Practical Aspects of Charging Phenomena in XPS as Demonstrated in Oxidized-Al Films on Al and Al Alloys

D. R. Baer, C. F. Windisch Jr., M. H. Engelhard, and K. R. Zavadil[1]
Pacific Northwest National Laboratory, Richland, WA 99352, USA
[1]Sandia National Laboratoratories, Albuquerque NM, USA

(Received November 25, 2001; accepted May 8, 2002)

Understanding the surface and interface structure, composition and chemistry of insulating materials has long been of importance in surface analysis. The relevance of insulating surfaces to the environment, and the increasing use of newer and more complex oxide films in electronic and optical applications significantly increases the information needed about these materials. Through a series of examples using Al-oxide films, this paper summarizes some conceptual and practical issues related to analysis of insulators, including vacuum-level and Fermi-level referencing, charge buildup at interfaces, the use of charge neutralization, the impact of electron and ion-beam damage, and the influence of impurities on oxide properties and measurements. Many of the measurements are understood through consideration of potential variation through a specimen. Current results, along with many in the literature, demonstrate that surface charging is not a problem that can be readily solved and ignored, but is a tool providing important information about materials and films.

1. Introduction

Surface analysis of insulators. The ability of surface analysis methods to provide fundamental information about the composition and the chemical and physical structure of insulating films and materials surfaces has been an important aspect of the development of x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and other surface methods. The careful examination of the surface of catalysts was one of the initial application areas, but corrosion films, and insulating layers on electronic components have also received considerable attention. The development of new types of composite ceramics and polymers, the emerging areas of nanoscience and nanotechnology, the increasing need to understand the surface reactions that occur on environmentally important minerals and aerosols, the search for new types of electronic and optical materials, and the need to make careful analysis of insulating materials or system components are of increasing importance.

A variety of methods have been developed to enable analytical techniques that involve the use of incident and/or secondary charged particles for the analysis of surfaces to be applied to insulating materials. Some new XPS instruments, for example, provide advanced versions of charge compensation systems that facilitate getting "charge compensating electrons" to the critical location. This is particularly important for instruments with high spatial resolution and, in general, has made charge compensation much more routine and repeatable. Some of the challenges of charging in relation to high-resolution imaging have been examined by Fulghum and co-workers in a series of papers [1].

In spite of the need, importance and advances in technique, the ability to collect and interpret data from insulating materials and layers is often a challenge and, consequently, the direct or indirect subject of considerable research attention. Recent papers by Cazaux have explored some of the basic principles leading to charge buildup [2] and others have examined charging issues on specific systems (e.g., Vereecke and Rouxhet [3]). The ASTM committee E-42 on Surface Analysis has developed a guide summarizing methods of charge compensation and referencing in XPS[4], and ISO Technical Committee 201 on Surface Chemistry Subcommittee 5 is developing a standard for reporting such data.

Although methods of charge compensation and accurate data collection have improved significantly, and analysis of insulating materials is often routine and can be highly reproducible (especially for similar samples with similar levels of surface contamination), our understanding of the processes involved and the nature of spectra that can be collected from insulators indicate that there is no ideal or fundamental solution to charging and charge referencing issues. Rather, the binding energies measured from insulators and the way that a specimen builds up or dissipates charge contain information about the specimen including contamination or doping, thickness, surface and bulk conductivity and other chemical and physical properties. To a significant degree, specimen charging can be used as a tool to obtain information often not readily obtained by using surface spectroscopies in the standard manner.

Corrosion films. Because corrosion often involves the formation of insulating films, charge buildup during analysis of these oxide and corrosion films is a potential complication in such studies. A recent interest in improving the corrosion and stress corrosion behavior of Al and Al alloys in applications ranging from electronics to transportation (aircraft and lightweight automobiles) has led to many studies of oxidized Al films created by a variety of different methods. In this paper, we use oxidized-Al layers on Al substrates to demonstrate some of the challenges of charge compensation and charge referencing and to suggest how they can be used to learn more about the layers being studied. Some of the data are from our current research, but we also draw from some of the interesting work on these films already in the literature.

