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SURFACE CHEMISTRY

G. A. Somorjai

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INTRODUCTION

In recent years there has been a remarkable progress in our understanding of the structural properties of solid surfaces. Most of the important advances were due to studies carried out on well characterized single crystal surfaces. There are several factors which have contributed to recent developments in surface science. (1) A variety of monatomic and diatomic solids (insulators, semiconductors, and metals) have become available in ultrahigh purity (<1 ppm impurities) and in single crystal form. (2) Vacuum technology has developed to the point where clean solid surfaces can be easily maintained in ultra high vacuum ($<10^{-8}$ Torr). (3) Several new experimental techniques have become widely used which have produced information about surfaces on an atomic scale. Among these new research tools low energy electron diffraction plays a prominent role. Just like x-ray diffraction may be used to study the bulk structure and thereby pave the road for the development of solid state science so is low energy electron diffraction probes the structure of solid surfaces and catalyzes the

development of surface science. In addition, other experimental tools such as electron spectroscopy using low energy beams, slow neutron [Boutin & Prask (1)] and molecular beam scattering studies and electron spin resonance [Chung & Haneman (2) and Taloni and Haneman (3)] studies of surfaces have provided further assistance to carry out more definitive investigations.

This review will be concentrating on investigations which were carried out on clean single crystal surfaces under well defined experimental conditions. It will be divided into two parts. In the first part studies concerning the properties of "clean" solid surfaces will be discussed. These will include studies of surface structure, surface phase transformations and the dynamics of surface atoms (mean displacement, surface diffusion, and vaporization). In the second part we shall discuss gas-solid interactions. These include molecular beam scattering studies from well defined surfaces, the investigations of the elementary steps of adsorption and surface reactions. Here, we shall discuss recent advances in

relatively simpler surface reactions such as photodecomposition, space charge limited reactions, and oxidation. Since the contribution of field emission and field ion microscopy to surface chemistry have been reviewed in this series only recently [Müller (4)] these fields are not treated here.

STUDIES OF CLEAN SURFACES

Properties of Clean Surfaces

The definition of a "clean" surface depends to a large extent on the experimental tool which is applied to investigate its properties. Using low energy electron diffraction techniques which have been reviewed by Lander (5) jointly with a mass spectrometer one could detect ordered impurities on the surface in concentrations of about 5% of a monolayer [Lyon & Somorjai (6)]. Using Auger electron spectroscopy (to be discussed later), one may detect low atomic weight impurities which comprise 1% of a monolayer. Electron spin resonance techniques could be used to monitor $\sim 10^{12}$ spins/cm^2, i.e., less than 1% of a monolayer [Haneman (7) and Sancier (8)].

Other techniques which have been useful to detect surface impurities are spark source mass spectrometry, and He^3 activation analysis [Markowitz & Mahony (9)].

Since the surface can be contaminated by either the adsorption of gases from the ambient or by the out-diffusion of bulk impurities several techniques should be applied to ascertain its cleanliness.

As a result of the application of different experimental tools to studies of clean single crystal surfaces several new surface phenomena have been discovered. Low energy electron diffraction studies revealed that the arrangement of surface atoms could be different from the arrangement of atoms in the bulk unit cell [Schlier & Farnsworth (10), Lander (5), Hagstrom, Lyon & Somorjai (11)]. The surface can undergo structural rearrangements as a function of temperature while no such transformation occurs in the bulk of the solid. The surface structures which form are either ordered or disordered [Lyon & Somorjai (6)] they have well defined temperature

ranges of stability. Measurements of the Debye-Waller factor for surface atoms using low energy electrons [MacRae & Germer (12) and Lyon & Somorjai (13)] showed that the mean displacement of surface atoms is different from that of atoms in the bulk. This confirms the results of several theoretical calculations [Clark, Herman & Wallis (14) and Maradudin & Melngailis (15)]. There are also experimental evidence that there is an appreciable net displacement between the first and second atomic layer at the surface [MacRae & Germer (16) and Feinstein & Shoemaker (17)]. Thus, it seems that the lattice vibration spectrum of atoms in the surface layer is different from that of atoms in the bulk.

