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Mini-Review

Electron and Neutron Beam Irradiation Effects in Homogeneous and Nanostructured Oxides

Diana Nesheva*

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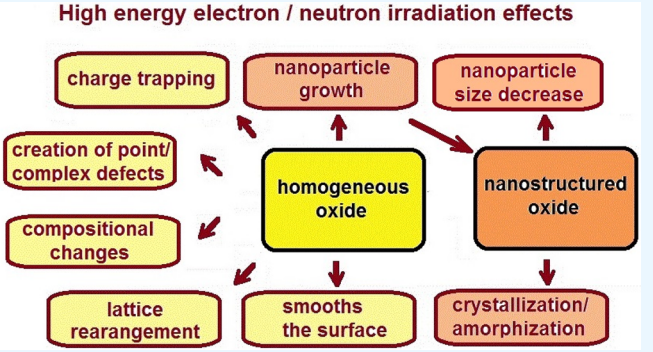
ABSTRACT: Oxide-based materials have a variety of applications in chemical sensing and photocatalysis, thin-film transistors, complex-oxide field-effect transistors, nonvolatile memories, resistive switching, energy conversion, topological oxide electronics, and many others. The radiation resistance of these materials in such devices plays an important role in device operation in radiation environment, and this attracts much attention in the research area. In spite of damage in a number of cases high-energy particles may have a beneficial effect on the target. In this mini-review article examples of both creation of defects and beneficial changes in the structure and properties of homogeneous and nanostructured oxides caused by high-energy electron and neutron irradiation are given by considering some recently published results. First, the attention is turned to ionizing and displacement effects of electron and neutron irradiation in homogeneous bulk and thin-film oxides reported in the literature. Then, the effect of electron and neutron irradiation on nanostructured oxides and semiconductor nanoparticles embedded in an oxide matrix is regarded. Considerable attention is paid to silicon oxide layers since they are widely used in microelectronic products, which are among the most manufactured devices in human history. Processes of irradiation-induced lattice rearrangement, compositional changes, growth of nanoparticles and their size reduction, creation of point defects and their complexes, electron−hole generation, and charge trapping are discussed.



1. INTRODUCTION

The resistance of materials and devices to radiation is of crucial importance in various applications. The terms "radiation resistance"/"radiation hardness" describe the ability of a material or structure to keep its properties upon exposure to radiation. Irradiation of solid-state materials with energetic particles (electrons, protons, ions, neutrons) normally gives rise to formation of defects. It may induce amorphization, recrystallization, and annealing thus changing various properties of three-dimensional (3D) solids and disturbing the device operation. For example, in a nuclear reactor, the materials and devices are exposed to neutron and gamma irradiation while in space the radiation environment consists of highly energetic electrons (energies up to ∼7 MeV), protons (energies extending to hundreds of MeV), and small amounts of low-energy heavy ions.[1]

Oxide materials have multiple applications in electronics and optoelectronics, sensing and photocatalysis, environment and human health diagnostics, etc. Among them are thin-film transistors and complex-oxide field-effect transistors, nonvolatile memories, resistive switching, oxide materials for photocatalysis, energy conversion, topological oxide electronics, and many others.[2] The radiation resistance of oxide materials in such devices plays an important role in device operation in radiation environment, and this attracted much attention in this research area. In particular, much effort was addressed to study and improve radiation hardness of metal-oxide-silicon (MOS) structures and microelectronic elements since they have applications in many areas of human life. Some of these devices are operated in airplanes or space environments or close to reactors in nuclear power plants where the radiation level can be quite high and can cause device degradation. Frequently this is due to radiation-induced changes in the oxide layer. Therefore, investigations for obtaining information for the behavior of oxide materials under extreme radiation conditions are important.

A promising way for development of materials and devices with good radiation resistance is production and usage of materials with reduced dimensionality. It has been ascertained that low-dimensional materials, which are among the subjects of

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interest in the mini-review, have better resistance to energetic (ionizing) radiation than three-dimensional ones and could be successfully used in fields such as medical diagnostic imaging and therapy, material processing, space and avionic applications, nuclear power plants, etc. Contrary to the case of irradiation of three-dimensional systems with high-energy particles, when much energy can be dispersed in the sample, normally only a small part of the particle energy is deposited onto the nanosystem and the total amount of damage to a nanoscale object decreases with the particle energy.[3] Nanoparticles play an important role in enhancing radiation resistance by providing extra sinks for irradiation-induced point defects, called "self-purification", as well as by maintaining the mechanical strength by pinning dislocations. The self-purification process will be considered in subsection 4.1.

It is important that, in spite of the damage in a number of cases, irradiation, especially when combined with heat treatment, may be useful and have a beneficial effect on the target. For example, electron beam irradiation is used as a valuable laboratory tool giving possibilities for investigation of the generation, evolution, and annealing of the radiation-induced defects in semiconductor devices. It can penetrate a wide range of materials and deliver the required irradiating dose in a few seconds, and thus the entire process can take place in minutes with no chemical residuals or induced radioactivity remaining in the processed products. Irradiation with high-energy particles has been applied for the modification and synthesis of various materials, in particular, nanomaterials.[1,3]

The purpose of the mini-review is to draw attention to the two ways in which the irradiation of oxide materials with energetic electrons and neutrons can affect their properties. It can cause deterioration of some properties of materials by damaging their structure, an effect which is usually given attention, but the irradiation can also have beneficial effects. The mini-review will not summarize all published results on the topic; some recent results giving interesting examples of the two types of impact of electron and neutron radiation on the properties of popular oxides with many real and potential applications will be considered. More attention will be given to displacement effects, but some data concerning ionizing effects will also be presented. The mini-review will start with a short consideration of the production of defects in solids under fast electron and neutron irradiation (Section 2). Then, the attention will be turned to some ionizing and displacement effects of electron and neutron irradiation in homogeneous bulk and thin-film oxides reported in the literature (Section 3). In the last Section 4, the effect of electron and neutron irradiation on nanostructured oxides and semiconductor nanoparticles embedded in an oxide matrix will be discussed.

