frequency bands (below 1300 cm^{-1}) all remained (Figure 3c), implying a stronger interaction between this material and the Si. The formation of silicate type species in the high-temperature oxidative environment during deposition would account for the adherent species. Indeed, the infrared spectrum of Zn_2SiO_4 published in the Sadtler handbook[30] is very similar to the low-energy infrared profile observed from our films deposited on Si substrates. Considering that a myriad of $Si_xO_y^{n-}$ species exhibit a series of infrared bands[30] below 1200 cm^{-1}, it seems reasonable to attribute the low-frequency bands of the films on Si to silicate species. This might also account for the shifts in frequency observed for these bands under different deposition conditions. Different experimental conditions could give rise to slightly different $Si_xO_y^{n-}$ species. Moreover, this would be consistent with a mechanism whereby an original silicate-type species is formed during the initial stages of deposition. Subsequently, purely physisorbed thallium species, including Tl_2O_3 (which has no bands in the mid-infrared) and Tl_2CO_3, are deposited over this silicate layer. X-ray diffraction analysis of the swabbed substrates revealed no distinguishable peaks, indicating that the remaining films were amorphous.

Results from an XPS analysis of a film grown on Si using Tl(acac) (Table II) supported the hypothesis that physisorbed Tl_2O_3 and Tl_2CO_3 were deposited over an initial thallium silicate layer. A spectrum of the as-deposited film was similar to that grown on MgO, which suggested the presence of both oxide and carbonate on the surface as discussed above. The spectrum of the swabbed sample contained significant differences from that of the as-deposited material. First, the high-energy C peak attributed to the carbonate species was not present; this was consistent with the infrared data showing the removal of bands in the 1300–1400-cm^{-1} range by swabbing. Second, the spectrum of the swabbed sample contained a Si peak at a binding energy consistent with oxidized Si.[31] This was also in agreement with infrared data indicating the formation of a silicate from the interaction of the film and substrate. The absence of Si in the spectrum of the as-deposited sample could have been the result of its being covered by a subsequent layer as suggested above or the relatively low sensitivity of Si in the X-ray photoelectron spectrum. For the swabbed sample, the absence of the low-energy O(1s) peak indicated that the surface region was not similar to that of Tl_2O_3.

Depositions on Other Substrates. Depositions were carried out on other substrates in attempts to produce continuous films at lower quantities of deposited material. On Al_2O_3 at 450 °C, CpTl gave a film whose appearance and X-ray pattern were similar to those of material deposited on MgO. On a buffer layer of $SrCO_3$ deposited on MgO, CpTl also gave a discontinuous black film whose strongest peaks in the X-ray pattern were found at 2θ = 34.00° (d = 2.634 Å) and 29.36° (3.039 Å).

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Registry No. Tl_2O_3, 1314-32-5; thallium acetylacetonate, 14219-90-0; dimethylthallium acetylacetonate, 15350-61-5; cyclopentadienylthallium, 34822-90-7.

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Surface Characterization Study of InP(100) Substrates Using ISS, AES, and ESCA. 3. Experimental Artifacts

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A surface characterization study has been performed on InP(100) substrates. Both solvent-cleaned, native oxides and sputter-cleaned InP have been examined by using multiple surface characterization techniques including ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), and electron spectroscopy for chemical analysis (ESCA). The data obtained indicate that the results may be difficult to interpret due to experimental artifacts including compositional alteration by ion sputtering and electron stimulated desorption (ESD) and chemical state alteration. This combination of techniques is powerful because ISS, AES, and ESCA probe varying depths beneath the surface. When used carefully, these techniques yield a nondestructive depth profile of the near-surface region of the sample.

Introduction

Ultrahigh-vacuum (UHV) surface analytical techniques have grown in popularity and use in the past 20 years. Today, it is fairly common for an analytical laboratory to have a stand-alone, computer-interfaced Auger electron spectroscopy (AES) or electron spectroscopy for chemical analysis (ESCA or XPS) system. Other UHV surface analytical techniques including secondary ion mass spectrometry (SIMS), ultraviolet photoelectron spectroscopy (UPS), scanning Auger microscopy (SAM), scanning electron microscopy (SEM), and electron dispersive X-ray analysis (EDX), ion scattering spectroscopy (ISS), etc., are also being used more extensively. Although the development of the field of surface science is still in its early stages, the power of these techniques has been demonstrated and is generally accepted. Unfortunately, a belief has developed that the sample is inserted, an automated analysis is performed, and the concentration or other desired information is read off a computer screen or an X–Y plot. The goal of this paper is to describe some of the experi-

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mental and interpretational problems encountered in using UHV analytical techniques for analyzing surfaces of III–V compounds.

