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Radiation effects on lead silicate glass surfaces

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Radiation-induced changes in the microstructure of lead silicate glass were investigated *in situ* under Mg K_α irradiation in an ultra-high vacuum (UHV) environment by X-ray photoelectron spectroscopy (XPS). Lead–oxygen bond breaking resulting in the formation of pure lead was observed. The segregation, growth kinetics and the structural relaxation of the lead, with corresponding changes in the oxygen and silicon on the glass surfaces were studied by measuring the time-dependent changes in concentration, binding energy shifts, and the full width at half maximum. A bimodal distribution of the oxygen XPS signal, caused by bridging and non-bridging oxygens, was found during the relaxation process. All experimental data indicate a reduction of the oxygen concentration, a phase separation of the lead from the glass matrix, and the metallization of the lead occurred during and after the X-ray irradiation.

1. Introduction

Today, lead silicate glasses are basic materials used in electronic and optical technologies such as electron multipliers [1] and microchannel plates [2]. They are bombarded by primary electrons or photons, with different energies, in a vacuum so that the secondary electrons are amplified. Since oxide glasses containing heavy metals have a very high coefficient of the intensity-dependent part of the refractive index [3], they are important candidates as new technological glasses for application in infrared transmission, non-linear optic and magneto–optical devices [4–6]. However, radiation-induced microstructural modifications, such as phase separations [7], electrical polarization [7, 8], and charge trapping [9], contribute to electrical breakdown in lead silicate glasses. These modification induced property changes are the characteristics used by radiation sensors. The long and short range motions of Pb^{2+} ions in irradiated lead silicate was reported by Dutta *et al.* [10] through thermally stimulated polarization current (TSPC) and depolarization current (TSDC) measurements. However a metal film has to be grown onto the irradiated glasses to ensure ohmic contact for the current measurements across the glass by TSPC/TSDC. We have utilized XPS to study the irradiation-induced phenomena in lead silicate glasses under an UHV environment which enables us to eliminate the confusion caused by the interface between the irradiated glass and the metal film.

2. Experimental procedure

The surfaces of five lead silicate glasses were investigated using X-ray photoelectron spectroscopy (XPS). Glasses having the general composition x PbO: $(100 - x)$ SiO_2, where $x = 25$, 30, 40, 45, and 50 mole %, were melted in silica crucibles in an air-atmosphere furnace following the procedure reported elsewhere [11]. Cylindrical bars of the prepared glasses were then cut into disks 12 mm in diameter and 1 mm in thickness, and subsequently polished. After having been cleaned using acetone and methanol, these glass samples were then individually mounted in a twelve sample carousel holder, which allows for sample changing, by rotation, within the UHV environment. Auger electron spectroscopy (AES), X-ray irradiation and XPS were performed in the UHV chamber. The base pressure of the chamber during the experiments was maintained at $1.33–3.99 \times 10^{-7}$ Pa. A pass energy of 50 eV was used to provide a 1 eV resolution.

The surface compositions of the samples were detected by Auger electron spectroscopy (AES). The major problem of performing AES measurements on insulators is surface charging caused by the emission of Auger and secondary electrons. The production of positive or negative surface charges is determined by the difference between the number of primary electrons injected into the sample and the total number of Auger and secondary electrons leaving the surface. The procedure that we used to prevent surface charging was to apply a defocused electron beam to reduce the electron flux.

The Pb 4f, O 1s, and Si 2p core electrons emitted from the glass surface (through a photoelectron process) were measured and recorded for five samples using a Perkin–Elmer model 560 spectrometer with a Mg K_α source, operated at 300W. The glass samples were continuously exposed to the X-ray irradiation for

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typical time periods of 2.5 h and the XPS spectra were collected at different points during the continuous irradiation in order to study the evolution of the chemical environmental changes of the elements on the surface of the glass sample. The shift of the binding energy due to the surface charging effect, even after being neutralized by a low energy electron flood gun, was calibrated by assuming that the binding energy of C 1s to always be 284.6 eV [12]. The binding energy of each element was determined at the centre position of its XPS peak, after the deconvolution of the spectrum. The experimental uncertainty of the XPS binding energy was about 0.10 eV. The concentration of each element was calculated by the peak area obtained by a curve fitting program, with the photoelectron yield of the element also being taken into account. The accuracy of the relative concentration of each element on the surface is ± 0.5%.

