PHILOSOPHICAL MAGAZINE LETTERS, 1989, VOL. 60, NO. 1, 31–36

Diffusion during electron-beam-induced reduction of tungsten trioxide

By S. R. SINGH and L. D. MARKS

Center for Surface Radiation Damage Studies, Department of Materials Science & Engineering, Northwestern University, Evanston, Illinois 60208, U.S.A.

[*Received in present form 4 March 1989 and accepted 5 April 1989*]

ABSTRACT

We report experimental results on the kinetics of the electron-beam-induced reduction of WO_3 by *in situ* high-resolution electron microscopy. Electron-beam irradiation of WO_3 results in complete reduction to W. The process is surface-initiated through desorption of oxygen from the crystal surface, and the subsequent growth of tungsten was found to be a diffusion-controlled process. The damage rate follows a para-linear curve, that is, an initially parabolic damage rate degenerating into a linear rate. The epitaxial relationship between WO_3 and W was found to be $(001)_{WO_3}//(110)_W$. The WO_3 lattice has a critical nucleus size of about 2·6 nm.

§1. INTRODUCTION

It is now well established that desorption induced by electronic transitions (DIET) of oxygen occurs from maximally valent transition metal oxide systems (Tolk, Traum, Tully and Madey 1983). It has recently been shown that high-resolution electron microscopy (HREM) can be a complementary technique to surface science studies (Marks 1983, Marks and Smith 1984). HREM provides a unique opportunity for the study of radiation damage in crystals, since discrete stages of the damage processes can be observed directly. To date, analyses have been purely qualitative in character, attempting to identify the end products and their epitaxy and not focusing on the kinetics of the processes, for example for previous studies of damage of WO_3 see Petford, Marks and O'Keeffe (1986), Smith, McCartney and Bursill (1987) and Liu and Cowley (1988).

In this Letter, we present the first evidence for a fundamentally new mechanism for the structural transformation during DIET from tungsten trioxide single crystals using high-resolution electron microscopy (HREM) *in situ* experiments to monitor the kinetics of the damage. Oxygen desorption from the surface of WO_3 crystal can be accounted for by the Knotek and Feibelman (1978) model, or a similar mechanism, but complete annihilation of the WO_3 lattice and subsequent growth of W was found to be a diffusion-controlled process.

§2. EXPERIMENTAL PROCEDURE

For HREM, samples of WO_3 powder were dispersed onto a holey carbon film supported on a copper grid. An isolated particle was chosen for more exact treatment of the kinetics, because when two such crystals impinge on each other, the electron-beam-induced surface migration of reaction product can lead to misleading results. The *in situ* HREM measurements were performed in a Hitachi H-9000 high-resolution electron microscope operating at a vacuum of 10^{-7} Torr and at an accelerating voltage of

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300 kV. An oriented crystal was irradiated at an electron flux of about 10 A cm^{-2}, and time-sequence photographs recorded at various electron doses. The lattice fringe spacings and orientations in the micrograph were determined from the corresponding optical diffractogram. The kinetics of the process were evaluated by plotting the linear dimension of the WO_3 crystal against time.

§ 3. Results

Figures 1 (*a*)–(*e*) show some of the HREM pictures from a time sequence of a WO_3 crystal. The crystal is in the [100] orientation and shows crossed lattice fringes corresponding to (001) planes ($d_{001} = 3{\cdot}83$ Å) and (020) planes ($d_{020} = 3{\cdot}75$ Å). Figure 1 (*a*) was recorded after about 5 min of electron irradiation. This time was required for proper orientation of the crystal. In this figure the WO_3 crystal lattice starts to disappear from the edges (surface) of the crystal. The optical diffractogram inset in fig. 1 (*a*) is from the WO_3 crystal. In fig. 1 (*b*), the WO_3 crystal has further reduced in size. The damaged region in fig. 1 (*c*) is covered by W (110) fringes which surround the WO_3 crystal. The orientation relationship between WO_3 and W is $(001)_{WO_3} /\!/ (110)_W$. Additional evidence from selected-area diffraction ring patterns indicated that the produce was W, not WO or β-tungsten, although the later could be produced by further oxidation of the W; these results will be reported in more detail elsewhere. In fig. 1 (*d*) the WO_3 crystal size is just about the stable critical nucleus size of the WO_3 lattice which is found to be about 2·6 nm. Immediately after this sequence the WO_3 lattice completely disappeared. Figure 1 (*e*) shows the final W crystal. The size of the WO_3 crystal was evaluated from the time-sequence photographs and a graph was plotted of variation of the linear dimension along the *b* and *c* axes with time. The graph is shown in fig. 2 and follows a para-linear curve. The overall behaviour of both the curves is the same, and the deviation from an exact path is due to shape anisotropy of the particle. This figure shows that, initially, damage follows a parabolic law which degenerates into a linear rate law. The parabolic damage/growth indicates diffusion control, whereas linear damage/growth indicates that reaction at the WO_3/W phase boundary is rate controlling. The diffusion constant evaluated by the Rosenburg (1960) method is $5{\cdot}4 \times 10^{-14}$ cm^2 s^{-1}.

