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Abstract
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Keywords
electrodes, impurities, segregation, aluminum, surface phenomena, etching, Auger electron spectroscopy

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Development of Surface Impurity Segregation during Dissolution of Aluminum

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ABSTRACT

Caucustic dissolution, when used as a pretreatment for etching of aluminum in chloride solutions, is observed to increase the rate of pit nucleation. Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy were used to measure the composition in the near-surface region of 99.99% purity aluminum after dissolution in 1 N NaOH at room temperature. During dissolution, concentrations of impurities such as Fe, Cu, and Ga were found to accumulate continuously within a layer less than about 10 nm thick adjacent to the surface, because they dissolved more slowly than did aluminum. Impurity concentrations on the order of 1 atom percent (a/o) in this layer, much higher than equilibrium values, were found after 40 min dissolution. It is argued that the large impurity concentrations are consistent with a highly defective region in the metal near the metal/oxide interface, which has been detected using positron annihilation measurements. Dissolution produced a scalloped surface topography with typically 30 nm high ridges separated by 130 nm. A simulation of BBS measurements based on scattering from spherical particles was developed to test for the possibility of preferential impurity segregation to ridges. No such segregation was detected, supporting this is not the reason for the strong tendency for pit nucleation to occur on ridges, as has been observed previously.

Introduction

Caucustic dissolution of aluminum, when used as a pretreatment for anodic etching in aqueous chloride solutions, is found to produce an overall increase in the pit number density. For this reason it is used industrially in the manufacture of aluminum capacitor electrodes, for which enhancement of the surface area is desirable.

Several surface changes caused by dissolution may contribute to this increased susceptibility to pitting. Bond et al. showed that pits may initiate near microsegregated iron, copper, and silicon impurities in high purity aluminum. It is possible that elevated near-surface concentrations of these impurities are present after dissolution in NaOH, since concentrations of elements less reactive than the metal are typically enhanced by dissolution. Aside from composition effects, recent positron annihilation

References

23. J. R. Cameron, ibid., 90, 839 (1953).
measurements on aluminum dissolved in NaOH revealed a highly defective layer within about 10 to 20 nm from the oxide/metal interface, within which the concentration of vacancy-type defects was estimated to be on the order of 1%. It is possible that these defects serve as pit nucleation sites, perhaps by disrupting the structure of the overlying protective oxide film.

Sodium hydroxide dissolution also alters the surface topography of aluminum: after exposure to NaOH, a microscopic mosaic of ridges is found on the surface which surrounds scalloped depressions. These “scallop cells” (depressed areas bounded by ridges) are 0.1 to 1 μm in width and the ridges are 10 to 100 nm high. Similar topographies are formed by chemical polishing and electroplating. Also, when the metal is anodically oxidized in acidic solutions, a scalloped surface texture is found on the metal surface underlying the oxide film. Cuff and Grant found that, for a constant time in a chemical polishing solution, the scallop cell width increased with increasing metal purity, and suggested that impurity concentrations were strongly elevated on ridges compared to the cell interior. They argued that the cellular pattern was the surface manifestation of a three-dimensional network of impurities in the bulk metal. Thompson et al. and Lin and Hebert subjected aluminum surfaces which had been pretreated by acid anodizing and caustic dissolution, respectively, to anodic polarization in chloride ion containing solutions. They both noted a strong tendency toward pit nucleation on ridges as opposed to within the cells (Fig. 1). Understanding the preferential attack of these very small ridges would be of significant interest, since nanometer-scale compositional or structural inhomogeneities in the oxide or the metal may be involved.

In the present work, the concentrations of impurities near the surface of high-purity (99.98%) aluminum were measured after dissolution in NaOH, in order to determine whether the increased susceptibility to pitting could be correlated with surface composition changes. Impurities were measured using Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES). Using the former technique, the surface composition was determined as a function of dissolution time. This allowed a mole balance on impurities to be made which gave information about the mechanism of their retention during dissolution. In order to determine whether impurities were laterally segregated to ridges, the backscattering spectra were modeled using two simulations: one which assumed that the impurities were present in a uniform flat layer adjoining the surface, and another which took them to be localized in spheres tens of nanometers in diameter. The sphere model approximated impurity segregation in ridges. To the authors’ knowledge the detection of lateral concentration variations associated with protrusions is an extension of the capabilities of RBS.

