

# Phase transition kinetics in DIET of vanadium pentoxide

## I. Experimental results

R. Ai, H.-J. Fan and L.D. Marks

*Center for Surface Radiation Damage Studies, Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA*

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Experimental results of the kinetics of phase transformation in vanadium pentoxide during surface loss of oxygen from electron irradiation are described. Phase transformations under three different regimes were examined: (a) low flux; (b) intermediate flux and (c) high flux. Different phase transformation routes were observed under different fluxes. In a companion paper, numerical calculations are presented demonstrating that these results are due to a mixed interface/diffusion controlled phase transition pumped by surface oxygen loss.

### 1. Introduction

It is now fairly well established that many oxides, primarily maximal valence transition metal oxides, damage in the electron beam of an electron microscope [1–4]. The damage process typically occurs more at lower accelerating voltages than at higher voltages, and is therefore due to low energy excitations [6–10] rather than knock-on damage [5]. Whereas it is possible for reactions to also take place with the ambient gases in a microscope [11] or the sample substrate [12], the same processes normally take place under UHV conditions [11]. The typical phase transition route is from the parent oxide to a lower oxide (or metal) which is a supergroup of the parent [13], analogous to an inverse oxidation process with diffusional rather than displacive phase transitions, with in many cases an epitaxial relationship between the parent and the lower oxides or metal [4,14].

Whereas the route and the epitaxial orientations are now fairly well established for most of the transition metal oxides, details of the kinetics have not as yet been published in any detail. Some studies [15,16] have indicated that the major process taking place is diffusional, but the

exact role of thermal versus athermal diffusion in these systems has been unclear.

The intention of this paper is to present in some detail experimental results for vanadium pentoxide ( $V_2O_5$ ). Two earlier reports on vanadium pentoxide have appeared [4,16], similar in many respects although the exact routes of the phase transitions differ and appear to contradict. We show here that the exact character of the phase transition is a strong function of the electron beam flux, which reconciles this apparent conflict. In a companion paper we analyze in some detail the numerical solution of a representative model of the diffusion problem involved, reproducing semi-quantitatively the experimental results.

### 2. Experimental method

Samples of high purity  $V_2O_5$  powders were crushed, dispersed in methanol and deposited onto a holey carbon film supported on a copper grid. The samples were baked on a mild light bulb immediately before examination in a Hitachi H-9000 electron microscope to minimize hydrocarbon contamination during conventional mi-

croscopy. These samples were then examined along [001] in a vacuum of  $10^{-7}$  Torr at a 300 kV accelerating voltage with a magnification of 400K for different electron beam fluxes, calibrated via a Faraday cup combined with the exposure meter of the microscope. The kinetics of the growth of the new phases were measured as a function of time. During the experiment, care was taken to minimize exposure of the samples during initial tilting of the crystal to [001].

### 3. Results

Before presenting details of the kinetics, we should first note that the phase transition route was beam flux dependent. Three different types of results were obtained:

(a) Low flux regime, flux  $< 1.5$  A/cm<sup>2</sup>. In this regime, the route was  $V_2O_5 \rightarrow V_4O_9 \rightarrow V_6O_{13} \rightarrow VO$  as reported previously [4], and see fig. 1. The epitaxial relationships are described in a previous paper [4]. The phase transformation was initiated at the surface. Both  $V_4O_9$  and  $V_6O_{13}$  were metastable. They were present initially, but vanished with increasing radiation time, a point we will return to later. The final stable phase was VO.

(b) Intermediate flux regime,  $1.5 < \text{flux} < 1.9$  A/cm<sup>2</sup>. In this regime the  $V_6O_{13}$  phase was not observed at all, and the route was  $V_2O_5 \rightarrow V_4O_9 \rightarrow VO$  as shown in fig. 2. The phase transformation was also initiated at the surface and extended into the bulk with a clear reaction front. Similarly,  $V_4O_9$  vanished with increasing radiation time and the final stable phase was VO.