3. Experimental results

X-ray irradiation-induced phase separation to the extent that neutral lead is separated from the glass but is still partially coupled to the oxygen is clearly observed in all five samples. The higher the PbO concentration in the glass, the clearer the phase separation. The AES results suggest that nuclei of metallic lead exist in the glass before the X-ray radiation. As is shown in Fig. 1, where the AES spectra of 25PbO:$75SiO_2$ and $45PbO{:}55SiO_2$, and $50PbO{:}50SiO_2$ are marked with the LMM silicon, KLL oxygen, KLL carbon and NOO lead signals [13], the intensity of the lead signal increased with increasing PbO content in the glasses. The existence of metallic lead in the sample was also shown by the positive chemical shifts for the lead signals listed in Table I. As an example of phase separation, Fig. 2 shows the XPS spectra of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ for the $50PbO{:}50SiO_2$ glass composition at different irradiation times. From Fig. 2, we can see that two shoulder peaks with lower binding energies appear as the glass sample is continuously exposed to the X-ray irradiation, and the intensities of the shoulder peaks grows with the irradiation time. By comparing the recorded XPS spectra of Pb 4f with the standard ones [14] of pure lead and lead in lead oxide, it is easy to assign the XPS peaks with higher binding energies to the Pb^{2+} ions (coordinated by oxygen) and to attribute the shoulder peaks with lower binding energies to neutral lead atoms. This suggests that the chemical environment around Pb in the glass was changed by the X-ray irradiation and that some Pb–O bonds break under the irradiation, resulting in the formation of neutral lead (Pb^o). The binding energies and intensity expressed in terms of the peak areas of Pb^o 4f and Pb^{2+} 4f are obtained from the deconvolution of the corresponding XPS spectra using a curve-fitting program. As an example, Fig. 3 shows a deconvoluted XPS spectrum of Pb 4f for the glass composition $50PbO{:}50SiO_2$. The relative concentration of neutral lead to that of total lead on the glass surface can be determined from the corresponding XPS peak areas of Pb^o 4f and Pb^{2+} 4f i.e., $[Pb^o] = A_{Pb^o}/(A_{Pb^o} + A_{Pb^{2+}})$, where A_{Pb^o} and $A_{Pb^{2+}}$ are the peak areas of Pb^o 4f and Pb^{2+} 4f respectively. Fig. 4 shows the relative concentration of neutral lead on the surface of the $50PbO{:}50SiO_2$ composition glass as a function of irradiation time. It can be seen that the concentration of neutral lead on the surface increases with increasing irradiation time and saturates after 2 h