**Experimental**

Aluminum foils were 100 μm thick and annealed. The typical grain size was 100 μm. A composition analysis with spark-source mass spectrometry revealed concentrations on the order of 10 wt-ppm of Cr, Cu, Fe, Ga, Mg, Si, and Zn metallic impurities. Dissolution was carried out at room temperature (25°C) aqueous 1 N NaOH solution. The solution was not circulated during dissolution, but copious gas evolution occurred from the aluminum surface.

Surface composition was measured with RBS, which is nondestructive and has a sensitivity of about 0.001 atomic fraction for some of the common heavier impurities (Cu, Fe, Ga, Pb) present in high purity aluminum. The RBS system consisted of a RBS 400 endstation with a 1 MV tandem accelerator (Charles Evans and Associates). Spectra were acquired using beams of alpha particles (4He) directed normal to the sample surface, with an energy of either 1.0 or 2.275 MeV. For each beam energy, spectra were measured by detectors positioned at both a near-normal angle (160°, measured from the direction of the incident beam) and a grazing angle (102° for the 1.0 MeV beam and 110° for the 2.275 MeV beam). 200 μC of “He” ions were used to accumulate the spectra. The detector resolution was 20 keV full width at half maximum (FWHM). Some additional measurements to confirm peak assignments in RBS were carried out with time-of-flight secondary ion mass spectrometry (TOF-SIMS) (Charles Evans and Associates).

AES, which has greater depth resolution but poorer sensitivity than RBS for the metallic impurities (Fe, Cu, Ga) being investigated, was used to help confirm the impurity concentration distributions. The base pressure in the Auger system (PHI 4300) was 2 × 10⁻¹⁰ Torr. The 100 nm diam electron beam (energy 10 keV, current 200 nA) was rastered over an area of several hundred μm², and reported spectra were averaged over this area. MATLAB software was used to fit the spectra over 25 channels of data near each transition of interest. Concentrations were determined as a function of dissolution time. In order to determine whether impurities were laterally segregated to ridges, the backscattering spectra were modeled using two simulations: one which assumed...
determined by optimizing the fit to the spectra of the corresponding pure components; in all cases the residual of the fit was smaller than 0.1%. For impurities, tabulated sensitivity factors were used for conversion of spectra to atomic percent (a/o). The two overlapping Al transitions, metallic Al at 1400 eV and oxidized Al at 1392 eV, were separated with principal component analysis, using different sensitivity factors for metallic and oxidized Al. Depth profiling was accomplished by Ar ion beam at an angle of 36°, and employed a Zalar rotation stage to minimize shadowing by surface roughness. The energy and current of the Ar beam were 4 keV and 3 μA.

Results and Discussion

Auger electron spectroscopy measurements of surface composition.—Auger spectra were acquired during sputtering through the oxide film and the region beneath the film, on a foil which was treated in NaOH for 40 min. The depth profiles of Al and O are shown in Fig. 2, and those of the impurities in Fig. 3. Significant concentrations of Cu, Fe, Mg, and Zn impurities near the surface were found. Appreciable noise is present in the impurity spectra in Fig. 3; however, as mentioned in the Experimental section, each concentration does not represent a measurement at a single energy, but a fit over 25 energy channels to the spectra of the pure components. Since the residuals of these fits in all cases were smaller than 0.1%, the measured concentrations were considered to be significantly larger than the detection limits. The oxide/metal interface was located at the point where the Al (oxide) and Al signals had decayed to 50% of their maximum values, at a sputtering time of 60 s. Two estimates of the sputtering rate were obtained from standard samples: 5.2 nm/min based on SiO₂, and 4.8 nm/min from anodic aluminum oxide films. Thus, the oxide film thickness was apparently 5 nm. All impurities may have been present in both the oxide and the metal. Concentrations of Zn and Mg were apparently highest at the film surface and decreased toward the metal interface, while the Cu concentration was highest at the metal/film interface and decayed toward the bulk metal. Oxygen was detected surprisingly deep in the metal, at concentrations which were larger than the sum of all the metallic impurities and aluminum ions. Possibly this persistence of oxygen can be attributed to readsorption during sputtering. On the other hand, a recent Auger and SIMS study of aluminum which did not employ sputtering also found deep oxygen, which the authors attributed to the presence of subsurface defects containing oxygen.

