Surface Phases and their Influence on Metal-Oxide Interfaces

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Abstract

Monolayers adsorbed at surfaces and interfaces can have dramatic effects on materials properties. This project is concerned with the bonding, structure and morphology of such layers on metal surfaces and with their effects on oxidation kinetics and metal-oxide adhesion. The proposed work is basically a study of the 'metallurgy' of 2-dimensional systems with emphasis on the properties of binary adsorbed layers. A range of experimental techniques, now available to the principal investigator's laboratory, will be brought to this problem including electron diffraction, atomic force and tunneling microscopy, environmental scanning electron microscopy and secondary electron spectroscopies. It is our intention to try to extract information on adsorbate interaction parameters through comparison of the results with model predictions; initially simple pair interaction potentials will be used, hopefully increasing in level of sophistication as collaborations develop.

Atomic steps on single crystal surfaces are known to have a major influence on the nucleation and growth of overlayers and this is being exploited by a number of research groups to produce epitaxial electronic materials with unusual morphologies. We propose to extend these ideas to metal oxide systems and to build on our previous work on atomic step interactions on metals to form atomic step arrays as preferential sites for surface nucleation of oxides and other compounds. Atomic steps may also introduce finite size effects on 2-dimensional phases. This will be explored by probing phase coexistence and morphology over ranges of vicinal surfaces with systematically increasing step density. There is little previous work on these effects on metal surfaces although the literature contains many references to the probable influence of atomic steps on surface phase transitions and oxide growth. Metal substrates, patterned using optical and e-beam lithography methods, will be used to obtain interesting atomic step modulation patterns.

Wetting, de-wetting and adsorbate spreading phenomena have their detailed explanation in the relative bonding of different adsorbates to surfaces and interfaces. Such phenomena are well studied in liquid systems and their importance has been recognized in the production of multilayer solid materials. Adsorbed (or segregated) monolayers at metal-oxide interfaces are also known to have a strong effect on adhesion and the degree to which the

oxide protects the underlying metal from further oxidation. The relationship between oxide morphology and the distribution of surface and interfacial phases is however not well studied; it will be one of the issues addressed in the proposed work.

Summary of Previous Work

Specific Project Objectives

- (i) The investigation of the stable phases of S and O (and other adsorbate pairs) on transition metal and alloy surfaces and the measurement of the thermodynamic properties of these 2-dimensional binary systems,
- (ii) The detection of the morphology of mixed or coexisting surface phases,
- (iii) The measurement of the effect of S adsorbed submonolayers on the nucleation and growth of metal oxides,
- (iv) The effect of S submonolayers on the adhesion and morphology of oxide-metal interfaces,
- (v) The influence of surface defects, principally atomic steps, on the above questions.

2-D Phase diagrams

The literature on structural and thermodynamic aspects of adsorbed phases on metals is very extensive(1). The relationship between substrate and overlayer structure has been followed by many techniques, the contributions from electron diffraction methods being most numerous. Adsorption isotherms and, in a few cases, isosteres have also been reported; from these one can extract information on heats of adsorption and the way this quantity changes with structural transitions. The number of studies which deal with adsorbed layers of 2 or more components is, on the other hand, very limited although the 2 or more component situation is probably more frequently encountered in important surface reactions such as oxidation and other corrosion processes. In our work to this point we have tried to establish a framework for describing phase equilibria for binary adsorbed layers, have made some studies of coexisting phases on Ni and NiFe alloy surfaces, and have tried to make the connection between the mode and rate of oxidation and the presence of the adsorbed phases. The effect of interface adsorbates at metal-oxide boundaries has also been a focus of our work. In our work we are trying to identify and study fundamental surface and interface properties that are important in gaseous corrosion processes and metal-oxide bonding.

Figure (1) indicates the set of variables that can normally be controlled or measured most readily in experiments dealing with 2-component adsorbed layers at surfaces or interfaces(10). In contrast with most 3-dimensional binary alloy systems the average density in (pseudo-) 2-dimensional layers at surfaces can be varied over a very wide range. In other words, a broad range of average coverage is normally accessible so that there are apparently an infinite number of constant coverage 2-dimensional diagrams that one could explore. We need to remember however that in choosing model systems that most closely correspond to real gas phase corrosion situations, the surface coverage will tend to 'saturate' at particular values over ranges of gas partial pressures (or component chemical potentials). This can be rationalized in terms of the strong adsorbate-surface interaction energies as well as those between adsorbates; the latter are largely responsible for adsorbate ordering. For example, for both Ni and NiFe alloy surfaces well defined superlattice structures of O, S, or O-S mixtures occur at coverages such as $1/4$, $1/2$ or $1/2$ monolayers(2)

Figures (2) and (3) are phase diagram sections for coadsorbed S and O from work done during the current grant period (2) while figure (4) shows data on transition temperature for a coverage of $1/4$ monolayer on Ni(111). These suggested diagrams are derived principally from LEED and electron spectroscopy observations. Taking as an example the case of S and O coadsorbed on Ni(111) at a constant total coverage of $1/3$ monolayers, there is apparently a low temperature miscibility gap in which 2 ordered phases coexist while these merge to a single homogenized phase with the same superlattice relationship to the substrate; this single phase undergoes a disordering transition to 'lattice gas' at higher temperature. It must be emphasized however, that the observations that form the basis of this diagram are indirect; they consist of observations of electron diffraction patterns from which overall symmetry properties can be derived and measurements of the temperature dependence of superlattice beam intensities. Examples of the diffraction patterns from the $1/3$ monolayers surface are shown in figure (5) while figure (6) shows the temperature variation of the $(1/3, 1/3)$ beam from this structure.