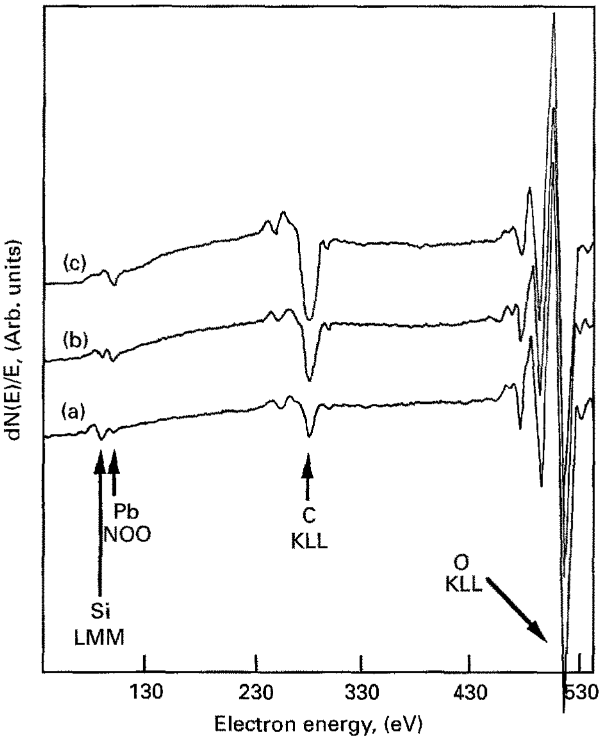

Figure 1 The AES spectra of (a) $25PbO{:}75SiO_2$, (b) $45PbO{:}55SiO_2$, and (c) $50PbO{:}50SiO_2$.

TABLE I Chemical shifts of NOO lead Auger signals

Sample ratio $PbO{:}SiO_2$	Location of NOO Lead eV
25:75	92.3
30:70	92.4
40:60	92.6
45:55	92.6
50:50	95.3
55:45	95.3

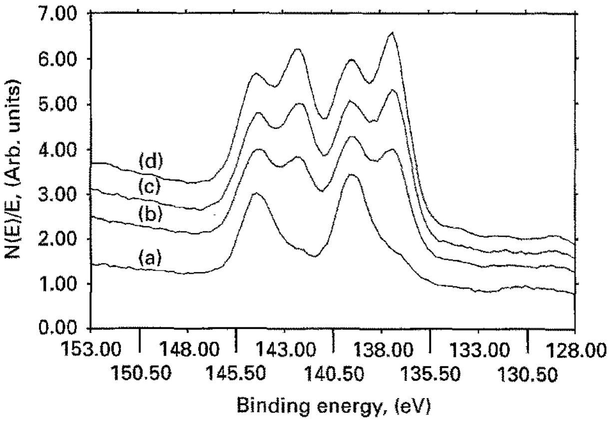

Figure 2 XPS spectra of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ for glass $50PbO{:}50SiO_2$ recorded at different irradiation times. Spectra were recorded starting at (a) 0 min, (b) 60 min, (c) 90 min, and (d) 120 min.

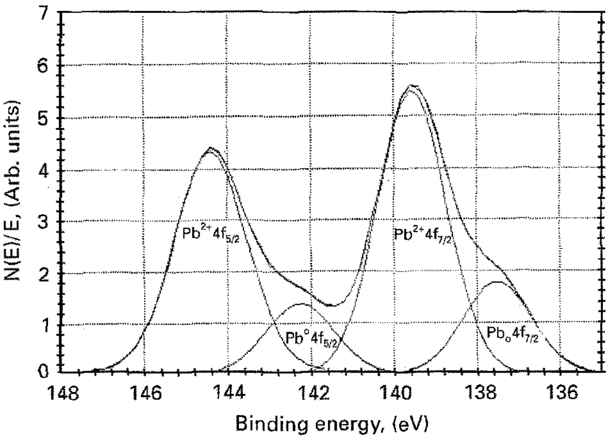

Figure 3 A deconvoluted XPS spectrum of Pb 4f for glass 50PbO: $50SiO_2$.

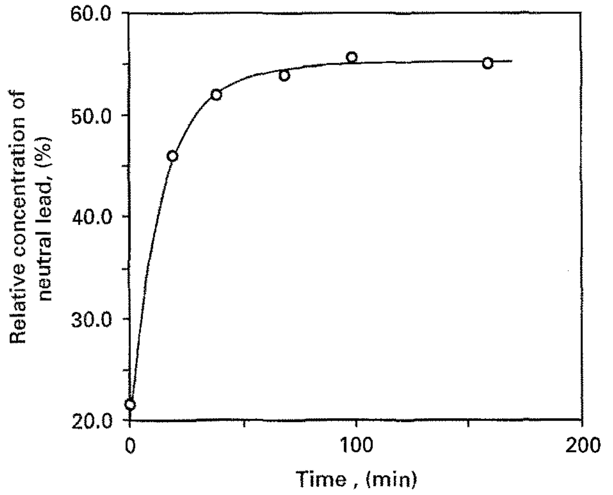

Figure 4 The relative concentration of neutral lead from all lead species on the surface versus irradiation time.

