ELECTRON IRRADIATION EFFECTS IN GLASSES AND OTHER INSULATORS

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ABSTRACT

This review attempts to summarize the physical property and compositional changes induced in insulating materials--primarily silicate glasses--by energetic electrons. A primary characteristic of electron irradiation is the production of simple defects; for electrons of MeV energy these are mostly isolated vacancies and interstitials. For this reason, electron irradiation has been preferred for fundamental studies of defects. Typical experiments and their interpretation are presented.

1. INTRODUCTION

Something on the order of 99.9% of the energy of MeV electrons is expended in ionization processes. The remainder is utilized in Coulomb encounters with atomic nuclei which may or may not result in a displacement, depending on the threshold energy, E_d, for displacement and the electron energy, E. Almost all electrons of the energies dealt with in this paper must be treated as relativistic particles. For illustration, the relativistic increase in mass is 1% of the rest mass for each 5 keV of kinetic energy [1].The classical Rutherford cross-section for displacement has to be modified because of the relativistic electron velocity The formalism for the appropriate equations for collision cross-section and energy transfer has been dealt with in earlier work[2-5]. In this paper we will demonstrate the utility of electron irradiation in the determination of threshold energies (E_d) in materials; the volume and density changes produced by network compaction; and the alteration of composition in alkali-containing silicate glasses in the region traversed by the electrons. We will not describe in detail the optical absorption centers as these matters have been adequately covered in many papers and reviews[6]. An important feature of electron irradiation is the magnitude of the energy transfer to target atoms. For MeV electrons this value, for typical silicate glasses, is on the order of several hundred eV. This is to be compared with the several hundred keV transferred by fission-reactor neutrons and 44 keV from 100 keV argon ions. The relatively low energy transfer for electrons means that the defect density in the collision vicinity is very small. This is one of the attractive features of electron-irradiation for the purposes of studying defects.

2. ILLUSTRATIVE EXPERIMENTS

Displacement Threshold Measurements

An early--apparently the first--measurement of a displacement threshold energy in an insulating material was made for crystalline α-Al_2O_3[3]. As in all such determinations, a physical property which varies in magnitude with the energy transfer to lattice atoms is required. For Al_2O_3, this is the optical absorption band at 205 nm. Figure 1 shows a comparison of the measured optical density per unit path length, for various values of the computed oxygen displacement cross-section, as a function of the electron energy. The best fit to the data is found for an E_d value of 70 eV. If an Al displacement caused the 205 nm absorption, the data would yield a value for E_d of 40 eV; however, it is now considered that the displacement of O is responsible. Similar experiments in MgO and $MgAl_2O_4$[7] have given values of about 59 eV for the displacement of O in those materials. Threshold measurements of the electrical conductivity in diamond have resulted in the determination of an E_d of 35 eV for C[8].

An attempt was made to measure E_d in fused silica using the optical absorption at 215 nm (E`-center) as a monitor[5]. It was found that lower energy electrons produced appreciably higher concentrations of E`-centers than did higher energy electrons. The data is shown in Fig. 2 for CFS 7940 and CFS 7943, "wet" and "dry" synthetic fused silica glasses, respectively. It was not possible to fit these data to any theoretical curve which would describe the direct displacement of an atom by the incident electron. The dashed line is the stopping power in silica glass for electrons of various energies, normalized to 2 MeV. This curve represents the damage produced by the energy lost by the electrons in predominantly ionization processes; the CFS 7943 data gives a good fit to these data and less good for the CFS 7940 data. These observations have been confirmed and extended by Pfeffer[9] who used thermally grown SiO_2 films ("wet" and "dry") on Si and electron energies as low as 30 keV. He concluded that ionization processes were dominant in defect creation for electron-irradiated silica. This is to be contrasted with the situation for ion-bombarded fused silica where the defect creation by the collisional part of the ion energy is several

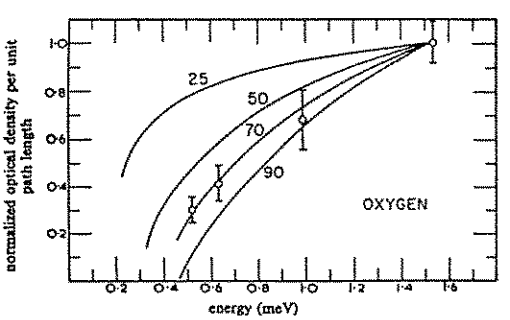

Fig. 1 *Optical density per unit path length vs effective electron energy incident on Al_2O_3 (normalized to 1.54 MeV) compared with calculated cross-section assuming the indicated values of E_d. The best fit to the data is obtained for $E_d = 70$ ev (after Ref. 5).*