2. GENERAL RADIATION EFFECTS IN THREE-DIMENSIONAL SOLID MATERIALS UNDER IRRADIATION WITH ENERGETIC ELECTRONS AND NEUTRONS

In order to make the further consideration of the effects of electron and neutron radiations clearer, we start with a short description of some characteristics of the electron and neutron irradiation and the ways they interact with solids. Electrons are light charged particles while neutrons are heavier neutral particles. For a kinetic energy of 1 MeV, the electron is relativistic (0.94c, where c is the speed of light in vacuum) with radiation path in air of 319 cm.[4] For the same energy, the heavier particles are slower, and the neutron radiation path in air is approximately 39 cm (see Table 1).

Table 1. Some Key Characteristics of Electron and Neutron Radiations with Kinetic Energy E_k = 1 MeV, Including Charge, Mass, and Range in Air[a]

Characteristic	Radiation energy E_k = 1 MeV	
	Electron	Neutron
Charge	−1	neutral
Mass (amu)	0.000 548 58	1.008 665
Velocity (cm/sec)	2.82×10^{10}	1.38×10^{9}
% Speed of light	94.1%	4.6%
Range in air (cm)	319	∼39
Relative displacement damage	0.01	2

[a]Adapted from ref 4.

There are several general types of radiation effects on three-dimensional solids.

(1) *Atom displacement* from the position in the lattice structure of the material, which is frequently called "displacement damage". It is due to the collision between an incoming particle and a lattice atom, which may result in displacement of the atom from its original lattice position provided the lattice atom receives sufficient kinetic energy (Figure 1). Displaced atoms may leave lattice vacancies, occupy interstitial positions, cause interchange of dissimilar atoms in the lattice structure, or may form Frenkel pairs, dislocations, or clusters. A single incident particle can cause a cascade of collisions that are related to both the incident particle and secondary particles. The collisions occur along the tracks of the incident particles, the tracks of the created secondary particles, and in clusters formed at the end of these tracks.

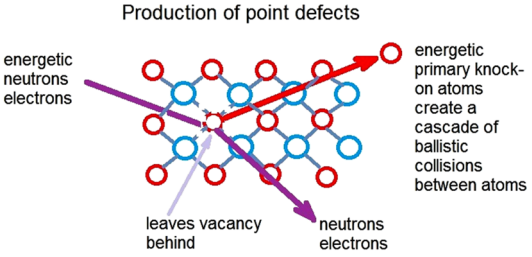

Figure 1. Illustration of defect production from ballistic processes. Energetic neutrons/electrons displace atoms leaving vacancies behind. Energetic primary knock-on atoms may create cascade ballistic collisions between atoms.

(2) *Ionization*. This is the process of removing or adding an electron to a neutral atom, thus creating an ion. The term is also used when an electron is removed from a partially ionized atom. The charged radiations, in particular, electron beams, can directly ionize solids while neutrons cause ionization indirectly by producing charged particles.

(3) *Impurity production*. It refers to radiation-caused transmutation of nuclei of the irradiated material into other nuclei that may be radioactive. Electrons do not directly cause impurity production, while neutrons cause it through neutron capture and fission. Neutron capture by the nucleus of an atom in the target changes either the

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chemical nature of the atom and thus an impurity atom appears or changes the isotope present. The nuclear reaction occurs when the incoming neutron has extraordinarily high energy.

Large energy transfer from energetic particles to a small volume of the irradiated material can result in thermal heating, and this could stimulate various lattice changes (bond breaking, atom and defect diffusion, ordering, cluster formation, etc.). A comparison of the effects of electrons and neutrons is presented in Table 2.

Table 2. Radiation Effects and the Way of Interaction of Electrons and Neutrons with Solid Materials[a]

Radiation effect	Electron	Thermal (eV) neutron	Fast (MeV) neutron
Atom displacement	Some displacement	Yes, Indirectly	Multiple displacement via scattering reactions; can cause displacement of "knock-on" atoms
Ionization	Directly	Indirectly	Indirectly
Impurity production	No	Directly by absorption reactions (mostly thermal neutron), also may lead to more radiations	
Energy release	Localized heat deposition	Indirectly	Indirectly

[a]Adapted from ref 4.

3. ELECTRON AND NEUTRON IRRADIATION OF AMORPHOUS AND MICROCRYSTALLINE OXIDE FILMS AND BULK MATERIALS

3.1. Electron Irradiation. *3.1.1. Irradiation-Induced Ionization of Atoms and Generation of Lattice Defects That May Disturb Device Operation.* In this subsection attention will be paid to both ionization of atoms and irradiation-induced generation of point defects and their complexes in SiO_2, ZnO, and SnO_2, which may disturb the operation of a device containing such films. Most attention will be paid to amorphous silicon dioxide, as it is used for many years in microelectronics, in particular, as a channel layer in field effect transistors (FETs). A type of FET known as metal-oxide-semiconductor FET is probably the most manufactured device in history. Its stable operation under irradiation with energetic particles is of great importance, and a large number of investigations has been performed to study ionizing effects and displacement in silicon oxide layers. Silicon oxide is mostly used in FETs, and therefore significant attention will be paid in the mini-review to electron and neutron radiation effects in silicon oxide layers. In Subsection 3.1.1 ionizing and displacement effects of electron beam irradiation of Si-SiO_2 structures and ZnO thin films, which may cause problems in the electronic and optoelectronic elements, will be addressed. A more detailed consideration of the research in the field of the electron beam damage in oxides and the popular damage mechanisms can be found in ref 5.