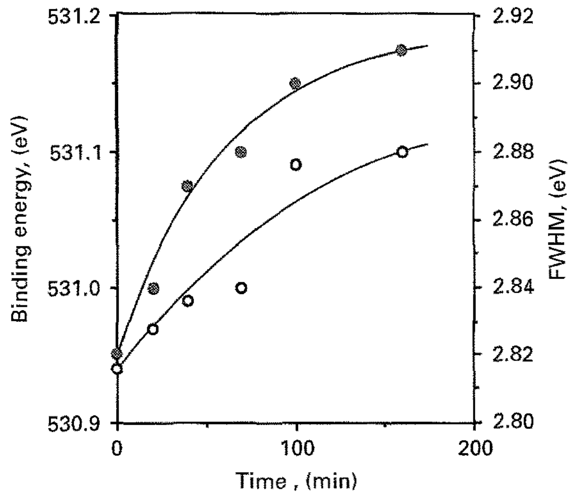

Figure 5 Plots of; (○) binding energy and; (●) Full width at half maximum (FWHM) of O 1s against irradiation time.

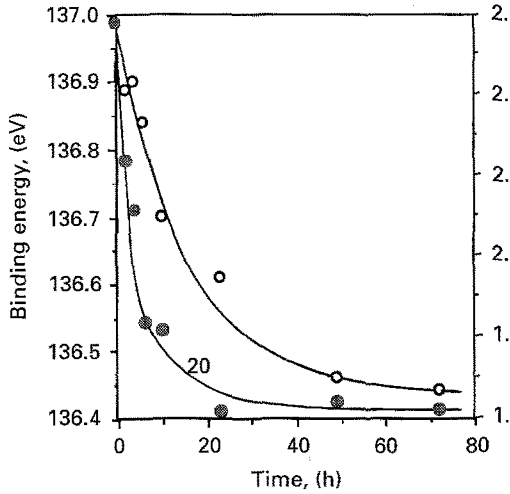

Figure 6 Dependencies of relaxation time on the; (●) FWHM and the; (○) binding energy of Pb° $4f_{7/2}$ for glass $50PbO:50SiO_2$.

irradiation. Fig. 4 also shows that some neutral lead species already exist in the glass before the X-ray irradiation which is consistent with the AES results presented in Fig. 1. This is perhaps a result of the glass preparation conditions.

The corresponding chemical environmental changes of oxygen at the glass surface during the X-ray irradiation were also observed. The binding energy and the full width at half maximum (FWHM) of the O 1 s peak increases with continual irradiation, and tends to saturate after 2 h irradiation (as is shown in Fig. 5). There was no noticeable change in the binding energy for silicon photoelectrons observed in the XPS spectra.

Since the concentrations of lead, silicon and oxygen reached a steady state after two hours irradiation, the X-ray irradiation was terminated after about $2\frac{1}{2}$ h. In order to understand the relaxation behaviour of neutral lead induced by the X-ray irradiation, the XPS spectra were recorded again after an interval of a few hours.

It was found that the position and the shape of the Pb^{2+} $4f_{7/2}$ peak remained unchanged and that those of the Pb° $4f_{7/2}$ peak changed during the relaxation. Fig. 6 shows the dependence of the FWHM and also the binding energy of the Pb° $4f_{7/2}$ of the 50PbO: $50SiO_2$ glass on the relaxation time. From this, it can be observed that the shape of the Pb° $4f_{7/2}$ peak became continuously narrower until its FWHM finally reaches after about 20 h after the termination of the X-ray irradiation a value of 1.81 eV . Also, it is observed that the binding energy of the Pb° $4f_{7/2}$ decreased slowly and finally (after 50 h) reached 136.45 eV which is approximately the same value as that of pure lead metal [14].

