X-Ray Photoelectron Spectroscopy Study of Passive Layers Formed on Pb-Sn and Pb-Sb Alloys

JING XU, XIAOGANG LI, XINGBO LIU, CHAOFANG DONG, NATHANIEL DEEM, and EVER BARBERO

In this article, passivated Pb-Sn and Pb-Sb alloys with different compositions were studied by X-ray photoelectron spectroscopy (XPS). The passive films were found to have a double-layer structure. Both Sn and Sb were found to play an important role during the growth of passive film, which resulted in different compositions of passive films. The Pb oxides, Pb sulfate, Sn/Sb oxides, and Pb-Sn/Sb complex oxides (PbO_x·Sn_{1-x}O₂, PbSb₂O₆) were present in the passive films. Both Sn and Sb facilitated PbO_x (1 < x < 2) formation, which was considered to be very helpful to optimize the conductivity of passive films. It was also shown that the positions of peak signals of alloying Sn/Sb, Pb, and O were almost fixed, even though the contents of alloying Sn/Sb oxides were quite different in different specimens.

I. INTRODUCTION

LEAD alloys currently are the main grid materials for lead-acid batteries. Grids made by Pb-Sb alloys have good mechanical and casting properties and are easy to process. The Pb-Sn alloy has a low casting temperature and high mechanical strength. Moreover, alloying Sn improves the deep-cycle charging-discharging property of lead-acid batteries. Alloying Sn or Sb helps to form a passive film between the grid and the active materials pasted on plates (mainly positive plates). This passive film protects the grid from corrosion in the acid surroundings. The property of passive film is decided by its composition and structure. Extensive work has been done, and some instructive results have come up.^[1-6] Among them, the double-layer structure mode was very popular.^[6,7,8] In terms of the relationship</sup></sup> between the content of alloying elements and film conductivity, investigations were done in an alkali environment (pH = 9).^[5] However, the practical working environment of the grid is sulfuric acid; the composition and character of formed films in an acid environment are inevitably quite different from those in an alkali one. No research, though, has been performed in this area before.

In this article, X-ray photoelectron spectroscopy (XPS) was used to study the passive films grown on the surface of Pb-Sn and Pb-Sb alloys in sulfuric acid. The compositions and microstructures were studied, and the influence of the

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alloying elements on the passive films was also discussed. It was useful for further optimizing the properties of grids in Pb acid batteries. Simultaneously, it could also benefit the batteries' lifetimes in deep-cycle service by preventing grids from being corroded in the severe service environment.

II. EXPERIMENT

The electrolyte was a 4.0 mol/L H_2SO_4 solution prepared from analytical reagent (AR)-grade sulfuric acid and distilled water. Four Pb-Sn alloys and three Pb-Sb alloys with different compositions were used as the working electrodes. The alloys were cast from Pb (99.99 pct) and Sb (99.99 pct) or Sn (99.9 pct). The compositions of the alloys are listed in Tables I and II. A Pt plate served as the counter electrode. The reference electrode was the Hg/Hg₂Cl₂ electrode (saturated calomel electrode (SCE)) containing the same electrolyte as that in the test cell. All potentials reported here are referred to the Hg/Hg₂SO₄ reference electrode.

The surface of the Pb electrode was mechanically polished with Emery paper of successively decreasing grain size down to approximately 10 μ m. The electrode was then rinsed with distilled water and placed into the cell for the experiment. A cathodic polarization at -1.2 V for 20 minutes was performed to remove any oxidation products formed during the pretreatment. The working electrodes were polarized at 0.60 V vs SCE to develop a passive layer in 4Msulfuric acid for 1 hour, until a steady-state passive current was attained. After passivation, the samples were rinsed with distilled water, dried, and then transferred to the XPS spectrometer. Each sample was sputtered by an AG-21Ar⁺ gun in vacuum, first for 3 minutes, then for an additional 27 minutes, for a total of 30 minutes. The XPS was then used to study the passive film in these two different states. All experiments were carried out at 25 °C ± 2 °C. Electrochemical potentiostatic polarization was performed by using an EG&G PARC 273 potentiostat/galvanostat controlled by EG&G PARC 273 software (EG&G Technical Services, Inc.).

Surface analysis of the passive layers was carried out with a VG Scientific MKII (ESCALAB) apparatus, with the Mg K_{α} X-ray source ($h\gamma = 1253.6 \text{ eV}$; power = 2 kV × 12 mA).

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 Table I.
 Composition of Four Kinds of Pb-Sn Alloys (Weight Percent)

Material	11	13	14	15
Sn wt pct	0.532 pct	1.06 pct	1.57 pct	2.60 pct

 Table II.
 Composition of Three Pb-Sb Alloys (Weight Percent)

Material	22	24	25
Sb Wt Pct	0.510 pct	1.58 pct	2.59 pct

Sputtering of the sample surface was performed with a VG AG21 argon-ion gun under 4 kV accelerating voltage, 5 \times 10⁻⁷ mbar pressure, and 30 μ A/cm² current density. The sputtered area was 1 cm², and the X-ray beam size was 0.1 cm². Iterative Shirley curves and peak synthesis (using Gaussian–Lorentzian curves) were carried out with the Origin6.1 software. The values of the attenuation lengths of the electrons for the different elements were derived from literature data.^[9]

III. RESULTS

A. Microstructure of Passive Film

After anodic oxidation for 1 hour, the Pb-Sn and Pb-Sb alloys attained a passive film on their surfaces. The micro-features of samples 11 and 22 are shown in Figures 1 and 2. Figure 3 shows a cross-sectional microstructure of the passive layer on specimen 25, with the corresponding element distribution shown in Figure 4. It can be found from Figure 3 that there are two sublayers in the passive film.

