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SHORT NOTE

ENCAPSULATION, DIFFUSION AND DIET IN THE ELECTRON MICROSCOPE

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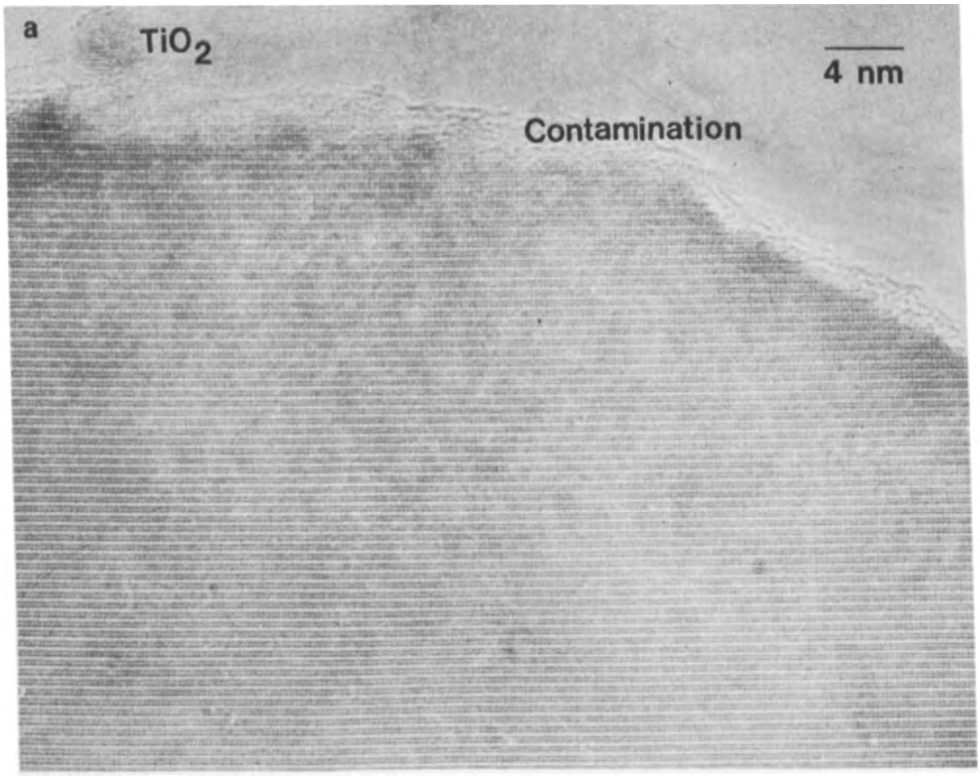
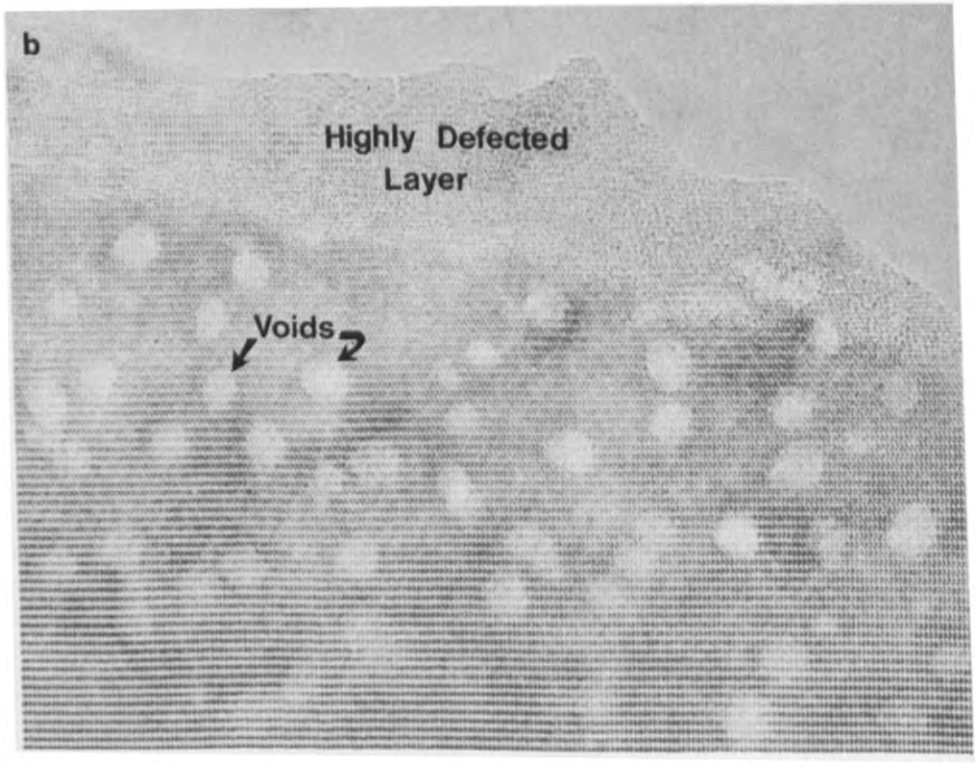
Observations of a large number of different oxides in the electron microscope clearly indicate that a crucial role is played by the presence or absence of encapsulating layers, either amorphous carbon, graphitic carbon or damaged metallic regions produced by DIET of the oxygen, and point defect diffusion in the subsurface region. In the presence of an encapsulation layer DIET slows by a factor which is related to the point defect migration through this layer.