A new peak (with a lower binding energy) related to O 1s develops and grows during the relaxation. The analysed binding energies and FWHM values of the O 1s for the glass of composition $50PbO:50SiO_2$ during the relaxation are tabulated in Table II. The relative concentration of the newly developed oxygen with a lower binding energy is also given in Table II. Fig. 7a shows the XPS spectra of O 1s recorded during the continuous irradiation and Fig. 7b shows the spectrum 4 h after the termination of continuous irradiation. A low binding energy peak clearly developed in Fig. 7b during the relaxation.

There was no binding energy shift observed for silicon during either the continuous X-ray exposure

TABLE II The binding energies and FWHM values of O 1s for glass 50PbO:50SiO$_2$ during the relaxation process

Relaxation Time (h)	BE (FWHM) for O$_h$* (eV)	BE (FWHM) for O$_l$* (eV)	Relative concen. of O$_l$ (%)
0	531.10 (2.91)		
2	531.29 (2.64)	529.94 (2.64)	14.00
4	531.28 (2.66)	529.93 (2.73)	14.76
6	531.29 (2.62)	529.90 (2.77)	15.14
10	531.30 (2.69)	529.84 (2.84)	18.07
23	531.25 (2.70)	529.84 (2.91)	18.69
49	531.24 (2.67)	529.85 (3.22)	20.17
72	531.20 (2.69)	529.80 (3.25)	21.00

* O$_h$ refers to the oxygen with higher binding energy and O$_l$ refers to the oxygen with lower binding energy.

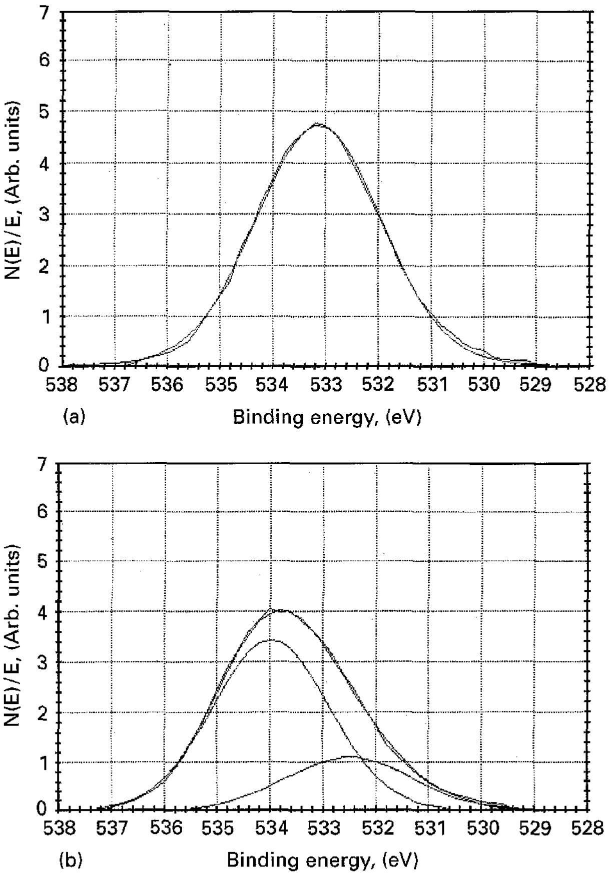

Figure 7 The XPS spectra of O 1s, (a) recorded during the continuous irradiation, (b) at 4 h after the termination of the continuous irradiation.

