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CERAMIC DECOMPOSITION UNDER IRRADIATION

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ABSTRACT

Our quantitative determinations of the decomposition of thin film and bulk ceramic materials during electron microscopy has shown that the radiation damage effect is a complex one depending upon the dielectric and thermochemical properties. In low melting temperature glasses for example much of the activity is due to field enhanced diffusion of low atomic weight species. This is particularly true of bulk specimens and for the case of binary soda-borosilicate glass the sodium depletion in the SEM can be quantitatively described in terms of this effect. Studies with thin specimens of refractory carbides show that in these materials the carbon depletion is due to direct displacement processes and that here the electric fields give rise to recombination effects.

The studies of ceramic thin films suitable for reference standards is continuing as a joint effort with the Rockwell Science Center. Work is in progress to describe the in plane crystallization that is observed in terms of the latent heat involved and the configurational entropy of the propagating interface.

MODELLING THE SEPARATE CONTRIBUTIONS TO THE DECOMPOSITION PROCESS:
This work was done by T.M.Walker as part of his MS Thesis

The decomposition of ceramics to electron irradiation can be generally described in terms of radiation damage from ionization and displacement effects. These processes can induce the redistribution of the constituent atoms internally (i.e. direct displacement or radiolytic decomposition) or the loss of particular elements from the surfaces (i.e. electron stimulated desorption) and will give rise to electronic and chemical discontinuities. These gradients in chemical and electrical potential will ultimately be eliminated by diffusional processes and it is the rates at which these competing processes operate that will determine the exact nature of the decomposition.

In this aspect of the program a finite element code has been developed to incorporate all of the anticipated effects, including the separate behavior of atomic species associated with their relocation in interstitial sites, for both bulk and thin film ceramics during and after electron exposure. In the approach which has been taken here all of these effects have been incorporated into a single analytical equation which describes the movement of atomic species. The equation is solved numerically to demonstrate how these different damage mechanisms effect the way in which mass is distributed and the manner in which the signal decays. The diffusion coefficient is a function of position, concentration, temperature and radiation dose, and is evaluated throughout the volume.

The source and sink terms on the right hand side of the equation represent the processes other than diffusion which can contribute to the redistribution of material. The other effects that are accounted for are Electron stimulated desorption (ESD), electric field-assisted atomic migration, atomic displacement and enhanced migration from radiation damage. With the exception of ESD, all of the effects take place throughout the volume, and are accounted for by unique constitutive equations.

Publications

This work has been submitted to J.Microscopy and a paper outlining the role of the electric field effect in soda silicate glasses is in preparation. Some of this work was presented by Mr Walker at the 1986 meeting of the Microbeam Analysis Society and was also presented at the 1987 EMAG meeting in Newcastle. This work was also the subject of an invited paper at the 13th Regional Meeting of the California Electron Microscopy Society.

REFRACTORY CARBIDE DECOMPOSITION: This work is being pursued by D. Medlin for an M.S Thesis.

One of the singular aspects of the decomposition behavior that has been studied is that of the direct atomic displacement of carbon in refractory carbides. It is interesting to note that the thermal decomposition of these materials involves the evaporation of the metal and yet there is a temperature dependance to the

decomposition process that releases the carbon which suggests the presence of a diffusion process. This work is continuing but preliminary calculations indicate that the observed behavior of vanadium, chromium and titanium carbide can be described in terms of a displacement mechanism if the specimen thickness and field induced recombination affects are accounted for.

Knock-on displacement is characterized by two quantities: The threshold displacement energy, T_d , which is the energy that must be imparted to an atom to remove it from its site, and the displacement distance, a , which is the separation distance between the interstitial and vacancy of the Frenkel pair that is created. Knowing the displacement energy and the energy of the incident electron, it is straightforward to calculate the displacement cross section, σ_d , although the displacement energy and displacement distance are not very well known for the refractory carbides. Two situations exist which give rise to somewhat different depletion behavior. When the displacement distance is greater than or equal to the specimen thickness, atoms require only one displacement event to be removed from the specimen. On the other hand, if the displacement distance is less than the specimen thickness, atoms may require several events to be removed resulting in a redistribution of the atoms within the specimen. In addition the possibility of field induced diffusion, in the direction opposite to the diffusion is also possible.

With the displacement distance greater than or equal to the specimen thickness, the theoretical depletion curve may be derived analytically. The rate of light element removal is simply:

$$dn/dt = -n \cdot \sigma_d \cdot i$$

When integrated, this equation becomes:

$$n/n_0 = \exp(-\sigma_d \cdot i \cdot t)$$

If the experimental data follows this exponential behavior, then we would expect the plot of $-\ln(n/n_0)$ vs. dose ($i \cdot t$) to fall along a straight line intercepting zero. The slope of this line would be equal to σ_d . Most of our data fits this behavior well. Table 1. gives the calculated cross section for each of the compounds studied, as well as the intercept, b , and correlation coefficient, r , of the line fit to the data.

Material	σ_d (barns)	b	r
TiC @ 298K	0.371	-0.151	0.981
TiC @ 143K	0.470	0.046	0.993
Fe ₂ O ₃	0.386	0.048	0.996
Cr ₃ C ₂	0.970	-0.028	0.999
Cr ₂ N	1.33	-0.068	0.998

Table 1. Damage Cross Section, Intercept, and Correlation Coefficient for Depletion Curves fit to $a/d \geq 1$.