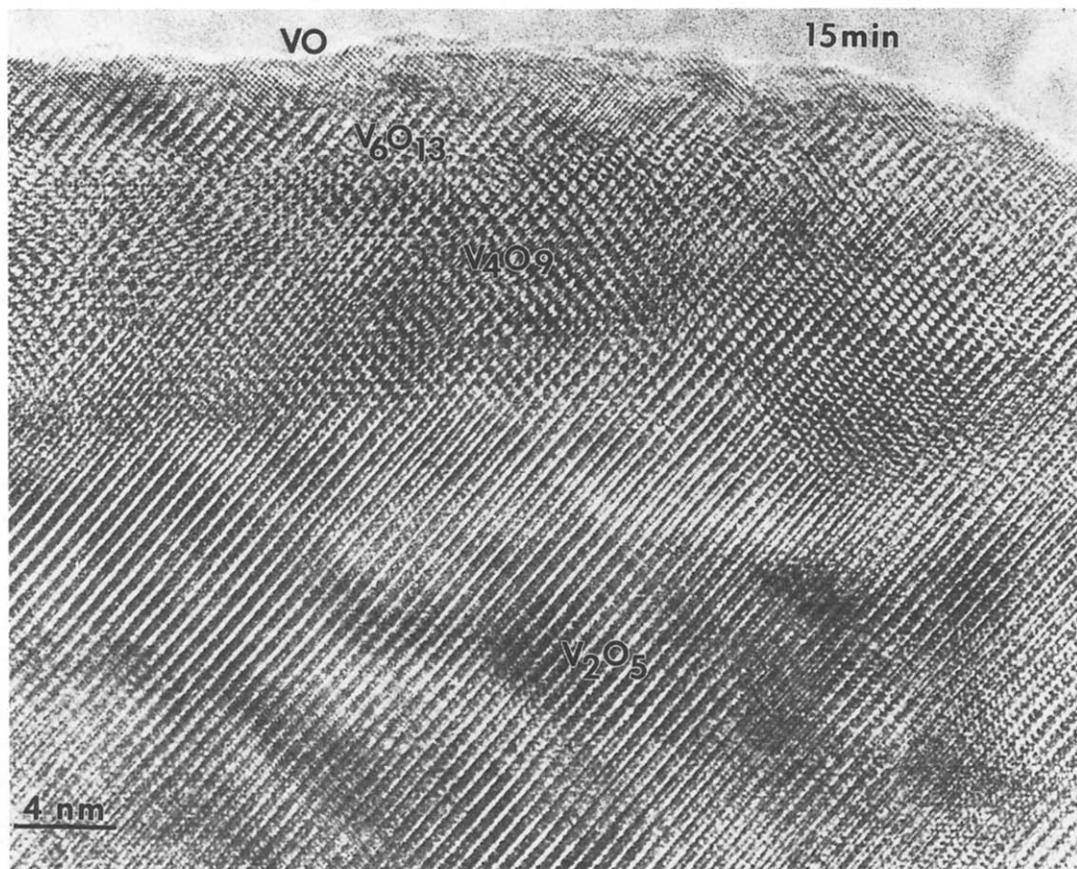


Fig. 1. HREM image showing typical phase transformation in the low flux regime. Flux  $< 1.5$  A/cm<sup>2</sup>.

