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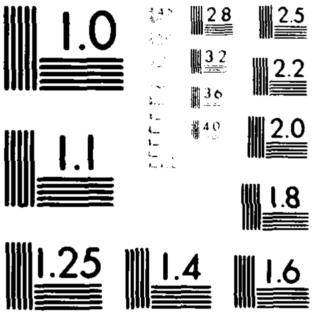
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INTERACTIONS OF MOLECULAR ION BEAMS WITH SURFACES

FINAL REPORT

DR. J. W. RABALAIS

SEPTEMBER 1980

U.S. ARMY RESEARCH OFFICE

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ion bombardment; ion damage; gun barrel erosion; metal erosion and corrosion; chemical reactions of beams with surfaces; sputtering; cluster formation at surfaces.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Reactions of N_2^+ ion beams with the surface of polycrystalline rhenium foil over the range 150-3000 eV have been studied by the techniques of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectrometry (TDS). The reactions produce a nitride layer of the type ReN_x, $0.21 \leq x \leq 0.40$, with x varying as a function of ion kinetic energy and depth into the surface. The nitride layer extends from the surface down to the penetration depth of the atoms, which varies from ~15 Å at 0.3 keV to ~76 Å at 2.5 keV ion energy. The

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product nitride and chemisorbed nitrogen on Re are distinctly different, exhibiting N_{1s} binding energies of 397.9 and 396.8 eV, respectively, and TDS maxima near 425 and 600 C, respectively. The value of x in ReN_x increases linearly with the nitrogen ion flux and reaches a steady state condition at a dose of 9.5×10^{16} ions/cm^2 which is determined by the opposing rate of nitride formation and the sputtering rate by impinging N_2^+ ions. An expression describing the rate of nitration as a function of the reaction cross section σ_r and the sputtering cross section σ_s is derived. The simplified expressions for the limiting cases of initial rates ($t \to 0$) and the steady state ($t \to \infty$) product concentration, which are used to interprete the experimental results, yield $\sigma_r \simeq 3 \times 10^{-18} cm^2$ for the $N_2^+ + Re\ (metal) \to ReN_x$ reaction at an ion impact energy of 500 eV.

Analytical expressions for the absolute cross sections of beam-surface reactions are derived and applied to the $N_2^+ + TiN \to TiN$ reaction over the kinetic energy range 0.25 - 3.0 keV. The theory predicts that the amount of reaction product, P, formed near the surface is a function of the collisional dissociation probability of the primary molecules, P_d, the reaction cross section, σ_r, and the cross section for product sputtering by the impingent reactant beam, σ_{sp}. For a dosage R_o of reactant molecules impingent on M_o target atoms,

$P/M_o = (\sigma_r P_d/A)R_o$ in the limit $R_o \to 0$ (initial reaction), and

$P/M_o^o = \{\alpha + (\beta/P_d^o)(\sigma_{sp}/\sigma_r)\}^{-1}$ in the limit $R_o \to \infty$ (saturation dose), where A is the surface area bombarded and α and β are stoichiometric factors for the product $M_\alpha R_\beta$. The techniques of x-ray and UV photoelectron spectroscopy (XPS and UPS), secondary ion mass spectrometry (SIMS), thermal desorption spectrometry (TDS), and depth-concentration profiling are used to characterize the reaction product and measure the product film thickness and composition for the reaction of N_2^+ with the (10$\bar{1}$1) face of a titanium single crystal. The measurements yield a film composition of $Ti_{0.89}N$ and show that the properties of the film, including its extremely high stability, are identical to those of commercial TiN. The reaction cross section is determined as $\sigma_{r,0.5} = 2.1 \times 10^{-16}$ cm^2 and $\sigma_{r,2.0} = 1.0 \times 10^{-16}$ cm^2 at primary N_2^+ kinetic energies of 0.5 and 2.0 keV, respectively. The formation and profile of the film near the surface, the interpretation of and uncertainties in the cross sections obtained, and comparison of this system to other N_2^+/metal systems are discussed.

