Materials subjected to fast neutron irradiation/Matériaux soumis à irradiation par neutrons rapides

Radiation aging of nonmetallic materials: specific aspects

Yves Limoge

C.E.A./D.E.N./D.M.N./S.R.M.P., C.E. Saclay, 91191 Gif-sur-Yvette cedex, France

Available online 18 April 2008

Abstract

Under irradiation, all materials experience various forms of structural evolution, from the simplest, associated with point defect creation and accumulation, to complex phase changes, either towards equilibrium or nonequilibrium structures. In nonmetallic ceramics the same processes are known or probable; however, the nature of bonding, partly ionic and partly covalent, as well as the complexity associated with the long range character of the Coulomb interaction, have long posed great difficulties in defect and aging studies under irradiation. Our aim here is to review the current state of knowledge, stressing the specific characteristics of nonmetallic materials, from primary defect creation to collective behavior, with respect to both experimental facts as well as to modeling perspectives. Given the broad field covered, we will illustrate the problem by choosing a few model materials, mostly oxides, in which the whole spectrum of phenomena has been handled. We will begin with threshold energy studies, then go to microstructure formation and evolution, radiation enhanced diffusion results, and lastly to phase changes. ***To cite this article: Y. Limoge, C. R. Physique 9 (2008).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Vieillissement sous irradiation des matériaux non-métalliques : une revue. Les matériaux soumis à une irradiation sont le siège d'évolutions structurales multiples, allant de la simple accumulation de défauts ponctuels, à des transformations de phase les menant à de nouvelles structures, que celles-ci soit ou non d'équilibre. Les matériaux non-métalliques n'échappent pas à ce schéma général, mais la nature de leur mode de cohésion, allant de la covalence à l'ionicité, jointe au caractère à longue portée de l'interaction coulombienne, compliquent fortement les études de vieillissement, tant expérimentales qu'en vue de la modélisation. Dans cette courte revue nous tenterons de présenter les implications de ces spécificités, telles qu'elles se manifestent aux diverses étapes du vieillissement. Nous aborderons ici à la fois les problèmes expérimentaux et les perspectives de modélisation. Cet article traitera donc successivement de la création des défauts primaires, qu'il s'agisse de l'effet des collisions ou de celui des interactions inélastiques, y compris sur la mobilité, des premières étapes de la réorganisation des défauts conduisant à l'apparition d'une microstructure d'irradiation, de l'impact de l'irradiation sur la mobilité atomique accélérée ou induite, enfin des divers changements de phase, d'origine statique ou dynamique, susceptibles de survenir. ***Pour citer cet article : Y. Limoge, C. R. Physique 9 (2008).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Keywords: Radiation aging; Nonmetallic materials

Mots-clés : Vieillissement sous radiation ; Matériaux non-métalliques

E-mail address: ylimoge@cea.fr.

Table 1
Experimental values of threshold energies and angular variations

	Cation [eV]	Anion [eV]; Temp. effect	Anisotropy	Methods
Al_2O_3	18–30	(40–) 90 decr. as T. incr.	not well known	H.V.E.M. + opt. abs.
MgO	50–60	44⟨001⟩, 64⟨011⟩ 46⟨111⟩ decr. as T. incr.	–	H.V.E.M. + opt. abs.
$MgAl_2O_4$	–	60; incr. as T. incr.	not known	opt. abs.
UO_2	40	–	not known	H.V.E.M.
SiC cubic 3C	20–40 direct 45–75 indirect	20–22	⟨001⟩ ∼ ⟨011⟩ ≪ ⟨111⟩	H.V.E.M. + opt., posit.
SiC hex. 6H	100–30	18–22		H.V.E.M. + opt., posit.

Displacement threshold energies in various nonmetals, '–' means not actually measured even if some publications state the reverse. For the original references see [3].