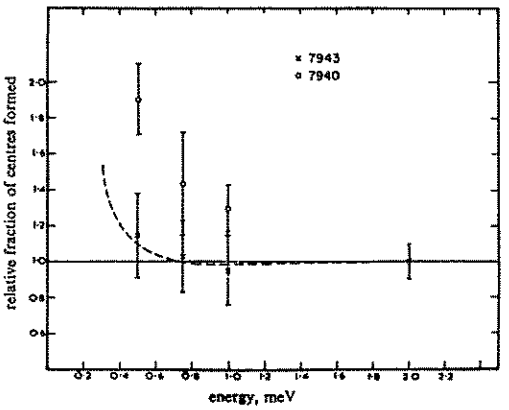

Fig. 2 *Relative fraction of 215 nm E'-centers formed vs incident electron energy. The dashed line is for the electron stopping power in SiO_2. O: CFS 7940; X: CFS 7943 (after Ref. 5).*

hundred times more effective than that of the electronic energy deposition[10].

Volume Changes

Volume changes as a result of electron irradiation of glass have long been known to occur; cracking of glass tubes containing beta-emitters for example. EerNisse and Norris[11] applied the cantilever-beam technique developed by EerNisse[10] to the study of the volume dilatation introduced by electron irradiation (18 keV) on SiO_2 layers thermally grown on Si.. Their results provided convincing evidence for the identification of the ionization-induced compaction as due to broken Si-O bonds. This structural defect was found to be the same for ion implantation, provided that the collisional damage from the ion-implantation was not too large. Additional structural damage was demonstrated for the interaction of electronic and collisional energy deposition. The maximum compaction, $\Delta V/V$, was about 3%, in agreement with that found for ion implanation[10]. Lattice expansion can occur in electron irradiated silica glasses at low fluences as first shown by Primak and Kampwirth[12] and attributed by them to an impurity effect. This effect was confirmed in another study by Norris and EerNisse[13] on bulk fused silica and was attributed to H as an impurity. Shelby[14] confirmed these observations in a measurement of density changes in γ-irradiated H-impregnated fused silica. This effect has also been demonstrated in alkali borosilicate glasses under ion implantation, where the expansion regime (with ion fluence) was shown to be proportional to the interstitial Na component[15].

An interesting and sociologically important study is that of radiation effects in nuclear waste glass used for encapsulation of high level nuclear waste products. Sato et al[16] have measured the density changes in electron-irradiated simulated radioactive waste glass and compared the results with those for fused silica and for the borosilicate Pyrex glass (Fig. 3). Using 2 MeV electrons and a flotation

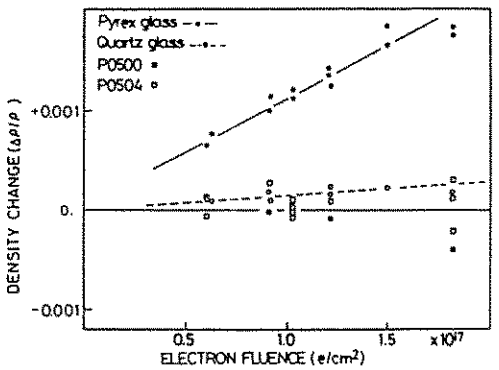

Fig. 3 *Fractional change in density ($\Delta\rho/\rho$) vs 2 MeV electron fluence for Pyrex., fused silica glass, and the simulated radioactive waste glasses P0500 and P0504 (after Ref. 16).*

measurement of density changes, they found a density change ($\Delta\rho/\rho$) of about 0.05% (compaction) for two waste glass formulations; this change was about the same as for fused silica glass. The density change for the Pyrex glass was much higher--on the order of 0.18%. It was estimated that the average energy of the electrons in traversing the sample thickness (0.5 mm) was about 1.9 MeV. These data are in qualitative agreement with cantilever-beam measurements of ion-induced stress in a similar nuclear waste glass and in Pyrex and fused silica[17].