During high-energy electron irradiation of MOS structures ionization of atoms in the oxide layer can take place and electron−hole pairs can be generated (Figure 2). If the energy of the generated electrons and holes is high (higher than the energy required for creation of an electron−hole pair), additional electron−hole pairs can be created. Thus, a single high-energy electron could generate many electron−hole pairs. Some electrons will recombine with holes, while most of the free

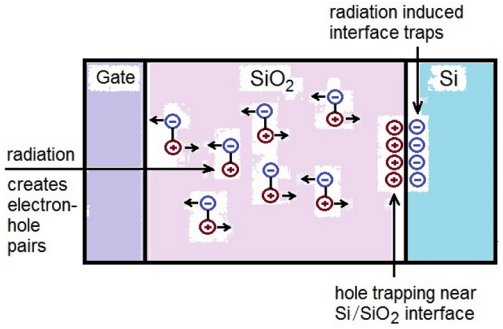

Figure 2. Sketch of the motion of electrons and holes produced under high-energy electron irradiation in the silicon oxide layer of a Si-SiO_2 structure.

electrons will rapidly drift to the gate (metal or polysilicon electrode) and the free holes will drift toward the Si/SiO_2 interface. During the drift to the interface, a part of the holes will be trapped in the oxide layer and form a positive charge (buildup of charge). Due to the lattice mismatch at the Si/SiO_2 interface and surface out-diffusion of oxygen in the oxide layer there is a large number of oxygen vacancies close to the interface that can act as trapping centers, and a part of the drifting holes will be trapped at the interface. The positive charge trapping in the gate oxide can result in the appearance of leakage current in the off-state condition while large concentrations of interface-trap charge can decrease the mobility of carriers thus causing degradation of timing parameters of an integrated circuit. These undesired effects of the electron irradiation can strongly disturb operation of the microelectronic and other electronic devices, and therefore during the years much effort has been addressed to ionizing radiation effects in electronics and hardening of MOS technology. A number of reviews and books in this area can be found in the literature [see, e.g., refs 6 and 7].

When the energy of irradiating electrons is high enough (MeV) they penetrate through the whole Si-SiO_2 structure and, together with electron−hole pair generation, they may generate radiation defects in the oxide layer, at the Si/SiO_2 interface, and in the Si wafer. Such defects are responsible for additional charge trapping that may strongly affect device operation. The most common group of radiation-induced defects in SiO_2 films are defects associated with oxygen vacancies called E' centers. The majority of these defects in undoped SiO_2 result from trapping of holes at neutral oxygen vacancies in the glass network. A brief review of the key experimental and theoretical results on creation of centers in amorphous SiO_2 can be found in ref 8. The traditional model of ionizing-irradiation-induced damage in SiO_2 at room temperature assumes a uniform generation of E'_γ centers in the SiO_2 bulk through the capture of irradiation-generated holes by oxygen vacancies. However, the traditional model has problems with the explanation of experimentally observed dose dependencies of the defect concentrations, especially at a low dose rate. A recent model for defect dynamics in irradiated Si-SiO_2 structures gives a better explanation of the dose dependences.[9] Because of the high level of lattice disorder in amorphous SiO_2 dispersive migration of the holes was assumed, which retards the generation of E'_γ centers. Decay of the diffusion coefficient was also assumed while the irradiation is applied. A recent complex study has given information about formation of oxygen vacancies under 1 MeV electron irradiation with a fluence of 1×10^{16} electrons/cm^2.[10] It is shown that, under the irradiation, Si−O bonds are broken and some oxygen

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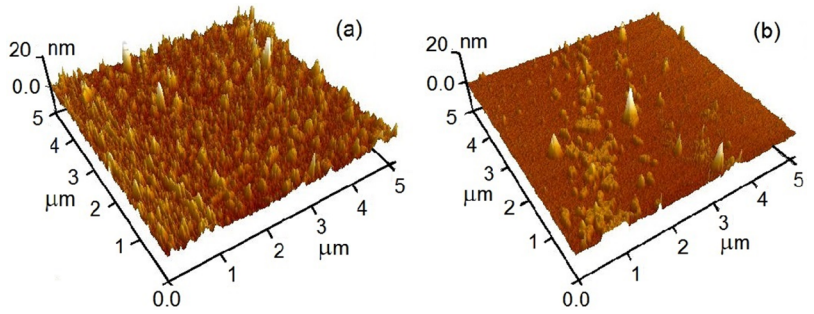

Figure 3. Three-dimensional 5 × 5 μm^2 AFM surface images of Si-SiO_x structures with 1000 nm thick homogeneous SiO_x film ($x \approx 1.8$): (a) non-irradiated and (b) 20 MeV electron irradiated with a fluence of 7.2×10^{14} electrons/cm^2. Reprinted in part with permission from ref 16.

atoms leave their position in the lattice network thus creating oxygen vacancies. An interesting result of this study is that the displaced atoms form negatively charged oxygen ions (O_2^{2-}) in the amorphous SiO_2 layer irradiated with 1 MeV electrons but 90 keV electrons do not provide enough energy for the formation of O_2^{2-} ions.

The radiation-induced defects at the Si-SiO_2 interface have also been investigated. The traditional model based on the obtained results assumes an irreversible conversion from E'_γ to P_b centers (P_b center is a trivalent Si atom playing role of fast trap) at the Si-SiO_2 interface through reactions with hydrogen molecules (hydrogen is released during long-term radiation exposure). Details on the generation of interface defects under MeV electron irradiation have been provided by a systematic investigation.[11,12] It has confirmed that 18 MeV electron irradiation generates new defects in the SiO_2 layer, most of which are positively charged oxygen vacancies (E′-centers). Besides, it generates various states at the Si/SiO_2 interface whose chemical nature and electronic position in the silicon band gap strongly depend on substrate doping.[12] Generation of neutral vacancy defects has also been noticed, but their concentration has been more than 2 orders of magnitude lower than the content of E′-centers. Besides, a shallow energy level situated at 0.18 eV below the conduction band bottom has been detected and related to a complex of oxygen vacancy trapped by an interstitial oxygen atom. It has been found that the density of these defects decreases with increasing electron irradiation fluence and deeper traps appear. For example, in Si-SiO_2 structures with n-type Si wafers (doped with phosphorus) activation energy of ∼0.40 eV has been obtained for such defects, and they have been attributed to a lattice vacancy trapped at a substitutional phosphorus atom or phosphorus-vacancy pair.