1. Introduction

Contrary to the case of metallic materials, the level of understanding of the behavior of most nonmetallic materials under irradiation is far from satisfactory, except for a few elementary semiconductors and some halides. Many difficulties contribute to this situation. From an experimental point of view, the high characteristic temperatures involved, (one of the main motivations for studying them), as well as the generally high impurity content, explain the frequently poor knowledge of the basic properties, even without irradiation. From a modeling point of view the situation is also more complex than in metallic systems, for three main reasons. Firstly, these systems are mostly compounds displaying very high ordering energies, so the properties of the different sublattices can be vastly different, and the interactions between their defects must be properly taken into account. Secondly, in most cases the bonding has a partially ionic character involving long range interactions. Lastly, the presence of a band gap induces many electronic effects unknown in metals, from point defect creation by purely inelastic energy losses, to multiple charge levels for a given point defect, changing both its mobility and its formation energy. However, the recent development of so called ab initio methods, based on a quantum mechanical handling of the electrons, frequently based on the Density Functional Theory (DFT), either in a time dependent or in a static approach, permits, in many cases, the quantitative calculation of the elementary properties, as well as the treatment in the near future of electronic excitations in a quantitative manner. The nature and aims of experiments have to evolve in order to take proper advantage of these new perspectives. In this article, we will try to show how they can be worth using in the various fields involved in irradiation aging studies, from defect creation to phase transitions.

2. Primary radiation effects and defect production

Contrary to metallic systems, both elastic and inelastic interactions can have an impact upon the defect population in non-metals, creating point defects or affecting their mobility.

2.1. Elastic interactions

During an elastic collision, as in metals, the impinging particle transfers kinetic energy to a target atom, the primary knocked atom, or PKA. If the transferred energy is high enough, higher than the *threshold energy* E_{thr}, the atom will, by definition, be permanently displaced, leaving a *vacancy* on the initial site, and possibly forming an *interstitial* on the arrest site. The threshold energy depends on the direction of the initial momentum transfer. In compounds, each sublattice has its own threshold; moreover, the displacement of a given species can be direct, or due to a collision with a moving atom which has already been displaced. In compounds with dissimilar masses, this can allow the displacement of the heavier atom at too low a primary energy to create a defect in a direct collision with the projectile.

In insulating ceramics, thresholds can be determined either by direct determination of the defect concentrations using various spectroscopies (positrons, optical measurements, EPR, conductivity), or by indirect methods, i.e. deter-

mining the number of defects clustered in the microstructure by electron microscopy, at a high enough temperature for defects to migrate. Here, high voltage electron microscopy (HVEM) offers the opportunity to create and observe damage in the same experiment. Relatively few systems have been studied, and Table 1 gives an almost exhaustive view of the available results. More complete reviews have been given by Pells [1] and Zinkle [2].

The values given here frequently display a very large spread, by a factor of up to two in the case of ionic compounds. The spectroscopic methods give the most specific values, but are frequently limited to anion defects. Depending on the specific behavior of the system, HVEM studies can determine both thresholds, (Al_2O_3, MgO), or not (UO_2). This method relies on the formation of visible damage, mostly dislocation loops, and therefore requires in ionic compounds the formation of defects on both sublattices. If a single sublattice is affected, the formation of visible clustering involves either the displacement of the counter ion, or the displaced species being neutral [4], in order to keep the charge of the cluster low. If the displaced species is charged, this can be achieved either by direct or indirect collisions, or induced by the electric field. The interpretation of the observations implies then a model of cluster formation including Coulomb interactions, which appears not to have been made on a quantitative basis up to now [5,6]. Relevant models have already been proposed for dislocation loop formation in halides under purely electronic loss regimes where only anions are displaced [4]; they could probably be applied here. This is probably one of the reasons behind the disparities seen in Table 1 in mostly ionic systems. As a general rule the thresholds appear to be controlled by the fact the sublattice involved is compact or not, not by the cohesive energy, being similar for both species for compact sublattices (MgO, ZnO), but much lower if structural vacancies or empty sites are present, either for the metallic ($MgAl_2O_4$, Al_2O_3) or the oxygen (UO_2) sublattice.

Numerical simulation methods are also used for threshold calculations, mainly by Molecular Dynamics (MD) using empirical potentials, but also by ab initio MD. In the former case the key point indeed lies in the potential used. In ionic systems formal charges are generally assumed for the particles, casting some doubt on the results. Indeed it has been shown that in Al_2O_3 the charge of the Al atom in an interstitial position decreases to 0.65e, from 2.35e in the stable one [7]. In some cases the potential itself is even fitted on the desired threshold. The ab initio methods are very computationally demanding but provide safer results. Their use for 3C-SiC has shown threshold values of 38 eV and 19 eV for the mean values, in rather good agreement with the experimental ones, even for marked anisotropy [8,9]. The values deduced from the best empirical models, are overestimated by 20 to 50%, depending on the direction [8,9].