InP is a direct-bandgap, high-mobility III–V semiconducting material used for optoelectronic and high-speed electronic devices.[1] The substrates are of interest because quality devices require epitaxially grown films of high-purity, low-defect concentration and precise thickness.[2] Ideally, growth of these films requires a substrate that is atomically ordered and clean. During the investigation of native oxides on InP substrates using ISS, AES, and ESCA,[3-5] a number of experimental difficulties due to sample perturbation by the primary beams were encountered. Since these difficulties affect the analytical results and most likely apply in surface studies of other group III–V materials, it is important that these experimental artifacts and their effects are recognized.

Hollinger et al.[6] showed that $In(OH)_3$ is decomposed to In_2O_3 under an ion beam while $InPO_4$ and In_2O_3 are not decomposed. Consequently, they concluded that depth profilling by ion sputtering is not an appropriate method for studying oxide layers at InP surfaces and used chemical etching in a following study.[7] Clark et al.[8] observed significant changes in the P 2p line shape during ion bombardment of thick oxide layers that they ascribed to changes in the oxidation state of phosphate by the ion sputtering. More recently, Thurgate and Erickson[9] found that the InP substrate is damaged at very low ion doses and eventually decomposed by an ion beam. Nevertheless, they believe that ion milling coupled with ESCA and careful curve fitting can be used to determine the nature of thin oxide layers on InP. Lau et al.[10] carried out a photoemission study of sputter-etched InP surfaces and found that sputtering with Ar^+ at 1–3 keV and low current density results in an In-rich surface. This study is in agreement with studies by Wada[11] and Tu and Schlier.[12] However, Achard et al.[13] claim that removing contamination layers from InP(100) surfaces with low-energy (250–400 eV) Ar^+ does not cause significant chemical damage to the InP surface. Alterations by electron beams have also been observed by Soonckindt et al.[14] Generally, the amount of primary beam-induced damage depends strongly upon the initial state of the surface and numerous experimental parameters.

Experimental Section

Sulfur-doped, n-type InP substrates with a carrier concentration of 8×10^{18} cm^{-3} oriented 2° off (100) toward (110) were used in this investigation. Substrates were obtained from Sumitomo Industries, Ltd., and CrystaComm, Inc. Before analysis they were ultrasonically solvent cleaned in toluene, acetone, trichloroethylene, acetone, and methanol (in that order).

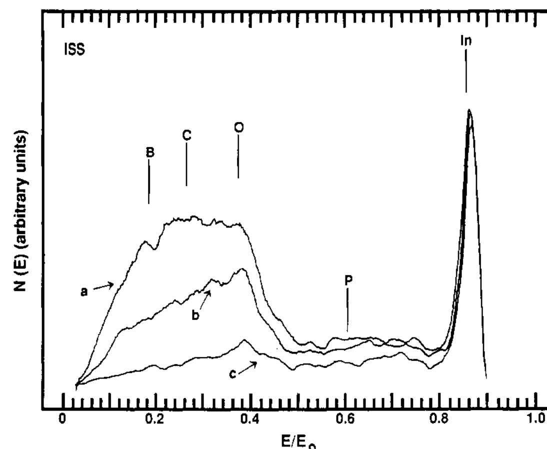

Figure 1. ISS spectra taken from the native oxide on InP(100) after 3-min sputtering periods using the same sputtering conditions as those used to take the ISS data.