§ 4. Discussion

During electron-beam irradiation oxygen ions or neutrals (defects) produced in the bulk, through the electron-beam-induced electronic transitions, cannot desorb from the surface. These defects can be annihilated at the surface provided they diffuse out of the bulk, giving rise to a defect flux towards the surface. As the present investigation was performed at room temperature, at which the equilibrium concentration of defects (vacancies and interstitials) is exceedingly small, thermally activated diffusional processes are negligible, and we have to presume the existence of electron-beam-assisted diffusion.

DIET alone cannot explain the complete reduction of the WO_3 crystal; if the damage rate depended solely upon the rate of formation of defects then the radius of the particle should scale as the cube root of the time (dose). The above experiments reveal that the total reduction of the WO_3 crystal is a multi-step phenomenon. The step sequence is as follows.

(1) DIET at the surface leads to oxygen desorption. This process may lead either to non-stoichiometry or to nucleation of W with a limited surface coverage.

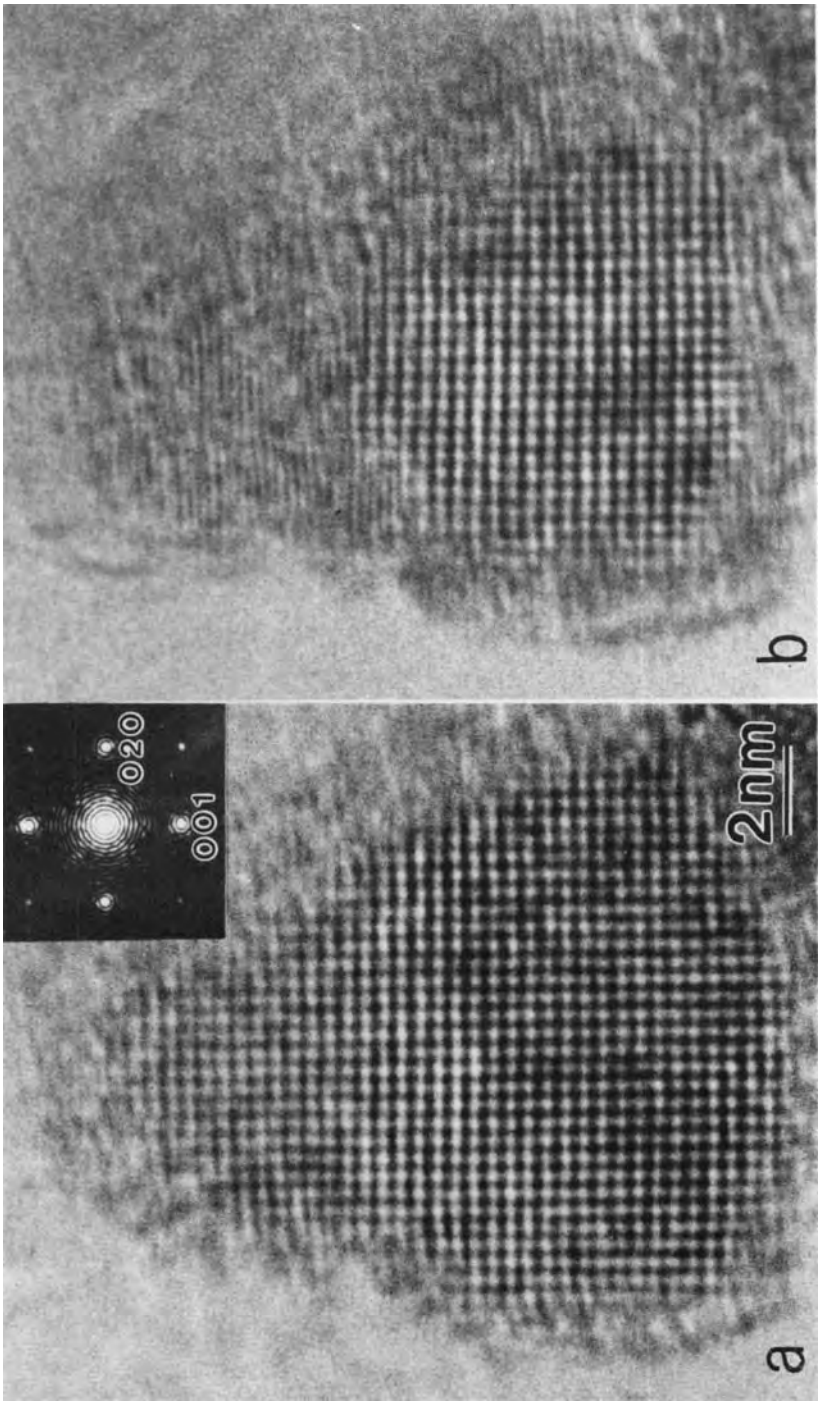
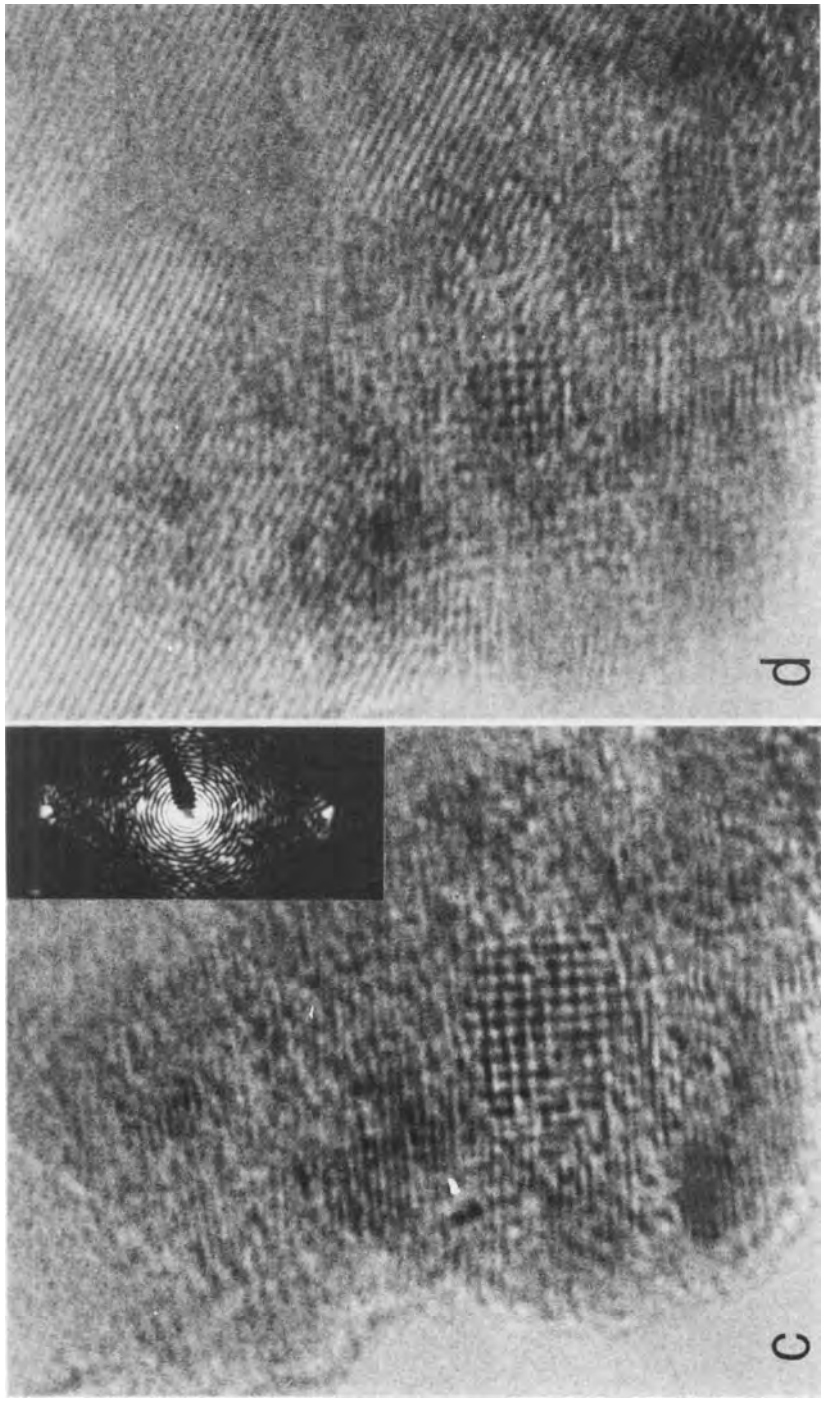