Quantitative interpretation of the Auger profiles requires knowledge of the sputtering depth resolution. This was estimated from the Al and Al (oxide) signals, since it is assumed that the transition from oxide to metal is actually sharp. The resolution was taken to be 9 nm, the distance over which the Al and Al (oxide) signals decayed from 84 to 16% of their maximum values. Since all the impurity profiles decay over distances which are comparable to this value, it is apparent that the true thicknesses of the impurity segregation layers cannot be estimated from the Auger profiles. The measured mean concentrations were about 1.0 a/o for Fe and Cu, and 0.3 a/o for Zn and Mg. These concentrations are much larger than the
Fig. 5. Part of backscattering spectra with grazing detector angle (102°), after dissolution for various times in NaOH. Edge energies for impurity elements: Fe, 0.8247 MeV; Cu, 0.8442 MeV; Ga, 0.8570 MeV. 

Table 1: Solubilities of the respective elements in aluminum metal, suggesting that the impurities were found in second-phase particles, or were accompanied by locally high defect concentrations.

RBS measurements of surface composition.—RBS was used to characterize surface impurity concentrations in as-received foils, and after immersion in 1 N NaOH at room temperature for 1, 5, 10, 15, 20, 30, and 40 min. Representative spectra measured with a near-normal detector angle (160°) are shown in Fig. 4, while Fig. 5 gives ones taken with a grazing angle (102°). The greatest elemental resolution was obtained with the detector positioned at the normal angle of 160°. As shown in Fig. 4, two peaks for metallic impurities could be distinguished. The peak on the left was due to iron, while that at lower energy was attributed mainly to copper, with gallium contributing a shoulder at low energy. The presence of both copper and gallium was confirmed with TOF-SIMS, and all three impurities were found in the bulk metal. Additionally, lead was detected in the 2.275 MeV, 160° spectra (not shown), at a concentration about 100 times lower than those of the other metallic impurities. Iron was the only metallic impurity found in the foil in the as-received condition; the others were detected only after dissolution. Figures 4 and 5 show that yields of all impurities increased steadily with dissolution time. Arai et al. also found strongly enhanced concentrations of iron, bismuth, boron, and magnesium impurities within a distance of about 20 nm from the surface of 99.99% Al foils. Light impurities such as zinc and magnesium which were found by AES would not have been detected with RBS.

Quantitative information about the spatial distribution of impurities was obtained by simulation of RBS measurements. Two models, which are referred to as the “layer” and “sphere” models, were used to simulate different lateral distributions of impurities along the surface. Simulations based on the layer model, which assumed that all impurities were present in a layer of uniform thickness adjacent to the surface, are described presently. For simplicity, the layer model approximated the impurity concentration profile by a uniform concentration of impurities within a layer of prescribed thickness. This approximation was valid because the impurity layers were extremely thin (less than 20 nm). Accordingly, the shape of the simulated spectra were found to depend more strongly on the detector resolution than on the shape of the concentration profile. As an additional simplifying approximation, oxide layers were not explicitly included in the simulations. The predicted spectra were found to be unaffected by the inclusion of an oxide layer, since the densities in atom/cm² of the oxide layer (7 × 10²³) and the metal (6 × 10²³) are comparable. Simulations using the layer model were carried out with RUMP software (Computer Graphic Service).

Figures 6 and 7 show experimental spectra along with the simulation based on the layer model, in the region of the iron, copper, and gallium peaks, for normal (160°, 1.0 MeV) and grazing (110°, 1.0 MeV) detector angles. Background levels were subtracted from the experimental spectra in the figure. In all simulations, the detector resolution was taken to be 20 keV (FWHM), in agreement with the experimental system. The aluminum edges of the experimental 1.0 MeV spectra, showed close agreement...
Fig. 7. Portion of backscattering spectra with grazing detector angle (102°) for aluminum after 40 min dissolution in NaOH. The solid line is the experimental spectrum and the dashed line the simulation, which was based on an impurity segregation layer 10 nm thick.

with simulations, thus demonstrating the absence of peak broadening due to the foil's surface roughness.