The passive films on the surfaces of the Pb-Sn and Pb-Sb alloys are all composed of small particle groups. These particles are the basic units of passive layers. They grew from Pb alloys, completely covering the surface of the alloys. This clinker-built assembling is shown, under scanning electron microscopy, to be uniform. The uncovered Pb alloys can be found in some parts of the stratification structure.

B. Composition of Passive Films

1. Composition of the Pb-Sn alloy's passive film

Using the sample no. 15 Pb-Sn alloy containing 2.60 wt pct Sn as an example, Figures 5(a) and (b) show the XPS survey spectra for the passive film that was sputtered for 3 and 30 minutes, respectively. The passive film after 3 minutes of sputtering was made up of C, O, Pb, Sn, and S. Carbon was considered to be the impurity introduced during sample preparation or analysis. In passive films after 30 minutes of sputtering, there is O, Pb, and Sn. There are no C1s and S2p peaks, and the O1s peak is much weaker than that after the 3 minutes of sputtering; however, the Pb4f and Sn3d5 peaks are slightly stronger than those after 3 minutes of sputtering. This illustrates that the passive film formed on Pb-Sn alloys has more than one layer.

To further explore the valency of Pb and Sn in the passive film, spectra of Pb and Sn levels in the passive films on 15# Pb-Sn alloys were studied. By using Gaussian resolution, Figures 6 and 7 show the Pb4f (Pb4f_{7/2} and Pb4f_{5/2}) and Sn3d (Sn3d_{5/2} and Sn3d_{3/2}) spectra after 30 and 3 minutes of sputtering of the passive films. According to binding energies of



5.00µn ⊨______ (*b*)

Fig. 1—(a) and (b) Micrographs of the passive layer in sample 11, containing 0.532 pct Sn, in the Pb-Sn alloy.

various signals of related materials in passivated Pb-Sn alloys, shown in Table III and Table IV, the Pb4f_{5/2} (nonsmooth curve in Figure 6(a)) is contributed by the signals of both PbSO₄ and PbO_x (1 < x < 2). Considering the statistical distribution of photo jumping and by using the fitting method to solution evolution, we could separate the measured curve into two smooth curves of the PbSO₄ peak around 140.1 eV and the PbO_x peak around 141.5 eV. Using the same resolution method, Figure 6(b) shows that the Pb4f_{5/2} peak is the sum of the Pb peak from both PbO (138.1 eV) and PbO_x (141.6 eV).

By using the solution-evolution fitting method, $\text{Sn3d}_{5/2}$ (nonsmooth curve in Figure 7) is found to be contributed by the Sn signals of both PbO_xSn_{1-x}O₂ (0 < x < 1) around 488.4 eV and of SnO₂ or SnO around 488.3 eV. The Sn peak in Figure 7(b) could be separated into PbO_x·Sn_{1-x}O₂ around 488.3 eV and into SnO₂ or SnO around 486.7 eV. The XPS, however, could not distinguish SnO from SnO₂ signals, because the peaks of these two Sn oxides have been found to be very close to each other.^[9]

Figure 8 showed the O1s spectra in the same passive film. Using the same solution-evolution fitting method, the O1s peak in Figure 8(a) is divided into five smooth curves corresponding to SnO₂ (530.6 eV), SnO (530.4 eV), PbSO₄ (531.9 eV), PbO_x (533.3 eV), and PbO_x $Sn_{1-x}O_2$ (534.0 eV). With the same



Fig. 2—(a) and (b) Micrographs of the passive layer in sample 22, containing 0.510 pct Sb, in the Pb-Sb alloy.



Fig. 3-(a) and (b) Cross-section micrographs of the passive layer in specimen 25, containing 2.59 pct Sb.



(b) 0 - 147 Sb - 136

Fig. 4-(a) and (b) Element distribution of the passive layer in specimen 25, containing 2.59 pct Sb.



Fig. 5-Survey spectra of passive films on the sample 15 Pb-Sn alloy containing 2.60 wt pct Sn: (a) after 3 min of sputtering and (b) after 30 min of sputtering.



Fig. 6—Spectra of Pb ($4f_{5/2}$, $4f_{7/2}$) in the passive films on the sample 15 Pb-Sn alloy, containing 2.60 wt pct Sn: (a) after 3 min of sputtering and (b) after 30 min of sputtering.



Fig. 7—Spectra of Sn $(3d_{5/2}, 3d_{3/2})$ in the passive films on the sample 15 Pb-Sn alloy, containing 2.60 wt pct Sn: (a) after 3 min of sputtering and (b) after 30 min of sputtering.

resolution method, the O1s peak in Figure 8(b) is the final result of SnO, SnO₂, PbO, PbO_x, and PbO_x \cdot Sn_{1-x}O₂.

Accordingly, the sample after 3 minutes of sputtering is mainly composed of SnO_2 , SnO, $PbSO_4$, PbO_x , and PbO_x .

Sn_{1-x}O₂, whereas the sample after 30 minutes of sputtering is chiefly made up of SnO₂, SnO, PbO, PbO_x, and PbO_x·Sn_{1-x}O₂. Among them, PbO_x (1 < x < 2) is a Pb complex oxide, and PbO_x·Sn_{1-x}O₂ (0 < x < 1) is a Pb-Sn complex oxide.



Fig. 8—Spectra of oxygen 1s in the passive films on the sample 15 Pb-Sn alloy, containing 2.60 wt pct Sn: (a) after 3 min of sputtering and (b) after 30 min of sputtering.



Fig. 9-Survey spectra of passive films on the sample 25 Pb-Sb alloy, containing 2.59 wt pct Sb: (a) after 3 min of sputtering and (b) after 30 min of sputtering.