An important tool in the study of 3-dimensional alloy phase diagrams has been microscopy, either optical or electron. Microscopy provides the 'direct' observations that provide a test of the conclusions on phase

Fig.(1) Two dimensional phase diagrams of binary systems can be represented on temperature T ($^{\circ}\text{K}$), composition χ (atomic fraction) and adsorbate coverage θ (ML) diagrams. The dashed lines indicates a plane of constant coverage on which some familiar features observed in 3-D binary systems are expected.

Fig. (2) Schematic T - θ - χ surface phase diagram for the $\text{Ni}_{60}\text{Fe}_{40}(100)\text{-S+O}$ system.

Fig. (3) Possible 2-D phase diagram for the $(\sqrt{3} \times \sqrt{3})R30^\circ\text{S+O}$ coadsorbed structure on Ni(111). The dashed line represents the order disorder transition which is possibly of first-order and the line with alternating dashes and dots represents a possible miscibility gap with a critical temperature representing the transition from the $(\sqrt{3} \times \sqrt{3})R30^\circ\text{S} + (\sqrt{3} \times \sqrt{3})R30^\circ\text{O}$ phases to the $(\sqrt{3} \times \sqrt{3})R30^\circ\text{S+O}$ phase.

Fig. (4) The variation of order-disorder transition temperature as a function of composition for the $p(2 \times 2)S+O$ coadsorbed structure. The bottom (upper) axis is the S (O) coverage. Note that this is not a phase diagram. The accuracy of T_c is indicated by the error bars, estimated from Intensity-T curve measurements and coverages determinations.

Fig. (5) LEED patterns of the coadsorbed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of oxygen and sulfur, (a) S coverage = 0.03, (b) 0.08, (c) 0.13 and (d) 0.20 monolayers. Taken at a primary beam energy of 82.1 eV. Note that the fractional beam size remains constant, but the background intensity varies with the S coverage.

Fig. (6) Plot of the intensity of the $(1/3, 1/3)$ LEED beam from a $(\sqrt{3} \times \sqrt{3})R30^\circ$ -S+O structure ($\theta_s = 0.15$ ML) as a function of temperature during heating. The order-disorder transition is not reversible. Note the beam intensity levels off within 10 K above the transition temperature.

coexistence from 'indirect' methods such as x-ray diffraction and thermal analysis. With the fairly recent development of scanning tunneling microscopy (STM) and low energy electron microscopy (LEEM) it is now possible to 'directly' observe the distribution and morphology of phases on crystal surfaces so that the topic of 2-dimensional metallurgy is poised for a significant step forward. In our laboratory we have gained considerable experience over the last several years in the use of the STM for the study of defects and mass transport processes; these studies have mainly been on semiconductor surfaces but we are now well situated to launch on an STM investigation of the morphology of 2-dimensional phases, interphase interfaces and transitions. Low energy electron microscopy would of course also be an extremely useful addition; this will be the focus of a future instrumentation proposal.

Kinetics of oxide growth

The initial stages of oxidation are greatly influenced by the presence of other adsorbates on the surface (2). Although this effect may not be of great importance in determining the thickness of oxide scales after very long exposure or service conditions the adsorbates probably continue to have a major effect on the adhesion at the metal-oxide interface (3). For special structures such as multilayer metal-oxide films they will have a dramatic effect on the film morphology. The effects of segregating or adsorbing impurities on oxide adhesion have of course been recognized as a major factor to be considered in the design of corrosion resistant alloys(3).

During the current grant period we have made a fairly detailed study of the effects of adsorbed sulfur on the kinetics of oxidation of Ni and NiFe single crystal surfaces. Using the results of the 2-dimensional phase coexistence studies, outlined in the previous section, we have explored the effects that various pre-coverages of S can have on the rate of growth and structure of surface metal oxide films for several substrate temperatures. The general conclusion is that while the same sequence of stages seems to occur (ie fast chemisorption, oxide nucleation and oxide thickening (4)) the overall rate is dramatically decreased by the presence of adsorbed S. Figure (7) shows some results for the rate of oxygen uptake on a Ni(111) surface with various pre-coverages of S at ~300K and at 440K. As noted, the general shapes of the oxygen uptake curves, for various S pre-coverages, are similar to that for the S free surface. However the onset of oxide nucleation is

Fig. (7) Oxygen AES intensity versus oxygen exposure on Ni(111) for sulfur overages of 0, $1/12$, $1/4$ and 0.4 ML at (a) 300 K and (b) 440 K; the exposure scale is logarithmic. Note the three-stage oxide growth on all but the 0.4 monolayer S covered surface, where oxygen chemisorption is prohibited.

delayed and the overall rate of oxide thickening is decreased in the presence of adsorbed S. Both of these effects can be rationalized on the basis of site blocking by the adsorbed S as described in some detail in reference (2b).