Although this paper does not focus on the corrosion phenomena, portions of new work associated with two corrosion-related studies are reported here. One set of work is focused on understanding the influence of alloy components and impurities on the stress corrosion cracking of lightweight Al alloys. In this work, the electrochemical, chemical and physical natures of the films that form were of interest. Materials that have been studied included Al, Al with Mg, and Al with Cu. In these studies, differences in the charging behaviors were observed, and we are beginning to examine systematically some of the electrical properties using surface charging phenomena. The second set of work seeks to understand the role of defects on passive film properties. In this case, films are formed on pure Al using an oxygen plasma, and the subsequent effect of electron beams to introduce defects was studied.

2. Experimental

The experimental conditions for the data reported here are summarized below:

Solution formed films. Oxidized Al films formed in pure water were produced using a transfer system that allows specimens to be moved from a PHI Quantum 2000 XPS system to an electrochemical cell without exposure to atmosphere [5]. Additional films were created by dipping samples in solution without use of the transfer system. The Quantum 2000 uses a hemispherical analyzer and a monochromatic Al K_α x-ray source. A patented charge compensation system is now used on the Quantum that involves both low energy electrons and low energy ions[6]. The sample can be either grounded or isolated from ground. Data has been collected with and without use of the flood gun and with the sample grounded and isolated from ground.

Plasma formed films. Plasma formed ultra-thin (30 – 50 Å) Al_2O_3 films on Al surfaces serve as reproducible, controlled mimics of passive oxide films on Al for corrosion studies. Electron irradiation is used to generate oxygen vacancies through electron stimulated desorption of oxygen. Irradiation was conducted with a Kimball Physics ELG-1108 gun (high output BaO cathode) and power supply. The spectroscopic data reported here was generated from 4.5-nm thick films. These films exhibit a self-limiting thickness, are amorphous, low density (1.98 g cm^{-3}), and stoichiometric[7]. They were cleaned in UV-generated O_3 prior to vacuum loading to remove contaminant carbon.

Two types of electron irradiation were used to introduce oxygen vacancies. Three hundred eV electrons directed normal to the surface produced defects that are within the oxide with apparent accumulation at the oxide-metal interface. Eighty eV electrons incident at an angle of 65° from the normal were used, in the presence of Cl, to generate defects at the oxide-vacuum interface. Fluence is determined by measuring the beam current on a biased electrode. A uniform beam of 13-mm diameter is formed and aligned on a phosphor. The imaged area in the XPS experiment is slightly larger than a 4-mm diameter spot in the center of this irradiation zone. These data were collected in a VG Hemispherical-based system using non-monochromatic Mg K_α x-rays.

3. Fundamental Observations about Charging and Insulators

Some important characteristics and issues related to making XPS measurements are listed here. Unless otherwise referenced, they are included in ref [2]:

- There is a significant difference between XPS measurements of conducting and non-conducting materials. It is well known that, for metals electrically connected to the spectrometer, the work function of the sample does not influence the measurements. Therefore, when Fermi levels are aligned, the binding energies of metallic specimens can be accurately defined and reproducibly measured. However, measurements on good insulators do not involve **Fermi-level** alignment, but are associated with the **vacuum level** at the specimen surface. In this case, the work function of the sample, the spectrometer and, where used, the electron neutralizer filament impact the measured binding energies. Although this is well represented in the literature, there are many consequences of this that are not always appreciated [8]. Furthermore, there are conditions where the specimen is resistive enough to influence measurements, but conductive enough to cause some confusion in both measurement collection and data analysis.
- Complex materials can set up differential charging in several ways including: differences in photoelectron yield, film or sample thickness, resistivity, charge trapping, contact variations [2]. As noted by Thomas, thin insulating layers may require special consideration [9].
- Charging is a 3D phenomenon – not just a surface phenomenon. Since x-rays penetrate microns into the material, photoelectrons are created within this depth, and charge build up can occur throughout this region, particularly at interfaces. In addition, variation of sample properties and x-ray flux along the surface cause variations in charge build up and retention [1].
- Charging can be expected for any insulator with conductivity less than $10^{-10}\ \Omega^{-1}\ m^{-1}$. Materials do not have to be great conductors to minimize charge buildup, but for low-conductivity materials or for materials with mixed conductivity (high and low), local charge accumulation and non-uniform potentials are likely. [2]
- The same processes involved in the charge buildup and transport in insulators can also lead to changes in composition and structure generally thought of as damage [2]. Although important, particularly for thin corrosion layers and passive films, these processes are not discussed in this paper. The overview of electron damage processes by Pantano and collaborators [10] provides a listing of the sensitivity of different materials to electron-beam damage. Both primary electrons incident on the surface and secondary electrons produced in the specimen being analyzed by incident particles or photons can have a significant impact on the damage behavior.
- For insulators, as well as semiconductors, **charge localization** can occur (particularly at defect sites and interfaces) and the fields created influence electron potentials. This is part of band bending for semiconductors and should be expected for insulating materials.
- Charge localization can be maintained during XPS analysis and is often an **intrinsic** property of the sample. Creative application of XPS and charge compensation methods can provide information about these properties.
- The measured binding energies of insulators are a mix of **intrinsic effects** (chemistry and charge localization) and the physics dependent effects of the x-rays and