Creation of defects under electron irradiation of metal oxide films and their composites such as ZnO, In_2O_3, SnO_2, and ZrO_2−Al_2O_3 was also the subject of numerous structural and optical (photoluminescence, spectroscopic ellipsometry, Fourier transform infrared (FTIR) spectroscopy) investigations.[13,14] In general, the defect formation observed is explained by bond breaking, while structural changes like amorphization are explained by excitation of the chemical bonds and subsequent atomic movements.[14] An enlargement of the *c*-lattice parameter of hexagonal microcrystalline ZnO has been observed upon irradiation with 10 MeV electrons at a fluence of 10^{16} electrons/cm^2 related to creation of complex defects.[13] A balance between the formation of defects and their annealing has been found, and the lattice of microcrystals has been relaxed when the fluence was increased twice. An interesting detailed mechanism has been suggested for the creation of the complex defects, which is based on the absence of emission bands corresponding to oxygen and zinc vacancies. It has been assumed that the electron energy is high enough to displace a Zn atom and the collision may give the Zn atom enough energy to knock out and displace the nearest oxygen atom. Then the O atom can knock out the nearest Zn, etc. If, after a number of steps, the last knocked-on Zn atom is far enough from the initial zinc vacancy (V_{Zn}) no immediate recombination will occur. Thus, V_{Zn}-Zn_O-O_{Zn} acceptor defects (where Zn_O is zinc antisite and O_{Zn} is oxygen antisite) and interstitial (Zn_i) donor defects may appear. The generation of the complex defects has resulted in undesired increase of the defect photoluminescence, which would disturb the performance of the layer in an optoelectronic light-emitting device, but the general conclusion is that ZnO is a material with high radiation resistance in which a significant fraction of the radiation-induced disorder disappears at room temperature.

A recent complex study of the effect of 3 MeV electron beam irradiation (5−15 kGy) of Co-doped nanocrystalline SnO_2 thin films on their microstructure and optical properties has revealed that the radiation resistance of these layers is lower than that of ZnO. Changes of the lattice constants, grain size, refractive index, extinction coefficient, and optical band gap of the films have been observed.[15] Generation of point defects or defect complexes, such as oxygen vacancies, migrating oxygen, and their clusters, has been assumed in order to explain the observed changes in structural and optical parameters. The observed significant changes of many film properties would be an obstacle for potential optoelectronic application of these films. However, the authors have pointed out that the changes of the optoelectronic properties of Co-doped SnO_2 film can be beneficial, as well; it has been assumed that the electron beam irradiation changes make the films suitable for application as radiation sensors.

3.1.2. Electron Irradiation Effects in Homogeneous Oxide Films That May Be Beneficial. In this subsection, examples of beneficial effects of the electron irradiation of thin films of various compositions (sub-stoichiometric and stoichiometric silicon oxide, Al_2O_3, TiO_2, Nb_xO_y, ZnO, and graphene) will be considered. Attention will be paid to electron beam-induced surface smoothening, film densification, a possibility for direct electron beam lithography on buried surfaces, changes in the electrical conductivity, and improvement of the chemical sensing properties.

The effect of the irradiation on the film surface roughness has been investigated when irradiating with high-energy (MeV)[16] and low-energy (keV)[17] electrons. It has been shown that the 20 MeV electron irradiation of Si-SiO_x (1000 nm) structures on crystalline Si substrate at room temperature (fluence 7.2×10^{14} electrons/cm^2, electron beam current 5 μA) significantly

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changed the SiO_x surface roughness. Three-dimensional atomic force microscopy (AFM) images of non-irradiated and irradiated Si-SiO_x samples are depicted in Figure 3.[16] It is seen that the surface of the non-irradiated layer (Figure 3a) is uniform and relatively rough; this is expected for films deposited by thermal vacuum evaporation at room temperature of the substrates. The surface of the irradiated film looks smoother (Figure 3b); it displays areas having very low surface roughness and areas with a slightly higher roughness. The root-mean-square (rms) roughness of the non-irradiated film and irradiated film is 2.38 and 1.4 nm, respectively.[16] It has been found that the roughness of the irradiated film equals that of films annealed at 700 °C. On the other hand, no significant roughness changes have been observed for the films annealed at 700 °C. These observations have indicated that, during the electron irradiation, due to energy transfer from the electron beam to the film lattice, a rearrangement of the surface atoms takes place resulting in smoothing of the SiO_x film surface. The irradiation-induced effect on the surface roughness is similar to the effect of thermal annealing, but as the electron energy is high bond breaking is probable and may have a contribution in the process of surface smoothing. The irradiation-induced smoothing, in combination with a parallel growth of Si nanoparticles in the SiO_x film, can be useful for the potential device applications of these structures.[18]

It has been shown recently that irradiation with low-energy electrons (1 keV) and high electron beam current (~300 mA) can also effectively change the surface roughness of low-density sputtered SiO_2 films on glass substrates (films thickness is around 100 nm).[17] The irradiation reduces the rms surface roughness of the sputtered films from 0.630 to 0.467 nm. Since the electron energy was very low, the rms reduction has been explained with thermally induced structural rearrangement owing to energy transfer from the electron beam whose current is quite high to the film lattice. No bond breaking is expected for the electron energy of 1 keV. An electron beam-induced increase in the density of the sputtered films from 1.87 to 2.25 g/cm^3 (typical for amorphous SiO_2) is also reported, but the irradiation does not cause changes in the density of SiO_2 films thermally grown on Si substrates (having density of around 2.65 g/cm^3). The observed density increase has been related to healing of the existing voids in the sputtered films facilitated by the electron beam. Sub-stoichiometric silicon oxide layers deposited by thermal evaporation in vacuum[16] are known to be of low density. The density of the sputtered SiO_2 layers in ref 17 is also low. This suggests that a reduction in surface roughness and an increase in density upon electron irradiation can be expected and be beneficial for oxide films with lower-than-usual density.