Adsorption, desorption, oxidation, and hydrogenation of carbon monoxide on polycrystalline rhenium foil along with the electronic structure of clean rhenium have been studied by x-ray (Al K_α) and UV (Ne I, HeI, and He II) photoelectron spectroscopyand thermal desorption spectrometry under UHV conditions. The valence band electron spectra of clean Re are compared with the density of states obtained from APW band-structure calculations and variations in the phtoionization cross sections as a function of photon energy are presented. X-ray induced Auger transitions below 1450 eV are indentified according to approximate calculations employing atomic energy level differences. Chemisorption of CO and O_2 at low exposures on clean Re is reported. The results show that O_2 is dissociatively adsorbed at 25°C and CO is dominantly molecularly adsorbed at 25°C, a portion of which is desorbed at 240°C and the remainder dissociated into carbide and oxide forms which desorb at 1060°C. The high temperature dissociated carbide and oxide species are the reactants during oxidation to CO_2 and hydrogenation to CH_4. Correlation of the molecular orbitals of adsorbed CO with those of gaseous CO and $Re_2(CO)_{10}$ suggests that the adsorbed molecule is terminally bonded to the metal via the C atom.

Instrumental Advances

The ion beam accelerator is now complete and we have obtained preliminary results from it. Preliminary studies of N_2^+ and N^+ on Mo have shown that the threshold for producing Mo_2N is ~8 eV, i. e., near the dissociation energy of N_2^+.

Studies with N^+ have shown that the reaction cross section actually increases at low energy and the product has been observed with N^+ energies as low as 3 eV.

Publications

1. "XPS, UPS, and TDS Study of Adsorption, Oxidation, and Hydrogenation of CO on Rhenium", *Surface Sci.*, *93*, 338-350 (1980).
2. "Interactions of Ion Beams with Surfaces: Dynamics of the Reactions of N_2^+ with Rhenium", *J. Chem. Phys.*, *72*, 6158-6163 (1980).
3. "Absolute Cross Sections for Beam-Surface Reactions: N_2^+ on Ti from 0.25 to 3.0 keV", *J. Chem. Phys.*, submitted.
4. "XPS and UPS Study of the Valence Band Structure and Chemisorption of Ti(0001)", *Surface Sci.*, *91*, 165-174 (1979).
5. "Clustering Distances in Secondary Ion Mass Spectrometry", Proceedings of the Second International Conference on Secondary Ion Mass Spectrometry, Springer-Verlag, N. Y., Stanford Univ., Stanford, CA, Aug. 27-31, 1979, p. 18-20.

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ABSOLUTE CROSS SECTIONS FOR BEAM-SURFACE REACTIONS: N_2^+ ON Ti FROM 0.25 TO 3.0 keV KINETIC ENERGY

by

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ABSTRACT

Analytical expressions for the absolute cross sections of beam-surface reactions are derived and applied to the $N_2^+ + Ti \rightarrow TiN$ reaction over the kinetic energy range 0.25 – 3.0 keV. The model assumes that the amount of reaction product, P, formed near the surface is a function of the collisional dissociation probability of the primary molecules, P_d, the reaction cross section, σ_r, and the cross section for product sputtering by the impingent reactant beam, σ_{sp}. For a dosage R_o of reactant molecules impingent on M_o target atoms, $P/M_o = (\sigma_r P_d/A)R_o$ in the limit $R_o \rightarrow 0$ (initial reaction), and $P/M_o = \left\{\alpha + (\beta/P_d)(\sigma_{sp}/\sigma_r)\right\}^{-1}$ in the limit $R_o \rightarrow \infty$ (saturation dose), where A is the surface area bombarded and α and β are stoichiometric factors for the product $M_\alpha R_\beta$. The techniques of x-ray and UV photoelectron spectroscopy (XPS and UPS), secondary ion mass spectrometry (SIMS), thermal desorption spectrometry (TDS), and depth-concentration profiling are used to characterize the reaction product and measure the product film thickness and composition for the reaction of N_2^+ with the $(10\bar{1}1)$ face of a titanium single crystal. The measurements yield a film composition of $Ti_{0.89}N$ and show that the properties of the film, including its extremely high stability, are identical to those of commercial TiN. The reaction cross section is determined as $\sigma_{r,0.5} = 2.1 \times 10^{-16}$ cm^2 and $\sigma_{r,2.0} = 1.0 \times 10^{-16}$ cm^2 at primary N_2^+ kinetic energies of 0.5 and 2.0 keV, respectively. The formation and profile of the film near the surface, the interpretation of and uncertainties in the cross sections obtained, and comparison of this system to other N_2^+/metal systems are discussed.

