CONF - 770642 -- 9

Isotope Effect in the Study of H-W(100) and O-W(100)
Chemisorption Systems Using SIMS

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Isotope Effect in the Study of H-W(100) and O-W(100)
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ABSTRACT

Large isotope effects were observed in the secondary ion yields when chemisorbed layers of H, D, ^{16}O , and ^{18}O on W(100) were sputtered with low energy Ne^+ ions. Higher isotopic mass in general lowered both the atomic ion yields (H^- , D^- , O^+ and O^-) and the molecular ion yield (WO_2^-), except for $\text{H}^+(\text{D}^+)$ where the converse was true.

The theory of secondary ion mass spectrometry (SIMS) is still not very well developed.⁽¹⁾ Quantitative interpretation of SIMS data is hindered by our lack of understanding of the basic mechanism. This isotope effect experiment is an attempt to acquire more information about the interaction between the escaping secondary ion and the target surface. Isotopes of the same element have practically identical bonding on the surface. But for the same escape energy, the heavier isotope which has a smaller escape velocity would be expected to interact more strongly with the electrons of the substrate. Hydrogen (^1H , ^2D) and oxygen (^{16}O , ^{18}O) layers chemisorbed on a W(100) single crystal surface at room temperature were examined. The isotope effect was expected to be more significant in these light adsorbate elements which have large percentage isotopic mass differences.

The experiment was performed inside an UHV system with the base pressure in the upper 10^{-11} torr range. The experimental setup and the sample cleaning procedures were described elsewhere.⁽³⁾ Adsorbate gas dosing was achieved by letting

*Work performed under the auspices of the U.S. Energy Research and Development Administration.

the gas in through a leak valve to establish a partial pressure in the 10^{-9} torr range. Low energy static mode SIMS employing low primary ion densities ($<20 \text{ nA/cm}^2$) and low incident ion energies (500 eV) was used to minimize the complication from radiation damage of the target surface. The incident angle was 45° . The secondary ions were detected with a quadrupole mass spectrometer which had an electrostatic energy filter in front to pass ions of energy roughly from 0 eV to 30 eV.⁽³⁾ The mass spectrometer could be programmed to alternately look at any two different ion species. The ion yields were monitored continuously during the whole gas dosing procedure until saturation.

Figure 1 shows the result for hydrogen and deuterium adsorbed on W(100) at room temperature. Both the $\text{H}^+(\text{D}^+)$ and the $\text{H}^-(\text{D}^-)$ yields increased monotonically with the hydrogen coverage until saturation. In spite of the fact that the work function gradually rose by over 0.8 eV as a result of the dipole moment of the adsorbed hydrogen atoms,⁽⁴⁾ the H^- to H^+ ratio was observed to be practically constant up to full coverage. This indicated that the ionization probability was not very sensitive to the dipole field generated by the surface atoms themselves though it can still be a strong function of the work function of the substrate metal. The D-W(100) system showed a similar behavior. The saturation yields, however, had vastly different values. $\text{D}^+(\text{sat})/\text{H}^+(\text{sat}) \approx 2.2$ while $\text{D}^-(\text{sat})/\text{H}^-(\text{sat}) \approx 0.17$ and the slope $\text{D}^-/\text{D}^+ \approx 0.095$ while $\text{H}^-/\text{H}^+ \approx 1.3$. The isotope mass difference resulted in an order of magnitude change in these ratios. But the most unexpected observation was that while the D^- yield was significantly lower than that of H^- , the D^+ yield was over a factor of two higher than that of H^+ .

The O-W(100) system was investigated in some detail.⁽²⁾ It was determined that the O^+ , O^- and WO_2^- yields all saturated approximately at one oxygen monolayer coverage and they were most sensitive to chemisorption bond changes. Other