2. Composition of the Pb-Sb Alloy's Passive Film

Using the sample 25 Pb-Sb containing 2.59 wt pct Sb as the example, Figure 9(a) presents the XPS survey spectra for the passive film that was sputtered for 3 minutes, which contains C, O, Pb, Sb, and S. The element C was considered to have been introduced to the sample during pretreatment. Figure 9(b) presents the XPS survey spectra for the same sample after having been sputtered for 30 minutes, in which O, Pb, and Sb are found. Compared with Figure 9(a), Figure 9(b) does not have C1s and S2p peaks, and the O1s/Sb3d peak decreased a lot. Similar to that of the Pb-Sn alloys, the passive film on the Pb-Sb alloys has a stratification structure.

Sample 25 was used to explore the spectra of Pb, Sb, and O in the passive film. Figures 10 and 11 showed the characteristic information of Pb and O/Sb in the passive film, where Figure 10 is for Pb4f (Pb4f7/2 and Pb4f5/2) and Figure 11 is for O1s/Sb3d. According to Table III, using the solution-evolution method, the Pb4f5/2 curve in Figure 10(a) is contributed by Pb in PbO₂, PbSO₄, and PbO_x (1 < x < 2). Among them, the Pb peak from PbO₂ is at about 137.6 eV, that from PbSO₄ is at about 139.7 eV, and that from PbO_x is at about 140.5 eV. The Pb4f5/2 in Figure 10(b) is contributed by the

Pb in PbO, PbO_x , and $PbSb_2O_6$. Among them, the Pb peak from PbO is at around 137.9 eV, that from PbO_x is at around 140.6 eV, and that from $PbSb_2O_6$ is at around 141.3 eV.

Because the Sb content in the passive film is very low, as shown by sample 25, Sb3d could not be clearly differentiated in Figure 11(a). Using the solution-evolution fitting method, the O1s peak is added up by oxygen in PbO₂, PbSO₄, PbO_x, and PbSb₂O₆. Among them, the binding energies of PbO₂, PbSO₄, PbO_x, and PbSb₂O₆ are 528.8, 531.5, 535.5, and 532.7 eV, respectively. According to Figure 11(b), the peaks of O1s, Sb3d_{5/2}, and Sb3d_{3/2} were separated first, and then the O1s and Sb3d peaks were each analyzed by the solutionevolution fitting method. The results showed that, in sample 25, the $Sb3d_{3/2}$ peak corresponds to Sb_4O_6 's feature spectra (531.8 eV) and the Sb3d_{5/2} peak corresponds to Sb₂O₄ or PbSb₂O₆'s feature spectra (around 540.0 eV). Both Sb₂O₄ and PbSb₂O₆ belong to noninteger-ratio complex oxides and have peaks that are so close, they cannot be distinguished by XPS. Peak O1s is contributed by oxygen in Sb₄O₆, PbO, PbO_x, Sb₂O₄, or PbSb₂O₆. Among them, the binding energies of Sb₄O₆, PbO, PbO_x, Sb₂O₄, or PbSb₂O₆ are 529.6, 531.1, 531.7, and 531.8 eV, respectively.



Fig. 10—Spectra of Pb $(4f_{5/2}, 4f_{7/2})$ in the passive films on the sample 25 Pb-Sb alloy containing 2.59 wt pct Sb: (*a*) after 3 min of sputtering and (*b*) after 30 min of sputtering.



Fig. 11—Spectra of O1s/Sb3d in the passive films on the sample 25 Pb-Sb alloy containing 2.59 wt pct Sb: (a) after 3 min of sputtering and (b) after 30 min of sputtering.

Table III. Peak Binding Energies of Different Lead Oxides

Fable IV.	Peak	Binding	Energies	of Materials	Concerned
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Element	Substance	Binding Energy (eV)
Ols	PbO, tetragonal	531.60
	PbO ₂	529.00
	PbSO ₄	531.50
	SnO	530.10
	SnO ₂	530.60
	Sb_4O_6	530.00
Pb4f _{7/2}	Pb	136.40
	РЬО	138.85
	PbO ₂	137.40
	PbSÕ₄	139.40
Sn3d5	SnO	486.90
	SnO ₂	486.65
Sb3d5	Sb₄Õ ₆	530.80

Accordingly, the sample after 3 minutes of sputtering is mainly composed of PbO₂, PbSO₄, PbO_x, and PbSb₂O₆, and the sample with 30 minutes of sputtering is composed of PbO, PbO_x, PbSb₂O₆, Sb₂O₄, and Sb₄O₆. Among them, PbO_x (1 < x < 2) is a noninteger-ratio complex oxide of Pb and

Compounds	Oxygen	Lead	Lead
	Signal	Signal	Signal
	(1s) (eV)	(4f _{5/2}) (eV)	(4f _{7/2}) (eV)
PbO _{tetragonal}	528.90	143.75	138.85
PbSO ₄	531.50	144.5	139.40

oxygen, Sb_2O_4 is a complex oxide of Sb and oxygen, Sb_2O_6 is a double-molecular oxides of Sb(III) and oxygen, and $PbSb_2O_6$ is a complex oxide of Pb, Sb, and oxygen.

C. The Influence of Sn and Sb on the Passive Film

1. The Influence of Sn on the Passive Film

Figure 12 shows the spectra of Sn level $3d_{5/2}$ and Sn level $3d_{3/2}$ in the passive films of the four studied Pb-Sn alloys (3 minutes of sputtering). Peaks 1 and 2 concern Sn $3d_{3/2}$ and Sn $3d_{5/2}$, respectively. The spectra of alloys with the higher Sn content (2.60 wt pct Sn) show only two peaks, denoted as 1 and 2 (Figure 12(a)). When the Sn content is decreased (1.57 and 1.06 wt pct Sn), it is shown that there are not only 1 and 2 peaks,



Fig. 12—Spectra of $Sn3d(3d_{5/2}(2) \text{ and } 3d_{3/2}(1))$ in the passive films on the Pb-Sn alloy after 3 min of sputtering: (a) sample 15, containing 2.60 wt pct Sn; (b) sample 14, containing 1.57 wt pct Sn; (c) sample 13, containing 1.06 wt pct Sn; and (d) sample 11, containing 0.532 wt pct Sn.