The 298K TiC data does not fit this simple model as well as

the other data. This is reflected in the relatively large magnitude of b and slightly smaller value of r for the best fit line. Secondly, our calculated value of σ_d is significantly lower than the value of 225 barns that would be expected for carbon in TiC based upon the results of Venables and Lye (1969) in Vanadium Carbide.

If the carbon that is lost is not in fact removed in one displacement, i.e. an atom requires several hits to be removed from the specimen, then the depletion occurs at a slower rate and if we take the specimen thickness to be a maximum of 1000 Å and the displacement distance to be a minimum of 5 Å, we estimate the maximum cross section to be 40 barns. Clearly the presence of an electric field, if it compensates the displacement process, will permit the cross section to be larger and this work is continuing to delineate this contribution more fully.

Publications

This work is being prepared for submission to Ultramicroscopy when the field calculations have been completed. The experimental studies in Vanadium carbide have already been published.

THIN FILM CRYSTALLIZATION PROCESSES: This work is being pursued by J.Heuer for a PhD Thesis.

The annealing of amorphous thin ceramic films to develop oriented crystalline ceramic specimens suitable as reference materials for this study is the other aspect of this work. The first effort has been to develop and characterize films of titanium dioxide which is a material in which electron stimulated desorption has been quantified. Crystallization, it seems, cannot be induced in these films when they are very thin and the thicknesses must be of the order of about 50nm for the films to crystallize. It is also apparent that when the thickness of the titania film is between this and about 200nm the crystallization occurs by the propagation of an interface in the plane of the film, which gives rise to a preferred orientation of $\langle 010 \rangle$ perpendicular to the plane of the film. These highly oriented microstructures are similar in many respects to those observed in silicon films after zone melting and represent a most promising method for the production of single crystal like films.

We have also observed that a reduction in film thickness gives rise to faceted growth. These thin films were prepared by reactive ion deposition with thicknesses ranging from 40-200nm which were accurately determined by ellipsometry. The films were completely amorphous and when annealed produced anatase, the low pressure metastable form, provided the film thickness is greater than about 40nm and grows in an oriented fashion at thicknesses less than about 150nm.

The details of the interface morphology are being investigated in a cooperative effort with the National Center for Electron Microscopy at Berkeley.

High Voltage TEM studies at the NCEM of the thin film

crystallization indicate that the amorphous to crystalline transformation in titania corresponds quite closely to the solidification that might be expected from the melt at the same undercooling. This conclusion is based upon direct measurements of the interface velocity during the transformation, using in-situ techniques which also serve to provide measurements of the latent heat of crystallization and the activation energy of the process which in fact controls the growth.

Observations of the crystallizing of anatase from amorphous Titania indicates that for thicknesses below about 300nm the interface is faceted on {011}. The derivation of the free energy of this interface can be performed in much the same way as it was originally done by Wilcox (1970) for a sawtoothed interface. The configuration of the interface can be divided into four parts; the outer surfaces (s), the flat faces (f), the edges (e) and the corners (c).

The Free Energy of an interface with facets of length d in a film of thickness t can then be written as;

$$G = \frac{N_s.H_s}{T} + \frac{N_f.H_f}{T} + \frac{N_e.H_e}{T} + \frac{N_c.H_c}{T} - kT \ln \left[\frac{N!}{n_s!.n_f!.n_e!.n_c!.N_s-n_s!.N_f-n_f!.N_e-n_e!.N_c-n_c!} \right] + \int_0^T C_p dT - T \int_0^T \frac{C_p}{T} dT$$

N_s , N_f , N_e and N_c remain constant as the interface propagates and so this is a symmetrical expression which depends not upon the enthalpy (H) of the sites but the ways in which they can be distributed. In this expression N is the total number of sites and the lower case notation indicates the sites are occupied (i.e. n). It is straightforward to calculate the number of sites which exist at the outer surfaces ($N_s=4da/A$), the faces ($N_f=2td/A$), the edges ($N_e=t/a$) and the corners ($N_c=t/a$) as well as the total number of sites (N) and from the structure of the crystallizing material the molecular spacing along the edges and corners (a) and the atomic density in the plane which facets (A) can be determined.

The enthalpy values for the face sites will always be $L/2$ but the corner and edge values will be specific to the interface morphology. For anatase faceting on {011} the corner sites are $0.38L$ and the edge sites are $0.62L$ if the proportion of the site which borders the solid is taken as the proportion of the latent heat that has been released.

The behavior of the activation energy, for the propagation of this interface with distance, can be calculated numerically from these expressions and this work is continuing.

Reconstruction of Three Dimensional Structures From Electron Micrographs. This work was pursued by P. J. Hood for a PhD Thesis.

The radiation induced decomposition of a specimen in the electron microscope occurs in 3-dimensions and it is necessary to determine this geometrical distribution of the irradiation effect. The traditional approach is to use stereoscopic reconstruction in a stereo viewer and we are investigating the development of an automated approach based upon the use of image cues to enable us to make rapid determinations of these distributions.

This work has initially involved basic studies of the translation of images into feature-based forms and is being prepared for publication in Scanning.

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