secondary electrons (**extrinsic effects**) on overall properties of the sample. Therefore, for most insulating materials, there is no unique binding energy. (However, it is useful to add that in many circumstances similar specimens prepared in similar ways and analyzed in the same instrument can be reliably measured with good relative BEs.)

The establishment of non-uniform electric potentials along a specimen surface or in the depth of the sample causes peak shifting, peak broadening and often a loss of signal intensity. Therefore, the primary objective of the analyst collecting data is to establish a **uniform and stable potential** in the sample. Although this is often done with an electron flood gun, there are a variety of other methods that can be used sometimes as summarized in [4 and 9]. Once the stable conditions are established and the data collected, the second challenge when attempting to extract binding energy information involves determining an **energy reference**. With many modern instruments, establishing a uniform potential is less of a challenge than finding an accurate and useful **energy reference**.

4. Oxidized-Al Films

The oxide films formed on Al provide several examples of the difficulty of establishing a single energy reference for oxides, particularly films. A starting point for our understanding of much of the film data evolves from an analysis by Sambe and Ramaker [11]. They discuss the nature of an electrical double layer at the $Al\text{-}Al_2O_3$ interface and the impact on XPS measurements in different conditions, and point out the importance of a uniform shift in potential across a dipole layer formed at the metal-oxide interface. The impacts of such potential shifts were also used to explain thin-film observations in $Si\text{-}SiO_2$ by Baer and co workers [12]. For an ideally conducting system, the potential would be uniform, case Fig. 1a. The existence of charge double layers at the oxide-metal interface would cause a uniform shift in the energy levels of the oxide relative to that of the metal, case Fig 1b. A surface charge buildup or a contamination layer can also form a double layer and a potential shift. If, in addition to the interface dipoles, an electric field is established across the film by application of a flood gun at some potential relative to the grounded metal, a field may be established across the "insulating" film as shown in Fig. 1c. The potential diagram (a) will apply for metals or highly conducting systems. Diagrams (b) and (c) will apply for specimens sufficiently insulating to allow charge localization and the formation of dipole layers (assisted in some cases by image charges from the conducting metal substrate).

The difference between conditions (b) and (c) is the existence of a single potential applied to the sample or the application of two potentials, one due to contact of the metal substrate to ground (or any other potential) and the second associated with a potential of the electrons from the flood gun. The application of two potentials across a thin insulating film will create a potential gradient through the film and broaden and shift the peaks from the film.

This two-potential behavior [Fig.1c] is demonstrated in Fig. 2a for a film formed in water.