ESCA, AES, and ISS were performed using a double-pass cylindrical mirror analyzer (CMA, PHI Model 25-270 AR) contained in a vacuum system with a base pressure below 2×10^{-10} Torr. ESCA data were taken in the retarding mode with a pass energy of 25 eV by using Mg $K\alpha$ X-rays (PHI Model 04-151 X-ray source) and a computer-interfaced, digital pulse counting circuit[15] and digital filtering techniques.[16] AES data were taken by operating the CMA in the nonretarding mode with a 0.5-V_{pp}, 5-kHz oscillation applied to the outer cylinder. A 10-μA primary-beam current was focused to a spot approximately 0.5 mm in diameter. ISS was carried out in the nonretarding mode using a defocused primary beam of high-purity 1-keV ^4He ions (100 nA over an area 1 cm in diameter) and a scattering angle of 137 ± 6°. An ISS spectrum required 90 s for data collection, and the ion beam was turned off between runs. For ESCA, AES, and ISS, the CMA outer cylinder voltage, which is proportional to the energy of the detected particles, was generated by a Model 2701C Valhalla Scientific precision dc voltage reference. This voltage was monitored by a Hewlett-Packard digital voltmeter, Model 3465A. The DVM measured voltage agreed with the Valhalla set voltage within 0.01 V at all times, and the power supply was found to have less than 0.01-V variance for a given set point over a 24-h period, which is near the stability limit of the voltmeter. Annealing was performed by heating the back of the stainless steel sample holder with a filament located approximately 0.5 cm from the holder. The substrate temperature was determined by using an optical pyrometer (Thermalert I.R. Thermometer, Model SL300AC). Sputtering was done with 3-keV $^{40}Ar^+$ ions (100 nA over an area 1 cm in diameter).

Results and Discussion

Figure 1 shows three ISS spectra taken successively from a solvent-cleaned InP substrate. In ISS noble-gas ions of low molecular weight and moderate kinetic energy (0.5–2 keV) are scattered off a solid surface. Due to the chemical inertness of noble-gas ions, peaks in the spectra are due to ions scattered elastically off surface atoms. Therefore, the simultaneous solution of the energy balance and momentum balance generates a functional relationship between mass of the surface atom and the energy of the elastically rebounding ion at a selected scattering angle.[17,18]

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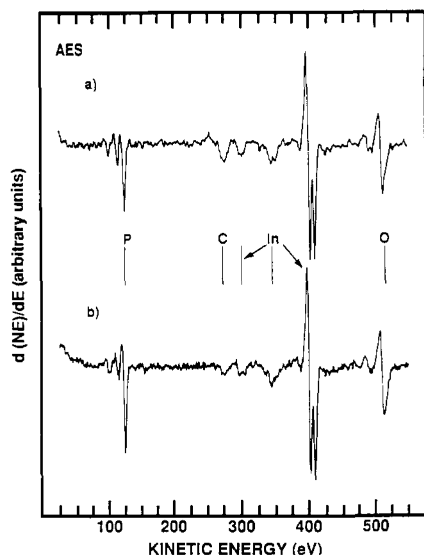

Figure 2. Auger spectra taken from the native oxide on InP(100) (a) before and (b) after ion sputtering for 6 min using $^4He^+$ and the same conditions used to collect ISS data.

This technique is highly surface sensitive, yielding compositional information about the outermost atomic layer since ions that penetrate beneath the surface have a high probability of being neutralized or scattered inelastically. Used in conjunction with other techniques of varying depth sensitivity, such as AES and ESCA, depth profiling information may be obtained. Even though ISS provides unique and important information about a surface, it has not been used as extensively as AES or ESCA in characterization studies of semiconductor materials.

Each spectrum in Figure 1 contains four peaks due to C, O, P and In appearing at E/E_0 = 0.23, 0.39, 0.60, and 0.89, respectively. Semiquantitative compositional information can be obtained from ISS spectra based on relative peak heights or peak areas.[17] The relative ISS cross sections of these elements increase significantly as mass increases. This point is demonstrated in a recent calibration study performed on the same system used in this InP study, which determined an O/Ag cross section ratio of approximately 0.045.[19] This value should be considered as only approximate since neutralization effects may vary from one type of sample to another. Considering the fact that In is about 8 amu more massive than Ag, the O/In cross section ratio would be slightly smaller than 0.045. Also, the cross section of C is slightly less than the cross section of O, and the P cross section lies between those of O and In. On the basis of these facts, small changes in the peak heights of light elements represent a significant change in the composition of the outermost atomic layer.

