₄	~ ZnO	No	Yes	Yes	No	[32]	
ZnCr ₂ O ₄	~ ZnO	No	Yes	Yes	No	[32]	
YBa ₂ Cu ₃ O ₇	~ BaO						
YBa ₂ Cu ₃ O _{6.5}	~ BaO						
$\langle 100 \rangle$		Yes	No	Yes	Yes	[20]	
$\langle 001 \rangle$		Yes	Yes	Yes	No	[20]	
LiNbO ₃	?	Yes	Yes	?	No	PS	
InP	In, In ₂ O ₃	?	No	Yes	–	[33]	
InAs	As, In ₂ O ₃	?	Yes	Yes	–	[33]	
InSb	In ₂ O ₃	?	No	Yes	–	[33]	
Class 3							
TiO ₂ $\langle 101 \rangle$, $\langle 110 \rangle$	Voids	–	–	–	–	PS, [14]	
CuO	Lower oxides	–	–	–	–	[30]	
Bi _x WO ₃	Disordering	–	–	–	–	[28]	
VO	Disordering	–	–	–	–	[34]	
Class 4							
Al ₂ O ₃	?	–	–	–	–	[35]	
NiO, clean (early stages)	Erosion	–	–	–	–	PS, [22]	
ZnCrFeO ₄ (early stages)	Faceting	–	–	–	–	[32]	
Class 5							
Material	Ref.	Material	Ref.	Material	Ref.	Material	Ref.
BaO	PS	BaCuO ₂	PS	BaTiO ₃	PS	CaTiO ₃	PS
Cr ₂ O ₃	PS	La _{2–x} Sr _x CuO ₄	PS	La ₂ SrCu ₂ O ₇	PS	Y ₂ O ₃	PS
UO ₂	[28]	U ₄ O ₉	[28]	TbO _x	[36]		

^{a)} Met. indicates metallization.

^{b)} PS indicates present study.

damaged rapidly along the [001] direction. The source of this directional effect remains a subject for further research. As described in preliminary

reports, a major role must be played by diffusional processes, whether they be thermal or radiation-enhanced [14,16,19–21].

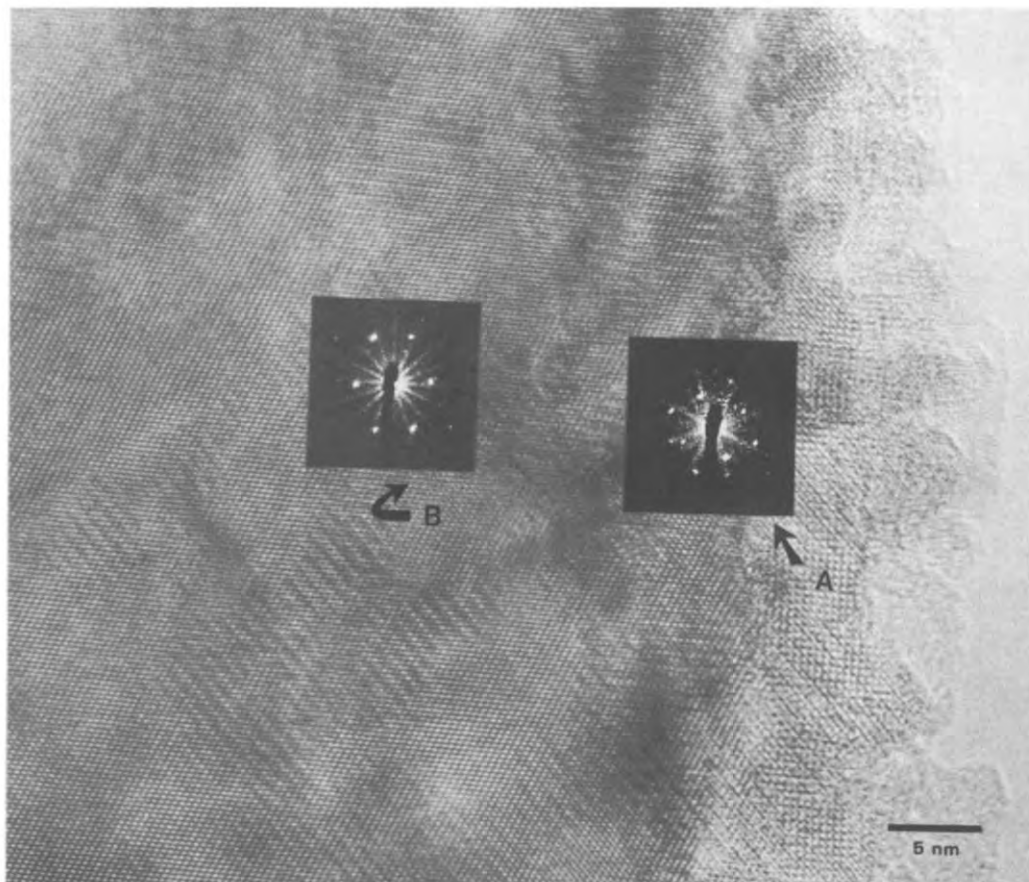


Fig. 4. TiO₂ (rutile) irradiated under high flux conditions along the $\langle 111 \rangle$ zone. Beam damage resulted in the surface transformation to α -Ti₂O₃ (marked A), as observed by the moiré fringe patterns. Optical diffraction patterns are inset.