Formation of amorphous SiO_2 around the interface between Al_2O_3 films and Si substrates has been detected upon electron irradiation at room temperature with 5 keV electrons.[14] It has been suggested that the electron bombardment causes bond breaking in the Al_2O_3 film thus providing neutral and/or charged oxygen for the SiO_2 growth. It is interesting that the growth, which was related to transport of oxygen and silicon atoms/ions, occurred during irradiation at room temperature. This observation has been explained assuming that the transport is assisted by charged and/or uncharged defects and a local electric field generated by the electron irradiation. This result is promising for making direct electron-beam lithography at buried interfaces.

It has been shown by in situ transmission electron microscopy that amorphous TiO_2 thin films, which are widely studied as potential resistive chemical sensors, photocatalysts, etc., have high sensitivity to electron beam irradiation demonstrating strong changes in their electrical properties.[19] It has been found that the material underwent an insulator-to-semiconductor transformation at fluence of ~4.5×10^2 electrons/nm^2 and transition to metallic conductivity at a fluence of 3.0×10^4 electrons/nm^2. The electron beam-induced conductivity increase, which is reversible upon reoxidation, has been related to the formation of oxygen vacancies and progressive formation of a conductive TiO_{2-x} phase. Since undoped TiO_2 thin films are highly resistive a controllable electron beam conductivity reduction could be useful for their sensing applications. Electron beam-induced oxygen reduction of Nb_xO_y thin films has also caused the film conductivity to increase, but the required fluence (1×10^6 electrons/nm^2) was higher than that in the case of TiO_2. The observed difference in the radiation resistance of these films could be useful when looking for materials with similar application, such as solar energy conversion, sensing, and optical systems, but operating in a different radiation environment. It is interesting that, in SiO_2 thin films, significant structural changes took place before the detection of resistivity changes. This has been explained with a somewhat different lattice transformation process (first silicon-rich particles appear and a long time after resistivity changes occur), which will be considered in more detail below.[19]

High-energy radiation has been applied to modify and/or enhance the sensing properties of low-dimensional oxides, which are very promising materials for gas sensors. Investigations of the sensing properties of ion-irradiated nanowire sensors based on "classic" ZnO and In_2O_3 have shown that, as in the case of three-dimensional materials, the ion-induced changes in the nanowire properties depend on the chemical composition.

Gas sensors based on graphene oxide and reduced graphene oxide (RGO) have attracted much attention because they can operate at room temperature. Pristine and platinum-functionalized RGO gas sensors were irradiated with 2 MeV electrons, and NO_2 gas-sensing measurements were carried out at room temperature.[20] It has been shown that, after irradiation of Pt-functionalized sample at a dose of 100 kGy, its response was increased relative to the response of the non-irradiated film. This improvement has been assigned to the formation of an optimum amount of defects and functional oxygen groups in the sample. When samples were irradiated at a dose of 500 kGy, the response was decreased because the electron beam caused the formation of a large network of connected defect sites.

3.1.3. Electron Irradiation Formation of Amorphous and Crystalline Silicon Nanoparticles. In recent decades, the growth of semiconductor and metal nanoparticles in a homogeneous oxide film has been studied actively because the presence of nanoparticles makes the composite films suitable for application in various types of more stable and reliable devices, such as third-generation solar cells, MOS-based nonvolatile memories, detectors of ionizing radiation, etc.[18] Therefore, a significant number of studies have been carried out on the radiation-induced nanoparticle growth. Because of the limited length of the mini-review our attention in section 3.1.3 will be mainly focused on the growth of silicon nanoparticles in silicon oxide layers.

Most frequently ion synthesis is used to form semiconductor or metal nanoparticles in various matrices. Although electrons are much lighter than ions and not as efficient as them, it has been observed that they also lead to the formation of nanoparticles. The first reports, published more than two decades ago, described growth of amorphous Si nanoparticles

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and nanocrystals of low density in a silicon dioxide matrix. Electron beams with relatively low energies (a few to several hundred keV) but with a high intensity (current density around and above 1 A/cm^2) and high fluences (from ~10^{21} up to >10^{23} electrons/cm^2) were applied. It has been concluded that Si nanocrystals can be generated in SiO_2 by using electrons with energy higher than 150 keV or combining lower-energy electron irradiation with heating the specimen to achieve a temperature higher than the crystallization temperature of Si.[21] Later experiments have shown that beams with electron energies higher than 1 MeV and much lower current densities (a few μA/cm^2; irradiation fluxes in the range from 5×10^{11} to 5×10^{13} electrons/cm^2 s) and electron fluences (around 10^{14} to 10^{17} electrons/cm^2) can also induce the formation of silicon nanoparticles in SiO_2.[10,11,19]

The effect of 20 MeV electron beam irradiation on the phase separation and Si nanocluster formation in homogeneous $SiO_{1.2}$ and $SiO_{1.3}$ films has been investigated at fluences of 2.4×10^{14}, 7.2×10^{14}, 1.44×10^{15}, and 3.6×10^{15} electrons/cm^2.[22,23] The irradiation at fluence of 7.2×10^{14} electrons/cm^2 has led to small changes in the optical constants and the formation of very small amorphous Si (a-Si) nanoclusters. The normalized pair distributions measured for the non-irradiated and irradiated SiO_x samples are shown in Figure 4. The intensity of the main

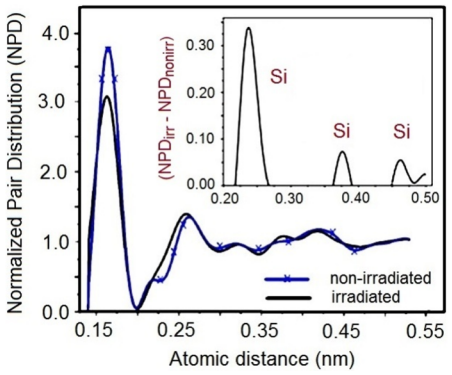

Figure 4. Normalized pair distributions measured for a non-irradiated sample and a 20 MeV electron irradiated sample. (inset) Difference between the two distributions. The irradiation fluence is 7.2×10^{14} electrons/cm^2.

peak at 1.63 Å characteristic of SiO_2 decreases upon electron irradiation, indicating that the number of Si−O bonds was reduced. The changes in the phase composition of the SiO_x are well-displayed in the difference between the two distributions plotted in Figure 4, inset. Three peaks, which coincide with the first three atomic distances in silicon, are observed. They indicate that the electron irradiation increases the relative amount of Si−Si bonds in the SiO_x films; i.e., a pure silicon phase was formed. It has been shown that the amount of the pure silicon phase created by the electron irradiation of the SiO_x films increases with increasing fluence. Investigations on the response to γ-radiation of MOS structures containing Si nanocrystals have shown that the presence of nanocrystals in the oxide layer ensures high sensitivity and good stability of such sensors/dosimeters.[18] Hence the obtained relation between the electron beam fluence and the amount of the pure Si phase could be useful in the preparation of MOS structures for fast electrons sensing/dosimetry applications.