The ISS spectra shown in Figure 1 have all been normalized on the basis of the height of the In peak. Spectrum a contains a broad peak due to B, C, N, and O, a very small P peak, a shoulder due to F and a large In peak. Spectra b and c were taken after sputtering the sample for 3-min intervals using the same conditions as those used to collect the ISS data. As discussed below, a portion of the native oxide layer including the contaminating species are removed quite rapidly during these fairly short sputtering periods. These data demonstrate that ISS spectra should be taken with the minimum beam fluence required to give a reasonable signal-to-noise ratio and that the sample should not be exposed to ion beam except during the data collection periods.

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Figure 2a,b shows Auger spectra taken before and after the ISS spectra shown in Figure 1a,b were taken. The substrate was exposed to the ion flux for approximately 6 min before the Auger spectrum shown in Figure 2b was taken. The ISS results in Figure 1 demonstrate that sputtering occurs at a significant rate at these surfaces. In agreement with the ISS data, the Auger data show a large decrease in the C signal. The AES O peak height does not change significantly with the sputtering treatment used. This fact appears to be at variance with the ISS results, which yield a large decrease in the O signal with the sputtering treatment. The apparent discrepancy is resolved by considering the fact that AES probes much more deeply than ISS. During ISS, the outermost few atomic layers are sputtered away, and O sputters away preferentially to the In. Therefore, the sputtered native oxide surface yields small C and O peaks and a comparatively large In peak in ISS. Since C is removed from the outermost few layers, it does not appear in the Auger spectra after sputtering. Although ion sputtering depletes the O in the outermost atomic layer, AES probes much more deeply and detects the subsurface O remaining in the native oxide that was not sputtered away. In fact, the fractional monolayer of O that was preferentially sputtered away is such a small amount compared to the total detected by AES that its absence does not influence the AES O-to-In peak-height ratio.

Interesting changes also occur with regard to the AES P peak during sputtering. Firstly, the P-to-In peak-height ratio increases with sputtering. This is primarily due to the removal of C- and O-rich layers, which exposes the more P-rich subsurface layers.[4] Second, very significant changes occur in the AES P peak shape. The P peak obtained from the surface before sputtering is characteristic of those obtained from a mixture of phosphates, biphosphates, and phosphide. The P AES peak shape changes considerably with chemical state. The P peak obtained from phosphates does not rise very much above the baseline, whereas it does for P bonded as InP.[20] Therefore, sputtering the native oxide surface causes the Auger P peak shape to become more phosphide like as more InP is detected in the Auger signal due to removal of the outermost surface layers. This peak-shape change introduces another problem with regard to quantification of the Auger data. It is preferable to use methods based on peak areas[21] rather than standard methods based on peak-to-peak heights[20] for semiquantitative estimation of the near-surface composition.

Alterations of surfaces can also occur while collecting Auger spectra by electron stimulated desorption (ESD).[22] This point is illustrated by the Auger spectra shown in Figure 3a,b, which were taken before and after exposure of a solvent-cleaned InP surface to the electron beam for 10 min under the same conditions used to collect Auger data. Spectrum a contains peaks due to O, In, P, C, and Cl. Cl is a common contaminant on solvent-cleaned InP surfaces, and C usually accumulates on air-exposed surfaces due to adsorption of hydrocarbon species. During electron beam exposure, significant changes occur. The Cl peak is reduced to about one-fourth of its original height, and the C peak height is reduced by about 20%. It appears that changes have also occurred in both the P peak shape and height, but more specific statements

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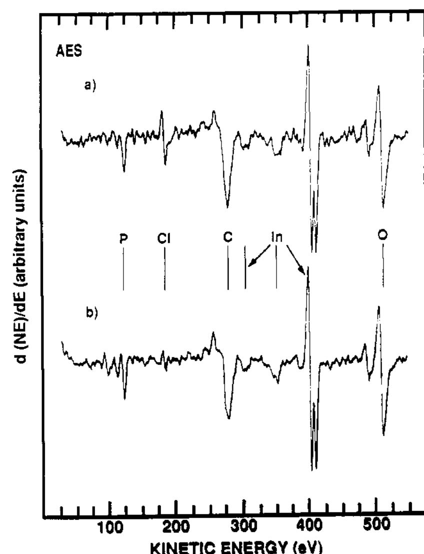

Figure 3. Auger spectra taken from a chemically etched InP surface (a) before and (b) after exposure to the electron beam for 10 min under the same conditions used to collect Auger spectra.

