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 O_2 , CO , CO_2 , AND H_2O ON INDIUM

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AES STUDY OF THE ADSORPTION OF
 O_2 , CO, CO_2 , AND H_2O ON INDIUM

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ABSTRACT

The adsorption of various oxygen-containing gases on clean polycrystalline In has been studied. For the In- O_2 system, the relationship between $N(E)$ areas and $dN(E)/dE$ peak heights for the In MNN Auger transition was found to be linear. At saturation, an oxygen/indium ratio of 3/2 was measured, consistent with the formation of the stable oxide In_2O_3 . Low coverage sticking coefficients were found to be ~ 0.014 for O_2 , ~ 0.004 for H_2O , $\sim 5 \times 10^{-5}$ for CO, and $\sim 2 \times 10^{-5}$ for CO_2 . In each case, chemical shifts and peak distortions in the $N(E)$ and $dN(E)/dE$ spectra have been measured for the gas-saturated In, the largest being ~ 3 eV for the MNN transition of O_2 -saturated surface.

NOTICE

I. INTRODUCTION

We report on the adsorption of a number of simple oxygen-containing gases (O_2 , H_2O , CO , and CO_2) on clean polycrystalline In surfaces using Auger electron spectroscopy. The published studies of In surface chemistry are almost entirely devoted to In-group VA semiconductors such as InP.¹ Studies of adsorption on the pure metal have been restricted to oxidation by O_2 exposure.²⁻⁴ We are interested in the adsorption properties of In with respect to other oxygen-containing gases because of our use of clean In as a sampling surface for impurity studies in tokamak-type fusion devices.⁵ This study reports measurements of sticking coefficients, saturation coverages, and dependence of the In MNN Auger structure on exposure.

II. EXPERIMENT

The apparatus used for these measurements was a standard PHI 590 Scanning Auger Microprobe. Samples were prepared from high purity indium wires and foils (>99.9%). The samples were sputter-cleaned with 0.5-5 keV argon ions until the relative surface concentrations of carbon and oxygen were less than 0.5 at.%. The gases under study, O_2 , H_2O , CO , and CO_2 , were admitted to a level of 10^{-7} to 10^{-5} torr for a designated period of time and then pumped out. During this time, pressure was measured with a nude Bayard-Alpert ion gauge, and the gas purity monitored with a quadrupole mass spectrometer. Both instruments were calibrated with a capacitance manometer over the range 10^{-6} to 10^{-4} torr. Gas purity was generally >99% with the

primary impurity being H_2O . Following pump-out to UHV levels (base pressure $<10^{-9}$ torr), Auger spectra in the $N(E) \cdot E$ and $dN(E)/dE$ modes were recorded. The primary electron beam current was kept low (10-50 nanoamperes) and rastered over a 200μ by 150μ area to reduce the possibility of electron beam effects. In no case were any beam-related effects noted. Atomic concentration results reported are calculated through use of $dN(E)/dE$ peak-to-peak values, and standard sensitivity factors.⁶

III. RESULTS

A. Oxygen

The measured dependence of oxygen coverage versus O_2 exposure is shown in Fig. 1. The oxygen coverage saturates after exposures $>10^4$ L at an O/In ratio of 1.5 consistent with the formation of the stable oxide,⁷ In_2O_3 . Figure 2 shows the dependence of the sticking coefficient versus oxygen coverage. The sticking coefficients were derived from the slopes of Fig. 1 with the assumption that an O_2 -saturated In surface is one monolayer equivalent of In_2O_3 or 4.1×10^{14} O atoms/cm² (see Fig. 2 caption). The derived sticking coefficient for O_2 on In falls smoothly from a low coverage value of .014.

The progression of the $In M_{4,5}N_{4,5}$ and $M_5N_{4,5}N_{4,5}$ Auger spectra is shown in the $dN(E)/dE$ mode from the clean to O_2 -saturated surface in Figure 3a. The $N(E) \cdot E$ clean and oxidized peaks are shown in Figure 3b. Accompanying the modification of the $N(E)$ peaks is a downward shift of 2.9 eV for $M_{4,5}N_{4,5}$ and

3.1 eV for $M_5N_{4,5}N_{4,5}$. The N(E) peak at 393 eV which is attributed to unresolved plasma-losses,⁸ is visible on the clean metal surface but disappears on the oxygen-saturated surface. The N(E) areas and the $dN(E)/dE$ peak-to-peak values were compared for the transition to the oxide, as illustrated in Fig. 4. The primary feature is the apparent linearity, i.e., for the $M_4N_{4,5}N_{4,5}$ transition the $dN(E)/dE$ sensitivity is independent of peak shape modifications due to oxidation. Comparing the N(E) spectra for the clean and fully oxidized samples, the peaks were broadened $22 \pm 5\%$ and the total area under the peaks decreased 20%.