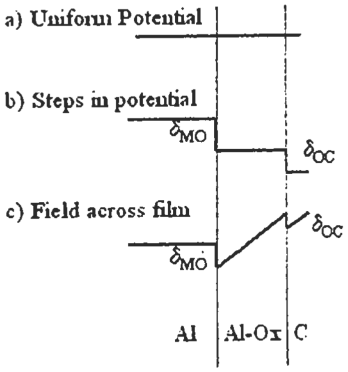

Fig. 1. Schematic drawings of potentials across an aluminum (Al)-oxidized aluminum (Al-Ox) and contamination layers (C): (a) Ideal uniform potential; (b) potential with dipole steps at metal-oxide and oxide-contaminant (or oxide-vacuum) interfaces; (c) potential with dipole steps and an electric field established between metal substrate and sample surface.

The oxidized Al 2p photoelectron peak at ≈ 75.5

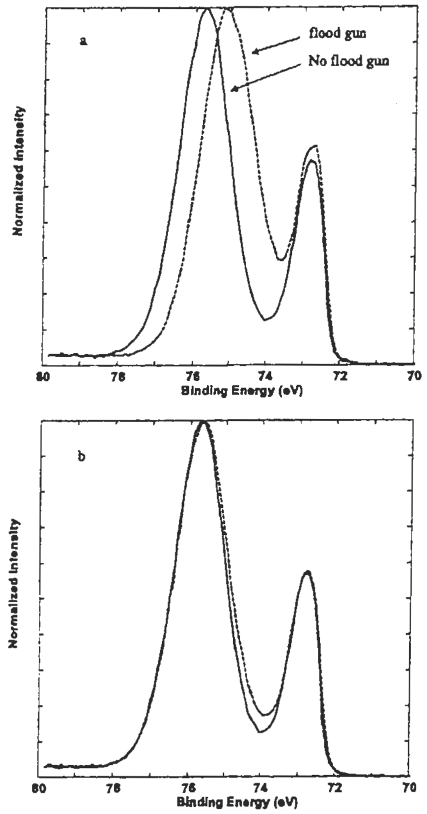

Fig. 2 a) Al 2p photoelectron peak for grounded film formed in water, with and without use of the electron food gun. b) Al 2p photoelectron peak for same film after 15 second Ar sputter, with and without use of flood gun.

eV for the grounded sample without application of the flood gun was shifted to about ≈ 74.9 eV and broadened when the flood gun was applied. Note that the metal peak at ≈ 73 eV does not shift. In contrast, after a very short sputter, the film is highly damaged and sufficiently conducting so that application of the flood gun electrons does not cause a shift in the potential of the oxide layer [Fig. 2b]. Although a highly conducting film with no charge buildup at the interface [Fig. 1a] is possible, some interface charge often remains at the surface [Fig. 1b] which is the condition we suspect in Fig. 2b. Observations of potential gradients across thin, oxidized Al films has been examined previously [13,14], and the difficulties of both grounding a substrate and neutralizing the film have been noted along with the suggestion that it may be useful to isolate such specimens from ground and treat them as pure insulators [15].

The application of flood gun electrons to the film on a grounded substrate can become a tool for examining properties of the films [16]. Work by Bart and co-workers [17] has shown that surface and bulk conductivity of different insulators can change the extent to which the flood gun can control surface potential. In our corrosion work, we are particularly interested in examining the impact of Cu on the properties of the film. For truly insulating films, the position of the oxidized photoelectron peak should shift as the potential of the flood gun is varied. We have conducted limited tests on this by changing the voltage of the flood gun from 2.2 to 3.2 V. We find that the peak shift correlates with the thickness of the oxide with higher content Cu films tending to form the thicker surface oxides [Fig. 3]. These results are consistent with minimal variation in film resistivity indicating, in particular, that the presence of Cu does not significantly increase the electrical conductivity of the film.