	Binding Energy (eV)					
Alloys	$\frac{Sn_{(ox)}}{3d_{3/2}}$ (Peak 2)	$Sn_{(ox)}$ $3d_{5/2}$ (Peak 1)	Peak 2'	Peak 1'	Peak 2– Peak 1	Peak 2'- Peak 1'
2.60 wt						
pct Sn	496.8	488.4			8.4	
1.57 wt						
pct Sn	496.0	487.6	501.7	493.2	8.4	8.5
1.06 wt						
pct Sn	495.8	487.4	502.6	494.1	8.4	8.5
0.532 wt						
pct Sn				-		
Tin oxide ^a	495.3	486.9			8.4	

Table V. Peak Binding Energies of Various Signals of Sn in Passivated Pb-Sn Alloys

but also 1' and 2' peaks (Figures 12(b) and (c)) in the spectra graphs. So, it is clear that the feature peaks correspond to different kind of Sn oxides. The binding energies corresponding to the Sn spectra of alloys are gathered in Table V. It can be seen from Table V that the difference between the two 3d energy levels of oxidized Sn (peak 2–peak 1) is 8.4 eV, and the difference between peak 2' and peak 1' is roughly 8.5 eV.



Fig. 13—Spectra of Pb4f in the passive films on Pb-Sn alloys after 3 min of sputtering. Note: sample 11 contains 0.532 wt pct Sn, sample 13 contains 1.06 wt pct Sn, sample 14 contains 1.57 wt pct Sn, and sample 15 contains 2.60 wt pct Sn.

The spectra of Pb4f and O1s in different Pb-Sn alloys are shown in Figures 13 and 14. The binding-energy peaks of Pb4f and O1s do not change with the variation of alloy composition. Based on the previous discussion, it is concluded



Fig. 14—Spectra of O1s in the passive films on the Pb-Sn alloy after 3 min of sputtering. Note: sample 11 contains 0.532 wt pct Sn, sample 13 contains 1.06 wt pct Sn, sample 14 contains 1.57 wt pct Sn, and sample 15 contains 2.60 wt pct Sn.

that the peak Pb4f is piled up by lead in $PbSO_4$, PbO, PbO_x, and PbO_xSn_{1 - x}O₂, and the peak O1s is the final result of oxygen in series of Pb oxides, Sn oxides, Pb sulfates, and complex oxides. The peak binding energies of the Pb4f and O1s signals are listed in Tables VI and VII.

Sputtering of the passive alloy surface was carried out in order to verify the quantity distribution of alloying Sn and the conductivity in the depth of the passive layers. Figure 15 shows the signal of Sn after 3 and 30 minutes of sputtering using a AG-21Ar+ gun.

It is easy to find that the binding energy of the Sn 3d peaks $(3d_{5/2} (2) \text{ and } 3d_{3/2} (1))$ shifts to the lower level when the sputtering time increased. This rule is true to all four Pb-Sn alloys tested, despite the differences of Sn concentration.

The Pb signals after sputtering for different times are presented in Figure 16. It is possible to get oxide reduction by argon sputtering, but, in this study, the reduction of Pb oxide (PbO) was not observed for pure Pb, even after 30 minutes of sputtering. The changes of the oxygen 1s signals can be observed in Figure 17. It shows that the O1s peaks of all four Pb-Sn alloys tested do not shift obviously after 30 minutes of sputtering. Also, the intensity of peak 1 decreases with the increase of sputtering time.

2. The Influence of Sb on the passive film

Figures 18 and 19 show the Pb4f and O1s/Sb3d spectra of passive layers in different Pb-Sb alloys. It is easy to find from Figures 18 and 19 that the peaks of the binding energies about Pb4f and O1s/Sb3d do not change, despite the variations of alloying Sb content. According to the discussion in the previous part of this article, the Pb4f peak is contributed by Pb in Pb sulfates, Pb transition oxides, and complex Pb oxides. Also, O1s/Sb3d peaks are contributed by the oxygen in Pb oxides, Pb sulfates, and Pb-Sb complex oxides. Tables VIII and IX gather the peak binding energies of the Pb4f and O1s/Sb3d signals from the Pb-Sb alloys. Combining the data listed in Tables VI and VII as well as the feature information shown in Figures 18 and 19, it is found that although the alloying Sb content changes, the binding energy of peak Pb4f_{7/2} is always at around 139.9 eV (\pm 0.1 eV), the peak of

 Table VI.
 Peak Binding Energies of Various Lead Signals

 From Passivated Pb-Sn Alloys

	Alloys			
Level	2.60 Wt	1.57 Wt	1.06 Wt	0.532 Wt
	Pct Sn	Pct Sn	Pct Sn	Pct Sn
Pb _(ox) 4f _{5/2}	145.4	145.2	145.1	145.0
Pb _(ox) 4f _{7/2}	140.4	140.2	140.1	140.0

 Table VII.
 Peak Binding Energies of the Oxygen Signal from Passivated Pb-Sn Alloys

	Alloys				
Level	2.60 Wt Pct Sn	1.57 Wt Pct Sn	1.06 Wt Pct Sn	0.532 Wt Pct Sn	
Ols (eV)	532.6	532.4	532.2	532.0	

Pb4f_{5/2} is always at around 144.8 eV (± 0.2 eV), and that of O1s is around 531.9 eV (± 0.1 eV). There is no obvious peak shifting. This illustrates that the alloying Sb has little influence on the Pb4f and O1s/Sb3d peaks.

Using an AG-21Ar+ gun to sputter the surface of three kinds of Pb-Sb alloys for 3 and 30 minutes with passive films in a vacuum, XPS was performed, and the spectra are shown in Figure 20. The binding-energy peaks of Pb4f ($4f_{7/2}$ (2) and $4f_{5/2}$ (1)) shift to the lower level when the sputtering time is increased. This rule is true for all three Pb-Sb alloys tested, despite the differences of alloying Sb concentrations. After deep sputtering (30 minutes), two other peaks appear at the high-binding-energy area, denoted as "a" and "b" in the spectra of Pb4f in Figure 20.