Measurements of the characteristic energy losses of electrons scattered by the solid surface indicate [Raether (18)] that the plasma frequency of electrons about surface atoms (surface plasmon) is much smaller than the plasma frequency in the bulk ($\omega_{surface} = \omega_{bulk}/\sqrt{2}$). Thus, the electron density distribution about atoms in the surface is different from that for atoms in the bulk.

These experimental results indicate that the surface often behaves as a separate solid phase with distinctly different properties from that of the bulk phase. The surface phase is well isolated by large potential energy barriers from exchange with the bulk or from evaporation into vacuum. Atomic rearrangements in the surface plane, however, can take place with relative ease since the activation energy for surface diffusion of ad-atoms or vacancies is appreciably smaller than the activation energies of bulk diffusion and vaporization for many solids. Most metals and semiconductors are expected to have a well-isolated surface phase. For ionic solids, however, atomic exchanges between the surface and the bulk is relatively unhindered due to the small activation energies for bulk vacancy (in alkali halides, II-VI compounds) or interstitial ion diffusion (silver-halides, etc.). Therefore, for these compounds the surface may not have structural properties different from that of the bulk crystals.

High energy electrons ($>10^4$ eV) may also be used to study the structure of surfaces [Simmons, Mitchell & Lawless (19); Siegel & Menadue (20)]. A high energy electron diffraction (HEED) technique which uses an electron beam at a grazing angle of incidence have been developed and promises to provide surface structural data in addition to that obtained by LEED. The notable advantages of HEED include a good control of the penetration depth of the incident beam and its possible application to studies of the structure of polycrystalline samples which cannot easily be studied by LEED.

Technique and Nature of Low Energy Electron Diffraction

A monochromatic beam of electrons of energies $1\text{-}10^3 \pm .1$ eV is used and focused onto the surface of a single crystal sample. The electron wavelength can easily be varied in the range roughly 0.4 Å–12 Å [$\lambda(\text{Å}) = (150/\text{eV})^{1/2}$] by changing the accelerating potential. The incident electrons have a large scattering amplitude (angstroms) due to their low energy and

charge and are back-reflected from the surface. After traveling a short field free path (~ 7 cm) the inelastically scattered electrons are retarded while the elastically scattered fraction which contains the diffraction information is post-accelerated (21) onto a spherical fluorescent screen where the diffraction pattern is displayed. Other detection techniques (Faraday cup) are also being used [Schlier & Farnsworth (22)]. For accelerating potentials smaller than ~75 volts, most of the electrons are back scattered from the surface plane. Thus, the diffraction pattern reflects the arrangements of atoms in the surface as the two dimensional character of the diffraction essentially dominates. At higher electron energies the fraction of electrons which penetrate a few atomic planes below the surface increases and the intensity of the diffraction features which are due to the periodicity of the atoms in the surface diminishes. Thus, at high beam voltages (> 150 eV) the diffraction pattern is more characteristic of the bulk

structure, i.e., the three-dimensional character of the diffraction becomes more pronounced (5). The fraction of elastically scattered electrons decreases rapidly with increasing electron energies from roughly 80% at 5 eV to about 5% over 75 eV and will depend on the material studied (5,6). The diffraction pattern can be viewed and photographed through a window. In the diffraction chamber which is a part of an ultrahigh vacuum system pressure of the order of 10^{-10}–10^{-9} torr can easily be maintained. Ultra high vacuum is necessary to avoid possible contamination of the sample surface during the experiments by the adsorption of gases from the ambient. Unlike x-rays which are scattered by the atomic electrons, the incident electrons are scattered by the crystal potential [Vainshtein (23)]. Thus, hydrogen atoms can be just as effective scatterers as heavier elements. Due to their large scattering amplitude which is several orders of magnitude higher than for x-rays, low energy electrons can be used to obtain high intensity diffraction

patterns from ordered surface structures composed of no more than 5-10% of the total number of surface atoms (5).