The examples so far have focused on effects of low voltage potentials applied by an electron flood gun. It is also possible to impact sample potential by creating defects and charge inside in a sample. It is actually possible to create shifts of the oxidized Al peaks in opposite directions as shown in Fig. 4. In this circumstance, higher energy electrons that will penetrate the oxide shift the peak in one direction, possibly by changing the dipole at the oxide-metal interface, while lower energy electrons at a glancing angle

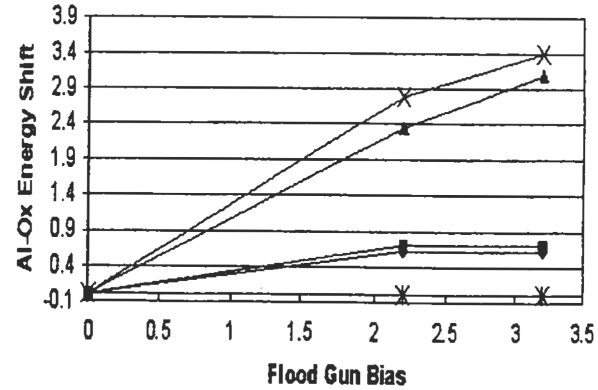

Fig. 3. Influence of the voltage of the flood gun filament on the measured Binding Energy of the oxidized Al 2p photoelectron peaks for oxides formed in water on different alloys. There are significant differences between the lack of variation for the sputtered film (※), a smaller shift for the thin films formed on pure Al (▼) and an Al 1%Cu alloy (■), and larger shifts for the slightly thicker oxides formed on Al 2% Cu (▲) and Al 4% Cu (X) alloys.

that enhance Cl sorption on the surface shift the peak in the opposite direction by changing the oxide-contaminant dipole. This data was collected with the specimen grounded and without flood gun application [Fig 1b].

The variations in the BE shifts produced by electron irradiation as a function of dose are shown in Figure 5. The shifts vary in two directions. Although the actual processes in the film may be complex, the overall impact of the 300 eV electrons was to increase the oxidized-Al BE. It is expected that the 300 eV electrons will create oxygen vacancies and leave electrons within the film. For many insulating materials, a high secondary electron yield near the surface leaves the surface positively charged while the subsurface builds up a negative charge [10]. However, the actual distribution depends on the secondary electron emission and the surface can sometimes be negatively charged. Fields built up within the film can also cause charge migration that result in charge accumulation at the substrate-oxide or oxide-surface interface. The observed shift in the BE is consistent with the stabilization of some of the positive charge at the metal-oxide interface effectively increasing the dipole δ_{MO} in Fig. 1b, consistent with the sign in ref. 11. As in the discussion above, a field gradient in the film should increase the observed line width, which is not observed in this measurement. This is also consistent with a change in the dipole layer at the metal-oxide interface. However, changes in BE could also be influenced by changes in the electronic structure of the damaged oxide due to the presence of the defects introduced into the band gap. Such defects may make the oxide more conductive and allow it to behave more like the sputter-damaged film in Fig. 2b. (After the 300 eV damage, the energy separation between the metal and oxide peak is approximately 3 eV, as observed for the sputter-damaged film.) At this point, we cannot definitively identify the cause of the BE shift.

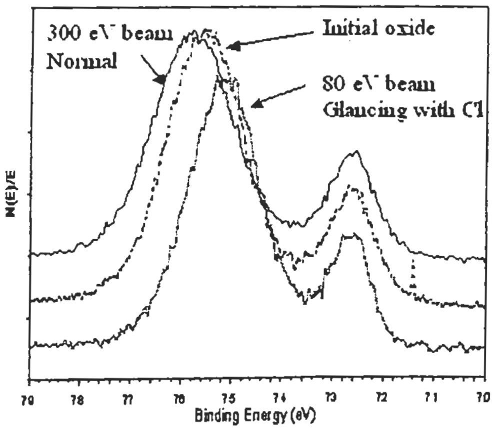

Fig. 4 Shifts in oxidized Al photoelectron peak due to incident electrons and surface adsorbates on plasma formed films.