The exposure of large-mirror substrates in space applications where they are exposed to a variety of radiation sources (Van Allen belt, solar wind, etc.) may result in surface compaction which alters the curvature. Rajaram et al[18] have examined the effects of 2 MeV electrons on the deformation of low-thermal coefficient glasses and ceramics (Optosil, Ti:SiO_2[ULE], Zerodur, Astrositall, Cervit). The experimental results of profilometer measurements are shown in Fig. 4 for 5 mm thick samples where the exposure was deliberately made non-uniform by inserting a 2 cm thick Al block with a 5 mm diameter hole between the accelerator window and the samples. The inset shows the interference fringes for Zerodur. The deformation is much larger for the ceramics than for the fused silica Optosil and the spread for the ceramics extends beyond the 5 mm defined beam. It is pointed out that lightweight mirrors for space applications may be as thin as 1-2 mm and the radiation-induced deformation may be significant; the spectrum of space radiation is said to be highly peaked at low energies which would be stopped in the near-surface region and thus cause greater deformation than higher energy particles.

Compositional Changes in Alkali-Silicate Glasses

The alkali-depletion from the surface of electron-bombarded glasses has long been-known and represents a major difficulty in applying Auger electron spectroscopy (AES) to the study of alkali-silicate glasses. The Na signal disappears with time due to the electron analysis beam (0.3-3 keV)[19-21]. Figure 5 shows the Na depth profiles resulting from 2.5 keV and 4.5 keV electron irradiations of soda-lime glass[22,23]. The Na depletion at the surface and the accumulation at depths corresponding to the electron

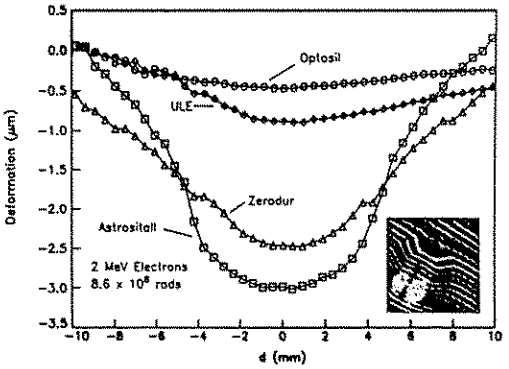

Fig. 4 *Surface deformation (diamond stylus measurement) vs lateral sample dimension for 2 MeV electrons (8.6×10^8 rad) incident on the indicated materials. The inset shows the interference pattern for a Zerodur sample after irradiation (after Ref. 18).*

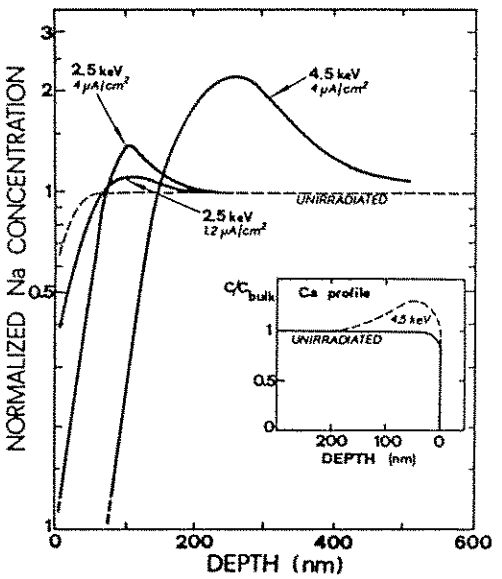

Fig. 5 *Sodium concentration vs depth for soda-lime glass after 2.5 keV and 4.5 keV electron irradiation at the indicated current densities. The inset shows the normalized Ca depth profiles for the 4.5 keV irradiation (after Ref. 22).*

range is evident in these profiles taken by means of the $^{23}Na(p,\alpha)$ nuclear reaction. The surface Na depletion (electron irradiation) is accompanied by a Ca surface accumulation as shown by the inset in Fig. 5. For 600 keV proton implantation (not shown), on the other hand, Na moves in the opposite direction and accumulates at the surface while Ca is depleted from the surface. The Italian investigators have shown[24] that the electric field established by electron irradiation, e.g. during AES experiments reaches a steady-state value inn a very short time (10^{-4}-10^{-3} sec) and that the alkali ions do not play a relevant role in the formation of the electric field. The analysis of the movement of alkali ions and Ca was done on the assumption that the interactions operative are between the alkali and Ca ions and the field created by the