Fig. 1



A series of time-lapsed HREM images of WO_3 crystal in [100] orientation. (*a*) After 5 min irradiation, inset shows the optical diffractogram from the image. (*b*) After 20 min irradiation. (*c*) After 115 min irradiation: inset shows the optical diffractogram from (110) lattice fringes of W. (*d*) After 160 min irradiation: showing stable critical nucleus of WO_3 crystal. (*e*) Showing complete disappearance of the WO_3 crystal.

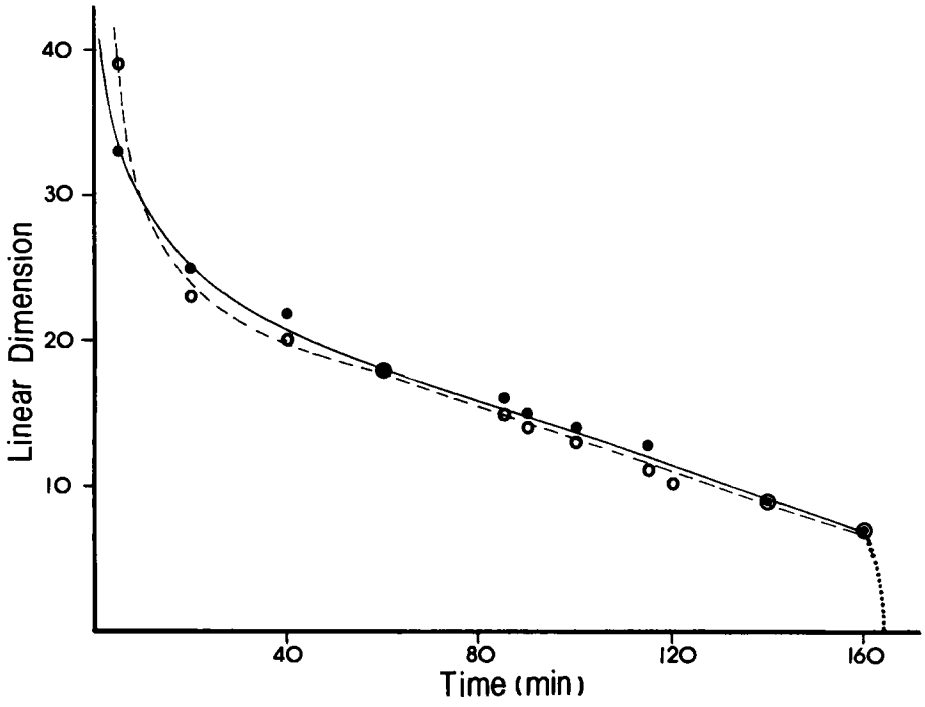
Further reduction of the WO_3 crystal stops because of the formation of the surface W phase which prevents direct escape of the oxygen.

(2) Diffusion of oxygen defects, interstitials or vacancies, charged or uncharged, through the surface W phase permits the reduction to continue. As mentioned above, this is electron-beam-assisted diffusion. The initial kinetics show a parabolic damage rate, which means that in the initial stage the W layer behaves as a semi-infinite diffusion system.

(3) The later part of fig. 2 shows that the kinetics of the damage is linear. Therefore the process becomes interface-controlled. This is expected because the diffusion-controlled process may become interface-controlled in a very small crystal (Christian 1975). During this stage the damage rate is slower than that in the parabolic regime.

From these experiments we see that the damage to the WO_3 lattice during electron-beam irradiation is a continuous process involving diffusion of participating species as the rate-limiting step and that this can be monitored directly by HREM.

Fig. 2



A graph of the linear dimension of crystal (in units of the number of (001) and (020) interplanar spacings) against time (dose) showing the kinetics of the damage process. The broken (--- and ○) and solid (—— and ●) lines are for kinetics along the *c* and *b* axes respectively. The dotted line indicates the dissolution of the critical nucleus.

ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research on grant number AFOSR-86-0344.

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