tungsten oxide ions saturated only slowly at very high oxygen dosages which made it difficult for reliable comparison of the effect of different isotopes at identical oxygen coverages. Figures 2 and 3 show the results for oxygen adsorption on W(100) at room temperature. The O^- vs O^+ plot (Fig. 2) has roughly two linear segments. The low coverage linear segment which has a higher O^-/O^+ slope was associated with oxygen atoms adsorbed randomly at fourfold sites. The high coverage linear segment which has a smaller slope was associated with the formation of the $p(4 \times 1)$ structure.⁽²⁾ The two oxygen isotopes ^{16}O and ^{18}O showed no distinct difference in these features. But the ^{18}O ions had smaller yields than those of the corresponding ^{16}O ions at all oxygen coverages. The saturation ratio $^{18}O^+(\text{sat})/^{16}O^+(\text{sat}) \approx 0.88$ and $^{18}O^-(\text{sat})/^{16}O^-(\text{sat}) \approx 0.66$. Repeated runs showed consistent results to within 20%. The WO_2^- yields gave the most surprising result. Figure 3 shows the variation of the WO_2^- yields with dosing time at room temperature. The saturation ratio $W^{18}O_2^-(\text{sat})/W^{16}O_2^-(\text{sat}) \approx 0.7$. It indicates a significant isotopic effect although the two ion species have insignificant percentage mass differences.

The secondary ion yield in general depends on the product of the sputtering coefficient and the ionization probability. The theory for the isotope effect in SIMS, especially for chemisorption systems, still has to be developed. The possibility of an isotope effect in the total sputtering coefficient has been speculated, although systematic experimental verification is still not available.⁽⁵⁾ But, theoretically, when the energy of the collision cascade generated by the primary ions propagates back to the target surface, there is a mass mismatch during the final momentum transfer to the adsorbed atom. If the last collision is between a single substrate atom of mass M_S and a single adsorbate atom of mass M_A , initially at rest, the maximum energy acquired by the adsorbate

atom is $(M_A/M_S)/(1+M_A/M_S)^2$ of the initial energy of the substrate atom. For two adsorbate atoms of mass M_{A_1} and M_{A_2} , the ratio of the energy transferred is $(M_{A_1}/M_{A_2})^{1/2} (1+M_{A_2}/M_S)^2 / (1+M_{A_1}/M_S)^2 \approx M_{A_1}/M_{A_2}$ when $M_{A_1,2} \ll M_S$. Since the binding energy is practically independent of the isotopic mass, the sputtering yields are expected to scale approximately by the same factor M_{A_1}/M_{A_2} , with the heavier isotope giving a higher yield. This may explain why experimentally the D^+ yield was 2.2 times the H^+ yield. But all other ion species containing the heavier isotopes had smaller yields. It seems that the decrease in the ionization probability dominated over the increase in the sputtering coefficient.

In a simple one electron picture, the secondary atomic or molecular ion escaping from the substrate surface interacts with the "selvage" of the substrate electron distribution that extends out from the solid edge. The probability of tunneling an electron between the escaping particle and the metal substrate depends on the transit time of the particle through the "selvage". In this experiment, for the same ion energy, the ions containing the heavier isotope had a longer transit time. Since the heavier isotope reduced the negative ion yields in all cases, neutralization by tunneling of electrons from the ions back into the substrate seemed to dominate the interaction. For O^+ , neutralization by electron attachment seemed to be the major interaction. In all these cases, the ions appeared to originate from the impact, and got partially neutralized on their way out. But for $H^+(D^+)$, it was not possible to separate the effect of ionization probability change from the mass mismatch effect.

The isotope effect of the WO_2^- yields is most intriguing. Since the $W^{18}O_2$ molecule is heavier than the ^{16}O counterpart by only 1.85%, only a very small isotope effect should result from the slight velocity difference between the two molecular species. But the isotope effect observed for WO_2^- was practically identical to that of the free negative oxygen ion. We suspect that the aggregate

of one tungsten and two oxygen atoms did not form a tightly bound entity until they left the substrate completely. If it was an O^- ion that carried the charge, it would have its own isotope effect independently. This mechanism of molecular sputtering has been suggested by Konner, et al.⁽⁶⁾ and Harrison, et al.⁽⁷⁾ The isotope effect result seems to support the proposed model.

The author would like to thank Drs. Myron Strongin and W. Brown for their very useful suggestions.

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FIGURE CAPTIONS

- Fig. 1. The $H^-(D^-)$ vs $H^+(D^+)$ plot at room temperature.
- Fig. 2. The O^- vs O^+ plot at room temperature for both ^{16}O and ^{18}O .
- Fig. 3. The WO_2^- yield as a function of time at room temperature for both ^{16}O and ^{18}O . The oxygen partial pressure was about 10^{-8} torr but different in the two cases.