3.2. NiO

A clean, freshly prepared NiO sample showed predominately ballistic damage at 300 kV in the form of surface erosion as shown in fig. 5a. This type of damage was completely suppressed by lowering the operating voltage to 100 kV. The effects of electron irradiation in NiO (rocksalt structure) were not found to be orientation dependent, most likely due to its cubic symmetry.

In isolated areas of the surface a doubling of the unit cell was also observed, as shown in fig. 5b. The doubled unit cell layer was more pronounced in specimens prepared, then left for a day in air before insertion into the microscope. This structure was also observed at an operating volt-

age of 100 kV and was not accompanied by mass loss, thus suggesting some mechanism other than ballistic, but not necessarily DIET. Image simulation showed agreement between this observed structure and a Ni₃O₄ spinel with a unit cell twice as large as that of NiO [22]. Previous surface science studies using chemical shift information have shown that NiO can be oxidized to produce Ni³⁺ at the surface, which was interpreted as the formation of a Ni₂O₃ surface phase [23]. It should be noted that neither Ni₂O₃ nor Ni₃O₄ are known stable oxide structures. We strongly suspect that both sets of data are describing the electron-stimulated surface oxidation of NiO to Ni₃O₄. The known catalytic activity of surface Ni³⁺ species [24] may also be the reason that damage resistant,

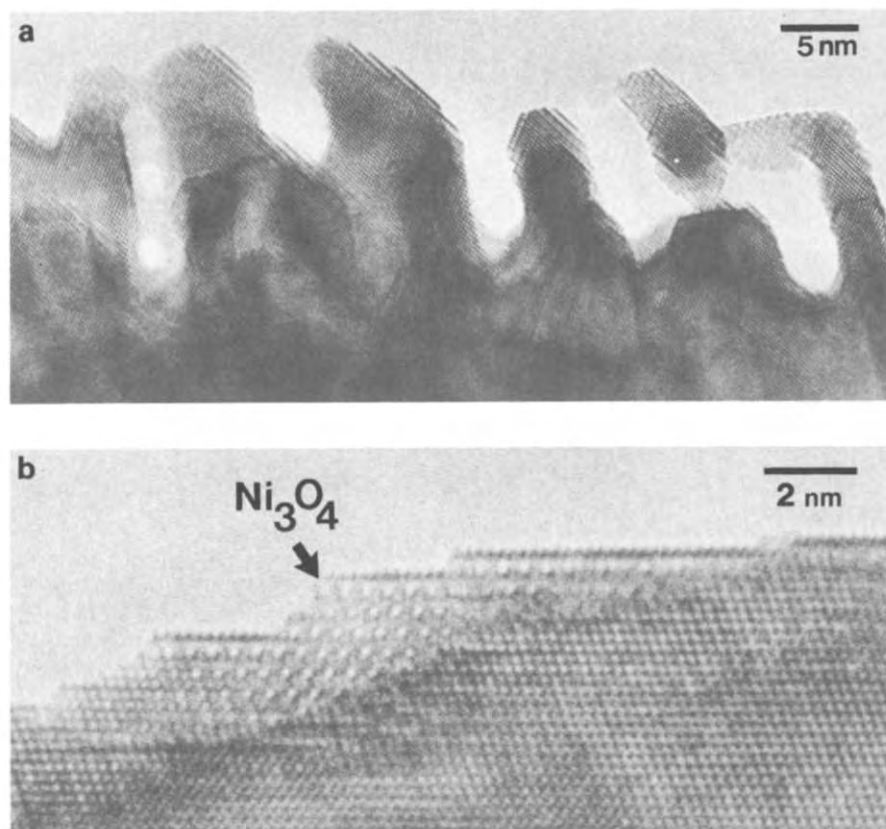


Fig. 5. (a) A clean, freshly prepared NiO sample irradiated under low flux conditions along the [110] zone at 300 kV for 2.5 h; beam damage was primarily ballistic in nature. (b) The same sample as shown in figure 5 after 1 h. A Ni_3O_4 spinel phase was observed in isolated areas of the surface.

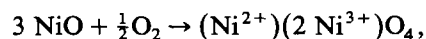
nonreactive carbonaceous encapsulating layers do not form on NiO surfaces.