2.2. Inelastic effects

2.2.1. Defect production

In insulators with a large band gap, electronic excitations can also result in defect production. This phenomenon, leading eventually to the radiolysis of the material, is known in various insulators, halides, hydrides, silicates, carbonates, etc. [10,11]. The key points here are: (i) a sufficiently long excitation lifetime in order to couple to atomic movements; (ii) an efficient mechanism allowing the electronic energy to be transferred into atomic displacements. Several processes are known to give rise to defect creation. The first proceeds through bulk exciton formation [12], and is proved in halides and silica [13]. Surface excitons created during a multiphoton process at specific sites could also result in surface defects [14]. A second surface process involves deep hole creation and Auger de-excitation [15]. Electron–hole pairs resulting from cation excitons can also lead to defect formation [16]. The surface processes are probably irrelevant for the bulk phenomena under consideration.

The availability of very high energy ions, so called swift heavy ions having an energy up to several GeV, opens the field of extremely high density of electronic excitations, at and above 10^4 eV/nm along the track. In this regime a whole range of radiation damage is induced, including atomic defect creation as in MgO [17]. The mechanisms involved are badly understood at the atomic level.

The excitonic mechanism, at work in many solids, is the more documented. It has, for example, long been thought that the phase separation, up to oxygen bubble formation, observed in silicate glasses, was due to the alkali or alkaline-earth oxide component, and could not be observed in pure silica. However, recent experiments have convincingly shown that inelastic effects during ion irradiation can create oxygen Frenkel pairs and oxygen molecules in pure silica too [18]. Recent ab initio calculations [19] have shown that molecules can indeed be formed by reaction between the highly mobile oxygen interstitials [20]. The overall yield of the process is of the order of 1 MeV of absorbed energy per stable Frenkel pair. Ab initio modeling, based on DFT alone, cannot tackle this creation step by inelastic interactions, since the DFT approach, now the one mostly used in solid state physics, is limited to the electronic

ground state. This is only possible in an approximate manner using constraint electronic state occupancies [21,22]. It is, nevertheless, probable that in the near future this approach will allow the calculation of the impact of inelastic losses for any material, thanks to the development of methods able to handle actually excitations, like time dependent DFT [23] or the many-body approach known as GW, extended to the calculation of the forces on the atoms [24,25].

2.2.2. Inelastic effects on defect mobility

Beyond defect production, and probably much more ubiquitously, electronic excitations in nonmetals also deeply affect mobility, generally enhancing it, either by lowering the migration energies or by changing the stable defect configuration [26]. Their impact is very critical for microstructure evolution, as will be shown below. Modern ab initio methods offer the opportunity to understand the origin of the effect and calculate the relevant atomic parameters. In SiO_2, both crystalline and amorphous, recent DFT calculations have shown that the migration energy of the oxygen interstitials decreases from 1.2 eV in the neutral state, to 0.1–0.35 eV in the -2 charge state [27,28]. Conversely, the migration energy of the oxygen vacancy, 4.1 eV in the neutral state, decreases to 1.9 eV in the charge state $+1$ and to 1.7 eV when bonded to an exciton [29]. One must stress here that current DFT based total energy calculations can fail in some cases by a large amount, even in very simple systems like silicon or SiO_2, due to concerns with the energetics of charged states of defects [30,31]. Here, too, significant progress is expected from the use of the more elaborate techniques mentioned above.

2.2.3. Inelastic effects and Fermi level determination

At equilibrium, the charge state of the point defects is controlled by the value of the electron chemical potential, i.e. the position of the Fermi level in the gap. This position, in turn, is controlled by the various impurities, comprising the defects themselves, and has therefore to be determined in a self-consistent manner [32], assuming an equilibrium state of the populations of defects and charge carriers. In doped semiconductors, or in most insulators which frequently display quite high impurity content, the influence of equilibrium thermal defects will generally be negligible. This can no longer be the case under irradiation at rather low temperatures, when defect concentrations exceed the equilibrium values by orders of magnitude. In this case the equilibrium assumption, as well as the notion of a Fermi level, is no longer valid. The charge states of defects are defined locally in a purely dynamic manner by the mobility of charge carriers between various localized states in the gap and valence/conduction bands. A proper treatment of this effect would certainly impact greatly on the understanding of the time evolution of cascades, as well as of the microstructure evolution discussed below.