Surface Science 91 (1980) 165–174

XPS AND UPS STUDY OF THE VALENCE BAND STRUCTURE AND CHEMISORPTION OF Ti(0001)

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Photoemission studies of the clean (0001) face of a titanium single crystal using UV and X-ray photoelectron spectroscopy (UPS and XPS) have revealed two maxima in the valence band density of states at ~0.5 and ~1.4 eV below the Fermi level. The 1.4 eV peak exhibits the following unusual characteristics: (i) Its photoionization cross section decreases rapidly as incident photon energy increases. (ii) Its UPS intensity is rapidly quenched by exposure to small doses of CO and N_2 but large doses of O_2 are required for the same effect. (iii) Its UPS intensity decreases rapidly upon heating from ~120 to ~240°C. The 0.5 eV peak does not exhibit this behavior. The temperature dependence of the 1.4 eV peak gives a near linear Arrhenius plot with an activation energy of 9.1 kcal/mole. This observed temperature dependence is that expected for diffusion of hydrogen during the $\gamma \to \alpha$ phase transformation of titanium hydride. The characteristics of this peak are consistent with its identification as photoemission from an electronic structure localized at the surface. This structure may be a titanium hydride layer near the surface.

1. Introduction

In the course of our investigations of the fundamental interactions of simple gases with clean metal surfaces, we have recently reported [1] details of the chemisorption of CO on (10$\bar{1}$1) titanium. Further investigations of the basal plane (0001) of a titanium single crystal have found its characteristics to be significantly different from either polycrystalline [2,3] or (10$\bar{1}$1) titanium [1]. This paper presents the first ultraviolet and X-ray photoelectron spectroscopic (UPS and XPS) study of the valence bands of Ti(0001). In particular, the dependence of the photoemission spectrum on incident photon energy, the temperature dependence of the valence band structure, and the different sensitivities to chemisorption of CO, N_2, and O_2 are described in detail. We have observed fine structure in the form of a well-defined peak in the Ti(0001) valence band photoemission spectrum which exhibits extreme sensitivity to surface contamination, chemisorption of gases, and temperature variations. Characterization of this structure according to its temperature dependence and comparison with density of states calculations suggests that it may be due to a phase transformation in titanium hydride. A recent LEED structure

Interactions of ion beams with surfaces: Dynamics of the reaction of N_2^+ with rhenium

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(Received 22 August 1979; accepted 22 February 1980)

Reactions of N_2^+ ion beams with the surface of polycrystalline rhenium foil over the range 150–3000 eV have been studied by the techniques of x-ray photoelectron spectroscopy (XPS) and thermal desorption spectrometry (TDS). The reactions produce a nitride layer of the type ReN_x, $0.21 \le x \le 0.40$, with x varying as a function of ion kinetic energy and depth into the surface. The nitride layer extends from the surface down to the penetration depth of the atoms, which varies from ~15 Å at 0.3 keV to ~76 Å at 2.5 keV ion energy. The product nitride and chemisorbed nitrogen on Re are distinctly different, exhibiting N_{1s} binding energies of 397.9 and 396.8 eV, respectively, and TDS maxima near 425 and 600 °C, respectively. The value of x in ReN_x increases linearly with the nitrogen ion flux and reaches a steady state condition at a dose of 9.5×10^{16} ions/cm^2 which is determined by the opposing rate of nitride formation and the sputtering rate by impinging N_2^+ ions. An expression describing the rate of nitration as a function of the reaction cross section σ_r and the sputtering cross section σ_s is derived. The simplified expressions for the limiting cases of initial rates ($t \rightarrow 0$) and the steady state ($t \rightarrow \infty$) product concentration, which are used to interpret the experimental results, yield $\sigma_r \simeq 3 \times 10^{-18}$ cm^2 for the $N_2^+ + \mathrm{Re(metal)} \rightarrow \mathrm{ReN}_x$ reaction at an ion impact energy of 500 eV.