The binding energies corresponding to the Pb spectra of alloys are gathered in Table X. It can be seen that the difference between peak 2' and peak 1' is 5.0 eV, and the difference between peak b and peak a is roughly 4.9 eV. It is then likely that peaks a and b are shifted from peaks 1' and 2'.

Figure 21 shows the spectra of O1s/Sb3d in a passivated Pb-Sb alloy after 3 and 30 minutes of sputtering. It is evident that the spectra of O1s/Sb3d in the Pb-Sb alloys are different from the spectra of O1s in the Pb-Sn alloys. The O1s/Sb3d peaks of passivated Pb-Sb alloys with a low Sb content (1.58 wt pct Sb and 0.51 wt pct Sb) shifted to the left-hand side after 30 minutes of sputtering, while this phenomenon is invisible for the high-Sb-concentration (2.59 wt pct Sb) sample. The less Sb in the bulk, the more shift of the O1s/Sb3d peak to the left-hand side. In fact, according to the spectra of O1s and Sn3d of passivated Pb-Sn alloys, O1s peaks do not shift after deep sputtering despite different Sn concentrations, but all Sn3d peaks shift to the left-hand side. Therefore, it is assumed that whether the peak O1s/Sb3d shifts or not depends on the concentration of alloying Sb in the passivated Pb-Sb alloys. The binding energies concerned are gathered in Table XI.

IV. DISCUSSION

A. Effect of Sn/Sb on the Composition of Passive Layers

1. Sn effect

From the spectra of Pb $(4f_{5/2}, 4f_{7/2})$ in the passive film, shown in Figures 6 and 10, it is found that there is no signal of pure Pb. This lack of signal could be due to a dismutation

reaction between Sn/Sb and Pb oxides in the passive layer. Take Pb-Sn alloy as example:

$$SnO_2 + Pb \rightarrow SnO + PbO$$
 [1]

Sn(IV), in SnO_2 , exists in the passive film with a strong reduction tendency. Sn(IV) in SnO_2 is able to oxidize pure Pb, while Sn(IV) reduces to Sn(II) with a redox reaction; therefore, it is impossible to have pure Pb in the passive film



Fig. 15—Spectra of $Sn(3d_{5/2}(2) \text{ and } 3d_{3/2}(1))$ in the passive films on the Pb-Sn alloy after 3 and 30 min of sputtering: (a) sample 15, containing 2.60 wt pct Sn; (b) sample 14, containing 1.57 wt pct Sn; (c) sample 13, containing 1.06 wt pct Sn; and (d) sample 11, containing 0.532 wt pct Sn.



Fig. 16—Spectra of Pb $(4f_{7/2}(2) \text{ and } 4f_{5/2}(1))$ in the passive films on the Pb-Sn alloys after 3 and 30 min of sputtering: (a) sample 15, containing 2.60 wt pct Sn; (b) sample 14, containing 1.57 wt pct Sn; (c) sample 13, containing 1.06 wt pct Sn; and (d) sample 11, containing 0.532 wt pct Sn.



Fig. 16—(Continued). Spectra of Pb $(4f_{7/2}(2) \text{ and } 4f_{5/2}(1))$ in the passive films on the Pb-Sn alloys after 3 and 30 min of sputtering: (a) sample 15, containing 2.60 wt pct Sn; (b) sample 14, containing 1.57 wt pct Sn; (c) sample 13, containing 1.06 wt pct Sn; and (d) sample 11, containing 0.532 wt pct Sn.



Fig. 17—Spectra of oxygen in the passive films on the Pb-Sn alloys after 3 and 30 min of sputtering: (a) sample 15, containing 2.60 wt pct Sn; (b) sample 14, containing 1.57 wt pct Sn; (c) sample 13, containing 1.06 wt pct Sn; and (d) sample 11, containing 0.532 wt pct Sn.



Fig. 18—Spectra of Pb4f in the passive films on the Pb-Sb alloys after 3 min of sputtering.



Fig. 19—Spectra of O1s in the passive films on the Pb-Sb alloys after 3 min of sputtering. Note: sample 22 contained 0.51 wt pct Sb, sample 24 contained 1.58 wt pct Sb, and sample 25 contained 2.59 wt pct Sb.

 Table VIII.
 Peak Binding Energies of Various Lead Signals from Passivated Lead-Antimony Alloys

Level	Alloys				
	2.59 Wt Pct Sb	1.58 Wt Pct Sb	0.51 Wt Pct Sb		
Pb _(ox) 4f _{5/2}	144.6	145	144.8		
Pb _(ox) 4f _{7/2}	139.8	140	139.8		

 Table IX.
 Peak Binding Energies of the Oxygen Signal from Passivated Lead-Antimony Alloys

Level	Alloys				
	2.59 Wt Pct Sb	1.58 Wt Pct Sb	0.51 Wt Pct Sb		
Ols (eV)	531.8	532.0	532.0		

for the thermodynamically stable system in Pb-Sn alloys, as well as Pb-Sb alloys.