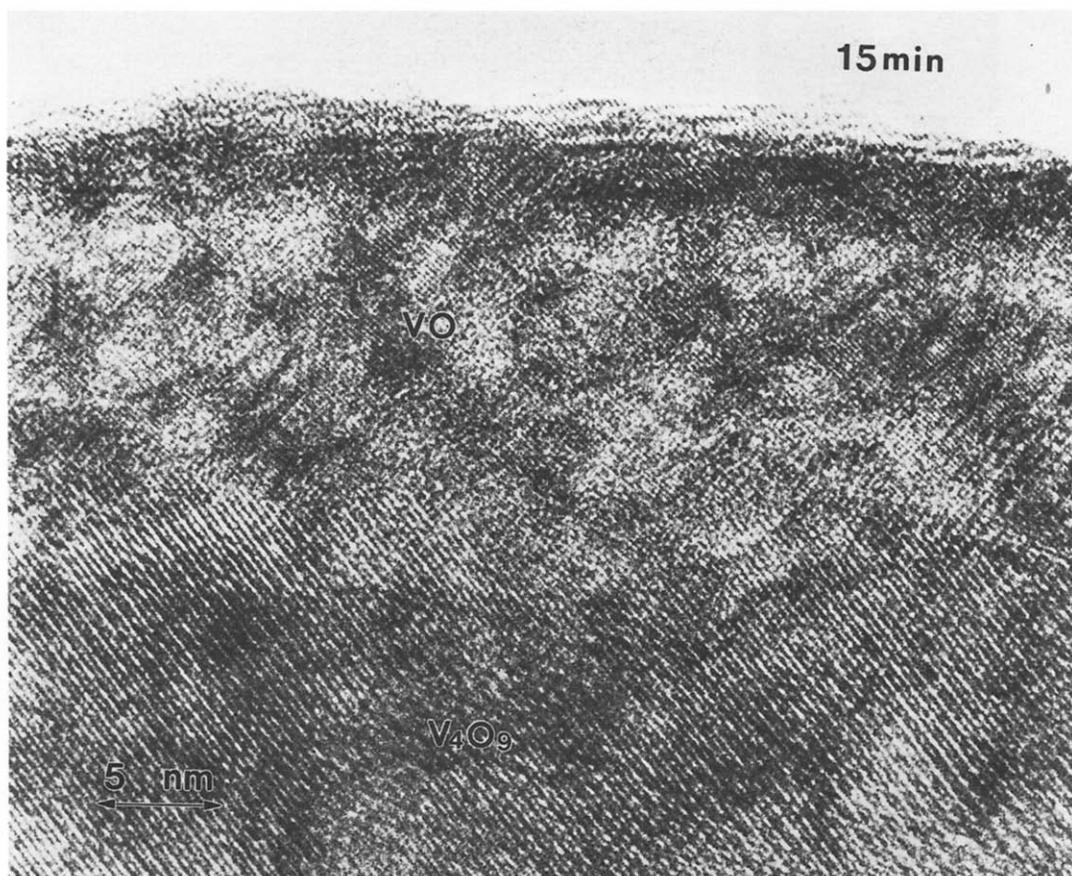


Fig. 2. HREM image showing typical phase transformation in the intermediate flux regime.  $1.5 < \text{flux} < 1.9 \text{ A/cm}^2$ .

(c) High flux regime, flux  $> 1.9 \text{ A/cm}^2$ . In this regime, the phase transformation occurred both at the surface and in the bulk (see fig. 3). Formed at the surface was a thin layer of VO which extended into the bulk with increasing radiation time. In the bulk,  $\text{V}_2\text{O}_5$  was transformed into  $\text{V}_6\text{O}_{13}$  with precipitation of VO. The precipitation of VO in  $\text{V}_6\text{O}_{13}$  was probably due to the supersaturation of oxygen vacancies in the bulk.

To show the data on the kinetics of the phase transition, we have chosen to plot the widths of the different phases as a function of time. Five sets of data are shown in figs. 4–8, labelled with the flux conditions used. The plots show that the phase transformations are a very complex process. The data could not be simply fitted by either linear (interface controlled) or parabolic (diffu-

sion controlled) functions [17]. Some general points can be noted. First, at the lower fluxes the dominant initial phase was  $\text{V}_4\text{O}_9$ , with only very small regions of  $\text{V}_6\text{O}_{13}$  and VO at the surface. With increasing radiation time,  $\text{V}_4\text{O}_9$  disappeared quite rapidly, being consumed by the  $\text{V}_6\text{O}_{13}$  and VO combined. The growth rates of both  $\text{V}_6\text{O}_{13}$  and VO were initially slow, however increased drastically as soon as  $\text{V}_4\text{O}_9$  vanished, indicated by the abrupt increase of the widths of these two phases at the onset of the disappearance of  $\text{V}_4\text{O}_9$ . This implies that the interface growth rate for  $\text{V}_4\text{O}_9$  is smaller than that for  $\text{V}_6\text{O}_{13}/\text{VO}$  (a point that will be returned to in the companion paper). This is more clearly seen in a plot of the growth rate of VO (linear fit to the data) as shown in fig. 9. The growth rate of VO was obtained by lin-

