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OXIDATION OF POLYCRYSTALLINE CHROMIUM BETWEEN 30°C AND 400°C

G. THURNER* AND P.H. HOLLOWAY
Department of Materials Science and Engineering, University of Florida
Gainesville, FL 32611, USA

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The formation of coalesced oxide films on atomically clean polycrystalline chromium has been studied with Auger electron spectroscopy and secondary ion mass spectrometry at temperatures between 30°C and 400°C. The data are consistent with an initialed chemisorption of oxygen on the clean Cr followed by nucleation of chromium oxide after 2 L of exposure followed by lateral growth to form a thin, coalesced, saturated oxide film about 0.8 nm thick at 30°C. The saturated oxide was thicker at higher temperatures, being about 80 nm thick at 400°C. Detection of a CrO^+ secondary ion was associated with chemisorbed oxygen, while O^- ion originated from chromium oxides based upon correlation with chemical changes in the low-energy Auger spectra. Heating of the coalesced oxide caused considerable changes in both the low-energy Auger spectrum as well as the secondary ion emission. Both these as well as time-dependent, reversible changes in secondary ion emission were interpreted as structural rearrangements of the chromium oxide resulting in relative changes of oxygen either adsorbed on the surface or incorporated into chromium oxide.

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1. Introduction

Oxidation of metals have been intensively studied over several decades [1, 2] both because of scientific interest as well as for technological purposes. Because essentially all metals are thermodynamically unstable relative to their oxides, formation of very thin continuous oxide layers, which protect the underlying metal from further oxidation, are essential. For understanding these phenomena, oxidation of chromium is particularly of interest since it is often used to form surface passivating oxide layers. Oxidation of Cr has been studied many times [3–10] with the general conclusion that at room temperature the sequence of reactions are dissociative, non-ordered chemisorption followed by nucleation and lateral growth of

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*Present address: Institute of Physical Chemistry, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria.

Cr_2O_3 to form a coalesced oxide. However studies starting from atomically clean surfaces of coalesced oxide on Cr at temperatures above 30°C are very limited. In fact most of the higher temperatures studies have only measured the rate of thickening of coalesced oxides. In the present work, we have investigated the oxidation of atomically clean polycrystalline chromium over the extended temperature range of 30–400°C. The techniques used in the study were Auger electron spectroscopy (AES) and static secondary ion mass spectrometry (SSIMS). Benninghoven [11] has shown that static SIMS, especially in combination with other surface analysis techniques, is a powerful method for study of surface reactions.

2. Experimental

A polycrystalline chromium sample ($1 \times 1 \times 0.1$ cm) of 99.95% purity was mechanically polished with 1 μm diamond paste and degreased with 1,1,1-trichlorethane, acetone, and methanol then blown dry with pure nitrogen. The sample was mounted on a heatable holder in an UHV-chamber with a base pressure of 5×10^{-10} torr. To obtain a clean chromium surface, the sample was sputtered with 1 keV Ar^+ until no impurities were detected by AES. The UHV-system was equipped with a Perkin Elmer/Physical Electronics Model 545 Scanning Auger Microprobe. A primary electron beam of 3 keV, 0.5 μA was used. The Auger spectra were recorded in the derivative mode with a modulation voltage of 1 eV peak-to-peak. For SIMS a 3M Company Model 610 Secondary Ion Mass Spectrometer was used with an ion gun (PHI Model 04-191) forming an Ar^+-primary ion beam of 25 μA and 1 keV. At the Ar partial pressure of 1×10^{-6} torr, more than 6 hours of sputtering was required to remove a chromium oxide film, formed at room temperature ($\approx$ 1 nm thick). To increase the secondary ion intensity under these static SIMS conditions the primary ion beam was rastered over an area ≈ 0.16 cm^2. For the oxidation experiments, oxygen (99.997%) was introduced into the chamber at a partial pressures of 5×10^{-8}–1×10^{-6} torr, with the ion pump almost completely throttled (estimated pumping speed of 10 l/s).