I. INTRODUCTION

Chemical reactions of active ions with surfaces at energies ranging from thermal to several thousand eV are an experimentally tractable new field of chemistry due largely to the arsenal of surface analysis techniques that have been developed in the last decade. The techniques of x-ray and UV photoelectron spectroscopy (XPS and UPS),[1-5] thermal desorption spectrometry (TDS),[6] and secondary ion mass spectrometry (SIMS)[7] have been employed for analysis of these reaction products at the surface. We have recently shown[2,3] that bombarding a surface with a low energy beam of molecular ions can induce chemical reactions between the ions and surface that do not normally occur between the neutral molecule and surface under ambient conditions. In such active ion bombardment (AIB) the kinetic energy of the molecular ion is used to overcome activation barriers that preclude reaction under ambient conditions. The unique feature of AIB is the ability to alter the *chemical nature* of a surface and to induce reactions through injection of specific mass and velocity selected ions at precise spatial locations (on a macroscopic scale) at known concentrations. The reactions of M, MO, and MO_2, where M = Si and Ge, surfaces with N_2^+ beams have been shown[1,2] to form nitrides which are similar to those of the type M_3N_4. In studies[5] of N_2^+ reactions with transition metals, it was found that metal nitrides are formed with all of the first row transition metals and that the yield of nitride decreases for second and third row metals. For many third row metals no reaction was observed.

This paper describes details of the reaction induced by N_2^+ ions on rhenium metal. Rhenium was selected for these experiments because N_2 does not adsorb on its surface until extremely high exposures are attained and it is in the center of the third row transition metals, a region where previous experiments have produced low nitride yields. XPS, TDS, and depth profiling data are used to characterize the rhenium nitride product and to determine the thickness of the nitrided layers, the initial reaction rate, and the steady state nitride/rhenium ratio as a function of N_2^+ kinetic energy over the range 150–3000 eV. This data enables derivation of the first reaction cross section for reaction of energetic N atoms with a Re surface.

Bombardment of a surface with low energy ions can result in ion penetration of the lattice with degradation of kinetic energy through collision cascades until the ions are eventually thermalized within the lattice. The ultimate fate[2] of these ions is determined by four processes, namely, (1) diffusion from the lattice, (2) entrapment as neutral species, (3) chemical reaction with bulk atoms, and (4) sputtering by the impinging N_2^+ ions. Process (1) is rapid for ions where the chemical affinity between the ion and target atoms is negligible, e.g., rare gas ions. Process (2) involving implantation of neutral species surely occurs; however, previous measurements[2,8] have shown that high ion doses are required in order to inject a sufficient quantity for detection by XPS. Processes (3) and (4) are therefore dominant opposing factors which determine the final nitride/metal ratio. The relative initial reaction rate [process (3)], and sputtering rate [process (4)] as a function of N_2^+ energy for the nitrogen–rhenium system have been deduced from this investigation.

II. EXPERIMENTAL

The experiments were performed in a bakeable ultrahigh vacuum chamber designed for maximum flexibility and versatility in the use of x-ray and UV photoelectron spectroscopy (XPS and UPS), Auger electron spectroscopy (AES), thermal desorption spectrometry (TDS), and active ion bombardment (AIB) of surfaces. Base pressures down to the 10^{-11} Torr range are obtainable by means of a combination of a 450 *l*/s turbomolecular pump, a 500 *l*/s ion pump, and a titanium sublimation

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XPS, UPS, AND TDS STUDY OF ADSORPTION, OXIDATION, AND HYDROGENATION OF CO ON RHENIUM