When the detector energy resolution assumed in the model spectra was set to 0 keV, the predicted yield for given impurities was independent of energy. This observation demonstrates the validity of the "surface energy approximation" for the small layer thicknesses under consideration; that is, the scattering cross section (probability) of given impurities was independent of depth. In this case, the integrated peak area for an impurity is proportional to the total number of impurity atoms per sample surface area, and is not affected by their spatial distribution (either laterally or in depth). Accordingly, area concentrations of metallic impurities were determined from the peaks in the spectra employing normal detector angles (160°, 2.275 MeV and 160°, 1.0 MeV), for which the elemental resolution was greater than for grazing detector angles (160°, 2.275 MeV and 160°, 1.0 MeV), for which the elemental resolution was greater than for grazing detector angles. The concentrations were adjusted until the shapes of the experimental and simulated spectra matched one another, with the integrals of the peaks in agreement to within 10%. Area concentrations of iron, copper, and gallium are shown in Fig. 8 for the various dissolution times. The nearly linear relationship between concentration and time, which is evident for all three impurities, is discussed below.

The thicknesses of impurity layers were determined by adjusting the simulation layer thicknesses for best agreement with experimental spectra. Given the 1.0 MeV, 102° spectra, rather than normal angle spectra were used because of their greater sensitivity to layer thickness. While varying the layer thickness, the impurity concentrations per unit area (i.e., the product of volume concentration and layer thickness) were kept constant at the values in Fig. 7. For all dissolution times of 5 min or greater, simulated peak heights were found to be within 10% of experimental values when layer thicknesses were chosen between 5 to 20 nm. The peaks became appreciably shorter and broader than those in experimental spectra when the thickness was larger than 20 nm. Also, for thicknesses larger than about 15 nm, the peak position was shifted to lower energy than the experimental peak by at least 10 keV. From these observations, it was inferred that the layer thickness was greater than 15 nm; it was not possible to establish a lower bound on the thickness. The layer includes a 5 nm thick oxide film, in which Fe and Cu impurities may not have been present. No variation of thickness with dissolution time could be detected, when the foil was dissolved longer than 5 min. For shorter dissolution times, the impurity peaks were too small to determine the layer thickness. The average impurity concentrations in the layer at 40 min were 0.4 Fe and 0.90 a/o Cu, closely comparable to the AES profile.

As mentioned above, surfaces after dissolution were not flat, but instead exhibited nanometer-scale roughness. They were covered by a mosaic of scallop cells which consisted of shallow, roughly circular depressions bordered by ridges (Fig. 1). After 10 min dissolution, the atomic force microscope (AFM) revealed that the characteristic cell width was about 600 nm, while typical heights and widths of ridges were 50 and 200 nm, respectively (Fig. 9). Two possible effects of such roughness on backscattering spectra were considered. First, roughness might artificially broaden peaks for impurity layers. However, this is unlikely, since, as stated above, no such broadening of the Al edge occurred. The other roughness effect would be present if, as proposed by Cuff and Grant, impurities were found preferentially at ridges. In this case, when a grazing detector angle was used, the path length of the beam after scattering from impurity atoms in ridges would be limited by the thickness of the ridge; thus, significantly narrower peaks would have been expected relative to those for flat surface, or for surfaces with no lateral segregation.

A simple model for backscattering spectra was devised to test for the possibility of impurity segregation to ridges. This model, which is described in detail in the Appendix, treated the ridges as spherical particles having uniform composition. The spherical geometry was chosen because it incorporated the essential feature of finite width, and yet, owing to its rotational symmetry, it was mathematically much simpler than a ridge geometry. Chu et al. also used a spherical model geometry to simulate the effect of impurity-containing protrusions on backscattering spectra; however, their simulation considered only normal detector angles, while the present one treated the detector angle as a parameter. The model sphere contained iron and copper at the same concentration, and no gallium. The inclusion of gallium was not necessary for the present purposes, since the impurity peak was compared to experimental spectra on the basis of its height, and the peak height was insensitive to the presence of gallium because of its low concentration relative to iron and copper (Fig. 8). Figure 10 shows the simulated spectral impurity peak according to the sphere model for the two detector angles of 102° and 160°. The peak shapes were determined by the parameter $\frac{f}{E}$, and the standard deviation of the
detector energy resolution. The resolution was taken to be that of the experimental system, 20 keV (FWHM), as was done in the layer model, and the energy loss rate \( f \) was taken to be that of pure aluminum, 250 eV/nm. Simulations were carried out for sphere radii \( R \) of 10 and 20 nm, the latter value representative of the ridge heights measured with AFM.