3. Results and discussion

3.1. Auger electron data

To follow the oxidation process, the ratio of the oxygen Auger signal at 510 eV over the chromium signal at 529 eV was measured versus oxygen dosage. Experiments at oxygen partial pressures between 5×10^{-8} and 1×10^{-6} torr showed that the surface oxygen coverage was dependent only on exposure at all oxygen partial pressures. The ratio of $I_{O(510)}/I_{Cr(529)}$ vs. exposure at temperatures ranging from 30°C to 400°C are shown in Fig. 1. In all cases a sharp increase in the oxygen/chromium ratio was observed at the beginning of the oxygen dosage followed by a saturation after oxygen exposures of 30 to 100 L. The exposure value at which saturation was reached increased with increasing temperature. Up to 300°C the oxygen/chromium ratio increased at all exposure values with increasing temperature. However, at 400°C the slope of the curve was lower and about 100 L

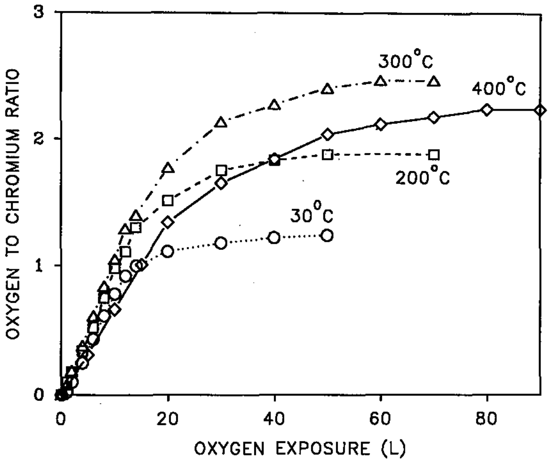


Fig. 1. Auger electron peak-to-peak height ratio $I_{Cr(529)}$, as a function of oxygen exposure at various temperatures.

was required to approach the same saturation value achieved with 50 L at 300°C. The increase of the saturation value with increasing temperature up to 300°C indicates that below 300°C the oxide layer was thinner than at least three times the escape depth of the Auger electrons (0.8 nm for 500 eV electrons measured by a CMA) [12]. The lack of further increase of I_O/I_{Cr} at 400°C indicates that the oxide thickness was larger than three times the escape depth. The form of the curves suggests that up to 300°C, the reaction mechanism is constant, with the oxidation going faster at higher temperatures resulting in a thicker oxide. At 400°C the amount of oxygen in the measured surface volume is smaller than for 200°C or 300°C data at exposures up to 40 L.

To demonstrate that the AES intensity ratio in Fig. 1 was influenced by the thickness of the chromium oxide increasing beyond the escape depth of the Auger electrons, the oxide thickness was analyzed with Auger sputter profiling. The sputter times required to reduce the O(510) Auger peak height to 50% of its original intensity are plotted versus oxygen exposure in Fig. 2. To estimate the chromium oxide thickness from the sputter time, we assumed that the thickness formed at 27°C and 20 L oxygen is 0.82 nm as found by Palacio et al. [10] leading to a chromium oxide sputter rate of 0.3 nm/min. Comparing the sputter data (Fig. 2) to the intensity data (Fig. 1) shows that there are significant inelastic scattering effects in the I_O/I_{Cr} for all temperatures above 30°C. This is true even for the 200°C data since the sputter data show the oxide thickness is double that at 30°C, yet the ratio of I_O/I_{Cr} for 200°C is only about 60% greater than for 30°C. This is consistent with inelastic scattering of Cr Auger electrons in the overlayer oxide [16, 17] since we assume the 30°C oxide is 0.8 nm thick and $\approx$ 500 eV electrons have escape depths of 0.8 nm [12]. At 300°C, a higher oxygen exposure ($\approx$ 200 L) was required to finish the reaction and the oxide thickness was about twice that

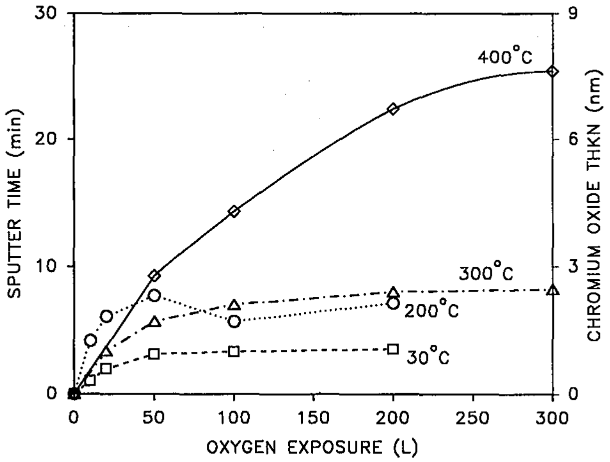


Fig. 2. Chromium oxide thickness from Auger electron sputter profiles as a function of oxygen exposure at various temperatures.

formed at 200°C. This trend continued at 400°C, but doses in excess of 300 L were required to form the saturated oxide which was more than three times thicker than at 300°C.