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Adsorption, desorption, oxidation, and hydrogenation of carbon monoxide on polycrystalline rhenium foil along with the electronic structure of clean rhenium have been studied by X-ray (Al K_α) and UV (Ne I, He I, and He II) photoelectron spectroscopy and thermal desorption spectrometry under UHV conditions. The valence band electron spectra of clean Re are compared with the density of states obtained from APW band-structure calculations and variations in the photoionization cross sections as a function of photon energy are presented. X-ray induced Auger transitions below 1450 eV are identified according to approximate calculations employing atomic energy level differences. Chemisorption of CO and O_2 at low exposures on clean Re is reported. The results show that O_2 is dissociatively adsorbed at 25°C and CO is dominantly molecularly adsorbed at 25°C, a portion of which is desorbed at 240°C and the remainder dissociated into carbide and oxide forms which desorb at 1060°C. The high temperature dissociated carbide and oxide species are the reactants during oxidation to CO_2 and hydrogenation to CH_4. Correlation of the molecular orbitals of adsorbed CO with those of gaseous CO and $Re_2(CO)_{10}$ suggests that the adsorbed molecule is terminally bonded to the metal via the C atom.

1. Introduction

Studies of carbon monoxide adsorption on transition metals [1] have provided important information in deciphering the basic mechanisms of catalytic oxidation and hydrogenation of CO to CO_2 and CH_4, respectively. Rhenium metal is frequently a component in industrial catalysts and, although catalysis on Re metal [2] and its alloys [3] has been studied, the mechanisms of such reactions on Re are not known. This paper attempts to determine the basic atomic interactions involved in such reactions through an investigation of the adsorption and desorption of CO on clean polycrystalline Re foil. The techniques of X-ray and UV photoelectron spectroscopy (XPS and UPS) and thermal desorption spectrometry (TDS) are used to identify surface species and monitor the reactants and products during the course of the basic reactions. Oxidation and hydrogenation as a function of temperature are performed within the UHV spectrometer environment.

During the course of these chemisorption studies it was found that the photo-

3

Clustering Distances in Secondary Ion Mass Spectrometry

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1. Introduction

The successful application of SIMS to chemical structure analysis is at present restricted by our rudimentary knowledge of two basic processes, i.e., the degree to which the detected secondary ion clusters reflect the virgin surface structure and the mechanism of cluster formation during sputtering. Some proofs have been offered for direct emanation of dimers and multimers from the surface [1]. Other works have shown that non-adjacent atoms on a surface can combine to form dimers and multimers upon sputtering [2]. Very low ion current and/or low impinging kinetic energy have been applied to avoid inducing molecular rearrangement during sputtering [3]. Our recent SIMS work shows that some molecular rearrangement occurs along with the characteristic fragmentation of the solid structure [4-7]. On the basis of these results, we propose that the bound secondary clusters are formed through potential interactions during irreversible adiabatic expansion of an activated region near the surface surrounding the impact site. The purpose of this work is to investigate the distances over which single atoms in a lattice can combine to form dimer clusters during sputtering.