3. Microstructural evolution under irradiation

As in metallic materials, irradiation *at a temperature where point defects are mobile* results in point defect clustering and microstructure evolution, up to the formation of dislocation loops, clusters and cavities; specific to nonmetals is the formation of metallic colloids by reduction of the cations. The effects depend on the temperature, damage rate, PKA energy spectrum, and flux. In ceramics, fundamental studies of radiation-induced microstructure changes are scarce compared with metallic materials. Insofar as a complete panel of characterization is desired in the prospect of a coherent understanding, and apart from alkali halides, most of these studies have been devoted to a few simple ceramics, nonamorphizable at medium temperature, free also of production of point defects via electronic excitations: MgO, α-Al_2O_3, $MgAl_2O_4$, as well as, to a smaller extent, SiC.

3.1. Electron irradiation

Experiments are usually carried out in HVEM and thus at very high damage rate, typically 10^{-3} dpa/s. Furthermore, as the energy given to atoms is very low and the threshold energies often very different for cations and anions, one can chose to displace both species, or mainly a single one, by adjusting the electron energy. In both MgO and α-Al_2O_3, interstitial dislocation loops are observed at low flux. In Al_2O_3 loops appear in the same way if only aluminium ions are displaced. Stathopoulos proposed that aluminium interstitials are precipitated between the basal {0001} or prismatic {10–10} plane, forcing simultaneous diffusion of oxygen to maintain stoichiometry and local electrical neutrality [33]. This is reminiscent of what was already known for alkali halides, even if in this last case the H center carries a zero charge [4]. Recent results show that this neutrality could be not a general phenomenon since

other results seem to point to charged defect clusters in fluorite structures in the same irradiation conditions [34,35]. Since the unit cell is complex and the energy of a dislocation is proportional to the square of the Burgers vector, pure edge faulted dislocation loops are nucleated. At large size they unfault by the passage of a partial shear dislocation resulting for instance in basal plane $1/3\langle 10\bar{1}\rangle$ perfect loops [36]. MgO, on the other hand, has a short stacking fault sequence. The loops, as soon as they can be observed by electron microscopy, are perfect with $1/2\langle 101\rangle$ Burgers vectors lying on $\{101\}$ plane [37]. At higher fluxes, voids and aluminium colloids are formed in α-Al_2O_3 but not in MgO. The reason for this different behavior is not clear. Experiments in SiC have to be performed at a comparatively higher temperature, but defect clusters have already been observed at 700 °C in 3C–SiC [38]. The $MgAl_2O_4$ spinel is very radiation resistant for the dislocation loops formed under irradiation are inefficient defect sinks, allowing more recombination, but also both sublattices can easily accommodate the displacements of the ions, due to the high concentration of either structural vacancies or empty interstitial sites they contain [39]. Moreover the complex chemistry (56 atoms per unit cell) results in a large loop nucleus size and consequently in a low nucleation rate.

3.2. Neutron and ion irradiation

Under cascade-producing conditions, the nucleation rate of loops is greatly enhanced. The effect is spectacular in the spinel, as loops are observed under irradiation conditions where they are not observed under electron irradiation. Indeed, $1/4\langle 110\rangle\{110\}$ loops preserving stoichiometry and $1/6\langle 111\rangle\{111\}$ loops with a nonpreserved Al/Mg ratio have been reported [40]. However, the incubation time for nucleation is still more than two orders of magnitude larger than in α-Al_2O_3, and the maximum number density of dislocation loops almost two orders of magnitude smaller [41]. No voids are observed in this spinel, but near grain boundaries, when under the same conditions voids aligned along [0001] direction can be seen in Al_2O_3 irradiated with neutrons [42]. This effect likely comes from the difficulties in forming a network of perfect dislocations in $MgAl_2O_4$. In 3C–SiC at high flux and temperature, the dislocations loops evolve and form a dislocation network. Cavities are observed above 1273 K, but along grain boundaries only, corresponding to a swelling amounting to $\sim$1% at 100 dpa and 1673 K [43].

3.3. Role of electronic excitations

Electronic effects can: (i) stimulate annealing of radiation damage in Al_2O_3 and MgO under proton irradiation; (ii) enhance metallic colloid formation in electron irradiated MgO containing iron or nickel; (iii) prevent amorphization under high-energy heavy ion irradiation. Concurrent electron and heavy ion irradiation lowers the nucleation rate of dislocation loops, but enhances the growth, in the Al_2O_3/MgO system [41]. According to Zinkle, it can be rationalized by using the electronic to nuclear stopping power (ENSP) ratio [2]. Later, it has been shown that the total ionizing radiation is more relevant, and under threshold elastic energy transfers could be the more important contribution [39]. The effect of electronic excitations in ceramics lacking the radiolytic mechanism is attributed to the role of charge states on the mobility of point defects or chemical species. The annealing of close Frenkel pairs is then stimulated, and the loop nucleation retarded due to the accelerated dissociation of small loops [2,41].