It is found from Tables VI and VII that the peak binding energy of Pb4f_{7/2} is always around 140.2 eV (\pm 0.2 eV), no matter how the alloy composition differs, and the peak



Fig. 20—Spectra of Pb $(4f_{7/2}(2) \text{ and } 4f_{5/2}(1))$ in the passive films on the Pb-Sb alloys after 3 and 30 min of sputtering: (*a*) sample 25, containing 2.59 wt pct Sb; (*b*) sample 24, containing 1.58 wt pct Sb; and (*c*) sample 22, containing 0.51 wt pct Sb.

binding energies of Pb4f_{5/2} and O1s are always around 145.2 eV (± 0.2 eV) and 32.3 eV (± 0.3 eV), respectively. This indicates that although alloying Sn can decrease the thickness of passive films, consequently increasing conductivity,

Table X. Peak Binding Energies of Various Signals of Lead in Passivated Lead-Antimony Alloys

Alloys	Binding Energy (eV)					
	Pb _(ox) 4f _{7/2} (Peak 2')	Pb _(ox) 4f _{5/2} (Peak 1')	Peak b	Peak a	Peak 2' – Peak 1'	Peak b – Peak a
2.59 wt pct Sb	142.8	137.8	155.9	151.0	5.0	4.9
1.58 wt pct Sb	142.7	137.7	155.9	151.0	5.0	4.9
0.51 wt pct Sb	142.8	137.8	156.1	151.2	5.0	4.9
Lead oxide ^a	143.75	138.85			4.9	
^a Reference 9.						



Fig. 21—Spectra of oxygen/antimony in the passive films on the Pb-Sb alloys after 3 and 30 min of sputtering: (a) sample 25, containing 2.59 wt pct Sb; (b) sample 24, containing 1.58 wt pct Sb; and (c) sample 22, containing 0.51 wt pct Sb.

it does not affect the peak position of Pb4f and O1s. Considering the fixed spectra of the Pb4f peak, despite the different Sn contents and the almost fixed spectra of the Pb4f peak after electron emission (shown in Figure 22), the conductivity of Pb-Sn alloys is good, although it decreases with decreasing Sn alloying concentration. It is worthy of mention that, in the spectra of Sn3d, Pb4f, and O1s, the main peaks do not change their positions, despite the different compositions of the Pb-Sn alloys (the concentration of Sn changes). This proves that although the Sn concentrations are different, the components in the passive films do not change.

2. Sb effect

From the composition analysis in Figures 9 through 11, it is found that PbO_x exists in the passive film on Pb-Sb alloys. As the concentration of the alloying Sb increases, Sb oxides and Pb-Sb complex oxides segregate at the grain boundaries. This leads to intergranular corrosion and depresses the continuity and uniformity of passive films, so as to increase the conductivity of passive films.^[10] In the spectra of Pb4f and O1s/Sb3d, all the main peaks do not shift, despite the different compositions of the Pb-Sb alloys (the concentration of Sb changes). This nonshifting illustrates that, although the alloying Sb concentration is quite different, components of the passive films do not change.

B. Effect of Sn/Sb on the Conductivity of Passive Layers

1. Sn effect

It is indicated in Figure 12 that peaks 1' and 2' seem to be shifted from peaks 1 and 2 and are related to oxidized Sn signals.

The parameters reported in Table V show that the shifting of oxidized Sn signals 1 and 2 to 1' and 2' attains roughly 5.6 eV (peak 1 to 1' or peak 2 to 2') for sample 14 (1.57 wt pct Sn) and 6.7 eV for sample 13 (1.06 wt pct Sn). These values are quite high, when compared to the shift of the binding energy, due to the increase of the oxidation state or to the bonding of Sn with a strongly electronegative ele-

 Table XI.
 Peak Binding Energies of Signals of Oxygen in Passivated Lead-Antimony Alloys

	Bir	nding Energ	gy (eV)
Alloys	Ols (Peak 1')	Peak a	Peak a – Peak 1'
2.59 wt pct Sb	530.6	539.8	9.2
1.58 wt pct Sb	530.0	539.2	9.2
0.51 wt pct Sb	528.6	537.8	9.2

ment, such as in SnF₄. It is reported that the shift of the Sn signals, when oxidized from SnO to SnO₂, is not significant and that the shift from SnO to SnF₄ is only 1.2 eV.^[9]

There are two possible reasons for the shift of the binding energy to higher levels. First, the change of either the oxidation state or the chemical environment of the element leads to stronger electronic binding, which is not the key point to explain the aforementioned experimental results (5.6 and 6.7 eV shifting, respectively). Second, the electrical conductivity of the sample decreases. The emission of electrons following X-ray irradiation results in the appearance of positive charges on the surface of the sample. If the sample (passive layer, in this case) has very low conductivity, the non-neutralized positive charges will increase the binding energy of electrons in the surface ions, and the XPS peaks will shift to higher energy levels. This phenomenon is called the electrical-charge effect (ECE). The ECE produces a stable surface potential on the sample, which fetters the electrons from escaping. Accordingly, the surface trail of electrons will have a higher binding energy, so that the XPS peaks will shift to the right-hand side. Hence, the passive layers of alloys with less than 1.57 wt pct Sn include positively charged zones because of their low electrical conductivity. The shifted peaks and nonshifted peaks correspond to the positive zones and noncharged zones. The conductivity of the passive layers decreases sharply when the Sn content decreases.^[11] For the sample 11 alloy, containing 0.532 wt pct Sn, no signal



Fig. 22—Spectra of Pb4f in the passive films on the Pb-Sn alloys before and after electron-beam sputtering: (a) sample 11, containing 0.532 wt pct Sn; (b) sample 13, containing 1.06 wt pct Sn; (c) sample 14, containing 1.57 wt pct Sn; and (d) sample 15, containing 2.60 wt pct Sn.

of oxidized Sn is observed, meaning that the nonconducting passive films contain no Sn oxide in the outer layer.

Electronic emission was purposely used on the sample surface to investigate the surface conductivity quantitatively and to prove the ECE in the Pb-Sn alloy. If the conductivity of the sample was low, the continuously ejected electrons could not be neutralized due to the insulation on the specimen. The phenomenon of "electron redundancy" would then show up on the surface of the samples. Therefore, the binding energy of electrons in the surface ions will decrease and the XPS peaks will shift to lower energy levels. Figure 22 shows the signals of Pb (levels $4f_{7/2}$ and $4f_{5/2}$) from the outer passive layers on the Pb-Sn alloys, sputtered with and without an electron beam (6 nA), respectively. It is shown that there is a lefthand shifting of the Pb4f peak for samples 11 and 13 after being sputtered by the electron beam. On the other hand, peak Pb4f shifts slightly to left-hand side for sample 14, and there is almost no shifting at all for the spectra of sample 15. These results indicate that as the Sn content increases, the quantity of low-conductivity zones in the passive layers decreases, and the conductivity of the passive films increases accordingly.