It is accepted that the formation of silicon nanoparticles under high-energy electron beam irradiation of amorphous SiO_2 is due to a process of Si−O bond breaking and formation of Si−Si bonds thus transforming a part of an a-SiO_2 layer to a-Si or a crystalline Si (c-Si) phase. Various mechanisms have been considered as responsible for this process.[21] For example, if the incident electrons have enough energy to produce an oxygen vacancy by knock out displacement, it is likely that O atoms are displaced rather than Si ones since each O atom is bound by two Si−O bonds while a Si atom is bound by four. Ionization of core electrons, ionization of valence electrons leading to covalent bond breakage, elevation of valence electrons to an exciton state, and collective excitation of valence electrons into plasmons have also been considered as possible mechanisms. The ionization of valence electrons of Si atoms can result in Si−O bond breacking and loss of O atoms. As a consequence, Si atoms will gradually aggregate into amorphous Si clusters. The cross section for valence electron ionization is about ten times larger than that for knock-on displacement, and therefore it has been accepted that the ionization of valence electrons of Si atoms is the dominating mechanism, but a displacement effect may also have a contribution to film reduction at high electron energies.

3.2. Neutron Irradiation. To date, a large number of investigations has been directed to studying the neutron radiation resistance of oxide ceramics and oxide dispersion strengthened alloys, which are promising structural materials for advanced reactor systems.[24] Considerable work has been devoted to the effects of neutron irradiation on silicon oxide and metal oxide binary compounds (SiO_2, ZnO, TiO_2, Al_2O_3, etc.), as well. Because of the limitations, in this section we shall pay attention to only a few of them, related to changes in the structure of crystalline ZnO, as well as changes in the structure of amorphous silica materials caused by high neutron irradiation fluences.

Zinc oxide crystals were used as a model material for studying neutron irradiation-induced defects in crystalline oxides and their impact on their properties.[25] Since crystalline materials have the best lattice order, it can be expected that the neutron irradiation, in particular, the irradiation with fast neutrons, will create a high density of different defects, which will affect many crystal properties. Indeed, the analysis of the results from positron annihilation spectroscopy measurements has indicated that the applied neutron irradiation induced an increase in overall defect content. The investigation of the carrier transport (concentration and electron drift mobility) has revealed that the neutron irradiation increases both shallow donors and deep acceptors and results in a strong compensation, which together with the observed neutron transmutation significantly affected the electronic properties of the crystal. The investigation of the optical absorption has shown that neutron irradiation caused a strong coloration of the samples; the increase of the irradiation times changes the color from colorless to dark gray/brown, which indicated a significant increase of the density of oxygen vacancies. It should be pointed out that the defect content does not simply scale with irradiation time. The conclusion is that the nature of the defects also changes with dose. The irradiation increases the defect density but also modifies the size and structure of the vacancy clusters. These important results have to be taken into account in considering neutron-irradiation effects in other oxides.

Silica-based glasses have a number of applications (fiber optic wave guides, laser optics for initiating fusion reactions, containers for radioactive waste, etc.) in which they are exposed to ionizing radiation, and therefore their radiation response has been studied for many years.[26] The great number of studies on

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the effect of the ionizing radiation on the optical properties of these glasses has shown that they have high radiation resistance, which is due to their high-defect structure in comparison with the crystals. When glasses are subjected to ionizing radiation the effects mainly result from ionizing electronic processes. New absorption bands appear due to centers formed by electron or hole trapping. Here we pay attention to a different investigation that reports results on the effect of neutron irradiation with high neutron fluences (10^{17} and 10^{18} neutrons/cm^2, neutron energy E > 0.1 MeV) on the structure of three different types of silica glasses (KU1, KS-4V, and Infrasil 301) with different OH concentration. A clear tendency of homogenization of the silica structure has been observed with increasing neutron fluence accompanied by a decrease of the average Si−O−Si angle in the lattice network.[26] These observations have confirmed previous theoretical studies and have shown that lattice damage such as irradiation-induced increase of the number of strained bonds and formation of new defects can be expected in silica glasses under high doses of neutron irradiation.

Neutron-induced void formation has been observed in the SiO_2 layers of Al_2O_3/SiO_2 multilayers at high irradiation fluencies (1 and 4 dpa, where dpa is the number of times that an atom is displaced for a given fluence) as the void size increased with increasing fluence. A strong accompanying silicon and aluminum diffusion within the multilayer has also been observed.[27] Less expressed interdiffusion has also been detected in a HfO_2/SiO_2 multilayer system, and in addition densification of silica in these multilayers during neutron irradiation has been found, which has been related to formation of silicon particles.