The low energy electron diffraction pattern is representative of the periodic arrangements of atoms on the surface. Analysis of the intensity of the diffraction features is necessary, however, to distinguish between several structures which could yield similar diffraction patterns, i.e., to determine the unique position of the atoms on the surface. Although accurate structure analysis cannot yet be carried out recent contributions by Boudreaux & Heine (24), McRae (25,26), and several groups in different laboratories [Gerlach & Rhodin (27); Gafner (28); Hirabayashi & Takeishi (29)] to the theory of low energy electron diffraction indicate that the formulation of a working model for structure calculations is imminent. We shall present some of the considerations which have played an important role in the development of a theory of LEED.

In the kinematic theory of scattering the intensity of the scattered waves is assumed small compared to the incident beam intensity and therefore multiple beam interactions are neglected. In view of the large scattering amplitudes of low energy electrons [McRae (30)] the applicability of the kinematic approximation in LEED studies has to be carefully examined. It is likely to be more applicable in the intermediate and high electron energy ranges (> 100 eV) where the strong inelastic scattering gives rise to pronounced absorption [Khan, Hobson & Armstrong (31)]. At low electron energies the intensity of the elastically scattered electron beam is comparable to the incident beam intensity and multiple beam interaction have to be taken into account. Experimental detection of in-plane resonance of the incident electrons in this energy range seems to confirm this [McRae & Caldwell (32)].

Studies of the wavelength dependence of the back-reflected specular (00) beam intensity revealed the presence

of "secondary" Bragg peaks (5). The differences in the electron scattering properties of the surface and the bulk are believed to be partly due to the asymmetry of the environment of the surface atoms (27) (i.e., mean displacement, electron density distribution) as compared to atoms in the bulk of the crystal.

The preparation of the single crystal surfaces is an important part of the experiment. Careless cutting and polishing can produce an amorphous surface layer as much as several microns thick [Lyon (33)]. In order to obtain the diffraction features characteristic of the single crystal surface the damaged surface layer is removed by ion bombardment [Farnsworth & Hayek (34)], chemical etching [Lander & Morrison (35)] or cleaving <u>in situ</u> [MacRae & Gobeli (36)]. Annealing the samples at elevated temperatures is also used to remove the surface damage.

Structure of Surfaces

The crystallography of two dimensional structures, symmetry operations and special conventions have been outlined by Wood (36). The arrangement of surface atoms which is identical to that in the bulk unit cell is called the "substrate" structure and is designated by (1 × 1). For example, the "substrate" structure of platinum on the (111) surface is designated Pt(111)–(1 × 1). Any other arrangement of surface atoms is called the "surface net" or "surface structure." When the unit cell of the surface structure is twice as long as the substrate unit cell along one crystallographic direction and the same length along the other direction it is designated (2 × 1). If the unit cell of the "surface structure" is twice as large as the underlying bulk unit cell, it is designated, (2 × 2). A (2 × 1) surface structure which is formed by an adsorbed gas such as oxygen on the (110) face of nickel, is designated, Ni (110) - (2 × 1) - O. If the unit cell of the surface net is rotated

with respect to the bulk unit cell, the angle of rotation is also specified. For example, for 45° rotation the same surface structure is designated by Ni (110) - (2 × 1) - 45° - O.