Since the discovery of methods of imaging surfaces in the electron microscope [1–5], a considerable interest has developed in understanding the atomistic processes whereby surfaces change. Very early on it became apparent that oxides, for instance tungsten trioxide [6,7], are damaged by processes known as desorption induced by electronic transitions (DIET), identical to the processes that are well documented in the surface science literature, e.g. refs. [8–10]. We have recently been extending from the original work [6,7] and have examined to date more than 25 different oxide systems. The intention of this note is to report two general results that we have found to have widespread significance during the surface damaging processes, namely the effects of encapsulation and diffusion of point defects on DIET.

The results reported here were obtained using a Hitachi H-9000 Electron Microscope. Operating with an accelerating voltage of 300 kV and a vacuum of 3×10^{-7} Torr, the microscope has a point-to-point resolution of at least 0.18 nm. Specimens were prepared by simple crushing of the oxide materials and depositing dispersed powder onto well pyrolized holey carbon films. To minimize or eliminate the initial contamination layer, these specimens were generally baked on a light bulb for 10–30 min before insertion in the microscope. This procedure, along with occasional mild baking of the microscope objective region, generally led to minimal contamination rates, presumably due to the dry turbomolecular pumping system of the instrument. However, in some unfavorable cases which are of importance for this paper, some contamination persisted.

We will not describe herein the behavior of all the systems that we have analyzed to date, certain specific systems being reported elsewhere. Our underlying purpose instead is to report the general results concerning encapsulation and bulk diffusion, which we make from figs. 1–3. Fig. 1 shows typical results for TiO_2 when there is no encapsulating layer. Substantial surface and bulk damage is observed, as evidenced by the highly defective, almost amorphous, surface layer and the subsurface voids which form after only a few minutes of beam exposure. Time-resolved observation showed that the voids and surface layer grew during continued irradiation. This growth indicates that point defects are migrating and aggregating by bulk diffusion, presumably in part due to the gradients set up by oxygen ejection from the surface. (There is also a process which leads to metal loss which we suspect is knock-on sputtering from the surface.) Fig. 2 shows for comparison an area of TiO_2 which was covered by a graphitic encapsulation layer and subjected to much longer beam exposure (2 h). Essentially no damage has