Homogeneous SiO_x (x = 1.2) films were irradiated by fast neutrons at a fluence of 4×10^{17} neutrons/cm^2.[28] It has been found that this fluence does not cause appreciable damage of the film surface; it remains very smooth, but the irradiation causes phase changes in the films. Fourier transform infrared (FTIR) transmittance spectra of three SiO_x films (non-irradiated, neutron-irradiated, and annealed at 700 °C) shown in Figure 5 give evidence of these changes. It is seen that the minimum of

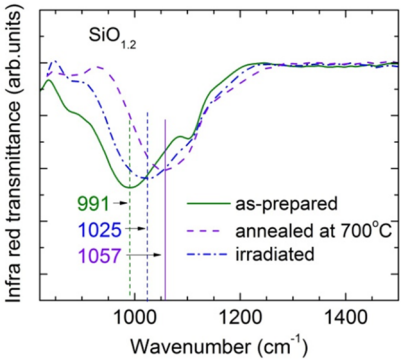

Figure 5. Comparison of infrared transmittance spectra of three SiO_x films: non-irradiated homogeneous film (solid olive), neutron-irradiated film (dash-dot blue), and a film furnace annealed at 700 °C for 60 min in an Ar atmosphere (dash violet).

the strong asymmetric stretching band has different positions. The position of this band gives information about the composition of silicon oxide films; when the oxygen content x is less than stoichiometric (x < 2) the minimum of the stretching band is shifted to the low frequencies ("red" shift) with respect to the position corresponding to SiO_2 (1080 cm^{-1}). The band minimum of the film annealed at 250 °C is situated at 991 cm^{-1}, which gives a value $x \approx 1.2$ for the non-irradiated homogeneous film. The thermal annealing at 700 °C causes a "blue" shift of the band to 1056 cm^{-1} (x_{matrix} = 1.7−1.8), which indicates that an incomplete phase separation and formation of pure silicon phase took place upon annealing. A considerable neutron-induced "blue" shift from 991 to 1025 cm^{-1} is also observed in the spectrum of neutron-irradiated films indicating that the neutron irradiation also causes phase separation and formation of a pure amorphous Si phase in the homogeneous samples.[28] A comparison of the FTIR results obtained on SiO_x films irradiated with fast electrons and neutrons has shown that the neutron irradiation causes stronger phase separation than the irradiation with fast electrons; the "blue" shift of the stretching band in the FTIR spectra of neutron-irradiated film is around 34 cm^{-1}, while in the electron-irradiated film it is only 3 cm^{-1}.[28] This observation confirms the much stronger relative displacement effect of neutrons (Table 1).

4. ELECTRON AND NEUTRON IRRADIATION OF NANOSTRUCTURED OXIDES

The last part of the mini-review is related to electron and neutron irradiation effects in nanostructured oxide materials. In the beginning (subsection 4.1) is a short consideration of the difference in the radiation behavior of homogeneous 3D and nanostructured (nanocrystalline and nanocomposite) materials. In the second subsection 4.2 two examples of electron-induced changes in the grain size of nanocrystalline oxide materials will be given. In the last subsection 4.3 electron and neutron irradiation-induced changes in the size of semiconductor nanoparticles embedded in an oxide matrix will be discussed.

4.1. Displacement Effects in Nanomaterials. In nanocrystalline materials of a given chemical and phase composition the decrease of the grain size results in a significant increase of the fraction of interfaces and triple junctions, which have disordered lattice structure. The great number of lattice defects in the interface regions facilitates an intense diffusion along the grain boundaries. At a grain size of around 6 nm, the fraction of interfaces in the entire volume reaches approximately 50% and further size decrease changes material microstructure—from nanocrystalline to nanocrystals embedded in an amorphous matrix of the same composition.[29] As in the case of homogeneous three-dimensional materials, it is assumed that upon bombardment of a nanocrystalline material by high energy neutrons and electrons effective displacement of atoms from their lattice positions takes place and interstitial atoms, vacancies, clusters of atoms and nanopores may appear. However, due to the existence of interfaces a competition of the radiation induced lattice disordering and removal of defects takes place. The interfaces favor an enhancement of the excess free energy and reduce the energy barrier for amorphization but they also facilitate the removal of radiation defects thus preventing amorphization.[29] When the grain size and the diffusion path of the radiation defects to interfaces are comparable one can expect very effective annihilation of the radiation defects and higher radiation resistance of a nanomaterial than that of its three-dimensional counterpart. The described difference in the radiation behavior of homogeneous 3D and nanostructured materials has been reported in a number of studies on radiation hardness of nanocrystalline materials of various compositions.[1,29]

4.2. Irradiation of Nanocrystalline Oxides. The research on the effect of irradiation with fast electrons and neutrons on

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the crystallite size of nanocrystalline oxides and semiconductor nanoparticles embedded in an oxide matrix is not very extensive. Most investigations have revealed a nanoparticle size decrease,[22,24,28] though a size increase has also been reported under neutron irradiation.[30]

Ensembles of ZnO nanocrystals were exposed to 6 MeV electrons at different fluences in the range of $(1-2.5) \times 10^{15}$ electrons/cm^2.[31] Characterization with X-ray diffraction has revealed that the initial size of the nanocrystals is ~46 nm and it gradually decreases with increasing electron fluence achieving a minimum value of 15 nm for the highest fluence. The grain size decrease has been confirmed by the observed quantum size increase of the nanocrystallite band gap from 3.29 to 3.42 eV. The investigation has shown that it is possible to control the size and shape of the nanocrystals in nanocrystalline oxide materials by using electron irradiation.

A zirconia-alumina $ZrO_2-Al_2O_3$ composite, which can have various applications related to its corrosion and shock resistance, high melting point, etc., was irradiated with 15 MeV electrons for 60 min at atmospheric pressure and low temperature (10 °C).[32] The composite consists of zirconia and alumina nanocrystals, which are miscible to a considerable amount. X-ray diffraction studies have shown that, before irradiation, the size of zirconia grains is 20 nm while the electron irradiation slightly reduced the size to 18 nm. This result shows that the grain size reduction depends on the composition of the oxide materials, i.e., on its bong energy/strength of the chemical bonds.