3.4. Modeling of the kinetics of microstructural formation and evolution

Kinoshita et al. carried out what seems to be the first, and probably the sole, attempt at quantitative modeling of the microstructure evolution in an oxide [44]. They use Kiritani's models of nucleation and growth of dislocation loops in metals under electron irradiation adapted to ionic crystals. This model uses a set of pseudo-chemical rate equations assuming that: (i) stoichiometry is always respected within the loops; (ii) stable nucleus of loops is a pair of cation interstitials; (iii) temperature is low enough to assume immobile vacancies. They show that C_L, the saturation number density of interstitial dislocation loops, is driven by the mobility of interstitials. At high temperature, where vacancies are mobile, they obtain an expression for the growth velocity of loops and show that, as in metals, it depends on the mobility of vacancies. Applied to MgO irradiated with 1 MeV electrons in the temperature range 300–1300 K, this model corresponds to a migration energy for interstitials of about 0.05 eV and 2.0 eV for vacancies, in qualitative agreement with known values.

This first approach is nevertheless still very crude compared to the complexity presented above. A full model should include certainly, at least in the most intricate cases: (i) the charge carrier concentrations, introducing equations for

them; (ii) the possible defect charge variations during jumps; (iii) the defect mobility in all charge states; (iv) the impact of the local electric fields induced by any local nonneutrality. Part of these hypotheses could indeed be removed for nonionic systems which display a lower ordering energy, like SiC. The connection of ab initio calculations, MD simulations and Monte Carlo/kinetic rate equation approaches, should now be able to open the way to a proper multi scale modeling of the microstructure formation, along the lines of the pioneering work by Uberuaga [45]. Including a proper description of the electric field effects in the mean field approach seems to us to be of great importance in this prospect.

4. Radiation enhanced diffusion (RED)

In metals irradiation enhances atomic diffusion through: (i) increasing defect concentrations above the thermal equilibrium ones; (ii) producing new kinds of atomic jumps, the ballistic ones, giving rise to so called ion-beam mixing. The latter term is temperature independent and dominates at very low temperatures. In nonmetals both terms must be present, combined with a third, complex inelastic effects on defect mobility already mentioned. The order of magnitude of the second term is 1 nm^2/(dpa/s), as in metallic systems. Ballistic mixing as well as some qualitative evidence of radiation enhanced or induced diffusion (RED), are known. Beyond ballistic mixing, RED has only been studied in MgO, using [18]O isotopic tracer for oxygen self-diffusion and Zn and Ca oxides for magnesium [46]. Under 2 MeV krypton ions irradiation, RED is observed. Above 1400 K the RED of oxygen displays an activation energy of 4.1 eV and a flux dependence given by an exponent amounting to 0.5. Below this temperature the flux dependence become more or less linear, with an exponent of 0.8 at 1373 K and 1.22 at 1173 K, and an activation energy of 0.35 eV. At high T the square root dependence is in agreement with a recombination regime. But then the activation energy should be of the order of 1.2 eV, half the know migration energy of vacancies, which is clearly incompatible with 4.1 eV. The low T result, with a low activation and a linear flux dependence, could be due to a regime of defect elimination on the sinks. However we know that the sink case normally sets in at high T and the recombination at low T, not the reverse.

Once more this puzzling result points to a better knowledge of the microstructure formation and evolution under irradiation, as well as to a determination of the sink strength.

5. Induced phase changes

In metals under irradiation one observes segregations of minority components on defect sinks, homogeneous or heterogeneous precipitation of a nonequilibrium phase, phase separation, bulk phase changes, order–disorder transitions, and amorphization. All these forms are a priori possible in nonmetals, and the importance of inelastic effects could enrich the list. Here too the knowledge is far less extensive than in metallic systems, and very few systems have been studied, the prototypical MgO and Al_2O_3 being again the best, if not the only, known, except for amorphization which is by far the most studied phase change.