For grazing detector angles, the spectral peaks simulated by the sphere model were found to be higher than those calculated by the layer model. This result was to be expected due to the limited beam path length through the sphere discussed above. Hence, when the detector energy resolution was set to zero, sphere model peaks were narrower and higher than the layer model peaks, for the same impurity concentration per unit area (i.e., spectral peak area). When the effect of detector resolution was included, differences in peak width between the two models were no longer discernable, but the peak heights were still appreciably different. The ratio of the peak height for the grazing angle to that for the normal angle was 2.7 for both 10 and 20 nm radius spheres, significantly larger than the experimental value of 1.4, and the ratio of 1.7 from the layer model. Evidently, the layer model represented experimental spectra more closely than did the sphere model. The clear differences in predicted peak height ratio for the layer and sphere models demonstrates the applicability of this technique for the detection of lateral concentration variations associated with topography.

While the impurity concentration may be somewhat higher on ridges than elsewhere, the present results show that they are not exclusively confined to ridges, as proposed by Cuff and Grant. However, even a moderate variation in impurity concentration along the surface may be sufficient to produce the variation in dissolution rate which gave rise to the scallop topography. Hence, the RBS results do not exclude that the scallops might be related to impurities. On the other hand, when the dissolved foil is etched, the preferred nucleation of pits on ridges is dramatic, very few pits being found away from the ridges. Explaining the location of pit sites solely on the basis of impurities would then require that nearly all impurities are associated with ridges, which contradicts the present backscattering results. Thus, alternative hypotheses for the enhancement of pitting at ridges must be sought. Possible explanations may be related to the local surface curvature at ridges, which may produce strain energy in the oxide film, or to the presence of defects in the metal near the metal/film interface, as discussed below.

Impurity retention during dissolution.—The surface concentration measurements provided by RBS allowed a mole balance on impurities to be made. The variation of
Fig. 10. Theoretical backscattering spectra at two detector angles for a spherical particle with radius 20 nm. The particle contained uniform equal concentrations of iron and copper in aluminum.

impurity surface concentration with dissolution time is expected to follow

\[ C_s = C_w + \lambda C_d t \]  

[1]

\( \lambda \) is the fraction of surface impurity atoms which are retained on the surface as the surrounding Al atoms dissolve; that is, \( 1 - \lambda \) is the ratio of the dissolution rate of an impurity to that of aluminum. The dissolution rate \( v \) was approximately constant at 0.22 \( \mu \)m/min, as determined by the weight loss measurements shown in Fig. 11. Thus the linearity of the data in Fig. 8 suggests that \( \lambda \) was constant for each impurity. To assess the tendency of impurities to be retained during aluminum dissolution, \( \lambda \) was set to unity in Eq. 1, and the bulk concentrations \( C_w \) were calculated from the surface concentration measurements in Fig. 8. The bulk concentrations obtained for iron, copper, and gallium were 39, 34, and 22 wt-ppm, respectively. The sum of these concentrations is 95 wt-ppm, about half of the nominal impurity content of 200 wt-ppm. The difference between the true impurity content and the estimate from Fig. 8 can be partly accounted for by light impurities such as Mg and Zn not detected by RBS. Hence, it appears that at least half, and perhaps all, of the Fe, Cu, and Ga impurities exposed at the surface by aluminum dissolution were not dissolved, but were retained in the metal.