B. Water

The adsorption of H_2O on In saturates after H_2O exposures $>10^4 L$ (Fig. 1), however the saturation coverage of oxygen is only in the range of 20-40 at.%. The derived sticking coefficient shows an initial rise after a low coverage value of .004, and then falls smoothly as saturation is approached (Fig. 2). The $dN(E)/dE$ peak progression from the clean metal to the saturated surface is shown in Fig. 5a. A strong third peak (405 eV) is evident at saturation, as is a downward shift of the initial peak in energy of ~3 eV. The N(E)·E spectra for the identical adsorption sequence is shown in Fig. 5b. Peak broadening of 20% is evident. The plasma-loss peak (393 eV), is absent from the saturated form. The other MNN peaks ($M_4N_3N_{4,5}$, $M_5N_3N_{4,5}$ at 350 eV and $M_4N_1N_{4,5}$, $M_5N_1N_{4,5}$ at 300 eV) are unaffected in general size and shape although they are very broad and difficult to measure.

C. CO, CO₂

The low coverage sticking coefficients for CO and CO₂ were measured to be 2×10^{-5} and 5×10^{-5} respectively (Fig. 2). These values are upper limits due to two factors. First, the amounts of gas needed to produce observable carbon or oxygen Auger signals (Fig. 1) were large (10^5 - 10^7 L), and H₂O or O₂ impurities in the inlet gas may be co-adsorbing. Secondly, the presence of two hot filaments in the UHV chamber may in some form activate either gas. As a precaution against this latter effect, we note that the results were independent of whether the mass spectrometer filament, which is very near the sample, was on or not. The measured values for oxygen and carbon coverage at saturation for CO adsorption were small: 24 at.% for O and 18 at.% for C; for CO₂ adsorption 32 at.% for O and 17 at.% for C.

The modification of the In peaks in the dN(E)/dE spectra is slight, and in the N(E) spectra changes are undiscernible. There was no measurable shift in the energy of the peaks. The only detectable change in the dN(E)/dE spectra is a reduction in the top half of the M₄N_{4,5}N_{4,5} In peak of approximately 40%.

E. Sequential Exposure: H₂O and O₂

Sequential exposures of water and oxygen, and vice-versa, were also undertaken. In the case of an H₂O exposure to an O₂-saturated surface, there was no change in the Auger spectra or saturation values. With the opposite exposure sequence, the spectra and the saturation values became characteristic of O₂ saturation ($<10^3$ L).

IV. DISCUSSION

The adsorption of O_2 or H_2O on In is accompanied by the following changes in the primary In Auger transitions: (1) a ~3 eV downward shift in energy; (2) disappearance of the plasma-loss peak at 393 eV; (3) a broadening of the peaks from 3 eV to 10.5 eV (FWHH); and (4) a 20% decrease of the peak intensity $\left[\int_{380}^{450} N(E) dE \right]$. These changes indicate the formation of an oxide (or hydroxide), and the concomitant disappearance of the free-electron density in the affected surface layer, which is at least the sampling depth of the ~400 eV Auger electrons (10-20 Å).

Chemical shifts in Auger spectra due to oxidation and, in particular, the 3 eV peak-shift with the oxidation of In, have been discussed by Wagner and Biloens⁹ in terms of polarizability changes which accompany the transition from metal to dielectric. The presence of O_2 or H_2O as interstitial or physisorbed species would not cause a sufficient change in dielectric constant to account for ~3 eV peak shifts.

The fading of the plasma-loss⁸ features (393 eV) on the Auger peaks is also evidence for a substantial decrease in the free-electron density in the surface layer. We have confirmed the disappearance of the plasma-loss peaks with oxidation by looking at energy loss spectra of 200, 300 and 400 eV primary electrons scattered from an O_2 -saturated In surface.