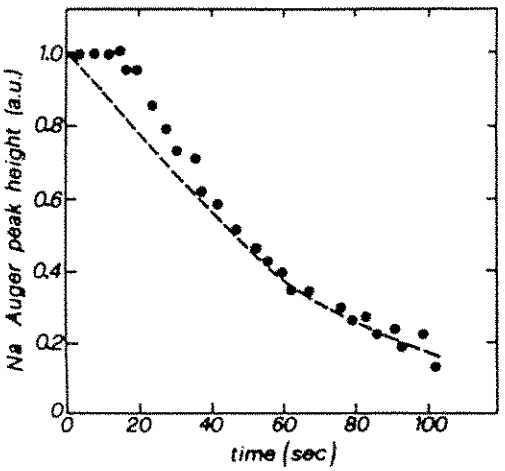

Fig. 6 *Experimental Na Auger signals from soda-lime glass (Ref. 26) compared with the calculated values (Ref. 25) vs time after electron irradiation at liquid nitrogen temperature.*

incident electrons as well as the surface positive charges formed as a consequence of secondary electron emission. Their analysis[25] provided excellent agreement with experiment[26] and showed that other possible interactions between the primary electrons and alkali and Ca ions were not relevant. The solution for the continuity equations for an assumed field strength of 10^5 V/cm yielded an effective diffusion coefficient for Na of 8×10^{-16} cm^2/sec. The comparison with experimental observations[27] of the decay of the Auger signal with time is shown in Fig. 6. The agreement is good except for the always seen incubation time for the onset of Auger signal decay which is not yet satisfactorily explained.

3. CONCLUDING REMARKS

This short review has not attempted to survey all of the interesting work on electron-irradiated insulators and glasses; this would tax my resources and the patience of the publishers. It is hoped that it will provide a stimulus for the reader to examine the covered topics and those not touched upon in greater detail.

4. ACKNOWLEDGEMENTS

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Profile

George W. Arnold has been with Sandia National Laboratories since 1961. He was previously with the National Bureau of Standards (1949-1950) and at the Naval Research Laboratory (1950-1961). He was a Fulbright Teaching Fellow in Egypt (Ein Shams University, Cairo; Assiut University, Assiut) in 1960-1961. Since 1984 he has also held the position of Visiting Professor of Physics at the University of Padova, Padova, Italy. He has been continuously engaged in studies of the interactions of radiation with materials (primarily insulators and semiconductors) throughout his professional career. Most of the earlier work was centered on the optical properties of materials (absorption and luminescence) and the effects of

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和文抄録

ガラスおよび絶縁体における電子線照射効果

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本論文では，物質原子のズレに要するしきい値エネルギーB_dの決定，網目の収縮による体積変化，電子の通過領域におけるアルカリケイ酸塩ガラスの組成改変，等への電子線照射の有用性を示す．MeV の電子線のエネルギーの 99.9% はイオン化過程に消費され，残りは，原子核との Coulomb 衝突に用いられ，原子のズレを生じることもある．この際，ターゲット原子へのエネルギー移動は数百 eV であり，核反応中性子に於ける数百 keV に比べると非常に小さい．この様に比較的小さいエネルギー移動のために衝突近傍での欠陥密度が低く，従って欠陥の研究に役立つ．最初の研究はα-Al_2O_3 結晶に対するもので，E_d は 70 eV であり，205 nm の吸収端の原因は Al ではなく O 原子のずれによるものであると考えられる．シリカガラスにおける 215 nm 吸収の原因である E′-センターは，低エネギー電子線により，多量に生成する．電子線照射シリカにおける欠陥生成にはイオン化過程が支配的な役割を果たしている．

ガラスの電子線照射による体積変化については古くから知られていきたが，高レベル核廃棄物ガラスへの照射は，0.1% 前後の体積収縮を引き起こし，この放射線照射効果は社会的にも重要な問題である．また宇宙応用における大面積ミラーは，様々な放射線に曝されるため，表面収縮により曲率が変化してしまうこともある．Optosil, Zerodur 等の低膨張ガラスやセラミックスに不均一な照射を行うと，後者で特に顕著に変形が生じる．宇宙応用に用いられる軽量ミラーの厚さは，1-2mm であり，放射線による変形は無視できない．また宇宙放射線は低エネルギーにピークを持つので，表面付近に留まり，高エネルギー放射線よりも，大きな変形を生じる原因になる．

照射によりガラス表面からアリカリが減少することは，Auger 電子分光 (AES) が適用しにくい原因でもある．Na プロファイルは，表面で減少し，電子線の到達深部で蓄積され，同時に表面で Ca が蓄積される．プロトン照射では，Na は表面に蓄積され，代わりに Ca が表面から減少する．AES において，電場形成は短時間で定常状態に達し，アルカリや Ca イオンの移動は電場形成に大きな寄与をしておらず，2 次イオン放出の結果，表面正電荷が形成される．Na の Auger 信号の時間減衰カーブは電場と Na の拡散係数の値をよく再現している．

（訳：京都大学　田部勢津久）