One of the important discoveries of low energy electron diffraction studies of recent years is that surface atoms may reside in surface structures of different kind. The presence of these structures is indicated by the appearance of extra diffraction features in the LEED pattern which are superimposed on the diffraction pattern of the substrate unit mesh predicted by the bulk unit cell. These surface structures are ordered or disordered. The ordered structures can be characterized by lattice parameters which are integral multiples of the unit cell dimensions which characterize the substrate. After several years of studies in different laboratories and considerable debate the presence of these surface phase transformations on semiconductor surfaces have been accepted to be attributed to ordered arrangement of the

surface atoms of the clean solid (5,10,35a,35b,36). Studies of clean germanium, silicone [Lander & Morrison (37)], gallium arsenide, and other compound semiconductor surfaces (~~36~~ 35b) have revealed the presence of several ordered surface structures with unit cells in the range of twice (2 × 2) to as large as eight times (8 × 8) the unit cell dimensions of the substrate. Although the first reports by Farnsworth et al (10) on the presence of these surface structures have met considerable scepticism further work in the field by several investigators have removed the possibility that they may be structures of possible surface contaminants. It should be pointed out, however, that since these surface structures are the property of the interface their formation or removal may well be catalyzed or inhibited by gases adsorbed on the surface.

Recently surface structures have been reported to exist on insulator surfaces as well. Charig (38) has reported on the appearance of surface structures on the c-face of Al_2O_3.

Surface structures have been discovered to exist on the surfaces of several face-centered cubic metals [Lyon, Mattera & Somorjai (39)]. The (100) and (110) faces of platinum (6,11), gold, palladium, and silver [Mattera, Goodman & Somorjai (40)] exhibit surface rearrangements as a function of temperature when heated in ultra high vacuum. Surface structures have also been detected on the (1120) crystal faces of antimony and bismuth [Jona (41)]. Palmberg, Rhodin, and Todd (42) have been able to produce the (5 × 1) surface structure of gold while epitaxically depositing the metal from the vapor onto different ionic single crystal substrates (MgO and KCl). Due to the more recent discovery of the surface structures on metal surfaces there is still some debate as to whether the surface structures are the property of the clean metal surface or are caused by surface impurities [Fedak & Gjostein (43); Somorjai (44)]. The properties of these surface structures and their complete reproducibility seem to rule out the possibility that they are impurity

structures. For example, the (5 × 1) surface structure of gold has been reproduced in six different laboratories by all the investigators who have been studying it.

The crystal faces with lower atomic densities are more likely to form surface structures at low temperatures. The formation of the surface structures seem to be surface diffusion limited, it is accelerated by prior ion-bombardment which produces weakly held mobile ad-atoms in large concentrations or by the presence of a temperature gradient (33) along the crystal surface. The surface structures have well defined temperature ranges of stability, their formation is reversible (33) or irreversible. Ordered surface structures appear at lower temperatures below roughly one-half the melting point of the solid (39). Disordered structures which give rise to ring-like diffraction patterns appear and are more stable at high temperatures on several metal surfaces (6,39,40). There are several semiconductor, insulator, and metal surfaces which do not exhibit the formation of surface structures. No surface structures have yet been found on

body-centered cubic metal surfaces [George et al (45); Haas et al (46); Pignocco & Pellissier (47)]. More work using clean metal surfaces should be carried out in order to understand the conditions necessary for ordered surface phase transformations or order-disorder transitions in the surface. It is apparent that the activation energy for surface diffusion, ΔE_{diff}, plays an important role in determining the rate and the nature of surface rearrangements (39). If ΔE_{diff} is small for surface atoms at kinks the surface structures may form as a function of temperature without ion bombardment. If ΔE_{diff} is large, ion bombardment, which increases the ad-atom and/or surface vacancy concentrations may be necessary to induce phase transformations in the surface.