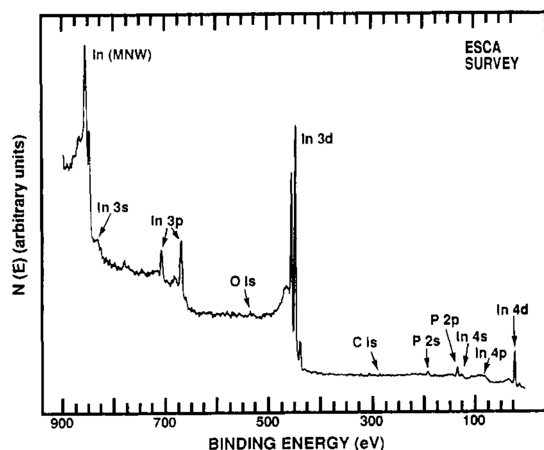

Figure 4. Survey ESCA spectrum taken from the sputter-cleaned and annealed InP(100) surface.

cannot be made in this case due to the low S/N ratio. Soonckindt et al.[14] have also observed changes in Auger peak shapes and positions with exposure of III–V surfaces to an electron beam.

ESCA is generally considered to be less destructive than AES or ISS because the X-ray flux is low, a small fraction of the X-rays interact with the near-surface region, and the nature of the interaction usually is less destructive than sputtering or ESD. However, as shown by the following example, problems can occur in performing ESCA on semiinsulating III–V materials that complicate data analysis and interpretation. This study was performed on the InP substrate after removal of contaminants by multiple cycles of sputter etching and annealing at 400 °C. A survey ESCA spectrum, an Auger spectrum, and an ISS spectrum taken from the cleaned substrate are shown in Figures 4–6, respectively. Peaks due only to In and P appear in these spectra.

After collection of a high-resolution ESCA spectrum, the first step in interpretation is adjusting the binding energy scale by a correction factor to account for the work function difference between the sample and the detector material and any charging effects. The magnitude of this correction is usually determined by selecting a surface species for which the binding energy is assumed to be known as the reference. Adventitious C is often used, but this may be

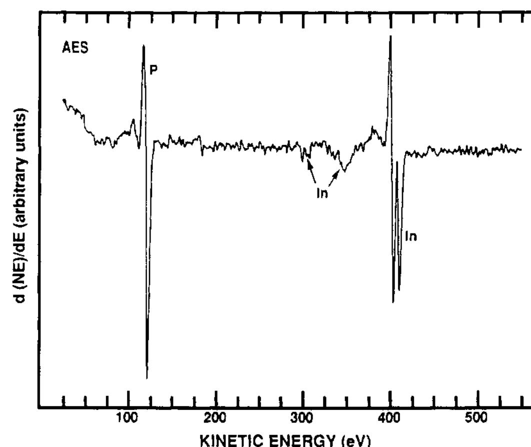

Figure 5. Auger spectrum taken from the sputter-cleaned and annealed InP(100) surface.

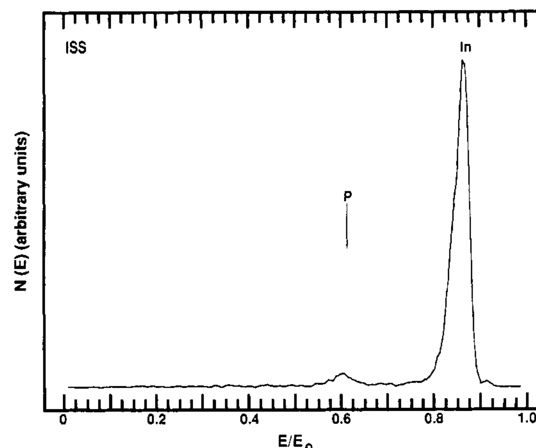

Figure 6. ISS spectrum taken from the sputter-cleaned and annealed InP(100) surface.