a
TiO_2
4 nm
Contamination


b
Highly Defected
Layer
Voids

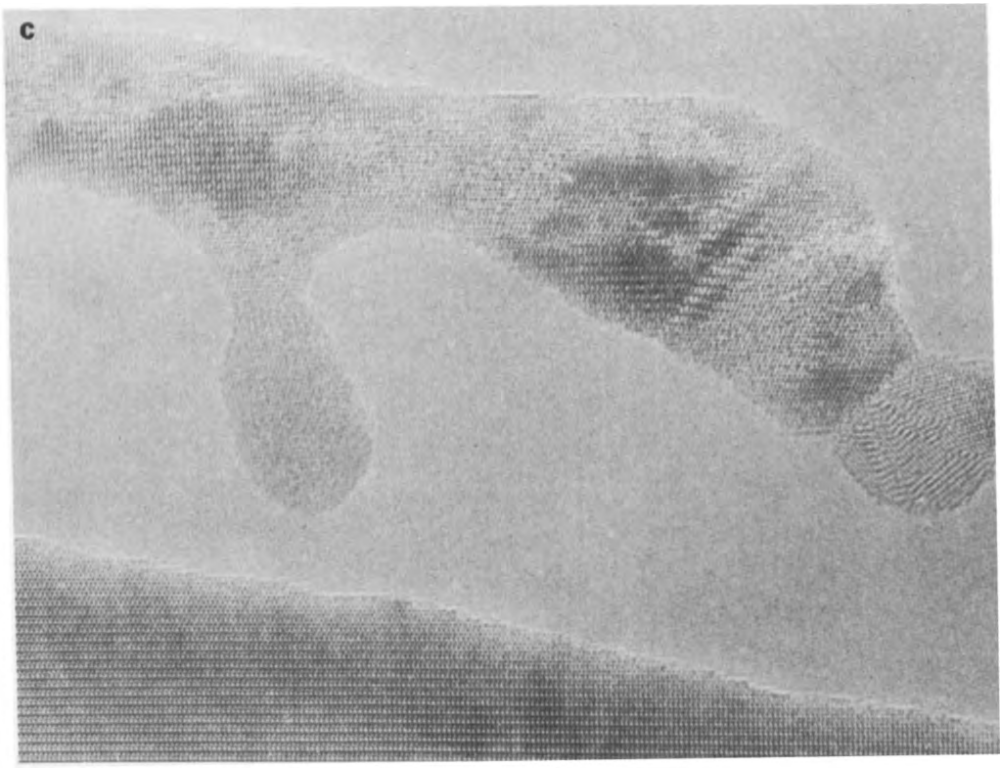


Fig. 1. Series showing damage induced in an unencapsulated [101] surface of TiO_2 (rutile): (a) initial undamaged surface; (b) a highly defected layer and voids form upon same surface during irradiation; (c) continued irradiation forms a hole due to the coalescence of voids.

taken place, and we can say that the damage rate is at least a factor of 200 times slower based upon the relative exposure times (we suspect that this figure is too low since we do not know when or if the surface would have been damaged). Results from TiO_2 show that formation of the highly defected surface layer is independent of the zone axis of irradiation for the major zones, although the subsurface defects differ from zone to zone. Clean surfaces oriented along [100] and [111] zones, for instance, formed superlattice periodicity and prismatic dislocation loops in the subsurface region with no evidence of void formation. The final result that we will show is of a trigonal modification of the high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ [11]. In this system ejection of oxygen from the structure (evidenced by an orthogonal distortion) leads to both chemical disordering of cation sites and diffusion of barium to the surface to produce barium oxide (see fig. 3).

Although only TiO_2 and $YBa_2Cu_3O_{7-\delta}$ examples are depicted in this note, our experience is that these results are quite general. The Nb_2O_5, $LiNbO_3$, MoO_3 and WO_3 systems all damage by formation of a metal encapsulating layer through desorption of oxygen. This type of irradiation damage was first observed by Petford et al. in WO_3 [7]. In all cases the metallic layer grew until quenched due to the inability of the desorbing oxygen to diffuse to the surface. Secondly, in the process of our studies no major damage has been observed when the surfaces are sealed by a layer of amorphous or graphitic carbon. Finally, the orthorhombic superconductor $YBa_2Cu_3O_{7-\delta}$ formed an amorphous surface layer with subsequent diffusion of the barium to the surface producing barium oxide. In this latter case the encapsulating layer is penetrable by diffusion, so quenching of the DIET processes did not take place.

We can understand these variations quite simply if we consider the difference between bulk and