To further study the early stages of oxidation, the Auger peaks at low kinetic energy were recorded with good energy resolution (≈ 0.25 eV) at several oxygen exposures (see Fig. 3). The Auger spectrum from a clean chromium surface consists of an intensive peak at 38 eV with little side structure. Exposure to oxygen causes this 38 eV peak to decrease in intensity until it vanishes at 16 L at 30 and 200°C, 20 L at 300°C, and 140 L at 400°C. With oxygen dosages as low as 2 L, a shoulder appears on the Cr peak at 34 eV and increases in intensity with increasing exposure, developing more slowly at higher temperatures. At an oxygen exposure of ≈ 4 L a new peak at 48 eV also appears at all temperatures, and it grew in intensity upon further oxidation. A small shoulder at 41 eV becomes visible after ≈ 8 L for $T < 400°C$ when the metallic peak intensity is sufficiently reduced. The original peak at 38 eV is identified in the literature as an $M_{2,3}VV$ Auger transition from clean chromium metal [13]. The peaks at 34, 41, and 48 eV have been previously reported to result from oxidation [14] but there is disagreement about their origins. Whereas Ekelund and Leygraf [3] consider the 34 eV peak to result from chemisorbed oxygen, Palacio et al. [10] believe it results from formation of an oxide.

It is well established that low temperature oxide formation occurs in three stages: (a) oxygen chemisorption, (b) oxide nucleation and lateral growth until coalescence, and (c) thickening of the continuous oxide film [8, 10, 15]. Palacio et al. [10] postulated that oxide nucleation was signified by the appearance of the 48 eV peak. In the present experiments, this would mean that the oxide nucleated at ≈ 4 L oxygen exposure for all investigated temperatures. The formation of a

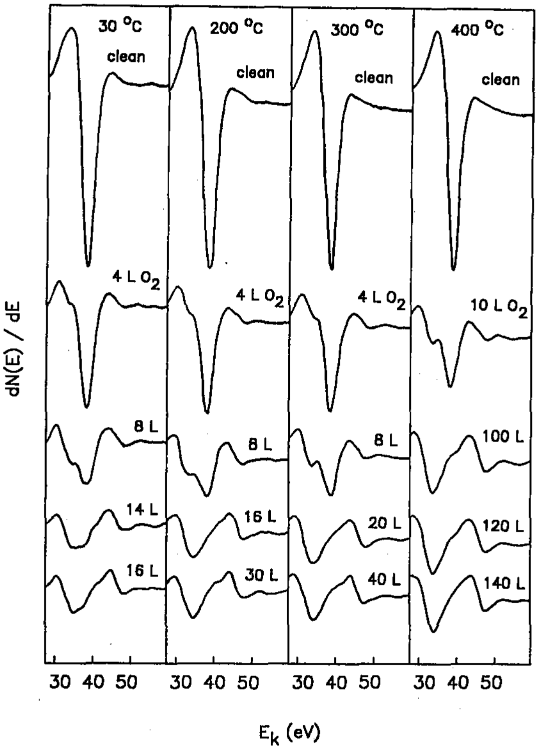


Fig. 3. Low energy Auger spectra after various oxygen exposures at 30, 200, 300 and 400°C.

continuous oxide film by coalescence of nucleated oxide islands was indicated by the disappearance of the metallic chromium peak at 38 eV. The metallic signal disappeared before the intensity ratio saturated because the escape depth of 38 eV Auger electrons (≈ 0.4 nm [12]) was smaller than the thickness of the oxide overlayer. Based on this argument, a continuous chromium oxide film was formed after 16 L at 30°C and 200°C, 20 L at 300°C, and 140 L at 400°C. This means that coalescence occurs very early for $30°\mathrm{C} \leq T \leq 300°\mathrm{C}$ suggesting a high nucleation density with small oxide islands [16]. At 400°C the situation is quite different since the late disappearance of the metallic chromium peak indicates that fewer oxide islands are nucleated and they remain isolated up to a relatively large exposure. These data agree well with classical nucleation theory with which suggests that nucleation occurs much faster at low temperatures and that the density of nuclei decreases with increasing temperature.