Three possible reasons are offered to explain the influence of alloying Sn on the conductivity of passive layers. First, the Sn seepage mechanism (SM) has been proposed by studying the redox kinetics process. The SM theory considers that Sn can decrease the thickness of passive films and improve the formation of the lead's transition oxide, PbO_x (1 < x < 2). The resistance of PbO_x is far less than that of either $PbSO_4$ or PbO_2 . Therefore, Sn can increase the conductivity of the whole passive film. Second, as the Sn content keeps increasing, many Sn oxides segregate at the grain boundaries, which leads to intergranular corrosion. This corrosion may depress the continuity and uniformity of passive films so as to increase the general conductivity of passive layers.^[12] Third, SnO₂ and SnO exist in the passive film. Since Sn⁴⁺, Sn²⁺, and Pb²⁺ ions have different radii, (0.71, 1.02, and 1.2 A, respectively), the doping of Sn will affect the grain structure, which can introduce some defects and, accordingly, introduce conductive channels.

2. Sb effect

The results of Figures 18 and 19 illustrate that the passive layers on the surface of Pb-Sb alloys have a high conductivity, and the quantity of zones with low electrical conductivity in passive layers decreases with the increase of alloying Sb, optimizing the conductivity of the passive films. The influence of alloying Sb to a passive layer's conductivity is similar to that of alloying Sn, that is, Sb can also help to form the Pb transition oxide PbO_x (1 < x < 2) with low resistance (compared to PbSO₄ and PbO). Sb³⁺ (existing in Sb₄O₆ and Sb₂O₄) and Pb²⁺ have ionic radii of 0.9 and 1.2 Å, respectively; the doping of Sb changes its grain structure. Accordingly, some defects are formed, which lead to available conductive channels.

Figure 23 is the spectra of Pb4f without and with electronbeam (6 nA) sputtering. It is shown that there is a left-hand shifting of peak Pb4f for sample 22 after the electron bombardment, with the shift of sample 24 being even smaller. Sample 25, with a high Sb concentration, almost does not shift at all.

C. Double-Layer Structure in the Passive Films

1. Pb-Sn alloys

Figure 4 indicates that there are two layers in the passive films of Pb-Sb alloys, while similar features were also found



Fig. 23—Spectra of Pb4f in the passive films on the Pb-Sb alloys before and after electron-beam sputtering: (a) sample 22, containing 0.51 wt pct Sb; (b) sample 24, containing 1.58 wt pct Sb; and (c) sample 25, containing 2.59 wt pct Sb.

in Pb-Sn alloys. This double-layer feature was also confirmed by the 3-minute and 30-minute Ar^+ sputtering tests. Figure 16 shows that the binding energies of the Sn 3d peaks ($3d_{5/2}$ (2) and $3d_{3/2}$ (1)) shifted to the lower level when the sputtering time increased. This is true to all four Pb-Sn alloys tested, despite their different Sn concentrations, meaning that the inner layer of the passive film is more conductive than the outer layer. Regarding the intensity of the peak, both signals 1 and

2 increased in intensity with the sputtering, which indicates that the Sn concentration increases from the outside to the inside. However, the degree with which the peak intensity increases is quite different for each signal, due to the different alloy compositions. In detail, the lower the Sn concentration in the bulk, the higher the differential gradient of the Sn content between the two layers of passive film. For instance, sample 15, with a high Sn concentration (2.6 wt pct Sn), has a negligible difference in the intensity of Sn signals between the outer layer and the inner one. On the contrary, the Sn signalintensity difference between the outer layer and the inner one for sample 11, with 0.532 pct Sn, is much greater than that of sample 15. As for the spectra of Sn in samples 14 (1.57 wt pct Sn) and 13 (1.06 wt pct Sn), besides the two main peaks of $Sn3d_{5/2}$ and $Sn3d_{3/2}$, the Sn 3d levels have other nonconductive peaks on the right-hand side. The two nonconductive peaks, however, do not show up any longer after 30 minutes of sputtering. These experimental results suggest that the inner layer has a higher conductivity than the outer layer.

Figure 17 shows that both signals 1 and 2 increased in intensity when the sputtering time increased, meaning that the Pb concentration increases from the outside to the inside. The amplitudes of the peak intensity, however, are different from each other due to various alloy compositions. The higher the alloying Sn concentration, the bigger the differential gradient of Pb content between the two layers of passive film. For example, sample 15, with a high Sn concentration (2.60 wt pct Sn), has a greater difference in the intensity of Pb 4f signals from the outer to the inner layer than that of sample 11, with 0.532 wt pct Sn. Furthermore, the existing state of Pb is quite different between the outside and inside layers. The Pb in the outer layer exists as $PbSO_4$, PbO_x , and $PbO_xSn_{1-x}O_2$, whereas the Pb in inner layer exists in PbO, PbO_x , $PbSO_4$, and $PbO_xSn_{1-x}O_2$. The alloying Sn with different concentrations can lead to a different quantity of PbO. even changing its equilibrium chemical coefficient, x (1 < x < 2). Naturally, the content and property of PbO_x itself will directly affect the conductivity of passive alloys.

The analysis of Figure 18 illustrates that the oxygen concentration lessens from outside to inside. Obviously, oxygen can react with the surface metal rather more easily than the inner layer metal, because oxygen needs to diffuse through the thick oxide layers before reaching the inside and reacting with the metal there. Therefore, the oxidation reaction in the solution was done as a step by step process of the diffusion of oxygen. Accordingly, Argon ion sputtering results show that the oxygen concentration of the outer layer is much higher than that of the inner layer.