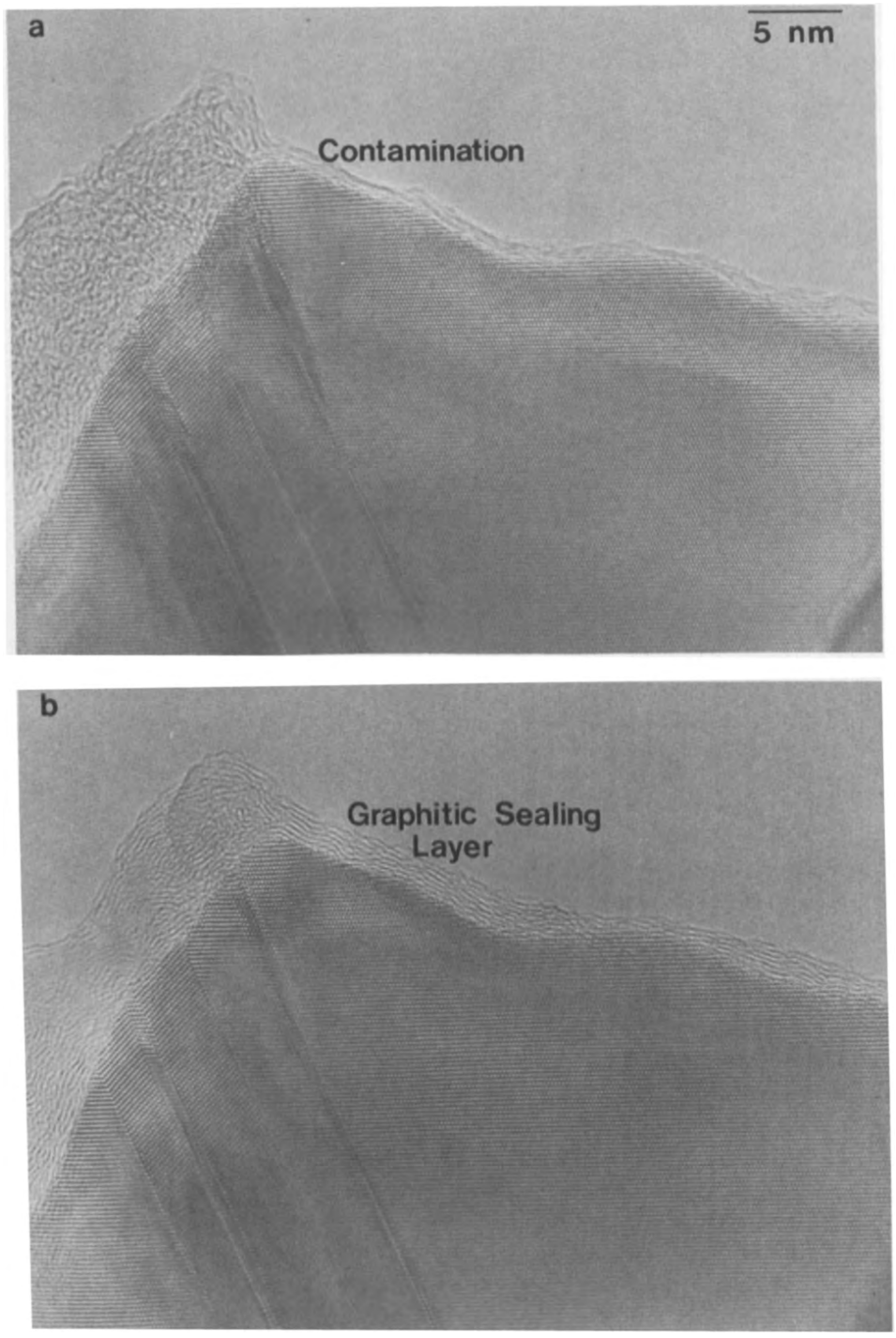


Fig. 2. Series showing damage induced in an encapsulated [111] surface of TiO_2 rutile: (a) initial unirradiated surface, (b) same surface after 2 h irradiation under the 300 kV electron beam.

surface knock-on as an analogy. For bulk damage, the knock-on atom must receive enough kinetic energy not just to overcome the energy barriers of bond breaking but to be able to produce a stable Frenkel pair, typically 20 eV. For surface sputtering however, the target atom only needs the en-

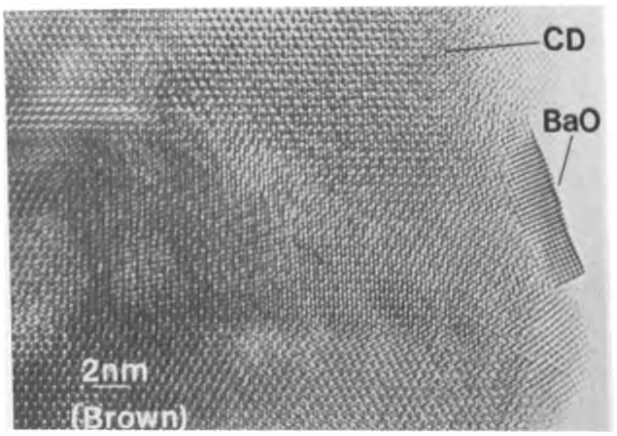


Fig. 3. Under irradiation by the 300 kV electron beam, BaO forms on the surface and chemical disordering takes place in the subsurface region as marked.

ergy required to break its bonds (assuming that it is knocked away from the surface), which is far less. In the case of electronic transition processes, bulk radiolysis is the analog of bulk ballistic damage, and DIET the analog of surface sputtering. When there is an encapsulation layer we can only lose oxygen by radiolysis, and since this requires far more kinetic energy for the atom it will be a far slower process whereas without the layer the faster DIET takes place. If the encapsulation layer allows sufficient point defect migration, then atoms can diffuse to the surface and then DIET, so that the damage is not arrested by the layer.

Conclusions: The presence of encapsulation layers plays a crucial role in DIET from oxides within the electron microscope, as does diffusion of point defects due to the gradients set up during DIET.

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