The instrumental width of the energy analyzer (~3 eV) did not allow the multiplet structure¹⁰ of the In MNN transition to be resolved, nevertheless 20% peak broadening was resolved as

the In oxidized. It has been suggested⁹ that the width of the peak is due to the lifetime of the two-hole state. This seems unlikely in view of the fact that the peak broadens as the transition to a dielectric occurs. Peak broadening may be due to a two-hole-induced Stark-type effect, which would cause multiplet splitting.

The 20% decrease in peak intensity $[\int N(E)dE]$ can be attributed to the decrease in number density of In atoms in the In_2O_3 lattice compared to pure In, if the electron inelastic scattering length remains constant.

The saturation of the O/In ratio at 1.5 during O_2 adsorption indicates that the chemisorption proceeds until a relatively uniform layer of In_2O_3 is completed. The thickness of the In_2O_3 layer is at least the sampling depth of the In Auger electrons (i.e. 10-20 Å or several times the electron inelastic scattering length¹¹). Previous ellipsometric³ and sputtering studies⁴ of the formation of In_2O_3 show film thicknesses in this range for O_2 exposures at pressures of 1 atm.

A range of values for saturation coverages was obtained after H_2O adsorption ($\text{O}/\text{In} = .25-.67$) that is considerably below the stoichiometric value (1.5) for In_2O_3 . Indium forms two stable hydroxides at room temperature, $\text{InO}(\text{OH})$ and $\text{In}(\text{OH})_3$. A uniform layer of either of these compounds is discounted because of the small saturation oxygen coverage. The formation of the monoxide (InO), suboxide In_2O , or sub-hydroxide InOH would lower the expected O/In saturation ratio to .3-.5. Studies of H_2O adsorption

on a chemically analogous surface, Al, show that both oxide and hydrated oxides are present.¹²⁻¹⁵ The detailed shape of the curve of sticking coefficient vs. coverage shown for H₂O on In in Fig. 2 is similar to the curve for H₂O on Al reported by Kruger and Pollack.¹² We note that the sticking coefficient vs. coverage curve for O₂ is also similar in both systems,^{12,16} and that ratio of low coverage sticking coefficients (O₂/H₂O) ~3 for both In and Al.

Evidently, there is little adsorption of either CO or CO₂ on In surfaces at room temperature. This result is consistent with the fact that there are no stable In carbides or carbonyls at lower temperatures. Weakly-bound adsorption may occur analogous to the situation observed for the low temperature adsorption¹⁷ of CO on Ag.

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617 (1976).

FIGURE CAPTIONS

Figure 1. Dependence of the oxygen coverage on clean indium as a function of exposure to various oxygen-containing gases. The oxygen coverage was derived from peak-to-peak values of $dN(E)/dE$ Auger spectra and standard sensitivity factors.⁶

Figure 2. Dependence of the sticking coefficient versus oxygen coverage for the adsorption of various oxygen-containing gases on indium. The sticking coefficients were derived from the slopes of the coverage vs. exposure curves given in Figure 1 with the assumption that an O_2 -saturated In surface is one monolayer equivalent of In_2O_3 or 4.1×10^{14} oxygen atoms/cm². The absolute value of the derived sticking coefficients may be in error a factor of 2-3, since the Auger measurements show that at least 10-20Å of oxide is present at saturation.

Figure 3. Progression of the primary In Auger peaks ($M_4N_{4,5}N_{4,5}$ and $M_5N_{4,5}N_{4,5}$) from the clean In (a) to O_2 -saturated surface (e). $N(E)$ Auger spectra from the clean In (a) and O_2 -saturated surface (b) are shown in the lower figure.

Figure 4. Comparison of the relative surface concentration of oxygen to indium calculated from the Auger $N(E)$ areas versus $dN(E)/dE$ peak-to-peak heights. The $dN(E)/dE$ modulation voltage was 3 V.

Figure 5. Progression of the primary In Auger peaks from the clean In (a) to H_2O -saturated surface (d). $N(E)$ spectra from the clean In (a) and H_2O -saturated surface (b) are shown in the lower figure.

Fig. 1. 786118

Fig. 2. 786119

Fig. 3. 786058

Fig. 4. 783350

Fig. 5. 786060