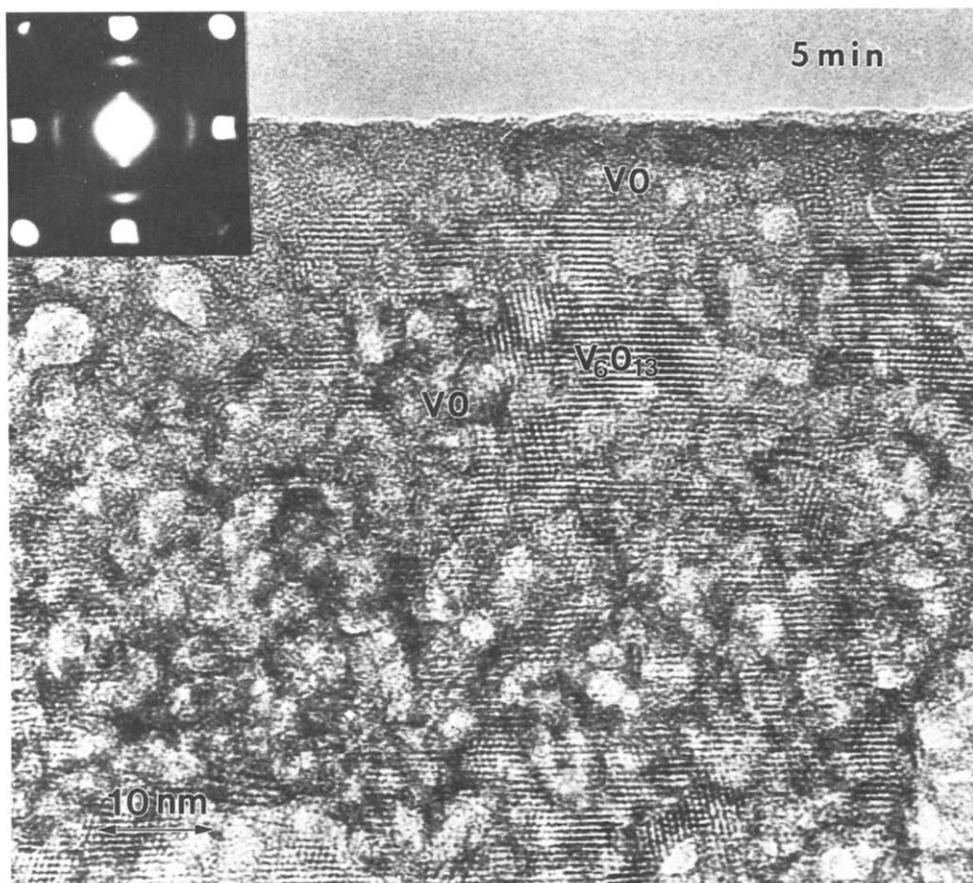


Fig. 3. HREM image showing typical phase transformation in the high flux regime. Flux  $> 2.0 \text{ A/cm}^2$ .

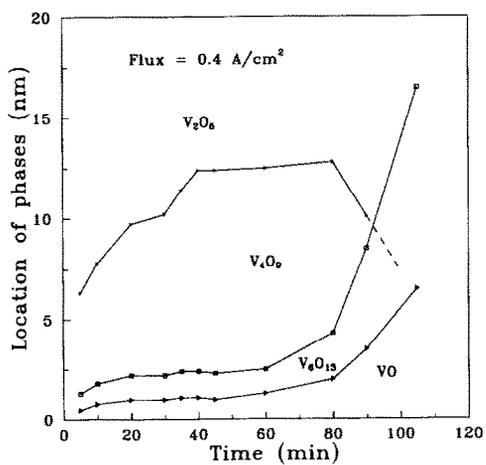


Fig. 4. Kinetics of phase transformation in  $\text{V}_2\text{O}_5$  under electron beam irradiation at a flux of  $0.4 \text{ A/cm}^2$ .

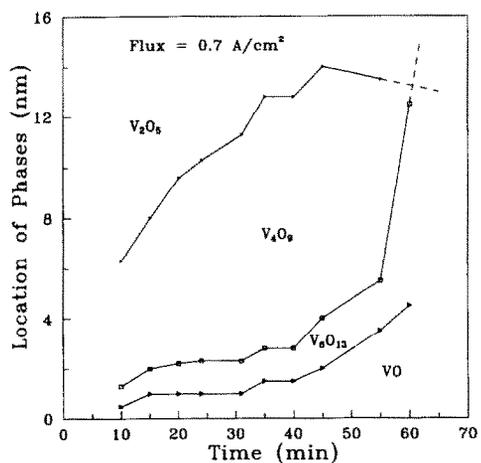


Fig. 5. Kinetics of phase transformation in  $\text{V}_2\text{O}_5$  under electron beam irradiation at a flux of  $0.7 \text{ A/cm}^2$ .

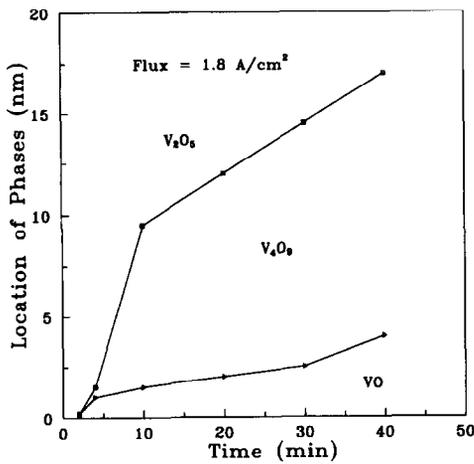


Fig. 6. Kinetics of phase transformation in  $V_2O_5$  under electron beam irradiation at a flux of  $1.8 \text{ A/cm}^2$ .