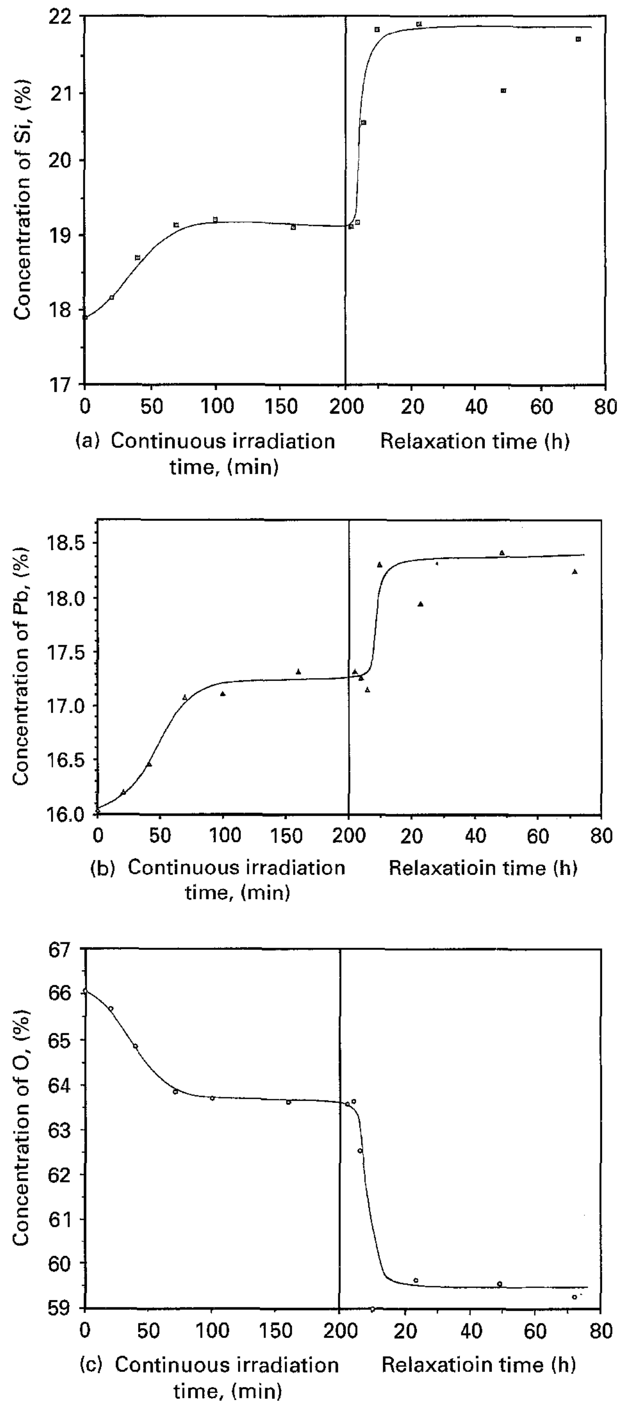

Figure 8 The irradiation effect and the structural relaxation are shown by the plots of concentration versus time. The time-dependence of lead concentration, oxygen concentration and silicon concentration are shown in (a), (b) and (c) respectively.

and the relaxation process. However, the silicon and lead signals gradually grew and the oxygen decreases with time, as is shown in Fig. 8(a–c). The relative concentration changes with time, clearly show the accumulation of lead and silicon and the depletion of oxygen on the surface during the irradiation and the relaxation, even though there is no degassing monitored by the ion gauge in the UHV chamber. A gradual increase or decrease at the beginning of each process (and later saturation) is a similar feature for the growth and decay curves in Fig. 8. This feature indicated that a stable stoichiometry is reached after a while in the glass.

4. Discussion

4.1. Surface modification of the lead silicate glass during X-ray irradiation

The experimental results during continuous X-ray irradiation indicate that the chemical environment around the Pb in the glass was changed by the X-ray irradiation and that the accumulation of silicon and depletion of oxygen on the glass surface were induced. Combined with the corresponding chemical environmental changes for the oxygen on the surface, which are a positive binding energy shift and a decrease in concentration during irradiation, we can infer that the formation of neutral lead was the result of the breaking of Pb–O bonds in the glass structure under the irradiation.