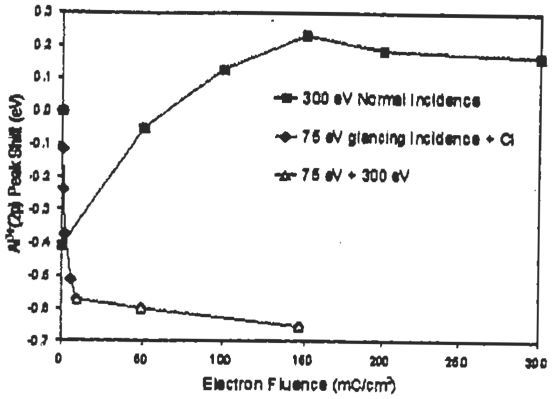

Fig 5. Oxidized Al peak shifts as a function of electron beam dose. The 300 eV irradiation increases the BE at high doses. The 75 eV glancing electron irradiation in the presence of Cl causes a decrease in BE. Adding 300 eV irradiation to the surface exposed to 75 eV electrons and Cl does not cause the BE to increase.

The sample as placed in the vacuum chamber had, by definition, a peak shift of 0.0. Low energy (50 eV) electrons were used to further clean this specimen, initially dropping the BE significantly below the initial value. We believe that this low voltage cleaning decreased the surface dipole δ_{OC} by trapping electron charge near the surface. The application of the 300 eV electrons eventually increased the BE to the initial value and higher for doses above 100 mC/cm^2.

A surface dipole can be produced by adsorbing Cl on the surface, most likely at surface defects generated by the electrons. This effect is shown in Figure 5, where a film is irradiated with 75 eV electrons at a glancing angle in the presence of atomic Cl. The BE of the oxidized-Al photoelectron peak decreases as a function of fluence from 0 to 10 mC/cm^{-2}, while the surface Cl concentration was found to increase (not shown). A maximum shift of -0.5 eV was measured. A similar effect is observed with the adsorption and electron-induced reduction of hydrocarbon contaminants. This surface dipole dominates the photoelectron peak energy as shown by subsequent irradiation of the surface at 300 eV and normal incidence in the presence of Cl°. As shown above, without the presence of the Cl, the 300 eV electrons were capable of eliminating the trapped surface charge effect of lower energy (50 eV) irradiation used to clean the surface. The data of Figure 5 shows that the energy shift remains and continues to decrease when the surface Cl (or C) is present. The surface dipole model (or surface charge transfer model) can be further tested by examining whether an electropositive species is capable of increasing the photoelectron peak energy. Work by Rodriguez and Hrbek [18] indeed confirms this as Cs was found to shift the oxidized-Al peak to the positive direction. These two sets of experiments demonstrate that the near surface and outer surface can each influence the measured BEs and they can be in opposite directions.

The effects described above are static in the sense that they are due to charge or damage sites in the films. In addition to these static-charging effects, there are transient effects associated with fields produced by ions formed during the photoelectric process and the ability of image charges to lower the BEs for very thin insulating oxide films on conducting substrates. The effects of the image charges vary with the film thickness and thus appear as variations of oxide Be as a function of thickness. Such effects were described by Wu et al. [19] for the Al-Al oxide system and theoretically examined for MgO by S. Altieri et al. [20]. These BE shifts are not present for more complex polarizable oxides where local charges created by the photoelectric process are more effectively screened [21].

5. Summary

Although most topics and issues related to specimen charging have been considered and there is little that is truly new, there are a wide variety of different consequences and new applications that will present unfamiliar challenges to many researchers. Although there is no ideal "solution" to charge compensation and referencing issues, it is possible to collect highly useful data, and, in many circumstances, creative application of charge control methods can provide an increased range of information about the materials of interest. The most general rule seems to be to minimize line width and enhance count rate while collecting the data and worry about referencing during the analysis. It is important to realize that surface contamination, film thickness and vacuum conditions can influence the extent of charging effects and that the Auger parameter and possibly valence band data can provide useful chemical state information that is somewhat immune from surface potential shift effects. Many of the examples in this paper focused on issues related to the special case of thin (sometimes) insulating films on conducting substrates where charge referencing can be challenging and considerable thought should be applied to modes of data collection.

Acknowledgements

This work was supported by the U.S. Department of Energy. Part of the work was conducted as part of the Center for Synthesis and Processing (CSP) program of the Division of Materials Sciences. Portions of the work were conducted in the William R. Wiley Environmental Molecular Sciences Laboratory, a national user facility operated for the DOE Office Biological and Environmental Research by the Battelle Memorial Institute.

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