While the inelastic scattering of electrons in thicker oxides explain why the I_O/I_{Cr} ratio was lower at 400°C, these effects could be additive with diffusion of O into the bulk of Cr. To determine whether oxygen diffused into the bulk of the sample at 400°C, the chromium was first dosed with 200 L of oxygen at room temperature to form a coalesced oxide film, then heated in base vacuum to 400°C. Changes in the $I_{O(510)}/I_{Cr(529)}$ ratio and the low energy Auger peaks are shown in Fig. 4. Whereas the $I_{O(510)}/I_{Cr(529)}$ ratio remained constant within 10%,

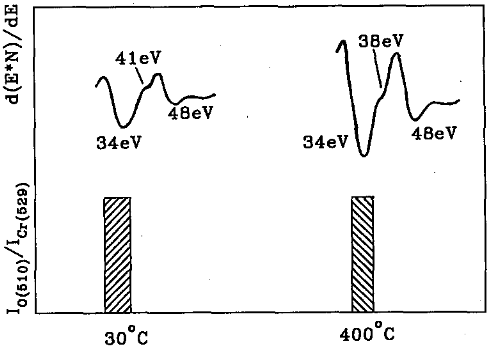


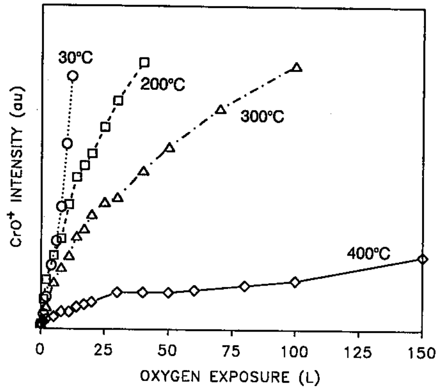
Fig. 4. Low energy Auger spectra and $I_{O(510)}/I_{Cr(529)}$ from a surface dosed with 200 L of oxygen at 30°C and subsequently heated in vacuum to 400°C.

remarkable changes in the low-energy spectrum occurred upon heating. The peak at 41 eV disappeared and the metallic chromium peak at 38 eV reappeared. The constant $I_{O(510)}/I_{Cr(529)}$ ratio indicates that the composition of the surface layer did not change, thus oxygen diffusion into the bulk during heating was insignificant. On the other hand, changes in the low-energy Cr Auger spectrum indicate a change in the structure of the chromium oxide. The absence of the metallic chromium peak (38 eV) after oxidation at room temperature indicates a continuous oxide film with a thickness larger than the escape depth of 38 eV Auger electrons ($\approx$ 0.4 nm). The appearance of the 38 eV peak after heating to 400°C means that, at least in some regions, the oxide thickness decreased below this escape depth. But since the total amount of oxygen remained constant (no change in the oxygen/chromium Auger ratio) this can only be explained by a separation of the continuous oxide film into an island-like film, with variable oxide thickness.

3.2. SIMS data

Only signals from Cr^+ and CrO^+ were detected in the positive static SIMS during the oxidation of the polycrystalline chromium sample. The dependence of the CrO^+ signal upon oxygen exposure at various temperatures is shown in Fig. 5. The CrO^+ signal increased with increasing oxygen dose, with larger increases at lower temperatures. The data show an inflection in the plot of I_{Cr} vs. exposure for 6 L at 30°C, 8 L at 200°C, 25 L at 300°C, and 30 L at 400°C followed in every case by a lower slope as the oxide saturated on the surfaces. The CrO^+ signal decreased after the oxygen was evacuated from the system, as shown in Fig. 6 for various oxygen exposures at room temperature.

Only O^- ions were detected in the negative SSIMS mode. As shown in Fig. 7, the O^- signal increased at very low oxygen exposures (2L), reached a maximum



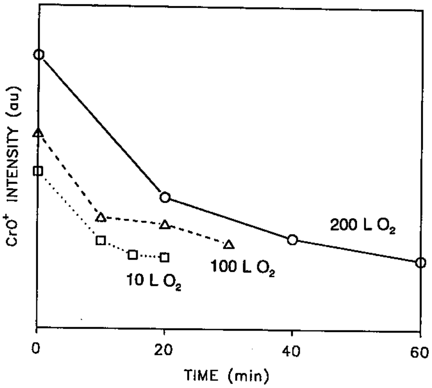


Fig. 5. Intensity of CrO^+ versus oxygen exposure at various temperatures

Fig. 6. Intensity of CrO^+ signal vs. time in UHV after dosing with oxygen (at 30°C) to 10, 100 or 200 L .