The binding energy shift will be considered by use of the charge potential model [15], where the alterations in the outer valent shell electrons change the nuclear attractive force on the core electrons. An increase in the outer electrons will reduce the nuclear attractive force between the nuclei and the core electrons, consequently reducing the binding energy of the core electrons. The same argument can be applied to the case in which there is a decrease in outer electrons.

The breaking of a Pb–O bond will result in the decrease of the outer electron density of oxygen in the Pb–O bond. In other words, the effective positive nuclear charge of oxygen in the Pb–O bond will increase with the breaking of the Pb–O bond. Consequently, the binding energy of O 1s increases with continuous irradiation. With prolonged and continuous irradiation, a great deal of neutral lead accumulated on the glass surface and formed a thin lead-rich layer, this is strongly supported by the fact that the surface of the sample apparently darkened after the irradiation. This lead-rich layer will protect the glass underneath the surface from any further damage by the X-ray irradiation. Therefore, the concentration of lead, silicon and oxygen on the surface reaches a saturation point after a certain irradiation (~ 2 h). The possible route for oxygen to be lost from the surface is via the formation of oxygen gas, as a result of free oxygens (created by Si–O and Pb–O bond breaking) combining. Oxygen depletion from the lead silicate glass after annealing was also observed by Rajopadhye *et al.* [16]. The accumulation of lead and silicon at the surface is the consequence of the depletion of oxygen. The onset of the nucleation of pure lead originates from the existence of Pb° in the sample before irradiation that is confirmed by the detection of Pb–Pb bonds by pulsed neutron scattering [17, 18] and XPS before the irradiation. The Pb° nuclei, initiating the phase separation under irradiation in the sample were also detected in AES higher PbO concentration samples.

4.2. Relaxation of lead and oxygen after the termination of X-ray irradiation

From Fig. 6, it was found that the position and the shape of the Pb° $4f_{7/2}$ peak changed after the termination of the continuous irradiation. In fact, this is the result of the relaxation of neutral lead after the termination of the continuous irradiation. The neutral lead atoms formed during the continuous irradiation are randomly distributed on the surface and they did not completely separate from the glass structure. At this point, they are still more or less influenced by the ligand field (established by the oxygen originally bonded to them) so the binding energy of the Pb° $4f_{7/2}$ is a little larger than that for pure lead metal. However, after the termination of the continuous irradiation, the neutral lead resulting from the irradiation will tend to segregate and metallize in order to minimize the energy of the system. This is the relaxation process of neutral lead. In this process, the neutral lead will gradually remove the influence of the oxygen ligand field and separate from the glass structure. The binding energy of Pb° $4f_{7/2}$ therefore decreases slowly while the relaxation proceeds and finally after a long relaxation time reaches the value of pure lead metal. For the same reason, the shape (i.e., the FWHM) of the Pb° $4f_{7/2}$ peak continuously narrows during the relaxation.

With the segregation and metallization of neutral lead during the relaxation process, the oxygen experiences corresponding changes in the chemical environment. Fig. 7 shows the XPS spectra of O 1s recorded during the continuous irradiation and at 4 h after the termination of the irradiation. From the spectra and the analysed results given in Table 1, it can be clearly seen that a shoulder peak with a lower binding energy appears and grows during the relaxation process. As discussed previously, the neutral lead atoms formed during the continuous irradiation are randomly distributed at the surface. They did not completely separate from the glass structure and are still more or less influenced by the ligand field of the oxygen originally bonded to them during the continuous irradiation. So, no definite behaviour of oxygen with lower binding energy can be obtained from the spectra at this period and all of our observations show that the binding energy and the FWHM of the O 1s peak increases with continual irradiation, as shown in Fig. 5. Lead reaches the steady state faster than the oxygen during continuous irradiation judging from the time-dependent concentration, binding energy and FWHM in Figs 4 and 5.