2. Experimental methods and results

The spectrometer chamber is pumped by a turbomolecular pump and a Ni-Ti sublimation pump providing a base pressure of 2 X 10^{-10} Torr. A primary ion current of 1 X 10^{-8} A over the energy range 0.2 - 3.0 keV was generated from a Varian ion gun. A binary system consisting of the mixed salt KCl-CsCl was chosen for the experiment; this system forms a solid solution in all proportions. For an ideal homogeneous solution, the average distance between metal atoms can be calculated from the concentration. The experiments were performed by monitoring the Cs_2^+/Cs^+ secondary ion ratio, R. With decreasing [Cs] the average distance between Cs atoms, r, will increase (and the average number of Cs atoms in the region over which the momentum is dissipated will decrease) and the clustering probability to form the Cs_2^+ dimer should decrease. When r is large enough that Cs atoms cannot be neighbors, all dimers observed are assumed to come from a recombination process. The SIMS intensity ratios Cs_2^+/Cs^+, R, as a function of [Cs] in the solid solution for different E_k's are shown in Fig.1. The average distances between Cs atoms, r, at the indicated concentration (assuming ideal mixing of the components) are shown at the top of the figure. It shows that R increases from 0.2 to 3.0 KeV as [Cs] increases. At constant voltage, these points form a reasonably straight line for low [Cs]; in this region R could be expressed as $R = a \cdot \log[Cs] + b$, where a and b are constants. Extrapolating these straight lines results in intercepts with the R=0 abscissa in the region of r∼200 A for He^+ and r∼400 A for Ar^+ bombardment. The R values for [Cs/K] > 0.1 deviate significantly from straight lines; these deviations are most likely due to the fact that the intensity of the monomer is $>10^6$cps. Nonlinearities can occur at such high count rates because the modular gain of the multiplier decreases and the amplification electronics beyond the channeltron begin to saturate as a result of pulse pile up. The Cs^+ and Cs_2^+ intensities from contamination on the sample holder were about 0.5 and 0.1 that observed from the most dilute sample ($[Cs]/[K] = 6.3 \times 10^{-4}$), respectively. Therefore the contribution to the Cs_2^+ signal from stray dimers due to migration along the surface was considered to be negligible.

3. Discussion

If sputtering is dominantly a momentum transfer process, the distances over which atoms combine during sputtering to form dimers should provide a measure of the size of the region over which the momentum is dissipated. Such a process can be studied by monitoring the intensity of secondary dimer clusters as a function of i) the distances r between the atoms in the lattice that make up the dimer and ii) the primary ion kinetic energy E_k and mass M. The experimental results suggest that the observed dimers are formed by combination of Cs atoms from non-adjacent sites during the sputtering process. If the detected dimers come dominantly from sites where two Cs atoms are accidentally adjacent, R would be independent of [Cs] because the probability of such sites existing is proportional to $[Cs]^2$. The results show that R is strongly dependent on [Cs] suggesting that the Cs_2^+ intensity obtained from accidentally adjacent Cs atoms or sputtering induced Cs migration is negligible. The convergence of the R versus [Cs]/[K] lines for different E_k

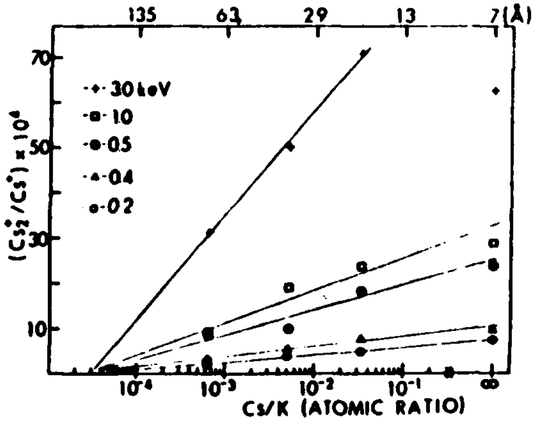

Fig.1 SIMS intensity ratio Cs_2^+/Cs^+ as a function of the Cs/K atomic ratio in the mixed salt solution KCl-CsCl. The primary ions are He^+ with E_k's ranging from 0.2 - 3.0 keV. The point for pure CsCl at 3 keV is neglected in the least squares fitting of the straight lines

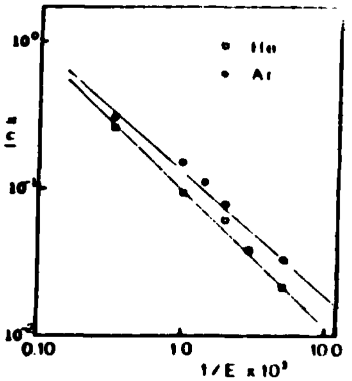

Fig.2 Plots of ln k versus $1/E_k$ assuming that k is proportional to the slope of the lines in Fig.1

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[1] On leave from The Res. Inst. Iron, Steel & Other Metals, Tohoku University, Sendai, JAPAN.