The retention of at least Fe and Cu is reasonable with regard to dissolution thermodynamics. The thermodynamic protection potentials of pure iron and copper against corrosion in pH 14 solution are, respectively, \(-1.0\) and \(-0.4\) V vs. the normal hydrogen electrode (NHE). Since the potential of aluminum in these experiments was between \(-1.4\) and \(-1.6\) V vs. NHE, iron and copper would not be expected to dissolve. On the other hand, the thermodynamic protection potential of gallium, which was detected by RBS but not AES, is \(-1.5\) V vs. NHE, comparable to the potential of aluminum during dissolution. Thus gallium retention, as well as that of the reactive Mg and Zn impurities found by Auger spectroscopy, would not be expected from thermodynamics alone. However, the kinetics of dissolution of these elements may be slower than those of aluminum, allowing them to accumulate on the surface.

The concentrations of Cu and Fe after 40 min dissolution, which were about 1 a/o, are much larger than the solubilities of these elements at room temperature (roughly 0.1 weight percent (w/o) for Cu and 0.001 w/o for Fe). Such high concentrations, if present in the metal, imply the existence of either second-phase particles or high defect concentrations near the metal surface.

Recent positron annihilation measurements on aluminum foils dissolved in NaOH have detected large increases caused by dissolution in the concentration of vacancy-type defects near the metal/oxide film interface. The defect layer thicknesses found after 10 min dissolution were about 10 to 20 nm, comparable to the upper bound on the segregation layer thickness determined in this paper, and the vacancy concentration in the defective layer was estimated to be the order of 1%. Hence, it appears that the metal is defective enough near the surface to hold very high impurity concentrations, without requiring the presence of second-phase particles.

As dissolved impurity concentrations in the metal near the surface built up during dissolution, a concentration gradient would have appeared favoring their diffusion toward the bulk. The segregation layer thickness would be determined by the depth to which the impurities diffuse. This diffusion length is given by Langer as roughly \( 2D/v \) (Eq. 3.7 in his paper). Hence the impurity diffusion coefficient could be estimated from measurements of dissolution rate and segregation layer thickness. Unfortunately, the uncertainty regarding the layer thickness measurements do not allow a reliable estimate of the diffusion coefficient to be made. One would expect, though, that diffusion would be significantly enhanced by the defective nature of the surface layer.

An alternative concept for impurity retention involves erosion and redeposition of impurities from solution. Here, as the nonreactive Cu and Fe were exposed on the surface by dissolution, rather than diffusing back into the metal, they would have been undermined by dissolution of the surrounding aluminum atoms, and would erode into solution. These elements would dissolve in the NaOH solution, and some would then redeposit on the metal surface. In order to explain the observed retention of Cu and Fe, at least half of the exposed impurities would redeposit. However, such an efficient redeposition process was considered unlikely, and the Auger spectra suggest the presence of Cu and Fe in the metal below the oxide, as opposed to on the surface. Thus the most probable retention mechanism is that the nonreactive impurities simply never leave the metal, and diffuse toward the bulk when their concentration near the surface builds up. After dissolution, the impurities are present within a relatively homogeneous but highly defective surface layer in which their
concentrations can be quite high. The increased susceptibility of the metal toward pitting may be related to the presence of these defects. It is not known whether the defects are associated with ridges between scallop cells, where pits preferentially form. Macdonald\textsuperscript{20} has discussed a mechanism for generation of voids at the aluminum metal/oxide interface near surface protrusions during anodic oxidation.

**Conclusions**

Dissolution of aluminum in sodium hydroxide solution is found to increase the rate of corrosion pit initiation during subsequent anodic etching in chloride solution. The work reported here used Rutherford backscattering spectrometry and Auger electron spectroscopy to measure near-surface concentrations of metallic impurities following dissolution in sodium hydroxide solution. It was revealed that nonreactive impurities (iron, copper, gallium) build up continuously during dissolution of aluminum in sodium hydroxide. The thickness of the impurity segregation layer in the metal was no greater than 10 nm. Within this layer, the concentrations of Fe and Cu after 40 min dissolution were about 1.8 a/o, much higher than their equilibrium concentrations in the metal at room temperature. They were most likely not present in second-phase particles, but were dissolved in the metal, their high concentrations being accommodated by large defect concentrations near the interface. Large subsurface defect concentrations after NaOH dissolution have recently been detected by the authors using positron annihilation measurements.