2. Pb-Sb alloys

Figure 20 illustrates that the inner layer of the passive film on Pb-Sb alloys is more conductive than the outer layer. The parameters reported in Table X show that the shifting of 1' and 2' to a and b attains roughly 13.1 eV (peak a to peak 1' = 13.2 eV; peak b to peak 2' = 13.1 eV) for the sample 25 alloy (2.59 wt pct Sb). These values are quite high compared to the shift of the binding energy due to either the increase of the oxidation state or to the bonding of Pb with a strongly electronegative element, such as in PbF₄. With X-ray photon electrons emission, the inner passive layer formed on the Pb-Sb alloy includes certain poorly conductive zones, which lead to "electron losses." The electron losses lead to positively charged

zones, which were reflected in the spectra with highbinding-energy peaks. In other words, peaks a and b, shifted from peaks 1' and 2', correspond to the positively charged zones, that is, the nonconductive zones. Therefore, although the conductivity of the inner passive layer is higher than that of the outer layer, the substance distribution of the inner layer is not uniform. This nonuniformity will lead to the coexistence of conductive and nonconductive zones; however, this phenomenon will not be observed in the outer passive layer. In terms of the intensity of the peaks, both signals 1 and 2 increased in intensity when the sputtering time increased for the three Pb-Sb alloys. This increase means that the Pb concentration increases from the outside to the inside and, based on the previous study, Pb has a different existence formation in the passive layers. The surface Pb exists as PbSO₄, PbO₂, and PbO_x, as well as a small amount of noninteger complexoxide PbSb₂O₆. The inside Pb exists as PbO, PbO_x, and PbSb₂O₆. The PbO₂ in the outside passive layer has a comparatively higher resistance than the PbO in the inner layer, being one of the reasons for the conductivity difference in the stratification structure. Also, the alloying Sb with different concentrations can lead to a different quantity of PbO, between the two layers of passive film; it can even change its equilibrium chemical coefficient, x (1 < x < 2). Naturally, the content and properties of PbO_x itself will affect the conductivity of passive alloys.

From the results of Figure 21, as the Sb concentration increases, the thickness of its passive layer decreases, and the quantity of nonconductive zones decreases. For sample 25 with good conductivity after 30 minutes of sputtering, the Sb3d peak does not shift after overlapping with the O1s peak, but when the Sb concentration is comparatively low (1.58 wt pct Sb and 0.51 wt pct Sb), there is a big difference of conductivity between the two passive layers. The inner layer shows better conductivity than the outer layer due to the composition of the inner layer. This is reflected in the XPS spectrum as the O1ds/Sb3d peak position shifts to the left-hand side. Moreover, similar to the spectra of O1s/Sb3d (denoted in Figure 21 as peak a) in the high-binding-energy region after 30 minutes of sputtering.

According to Table XI, the difference between peak a and peak 1' in Figure 21 is 9.2 eV. Based on the discussion in Section IV-B, this is a high value compared with the shift of the binding energy due to the chemical-environment effects. It is deduced that peak a is the right-hand shift of peak 1'. Using the nonconductive peak analysis offered previously, peak a corresponds to the positively charged zones (low conductivity) of the passive film. Therefore, although the conductivity of the inner passive layer is higher than that of the outer layer, the substance distribution of the inner layer is not uniform. This nonuniformity will lead to the coexistence of conductive and nonconductive zones, but this phenomenon is not observed in the outer passive layer. This viewpoint tallies with the discussion of the Pb4f spectra. Although the passive film's inner layer has better conductivity than the surface, due to its nonuniform structure and composition, there are nonconductive regions in this layer; however, no similar effect exists in the outside layer. This is in agreement with the spectrum's experimental discussion. In terms of peak intensity, the O1s/Sb3d peaks for the different Pb-Sb alloys clearly decrease after 30 minutes of sputtering. The reason for this decrease is the effect of the passive

layers' ability to block oxygen diffusion, meaning that the oxygen concentration in the outer passive layer is higher than that in the inner one.

V. CONCLUSIONS

An XPS study of the passive film developed on Pb-Sn and Pb-Sb alloys in 4.0 M H_2SO_4 at 0.6 V vs SCE has led to the following conclusions.

- 1. The passive film formed on both the Pb-Sn and Pb-Sb alloys has a double-layer stratification structure. The inner passive layer has a different composition compared with that of the outer layer. The outer passive layer on the Pb-Sn alloys is mainly composed of SnO₂, SnO, PbSO₄, PbO_x, and PbO_xSn_{1-x}O₂, while the inner layer is mainly composed of SnO₂, SnO, PbO, PbO_x, and PbO_xSn_{1-x}O₂. The outer passive layer on the Pb-Sb alloys is mainly composed of PbO₂, PbSO₄, PbO_x, and PbSb₂O₆, while the inner layer is mainly composed of PbO, PbO_x, PbSb₂O₆, Sb₂O₄, and Sb₄O₆.
- 2. Alloying Sn and Sb improves the conductivity of the passive film by pushing the formation of PbO_x (1 < x < 2), which has a resistance lower than both $PbSO_4$ and PbO.
- 3. The conductivity of the inner passive layer on the Pb-Sn alloys is better than that of the outer layer. The tin and oxygen concentration in the passive film decreases from the outside to the inside. Also, as the content of tin in the alloys increases, its difference gradient between the two layers increases.

4. The conductivity of the inner passive layer on the Pb-Sb alloys is better than that of the outer layer. Because of the nonuniformity of the elements' distribution, there are some nonconductive zones deep inside the passive layer which are not found in the outside layer. The Pb concentration increases from the outside to the inside, but the amplitude of the increase does not vary with the different Pb-Sb alloys.

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