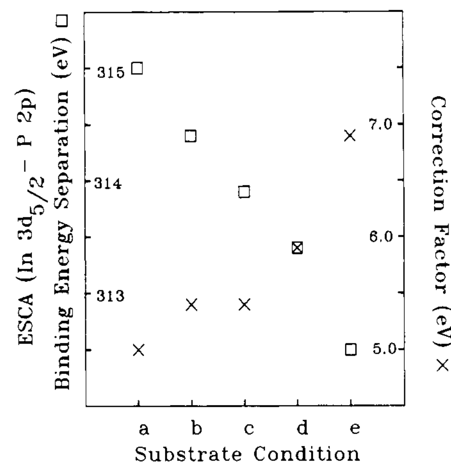

Figure 7. ESCA (In $3d_{5/2}$ − P 2p) binding energy difference (□) and correction factor (×) obtained after various sample treatments: (a) sputtered, annealed at 400 °C, and sputtered again; (b) annealed and exposed to X-rays for $^1/_2$ h; (c) exposed to X-rays for another 1/2 h; (d) exposed to X-rays for an additional 8 h, sputtered 2.5 h, annealed for 8 h; (e) exposed to X-ray for another 1/2 h.

a poor choice because its chemical state usually is not well defined or known. For the cleaned InP surface, either In or P must be chosen as the reference. The ESCA binding energy of the In $3d_{5/2}$ feature in InP is 444.5[3,23,24] and 443.8

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Table I. Treatments Performed on InP(100) Surface before Taking ESCA Data Shown in Figure 7

substrate condition	pretreatment
a	sputter, anneal 400 °C, sputter
b	anneal 400 °C, $^1/_2$-h X-ray exposure
c	$^1/_2$-h X-ray exposure
d	8-h exposure, sputter 2.5 h, anneal 8 h
e	$^1/_2$-h X-ray exposure

eV for In metal, and the P 2p feature in InP has a binding energy of 128.9 and 129.6 eV for elemental P.

Figure 7 shows the correction factor (×) required to move the In $3d_{5/2}$ binding energy to that of InP (444.5 eV) and the difference between the In $3d_{5/2}$ and P 2p binding energies (□) after the various sample treatments specified in Table I. Generally, the difference in binding energies between the In $3d_{5/2}$ and P 2p levels (□) decreases and the correction factor (×) increases as the X-ray exposure increases. If the X-rays do not alter the surface in some manner, then neither of these parameters would change with X-ray exposure. Furthermore, the magnitude of the change is so large that chemical state information cannot be extracted from the ESCA spectra.

Two possible explanations of the behavior shown in Figure 7 are that the X-rays are inducing a change in chemical state and/or charging or differential charging is occurring. Simple charging would just shift both the In and P peaks by the same amount. One possible reaction that might be induced by X-rays is the decompositions of InP to metallic In and elemental P. If the reactions were complete in the near-surface region, then (□) would decrease by 1.4 eV, which is considerably smaller than the observed decrease of 2.5 eV. However, this difference could be due to charging or differential charging of an insulating elemental P phase. The P 2p peak shape does change in progressing from a to e, and the change apparently is not reversible by sputtering or annealing treatments. These facts are consistent with the suggestion that an X-ray-induced chemical reaction occurs, but further effort will be required to understand this experimental artifact, which may be an important factor in numerous ESCA studies of InP surfaces.

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Summary

ISS, ESCA, and AES are important techniques for the characterization of III–V semiconductor surfaces and have been used in a large number of studies. However, the application of these techniques induces changes in these surfaces, and it is important for this fact to be recognized. This study illustrates the types of changes that occur and the extent of these changes during analysis of different types of InP surfaces including the native oxide and sputter cleaned and annealed surfaces. ISS removes the outermost surface layers by ion sputtering. Therefore, it is important to use a defocused primary ion beam and the minimum total dose to obtain a reasonable S/N ratio. AES results in alteration of the composition of the near-surface region through the ESD process. Similar to ISS, it is preferable to use a defocused electron beam or raster a focused electron beam and minimize beam exposure. The ESCA peak shifts, and possible X-ray induced reaction was not expected and is not well understood. Further experiments need to be performed in order to understand this phenomenon that affects interpretation of the ESCA data.

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