5.1. Segregation/precipitation

This process is, in metallic systems, the dominant source of phase change under irradiation, but does not seems to have attracted much interest in insulating ones; beyond the colloid formation in halides, only a few cases have been studied. Under 1.8 MeV electron irradiation of iron or nickel doped MgO at 923 K and above, metallic precipitates form, containing 30% of the initial doping. They mostly decorate dislocations, pointing both to cation transport and to a heterogeneous formation mode [47]. At this energy the iron cannot be displaced at a sufficient level and mainly oxygen defects are involved. The thermal equilibrium phase in these conditions of temperature and oxygen partial pressure is a solid solution of iron and magnesium oxides. Therefore if, according to the authors, Fe^{2+} is the migrating species, segregation and subsequent precipitation of Fe^{2+}, later reduced in metallic form by electron capture, should take place by a flux coupling mechanism with oxygen defects eliminating on sinks. A similar mechanism could be involved in Al colloid formation in alumina, even if the diffusionless mechanism proposed for colloid formation in halides by Jain could also be valid in this case [48]. A segregation of C interstitials on sink could occur in SiC, triggered by the well-known interaction of silicon interstitials with carbon dissolved in silicon [49].

5.2. Phase change and order–disorder transitions

Beyond flux coupling effects, the defects stored in the material under irradiation can also trigger structural changes, either order–disorder transformation or amorphization. Two systems have been thoroughly studied for induced order-disorder transitions: zirconia and the $MgAl_2O_4$ spinel. Zirconia has a complex phase diagram and, if undoped, displays at ambient pressure three phases: cubic, tetragonal and monoclinic as the temperature is lowered. Under irradiation by heavy ions, Bi and Xe of 800 keV, but not light ones or electrons, at ambient temperature, the low temperature monoclinic phase transforms into the tetragonal one [50]. This transformation is known to take place without irradiation under high pressure, which allow the proposal of a model based on the effect of stresses created by a high concentration of defects, probably oxygen vacancies, produced in dense cascades, but not by irradiation creating isolated Frenkel pairs [51].

We have seen that $MgAl_2O_4$ is very radiation resistant. Under neutron irradiation, or heavy ions whether swift or not, the cations sublattice becomes disordered, giving rise to a structural transition. Some controversy remains as to whether the disorder triggers a transition towards a cation disordered spinel structure with a random occupation of both kinds of cation sites, or a cubic rock salt like one with half a parameter cell, where the four octahedral sites are randomly occupied by the three cations and a vacancy [52]. A recent ab initio calculation has shown that the first case is lower in energy, kinetic constraints however could lead to the second case [53].

5.3. Amorphization

Amorphization, or metamictization, is the phase transition from a crystalline to a noncrystalline phase under irradiation. The resulting structure may be closely related to the structure of the glass formed, when possible, by a quench from the liquid phase, as in metallic glasses, or may not, as in SiO_2. It has been by far the most studied phase transition under irradiation in ceramics during recent years. The experimental character of the transformation are now well known and do not differ greatly from the ones already observed in semiconductors and metallic alloys. Numerous models have been devised to describe the *macroscopic* kinetics in the various regimes, starting from the silicon studies forty years ago, to the recent revival in the oxide field [54]. Basically, the amorphization is supposed to result from the accumulation of the damage coming from individual primary particles, whether in isolated Frenkel pairs or in a cascade regime. These models then describe at a macroscopic level the competition between accumulation and annealing processes along irradiation time. At the *atomic level* however, we are still lacking a model, even if the basis of the mechanisms at work are known.

Upon irradiation any kind of material can be amorphized if the temperature is sufficiently low, and the irradiation flux high enough [55]. However, the ease of amorphization differs greatly from one material to another. Some crystals, like quartz, are easily amorphized by 20 keV electron irradiation producing only isolated defects, probably broken bonds and oxygen Frenkel pairs, at a critical dose of much less than one dpa. Silicon carbide can be amorphized below 500 K at a dose of 0.3 dpa. Conversely the $MgAl_2O_4$ spinel needs heavy ions and dense cascades producing tens of dpa to amorphize, as well as low temperatures of the order of 100 K at most [56]. Simple oxides like UO_2, cannot be amorphized in experimentally accessible conditions, but only under the highest fluxes allowed in numerical simulations.

The various simulation studies made by molecular dynamics on model systems of metallic alloys have greatly elucidated the atomic mechanisms at work in the less covalent systems, at least in the Frenkel pair regime. Amorphization proceeds as soon as a sufficient concentration of defects has destabilized the lattice, through an elastic softening if the bonding is sufficiently isotropic. These defects can be either broken/reconstructed bonds in sufficiently covalent compounds, as in SiO_2 and SiC, or point defects, probably both interstitials and anti-site defects in ionic compounds having centro-symmetric bonding interactions [57]. The competition between build-up and thermal annealing results both in the specific form of the dose/temperature curve and the role of simultaneous electron and ion irradiation. Indeed if g is the mean defect production rate and E_a a typical migration energy, the build-up will stop at a temperature T_c where $T_c \approx -E_a/kLn(g)$. Simultaneous irradiation with electrons, or even light ions, is able to slow down or even prevent the transformation, by enhancing the defect mobility toward sinks or by increasing recombinations. This effect has already been observed in several oxides [2,58].