In order to assess the effect of the S on subsequent thick film growth and adhesion we have attempted to probe the location of the S as growth proceeds. From measurements of the intensities due to O and S Auger transitions both during growth and during sputtering we have concluded that the S remains concentrated in the metal-oxide interface region as continuous oxide film growth proceeds (2b).

Effect of S on oxide-metal adhesion

Complete prevention of oxide growth on metallic alloy surfaces is, in general not a very realistic goal. It may in fact be possible with extremely well controlled structures (such as single crystal thin films) to 'poison' the oxidation reaction with monolayer level adsorbates or implanted species but this will not be a long term solution to general corrosion problems. The data presented in the previous section clearly show that major changes in growth kinetics are in fact caused by S on a relatively short term basis and this could be of importance for the production of special oxide-metal structures.

We have found that continuous oxide films on NiFe alloy surfaces can in fact be unstable in the presence of S (5). In our experiments we used a beam of S₂ as the S source and found that at elevated temperatures the S would penetrate the oxide layer, strongly bond to the metal surface and displace the metal oxide. Under the right conditions the adsorbed S can form an ordered superlattice structure (see figure (8)). The phenomenon can be described as a solid state de-wetting process. The difference in energy between the S-metal and O-metal bonds seems to be sufficient to allow the S to radically change the morphology of the oxide in a manner similar what is commonly observed when surfactants are added to oil films on water. As in nearly all of the effects that we have investigated there is a real need for 'direct' observations of the structural changes taking place at the metal-oxide interface; as part of the work during the proposed new grant period we intend to carry out both scanning electron microscopy and atomic force microscopy studies of the effect.

Figure (8): Models of the surface morphology caused by exposing an oxide coated Fe-Ni surface to S at 500C.

Influence of Surface Defects on Surface Adsorbed Phases and Oxidation

It is well established that most solid state reactions are strongly influenced by crystalline defects. This is certainly true of many surface reactions. Systematic studies of the correlation between surface defects and surface adsorbed phase or oxide formation are extremely sparse. In our work we intend to look for such correlations by studying adsorbed phases on surfaces with well defined average step densities (vicinal surfaces). As described later these will be produced by a variety of different methods. To this point in the work we have made observations on the distributions of atomic steps mainly using electron and x-ray diffraction methods. We have found interesting atomic step clustering phenomena which are themselves influenced by adsorbates (6).

We have carried out a study of the structure of Ni surfaces vicinal to Ni(111) using both LEED and glancing incidence X-ray diffraction (at Brookhaven). Using a resistive anode detector we have measured the distribution of electron diffracted intensity near the (00) beam from a Ni vicinal surfaces as a function of temperature. The split beam changes to a single beam as the temperature is decreased as shown in figure (9). By fitting calculations, based on a 2-phase model of the surface, to the measured beam profiles we believe that the changes in LEED patterns with temperature can be attributed to an atomic step clustering transition in which there are major changes in the distributions of terrace widths and step heights on the surface. The variation of average step height with temperature, which is consistent with both the LEED and the X-ray data has been obtained. Figure (10) presents some conclusions on the way that the average atomic step height varies with temperature. (The transition occurred on Ni(111)5°[112] at ~560 K with some hysteresis). Preliminary data suggests that this transition is strongly affected by small concentrations of adsorbed S or O; this will be the subject of some future experiments.

FIG(1): Intensity plots, using a position sensitive detector, showing the variation of the splitting of the (00) beam at an electron energy of 40.7 eV from a surface rotated 5° from Ni(111) about the $[110]$ zone axis, ie Ni(111) 5° [110]. As temperature decreases the split beam merges into a single beam indicating the formation of larger terraces.

Fig(9): Step height versus temperature derived from fitting the LEED intensity variations shown in fig(8) with model terrace width distributions. Single atomic steps dominate at high temperatures while clustering takes place at lower temperatures.

PUBLICATIONS DURING CURRENT GRANT PERIOD

Publications with DOE support during current project.

Some of these publications involve development of techniques used in the central DOE project

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"Temperature Programmed Desorption Studies of Copper Ultra Thin Films on Sapphire (0001) Surfaces", Yaoguo (Gary) Ding, MS Thesis, Aug '91.

"Coadsorbed Structures of Sulfur and Oxygen on Ni(111) and their Effects on Oxidation", Jun Liu, PhD Thesis, May '92.

"Diffraction Studies of the Atomic Step Phase Transition of Ni(111) Vicinal Surfaces", Jae-Pill Chang, PhD Thesis, May '92.

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