Dissolution of high purity aluminum leaves a microscopic surface topography consisting of a mosaic of 10 to 100 nm high ridges. These ridges serve as effective sites for the initiation of small corrosion pits, and it has been suggested that elevated impurity concentrations can be found on them. To evaluate the lateral distribution of impurities with respect to the ridges, a simulation of backscattering from protrusions containing elevated impurity concentrations was developed. To the authors' knowledge, this simulation represented an extension of the capabilities of RBS for the detection of such lateral concentration variations. It was concluded that the impurities were not primarily confined to ridges, but were spread fairly uniformly along the surface. Hence lateral segregation of impurities is probably not the reason for preferential pitting on microscopic ridges. Alternatively, the enhancement of pitting by dissolution might be related to the defective nature of the metal near the interface, or to geometric features of the surface topography.

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**APPENDIX**

**Rutherford Backscattering Spectra of Rough Surfaces**

The model described here parallels that of Chu et al.\textsuperscript{17} in that in both models the surface roughness features are assumed to be adequately represented as spheres. The model of Chu et al. further assumed that the detector was positioned along the direction of the incident particle beam (detector angle of 180\(^\circ\)), and consequently a simple analytic expression for the scattering yield was obtained. The present model extends their treatment to arbitrary detector angles. It is now shown that the variation of spectral peak height with detector angle is appreciably different for the sphere and uniform layer models.

Figure A-1 shows the model geometry. The incident beam is directed along the surface normal, and the detector is oriented at an angle \(\Theta\) with respect to the surface normal (the "detector angle" is the supplement of \(\Theta\)). The elastic collision of the beam with a target atom occurs at point \(P_1\), and the points \(P_2\) and \(P_3\) lie on a plane perpendicular to the y axis. The scattering yield is given by

\[
H(E_i) = \sigma(E) \Theta S(E_i) N \left( \frac{d\sigma}{dE} \right) \Delta E_i \tag{A-1}
\]

The locus of scattering points \(P_i\), from which the beam exits the sphere with the same energy \(E_i\), defines a surface inside the sphere. \(S(E_i)\) is the area of this surface projected onto the plane of the incident beam, i.e., the xy plane. The energy dependence of \(\sigma\) is \(\sigma(E) = \sigma(E) S(E) E_i F\); \(E\) is the particle energy just before collision. Thus a normalized yield \(F\) is defined according to

\[
F = \frac{H(E_i)}{E_i^2 \Theta \Theta S(E_i) (Z,Z_\text{eff}/E_i)^2} \tag{A-2}
\]

The energy just after collision is \(KE\), where the kinetic factor \(K\) is smaller than unity because some of the particle's kinetic energy is transferred to the target atom. As the beam traverses the sphere, it loses energy at a constant rate \(f = dE/dx\). The distance the beam traveled by the beam before collision is \(L_1 = P_1 P_2 = (E - E_i)/f\), while the distance through the sphere after collision is \(L_2 = P_2 P_3 = (KE - E_i)/f\). Eliminating \(E\) between these two expressions, the detected energy is found to be

\[
E_i = KE_{\text{det}} - (K L_1 + L_2) f \tag{A-3}
\]

Thus, scattering events which contribute to the yield at a given energy \(E_i\) occur at points within the sphere having the same value of \(L = KL_1 + L_2\). These points lie on a surface whose defining equation is derived by calculating \(L_1\) and \(L_2\) in terms of the coordinates \(P_i = (x_i, y_i, z_i)\). The coordinates of \(P_i\) are \((x_i, y_i, z_i)\), and hence \(L_1 = (R_i - x_i^2 - y_i^2 - z_i^2)/z_i\) and \(z_i = z_i = z_i = l_1 \cos \Theta\). Solving the resulting quadratic equation for \(L_1\) and combining the solutions for \(L_1\) and \(L_2\), an expression for \(L\) is

\[
L = \pm \sqrt{x_i^2 \sin^2 \Theta + z_i^2 \cos^2 \Theta + 2x_i z_i \sin \Theta \cos \Theta - x_i^2 - y_i^2 - z_i^2 + R^2} \tag{A-4}
\]
For a given point \((x_0, y_0)\) on the xy plane, this equation implicitly gives the coordinate \(z_0\) of a point on the constant L surface.