An investigation of the effect of neutron irradiation by a flux of 2×10^{13} neutrons/cm^2·s for up to 20 h on the lattice structure, grain size, and clustering of amorphous nanoparticles of SiO_2 with size of 20 nm has established that the irradiation did not cause crystallization and did not stimulate formation of large clusters of nanoparticles.[30] However, particles of significantly larger size (70 nm) appeared, which could be due to irradiation-stimulated coalescence connected with excitation of the chemical bonds and subsequent atomic movements.[14]

4.3. Electron and Neutron Irradiation of Composite Oxide Films Containing Semiconductor Nanoparticles. As described above (Figures 4 and 5), phase separation and silicon nanocluster formation take place upon irradiation of homogeneous SiO_x films with high-energy electrons and neutrons. Experiments on the effect of high-energy electron and neutron irradiation of a(c)-Si-SiO_x composite films containing thermally grown amorphous (a-Si) or crystalline (c-Si) Si nanoparticles have revealed[22] a radiation-induced decrease of the a-Si nanoparticle size, which is illustrated in Figure 6; the irradiation-induced nanocluster formation is also shown in the figure. The nanoparticle size decrease has been concluded on the basis of the observation of a decrease in the effective refractive index of the composite films (Figure 7). Reasons for such decrease could be both reduction in the nanocluster size, leading to a decrease in the dielectric constant of the pure Si phase, and a reduction in the amount of the pure Si phase. Infrared transmittance data have shown that the relative amount of oxygen x in the SiO_x matrix and hence the amount of the pure Si phase decreased upon neutron irradiation. Besides, an irradiation-induced increase of the optical band gap of the Si nanoclusters has been observed confirming that neutrons have given rise to nanoparticle size decrease. It has been assumed that irradiation caused bond breaks, thus reducing some SiO_2 to SiO_x, and the free oxygen released moves to the Si nanoparticles and forms SiO_x on their surface and the a-Si nanocluster size

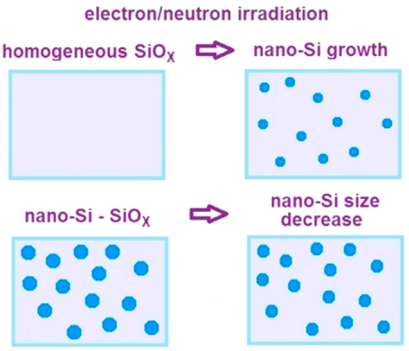

Figure 6. Schematic presentation of the irradiation-induced changes in homogeneous SiO_x films and composite films containing amorphous or crystalline Si nanoparticles embedded in a SiO_x matrix.

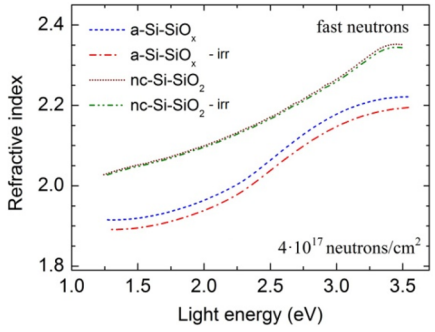

Figure 7. Dispersion curves of the effective refractive index of non-irradiated and neutron-irradiated composite films containing amorphous or crystalline Si nanoparticles. The curves of the films with Si nanocrystals are shifted up for clarity.

decreases. Complete disappearance of the smallest nanoclusters is also possible. While the irradiation-induced a-Si nanocluster size decrease is well-expressed, being a bit larger in the case of neutron irradiation, the observed changes in the composite c-Si-SiO_2 films were weak (Figure 7), which speaks about the high radiation resistance of those films.

5. CONCLUSIONS AND FUTURE OUTLOOK

The radiation response of oxide materials plays an important role in the operation of oxide-based devices in a radiation environment. This mini-review presents some recent results on changes in the structure and properties of homogeneous and nanostructured oxides caused by high-energy electron and neutron radiation. The related processes of irradiation-induced electron−hole generation and charge trapping, lattice rearrangement, creation of point defects and their complexes, compositional changes, etc. are discussed. Typically, electron and neutron irradiation of materials is considered as the cause of damage to materials, which may disturb device operation; for example, radiation may affect the operation of a number of microelectronic devices including SiO_2-Si structures. However, it is shown that radiation does not necessarily have only detrimental effects,; it can also have beneficial effects from a practical point of view. Examples of such effects are described in the mini-review such as ordering and annealing of existing defects, surface smoothing, and modification of oxide/silicon interface as well as compositional changes and appearance of new nanophases/modification of existing nanophases in oxide matrices, microstructural changes in nanostructured oxides, etc.

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These effects could be used for tailoring certain properties of homogeneous and nanostructured oxides.

The development of nanotechnology in the last few decades has led to the practical use of nanoscale and nanostructured materials in many areas of human life. However, the collected data on the behavior of these materials under irradiation with energetic particles, including the nanosized and nanostructured oxides, is quite limited as compared to the information on conventional materials. Much more knowledge is necessary of how the irradiation-induced defects affect the properties and radiation resistance of oxides. Investigations are required to get more information on the changes of the structure and electrical properties of oxide films that are used in nanoelectronics as transistor gate oxides, tunnel barriers in nonvolatile memories, and materials of memristive devices. Defect annealing and damage accumulation in nanosized oxides under irradiation should be explored in detail. Significant attention has to be paid for better understanding of the "self-purification", self-organized formation of surface nanostructures, intermixing at the interface between two materials in nanostructured oxides caused by irradiation with energetic electrons and neutrons. The accumulation of new information will allow us to evaluate the possibilities for different applications of nanosized and nanostructured oxides in radiation environments.

AUTHOR INFORMATION

Corresponding Author

Diana Nesheva − *G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria;* orcid.org/0000-0001-8667-3502; Email: nesheva@issp.bas.bg

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c00486

Notes

The author declares no competing financial interest.

Biography

Dr. Diana Nesheva is Full Professor at the Institute of Solid State Physics of the Bulgarian Academy of Sciences since 2011. For more than 30 years she has carried out active research on wide band gap semiconductors of various dimensionalities and zero-dimensional silicon. She has long-time experience in deposition of homogeneous and nanostructured thin films by using vacuum techniques, as well as in characterization of materials by applying a great variety of modern techniques. Her recent activity is on preparation and treatment with fast (MeV) electrons and neutrons of metal-oxide-silicon structures containing amorphous or crystalline silicon nanoparticles in the oxide layer. Such structures have potential applications as nonvolatile memories, UV detectors, and dosimeters of high energy radiation. Chemical sensing at room temperature based on nanostructured oxide and chalcogenide thin films is the second field of her recent research.

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