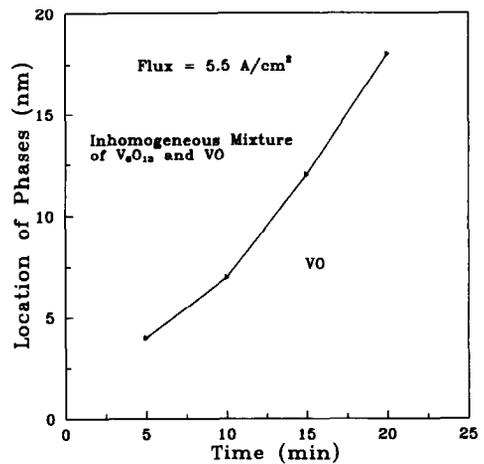


Fig. 8. Kinetics of phase transformation in  $V_2O_5$  under electron beam irradiation at a flux of  $5.5 \text{ A/cm}^2$ .

early fitting the kinetics curve of VO. The growth rate of VO in the low and intermediate flux regimes are very similar. However there is a clear break between the low/intermediate flux regime and the high flux regime.

#### 4. Discussion

It is appropriate to discuss here some of the errors and complications in the interpretation of

the experimental results. First, we have approximated the data in terms of straight fronts, whereas in reality the phase boundaries are not always flat, see for instance fig. 1. Secondly, the zero of the time axis is slightly uncertain, since there is damage while the specimen is being aligned for imaging. Thirdly it should also be noted that the specimen thickness is slowly increasing away from the edge so we do not have a true one-dimensional problem but a two- or three-dimensional problem.

Another point that should be mentioned concerns the interpretation of the data. The most

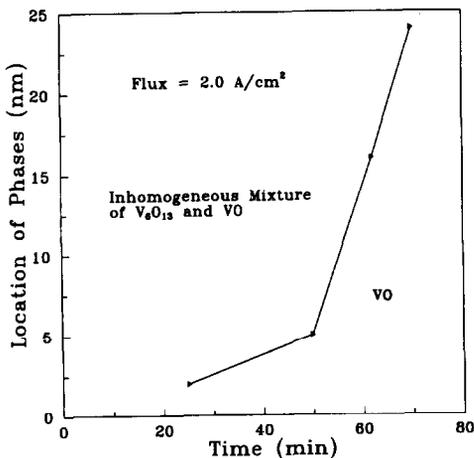


Fig. 7. Kinetics of phase transformation in  $V_2O_5$  under electron beam irradiation at a flux of  $2.0 \text{ A/cm}^2$ .

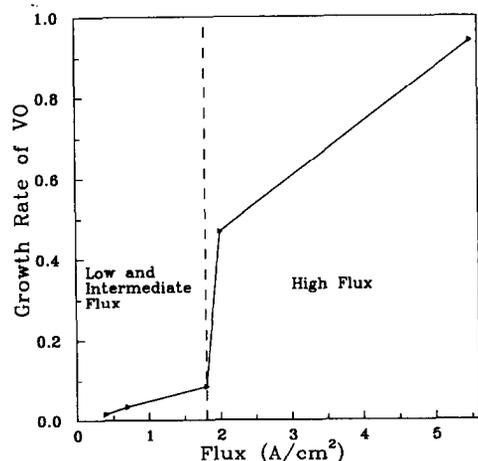


Fig. 9. Growth rate of VO as a function of electron beam flux.

obvious approach to take would be to fit the data by parabolic functions and extract a diffusion constant. However, as suggested by the experimental observation, the kinetics data cannot be fitted either linearly or parabolically. Indeed, the phase transformation process can only be described in terms of diffusion equations coupled with interface growth as described in the later paper. What is not so obvious is that the change in phase route also comes out quite naturally. The front appears to nucleate at the thin edge of the crystal and then propagate inward. This is probably due to a combination of easier nucleation in the thin region and the dipole orientation of the low energy excitations normal to the beam, although more analysis is needed.

Finally, it is worth repeating that the phase changes occurring herein are due to low loss electronic excitations. At lower voltages the rates increase, not decrease as they would for knock-on damage and the same type of phases have been observed for 1–3 kV electron damage [16]. (We cannot completely rule out knock-on assisted damage.) It should be mentioned that they are not due to any forms of contamination since they also take place in UHV [4].

### Acknowledgements

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