The normalized yield \(F\) was found by integrating \((E_0/E)^2\) over the projection onto the xy plane of the surface defined by Eq. A-4. For a point on the surface, \(E = (E_0 - tL)/K\). To carry out the integration, a grid of points within the circle \(x_1^2 + y_1^2 = R^2\) was constructed, and for each point the solution for \(z_0\) was found from Eq. A-4. The integrand at that point was set to zero if no solution for \(z_0\) existed, or if the solution lay outside the sphere. Otherwise the integrand was set to \((E_0/E)^2\) as calculated from \(x_1, y_1,\) and \(z_1\). Integration was according to Simpson's rule. Grids consisting of 400 points in both the \(x\) and \(y\) directions were existed, or if the solution lay outside the sphere. Otherwise the integrand was set to \((E_0/E)^2\) as calculated from \(x_1, y_1,\) and \(z_1\). Integration was according to Simpson's rule. Grids consisting of 400 points in both the \(x\) and \(y\) directions were to achieve smaller than 0.1% relative error with respect to the analytic solution of Chu et al.

To account for the broadening of the spectral peak by the limited energy resolution of the spectrometer, the predicted yield was transformed according to

\[
G(E) \left[= \frac{1}{(2\pi\nu E_0)^1/2} \int F(E') \exp \left[ \frac{-2}{2\pi^2 E_0} \right] dE' \right] \quad \text{[A-5]}
\]

where \(\nu\) is the standard deviation of the system energy resolution, which in the experimental system was 20 keV, the FWHM resolution, divided by 2.35. The predicted spectrum for a sphere with uniform equal concentrations of iron and copper impurities is shown in Fig. 7. The ordinate is \(2[(Z_1)^0 + (Z_1)^Fe]/[(Z_1)^0 + (Z_2)^Fe]\). The normalized yield is a function of the detector resolution in the figure is \(2[(ZG)^0 + (ZG)^Fe]/[(ZG)^0 + (ZG)^Fe]\).

LIST OF SYMBOLS

- \(C_i\): impurity concentration in the bulk metal, mol/cm³
- \(C_{i0}\): moles of near-surface impurity per unit surface area, mol/cm²
- \(D\): impurity diffusion coefficient, cm²/s
- \(E\): energy of particle just prior to collision with target atom, MeV
- \(e\): electronic charge, \(1.602 \times 10^{-19}\) C
- \(E_0\): beam energy, MeV
- \(E_s\): particle energy at detector, MeV
- \(F\): normalized scattering yield, dimensionless
- \(f\): rate of energy loss at beam traverses sphere, MeV/cm
- \(G\): normalized scattering yield as broadened by detector energy resolution, dimensionless
- \(H\): backscattering yield, number of particles
- \(K\): scattering kinematic factor: ratio of particle energy just after collision to that just before collision
- \(L\): beam path length in sphere before collision, cm
- \(L_s\): beam path length in sphere after collision, cm
- \(N\): volume density of atoms in the target material, atoms/cm³
- \(u\): dissolution velocity, cm/s
- \(R\): radius of sphere, cm
- \(S\): projected area onto incident beam of surface comprising points in sphere where collisions produce the same particle energy, \(E_0\)
- \(t\): time, s
- \(x_1\): coordinate of point where particle-target atom collision occurs, cm
- \(y_1\): coordinate of point where particle-target atom collision occurs, cm
- \(Z_i\), \(Z_f\): atomic number of projectile and target atoms
- \(z_1\): coordinate of point where particle-target atom collision occurs, cm
- \(\Delta E_i\): energy width of one channel of detector, MeV
- \(\lambda\): \(1 - \text{(rate of impurity dissolution)} / \text{(rate of aluminum dissolution)}\)
- \(\mu\): standard deviation of detector energy resolution, keV
- \(\theta\): angle between unit normal to surface and beam from sample to detector, "
- \(\sigma\): differential scattering cross section, cm²/atom-steradian
- \(\phi\): incident beam particle flux, particles/cm²
- \(\Omega\): solid angle of detector, steradian

REFERENCES

17. Ibid., p. 334.