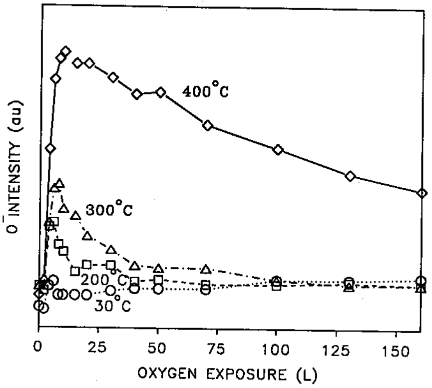


Fig. 7. Intensity of O^- versus oxygen exposure at various temperatures.

value at 6 L and 10 L for 30°C and 400°C, respectively, then decreased for longer exposures. Contrary to the CrO^+ signal, the O^- intensity was lower at lower temperatures and increased after evacuating the oxygen (see Fig. 8).

Benninghoven [11] reported several different secondary molecular ions during oxidation of polycrystalline chromium at room temperature, but because of the lower sensitivity of our SIMS apparatus we found only CrO^+. However Benninghoven [11] did not detect chromium oxide molecular species until exposures of several hundred L. In our experiments, the CrO^+ peak was detected at the lowest exposures investigated, which agrees well with the detection of the 34 eV (chemisorbed oxygen) Auger peak at only 2 L, and with our current understand-

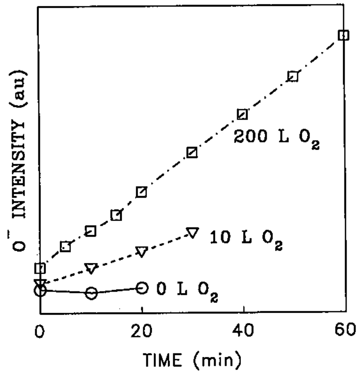


Fig. 8. Changes in O^- intensity vs. time in UHV after oxygen dosing (at 30°C) to 0, 10, and 200 L.

ing of oxidation [2, 15]. Based on the AES results, the CrO^+ ions detected during the first few langmuirs (0–25 L) of exposure probably originate from chemisorption oxygen rather than chromium oxide. The inflection in the CrO^+ intensity vs. exposure probably indicates a significant coverage of oxide on the surface. This is consistent with the observation of the 48 eV AES peak at low (4 L) oxygen exposures. The increase of the CrO^+ intensity at larger exposures correlates with disappearances of the 38 eV AES peak from metallic chromium, signifying the coalescence of oxide islands into a continuous oxide layer. On the other hand the increased O^- emission correlates with the nucleation of oxide islands, but O^- emission decreased upon coalescence of the oxide. The form of the O^- intensity versus oxygen exposure curves correlates well with changes of the work function, as measured by Sakisaka et al. [6]. These authors found that the work function initially decreased front the clean surface value upon chemisorption of oxygen, increased only slightly during oxygen nucleation, then increased dramatically to above the clean surface value upon growth of the oxide. The dramatic drop of the work function during chemisorption and oxide nucleation would explain the larger intensity of negative oxygen ions since it is well known that formation of negative secondary ions is assisted by low work function systems [11]. In addition, Sakisaka et al. [6] observed a time-dependent decrease of the work function when the sample was held in UHV after evacuation of oxygen. They postulated the decreased work function resulted from either oxygen diffusion into the bulk, cation migration toward the surface, or partial desorption of absorbed oxygen from the oxide surface. The decrease of the CrO^+ signal and the increase of the O^- signal, observed after evacuating the oxygen (see Fig. 6 and 8 respectively), also probably reflects these work function changes. The fact that the $I_{O(510)}/I_{Cr(529)}$ does not change during heating excludes the possibility of significant oxygen migration into or cation diffusion out of the bulk. In addition, cation migration, which is the dominant low-temperature transport mechanism during the thickening of the continuous oxide film [1, 2] should stop after the final passivating oxide thickness is reached. However, the time-dependent CrO^+ secondary ion intensity increase upon exposure to oxygen and decrease upon exposure to vacuum were observed even after the O AES signal saturated (e.g. at 200 L oxygen at room temperature). Therefore, desorption of adsorbed oxygen from the oxide surface is one possible explanation for reversible changes in the work function and secondary ion intensity. In addition though, the behavior of the O^+ signal upon standing in vacuum suggests another possible explanation. The increased O^- signal with time in UHV could result from an increased concentration of oxide and/or a decreased work function. Since conversion of adsorbed oxygen into oxide would probably result in both more oxide and a lower work function, this supports the concept discussed above. The only difference is that the oxygen would remain on the surface rather than desorb.