If the NiO specimens were left in air for approximately one week or more, they developed a reactive carbonaceous contamination layer on the surface. Electron irradiation in this case resulted in the reduction of the “dirty” NiO to epitaxial Ni on the surface regardless of beam orientation, contrary to the previously described results for clean NiO surfaces. As shown in fig. 6, islands of Ni form on the surface with a cube–cube epitaxial relationship. This behavior was greatly accelerated at 100 kV.

Ion-milled NiO samples showed similar behavior as described above for the “dirty” NiO samples. Ballistic knock-on damage could be observed in the form of mass loss from the surface and the

formation of holes (see also ref. [22]). Under high flux irradiation, islands of Ni were also identified. The threshold for this type of beam damage has been previously observed to be approximately 115 ± 5 kV [22]. It is suspected that the combined effects of ion beam damage and bond weakening by chemisorption of H_2O and other surface species has reduced the knock-on threshold in this case.

In summary, the beam damage observed in NiO does not indicate a DIET-initiated mechanism. Clean specimens revealed ballistic damage as well the oxidation of NiO to Ni_3O_4 , so that either oxygen has been introduced from the vacuum via the reaction:



or a defect reaction between the parent NiO and



Fig. 6. A “dirty” NiO sample irradiated under low flux conditions at 300 kV for 0.25 h. Islands of Ni have formed on the surface with a cube–cube epitaxial relationship.

Ni vacancies has occurred. In contrast, samples with a carbonaceous contamination layer indicated the reduction of NiO to Ni at the surface during irradiation. Ballistic phenomena were followed qualitatively; however, this mechanism could not account for the varied behavior of NiO to surface preparation conditions.

4. Classification of damage processes

A survey of the structural changes produced in oxide systems during in-situ electron irradiation reveals that many characteristics of electron irradiation damage appear to be consistently observed. Materials can be classified into at least five general categories as described below and in table 2:

Class 1: Materials which show surface-initiated phase transformation to a lower oxide.

Class 2: Materials which show phase transformation, but not to a lower oxide.

Class 3: Materials which show bulk-initiated beam damage.

Class 4: Materials which show surface-initiated beam damage.

Class 5: Materials which show no beam damage.

Nearly all the materials in Class 1 are maximum valency oxides. It is presumed that the Knotek–Feibelman DIET mechanism is primarily responsible for the radiation damage seen in these systems. A number of mechanisms may be operative for Class 2 materials, including ballistic, electronic, or thermal. III–V semiconductors are included because surface oxides are observed. Class 3 materials show extensive bulk damage, such as void and vacancy/interstitial loop formation, order/disorder, or bulk phase transformation, which may or may not be related to events occurring at the surface. Class 4 materials show features such as surface reconstructions, faceting, or surface erosion. As in Class 2, a number of mechanisms may be operating. Class 5 materials are stable

against prolonged electron irradiation. Where applicable, the materials are further described as to the identity of the new phase, whether the new phase wets the original, whether the new phase is formed epitaxially, whether diffusion or segregation is noted, or whether an amorphous layer is noted.

5. Discussion

After a review of the radiation damage processes observed in the electron microscope, it is clear that a number of contributing mechanisms are operative (see, for example, refs. [25,26]). Within the voltage range of a typical high-resolution microscope, 100–400 kV, it is virtually impossible to isolate and observe a single mechanism in operation. With careful experimentation, however, one can gain insight to the relative contributions of various mechanisms. Ballistic versus electronic processes can be identified by varying the electron energy and noting both the type and qualitative rate of any given structural modification. For example, the tendency of many of the Class 1 materials to undergo reduction consistent with the Knotek–Feibelman DIET mechanism was identified in this way. In contrast, MoO_2 was seen to “metallize” at 400 kV, but not at 200 kV [27]. This would be in agreement with surface sciences studies indicating that DIET should not be occurring in this material [3]. With a continuously variable voltage microscope, one can obtain qualitative information on the ballistic knock-on damage threshold limit. The questions of damage rates, the effect of electron flux and dose, bonding versus mass effects in ballistic processes, and the persistent questions of beam heating and other thermal effects remain for further study.

Other concerns which have been addressed in this paper are the beam orientation effect, beam-enhanced diffusion, and the state of the surface prior to irradiation. These processes are, as yet, admittedly not well understood. With respect to the state of the surface, observations such as the reaction of “dirty” NiO to form metallic Ni are examples of how electron-stimulated surface reactions can be studied in-situ in the electron

microscope. With the appearance of the UHV instruments, electron microscopy should become a major contributor in these areas.

6. Conclusion

The structural changes occurring in oxides during electron irradiation have been categorized. Two specific materials, TiO_2 and NiO, have been contrasted with respect to the mechanisms by which they are believed to undergo radiation damage in the electron microscope. It was seen that the electronic, thermal, and ballistic mechanisms by which oxides undergo radiation damage depend on a number of parameters, including sample preparation, crystal orientation, and electron flux.

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