The cascade regime, however, is frequently described in the so-called 'thermal spike' framework, which involves the formation of a molten core in the cascade followed by the quench through thermal contact with the surrounding cold matter. This approach is as difficult as in metals to prove or to disprove.

6. Conclusions

Here we have given a short survey of the basic phenomena involved in the aging of nonmetals under irradiation. We presented the main aspects of these materials under irradiation, defect creation, either elastically or inelastically, microstructural evolution due to defect elimination, radiation enhanced diffusion and phase changes under irradiation. In all cases we must stress that the number of systems *comprehensively studied in this prospect*, beyond halides, is tremendously small, except for amorphization. We showed how partial our knowledge remains of ballistic threshold values as well as of inelastic defect production rates. Similarly the inelastically induced defect mobility is detected, but badly understood. The formation and evolution of the microstructure from defects clustering and recombination, is the neglected key to the understanding of almost all the behaviors. Here, too, the level of knowledge is very scarce, and we lack proper models, i.e. including the important role of Coulomb interactions between charged species upon clustering. The same remark probably explains the unusual behavior of radiation enhanced diffusion in the sole system studied, MgO, for which the sink dominated regime could be observed at a lower temperature than the recombination one. The situation is bit less disappointing for induced phase transitions, particularly the amorphization one, which can benefit from the large number of studies done in the past on semi-conductors and metallic alloys.

References

[1] G.P. Pells, J. Nucl. Mater. 155–157 (1988) 67.
[2] S.J. Zinkle, C. Kinoshita, J. Nucl. Mater. 251 (1997) 200.
[3] Y. Limoge, A. Barbu, Def. Diff. Forum 237 (2005) 621.
[4] L.W. Hobbs, A.E. Hughes, D. Pooley, Proc. R. Soc. Lond. A 332 (1973) 167.
[5] G.P. Pells, D.C. Phillips, J. Nucl. Mater. 80 (1979) 215.
[6] G.P. Pells, D.C. Phillips, J. Nucl. Mater. 80 (1979) 207.
[7] E.A. Kotomin, A.I. Popov, Nucl. Instrum. Methods B 141 (1998) 1.
[8] G. Lucas, L. Pizzagalli, Nucl. Instrum. Methods B 229 (2005) 359.
[9] G. Lucas, in: Etude théorique à l'échelle nanométrique du carbure de silicium sous irradiation : modélisation classique et ab-initio, PhD Thesis, Faculté des Sciences, Poitiers, France, 2006.
[10] F.W.J. Clinard, L.W. Hobbs, in: V.M. Agranovich, A.A. Maradudin (Eds.), in: Modern Problems in Condensed Matter Physics, vol. 13, North-Holland, Amsterdam, 1986.
[11] N. Itoh, A.M. Stoneham, Materials Modification by Electronic Excitations, Cambridge University Press, Cambridge, 2001.
[12] D. Pooley, Proc. Phys. Soc. London 87 (1966) 245.
[13] K. Tanimura, T. Tanaka, N. Itoh, Phys. Rev. Lett. 51 (1983) 423.
[14] P.E. Trevisanutto, P. Sushko, A.L. Shluger, et al., Surf. Sci. 593 (2005) 210.
[15] M.L. Knotek, P.J. Feibelman, Phys. Rev. Lett. 40 (1978) 964.
[16] A. Lushchik, M. Kirm, C. Lushchik, et al., Nucl. Instrum. Methods B 166 (2000) 529.
[17] A. Lushchik, T. Kärner, C. Lushchik, et al., Phys. Status Solidi C 4 (2007) 1084.
[18] H. Hosono, H. Kawasoe, N. Matsunami, Phys. Rev. Lett. 80 (1998) 317.
[19] A.L. Shluger, J.L. Gavartin, M.A. Szymanski, et al., Nucl. Instrum. Methods B 166–167 (2000) 1.
[20] G. Roma, Y. Limoge, S. Baroni, Phys. Rev. Lett. 86 (2001) 4564.
[21] D. Ceresoli, O. Tosatti, S. Scandolo, et al., J. Chem. Phys. 121 (2004) 6478.
[22] J. Song, H. Jonsson, L.R. Corrales, Nucl. Instrum. Methods B 166–167 (2000) 451.
[23] M. Petersilka, U.J. Gossmann, E.K.U. Gross, Phys. Rev. Lett. 76 (1996) 1212.
[24] S. Ismail-Beigi, S.G. Louie, Phys. Rev. Lett. 90 (2003) 076401.
[25] S. Ismail-Beigi, S.G. Louie, Phys. Rev. Lett. 95 (2005) 156401.
[26] J.C. Bourgoin, J.W. Corbett, Radiat. Eff. 36 (1978) 157.
[27] Y.G. Jin, K.J. Chang, Phys. Rev. Lett. 86 (2001) 1793.
[28] G. Roma, Y. Limoge, Def. Diff. Forum 137 (2005) 127.
[29] J. Song, L.R. Corrales, G. Kresse, et al., Phys. Rev. B 64 (2001) 134102.
[30] P. Rinke, private communication, 2007.
[31] G. Roma, Y. Limoge, 2007, in press.
[32] G. Roma, Y. Limoge, Phys. Rev. B 70 (2004) 174101.
[33] A.Y. Stathopoulos, G.P. Pells, Philos. Mag. A 47 (1983) 381.
[34] K. Yasuda, C. Kinoshita, S. Matsumura, et al., J. Nucl. Mater. 319 (2003) 74.