Finally, the effect on the SIMS spectrum of heating of a sample with a coalesced room temperature oxide to 400°C was studied. Changes of the CrO^+ and the O^- signal are shown in Fig. 9 and 10, respectively, after dosing with 200 L of oxygen at room temperature followed by heating to 400°C for various times. In addition, points (a) and (b) in Fig. 9 correspond to heating a sample quickly to 400°C immediately after the 200 L exposure (point (a)) versus heating one after 200 L plus standing for 60 min in UHV (point (b)). Similarly, points (a), (b) and (c) in Fig. 10 correspond to 0, 10 and 60 min in UHV after the 200 L exposure. Remarkably, no matter what the strength of the CrO^+ or O^- signals were before heating, their secondary ion signals after heating to 400°C were the same, with the CrO^+ signal being very low and the O^- signal being intermediate. These results are more consistent with oxygen conversion to oxide plus oxide restructuring, rather than simple oxygen desorption. As pointed out during discussion of the AES results, a change in the structure of the oxide film takes place during heating. The chromium oxide apparently forms thick and thin clusters, but the poorly ordered or amorphous low temperature oxide may also be transformed into a more crystalline state at 400°C [2, 5]. Such structural changes

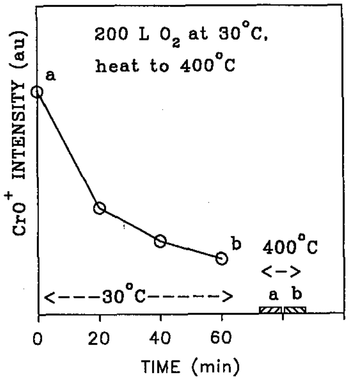


Fig. 9. Intensity of CrO^+ after oxygen dosing (at 30°C) to 200 L and heated to 400°C after (a) zero time, or (b) 60 min in UHV at 30°C.

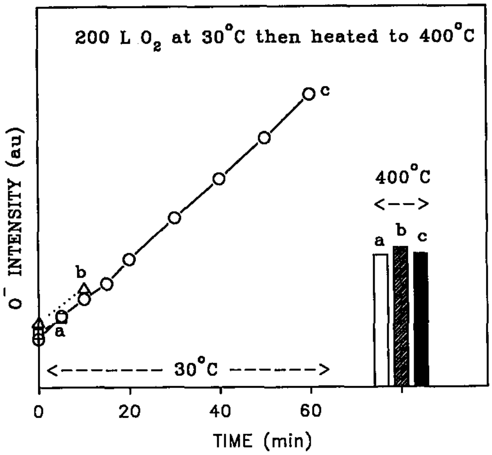


Fig. 10. Intensity of O^- after oxygen dosing (at 30°C) to 200 L and heated to 400°C (a) immediately after oxygen exposure, (b) after 10 min and (c) after 60 min at 30°C and heating to 400°C.

are associated with changes in the bond character and strengths, which play an important role in Auger emission and secondary ion formation.

4. Summary

Oxidation of atomically clean, sputtered polycrystalline chromium surfaces was studied by Auger electron spectroscopy and secondary ion mass spectrometry. Oxygen exposure cause the metallic Cr Auger electron peak at 38 eV to decrease in intensity along with a simultaneous development of a shoulder at 34 eV indicative of chemisorption of oxygen. These changes in Auger peak shape were accompanied by an increase in the intensity of the CrO^+ secondary ion, suggesting this species also originated from chemisorbed oxygen. At about 4 L, nucleation and growth of chromium oxide was detected by a continued decrease of the 38 eV Auger peak and development of new Auger peaks at 41 and 48 eV. Oxide formation resulted in emission of an O^- secondary ion which increased as the oxide coalesced on the surface. Upon allowing the oxidized surface to stand in UHV, the CrO^+ and O^- signals decreased and increased, respectively, indicating conversion of chemisorbed oxygen to oxygen bound in oxide. The effects of temperature on the Auger and secondary ion signals are consistent with these assignments since the oxide was thicker (increased O^- signal) but chemisorbed oxygen was less (reduced CrO^+ signals) at higher temperatures. Heating oxide formed at 30°C to 400°C resulted in restructuring of the coalesced oxide into an oxide layer with varying thickness, with near elimination of the CrO^+ signal and an intermediate O^- signal. The data show that oxygen does not dissolve in Cr upon heating to 400°C.

Acknowledgement

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