However, with the departure of neutral lead during the relaxation, the oxygens (originally bonded with this lead) become completely non-bridging oxygens with lone electrons. Therefore they show themselves in the XPS spectrum as O 1s with a lower binding energy and are clearly distinguished from the bridging oxygen in the initial glass structure. Even though the Gibbs free energy of PbO (-215.50 KJ mole^{-1} at 25 °C) is lower than pure lead (0 KJ mole^{-1} at 25 °C) and higher than SiO_2 (~ -837.4 KJ mole^{-1} at 25 °C), the dissociation of oxygen from Pb–O bond to form Si–O and Pb–Pb bonds is still energetically favourable [19]. This supposition of bonding and non-bonding oxygens can be supported by the results listed in Table 1 and Fig. 7b. The electron density on these non-bridging oxygens increases and therefore their binding energy decreases. On the other hand, the longer bond length of non-bridging oxygen provides larger delocalization of electrons, causing the FWHM of the XPS peak to increase. The assignment of this low binding energy peak to non-bridging oxygen is consistent to many workers (e.g., Sprenger *et al.* [20]). Except for those oxygens that rebond to silicon and non-bridging oxygens, the rest of the oxygens can form a gas and leave the surface during the relaxation process.

4.3. Response of silicon in the glass during irradiation and relaxation

There is no convincing explanation as to why the binding energy of the silicon signal did not shift during the irradiation and relaxation. It may be attributed to the relaxation of the three oxygens bonded to the silicon. Possible explanations are discussed below. Oxygen vacancies, created by the irradiation, are well known as E′ centres (≡Si↑ + adjacent Si with three relaxed oxygens) [21, 22] where two silicons and one oxygen vacancy are involved. Another route to E′ centre production is through an electron loss in an Si– Si homobond in a ≡Si–Si≡ structure which has been detected by neutron scattering [17]. The first silicon bonded to three oxygens has an unpaired electron (↑) and forms an SiO_3 pyramid structure. The nearby second silicon, with one electron lost, is bonded to three oxygens that are relaxed and coplanar with the silicon. Apparently the electron density of the first silicon (with an unpaired electron) changes little compared to the network silicons (≡Si–O). The electron density of the second silicon is reduced by the loss of one electron and the higher binding energy Si 2p signal is expected. However, since the outer shell electrons of the three relaxed oxygens bonded to the silicon cause the redistribution of electron density, around silicon, this reduces the effect due to the loss of one silicon electron. Consequently no binding energy shift was detected within the detection limit. These experimental results are consistent with the Molecular Linear Combination of Atomic Orbitals (MOLACO) theoretical calculation where only the electronic density of lead and oxygen are changed under the irradiation [23]. An other possible reason is that the SiO_4 tetrahedral structure is not easily changed under radiation compared to the Pb–O bonds, which is confirmed by the results previously discussed (i.e. the changes in binding energy and FWHM of the oxygen and lead). The final possible reason is that the XPS detects silicon 2p electrons, not the outermost 3p electrons where the significant change of the electron configuration occurs.

5. Conclusions

From the experimental results and the discussion above, it can be concluded that X-ray irradiation causes the breaking of the lead oxygen bonds in the lead silicate glass and results in the formation of pure lead. The concentration of pure lead on the glass surface produced by X-ray irradiation tends to saturation after about 2 h of continuous irradiation. Randomly distributed pure lead with a higher binding energy indicates the coupling between Pb^o and the non-bridging oxygen. Oxygen may form oxygen gas and become depleted from the surface. After the termination of the continuous irradiation, the observation of well-resolved non-bridging oxygens and a shift in the binding energy of neutral lead to that of pure metal lead indicates the segregation and the formation of a metallic lead layer on the glass surface. Some oxygen was still depleted from the surface during the relaxation process. The structural relaxation was clearly observed after about 20 h after the termination of the X-ray irradiation.

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