[35] K. Yasunaga, K. Yasuda, S. Matsumura, et al., Nucl. Instrum. Methods B.
[36] D.G. Howitt, T.E. Mitchell, Philos. Mag. A 44 (1981) 229.
[37] R.A. Youngman, L.W. Hobbs, T.E. Michell, J. Phys. (Paris) 41 (1980) 227.
[38] R.A. Oshima, C.Y. Nie, M. Komatsu, et al., Mat. Sci. Forum 196 (1995) 1237.
[39] K. Yasuda, C. Kinoshita, R. Morisaki, et al., Philos. Mag. A 78 (1998) 583.
[40] S.J. Zinckle, Nucl. Instrum. Methods B 91 (1994) 234.
[41] K. Yasuda, C. Kinoshita, M. Ohmura, et al., Nucl. Instrum. Methods B 166-167 (2000) 107.
[42] F.W. Clinard, G.F. Hurley, L.W. Hobbs, J. Nucl. Mater. 108-109 (1982) 655.
[43] Y. Katoh, N. Hashimoto, S. Kondo, et al., J. Nucl. Mater. 351 (2006) 228.
[44] C. Kinoshita, K. Hayashi, S. Kitajima, Nucl. Instrum. Methods B 1 (1984) 209.
[45] B.P. Uberuaga, R. Smith, A.R. Cleave, et al., Phys. Rev. Lett. 92 (2004) 115505.
[46] A.I.V. Sambeek, R.S. Averback, C.P. Flynn, et al., Mat. Res. Soc. Symp. Proc. 373 (1995) 293.
[47] S. Clement, E.R. Hodgson, Phys. Rev. B 36 (1987) 3359.
[48] U. Jain, A.B. Lidiard, Philos. Mag. 35 (1977) 245.
[49] S. Mirabella, A. Coati, S. Scalese, et al., Diff. Def. Data B 82 (2002) 195.
[50] K.E. Sickafus, H. Matzke, T. Hartmann, et al., J. Nucl. Mater. 274 (1999) 66.
[51] D. Simeone, G. Baldinozzi, D. Gosset, et al., Phys. Rev. B 70 (2004) 134116.
[52] K.E. Sickafus, J. Nucl. Mater. 312 (2003) 111.
[53] R.P. Gupta, J. Nuc. Mater. 358 (2006) 35.
[54] W.J. Weber, Nucl. Instrum. Methods B 166 (2000) 98.
[55] L.W. Hobbs, Nucl. Instrum. Methods B 91 (1994) 30.
[56] N. Yu, K.E. Sickafus, M. Nastasi, Mat. Res. Soc. Symp. Proc. 373 (1995) 401.
[57] A. Chartier, C. Meis, J.P. Crocombette, et al., Phys. Rev. Lett. 94 (2005) 025505.
[58] A. Meldrum, L.A. Boatner, R.C. Ewing, Nucl. Instrum. Methods B 141 (1998) 347.