Dynamics of Surface Atoms

Mean displacement of surface atoms.- Atoms at the surface are in an asymmetric environment which markedly affects their lattice vibration spectra. Calculations showed that the mean displacement of surface atoms in metals (14,15),

ionic [Benson et al (48)], or molecular crystal lattices [Alder et al (49)] should be different from that in the bulk. The technique of low energy electron diffraction has proved to be applicable to measure this effect. This is carried out by measurement of the Debye-Waller factor, i.e., the temperature dependence of the back-scattered diffracted electron beam intensity (13). The scattered intensity may be expressed as

$$I_{hk\ell} = |F_{hk\ell}|^2 \sum_{\ell,\ell'} \exp[i(\underset{\sim}{k}-\underset{\sim}{k}_o)\cdot(\underset{\sim}{u}_\ell-\underset{\sim}{u}_{\ell'})] \qquad 1.$$

where $|F_{hk\ell}|^2$ gives the scattered intensity from a rigid lattice in a particular direction (h,k,ℓ) and the exponential term arises from scattering due to lattice vibrations (13). Here $\underset{\sim}{k}$ and $\underset{\sim}{k}_o$ are the scattering vectors in the direction of the scattered and incident electron beams, respectively, and $\underset{\sim}{u}$ is the displacement vector. The summation is over all pairs of scattering centers ℓ,ℓ'. If we disregard thermal-diffuse scattering [McKinney et al (50)] and multiple scattering events (26) the scattered intensity can be rewritten as

$$I_{hk\ell} = | F_{hk\ell} |^2 \exp\left[(-16\ \pi^2 \cos^2\phi/\lambda^2)\langle u^2_{\Delta k}\rangle\right] \qquad 2.$$

where $\langle u^2_{\Delta k}\rangle$ is the component of the mean-square-displacement in the direction $\Delta \underset{\sim}{k} = (\underset{\sim}{k} - \underset{\sim}{k}_o)$, λ is the electron wavelength and 2ϕ is the angle between the scattering vectors $\underset{\sim}{k}$ and $\underset{\sim}{k}_o$. The exponential term is the Debye-Waller factor. Using the Debye model of lattice vibrations in the high temperature limit the mean square displacement is given by the equation,

$$\langle u^2 \rangle = (3N\hbar^2/Mk)(T/\theta^\infty) \qquad 3.$$

where θ^∞ is the Debye temperature at the high temperature limit, M and T are the atomic weight and temperature of the solid, respectively, N, k, and $\hbar$ are the Avogadro number, the Boltzmann and Planck constants, respectively. Combining Eqs. (2) and (3) we have

$$I_{hk\ell} = | F_{hk\ell} |^2 \exp\{-(12Nh^2/Mk)(\cos\phi/\lambda)^2[T/(\theta^\infty)^2]\} \qquad 4.$$

The temperature dependence of the scattered intensity can thus be used to measure the mean displacement of surface atoms or the surface Debye temperature. Most of the measurements reported so far were carried out with the specularly reflected

electron beam (00-reflection). For the specular reflection the scattering vector, $\Delta\underset{\sim}{k}$, is perpendicular to the surface plane. Therefore, the data yields only the vertical component of the root-mean-square displacement, $\langle u_{\perp} \rangle$. In order to measure the true surface displacement the $I_{oo}(T)$ measurements should be carried out at the lowest electron energies (13). At higher incident energies a large fraction of the electrons penetrate below the surface plane and the bulk Debye temperature is approached.

These studies have been carried out using Pt (13), Ni (12), Pd and Pb [Goodman, Farrell & Somorjai (51)], and Ag [Jones, McKinney & Webb (52)] surfaces. It was found that the mean displacement of surface atoms is 40-100 per cent larger than for bulk atoms. There is little difference between the surface mean displacements of different crystal orientations, $\langle u_{\perp} \rangle$ appears to be relatively insensitive to changes of surface structure or surface density (50). It is hoped that these studies will be expended to include ionic and semiconductor crystals as well.

Theoretical analysis of the mean square displacement of simple cubic and face-centered cubic crystals have been carried out (14,15). These calculations predict increased mean displacements of surface atoms essentially the same order of magnitude as found by the Debye-Waller measurements using low energy electrons. Maradudin and Flinn (53) have investigated the anharmonicity of surface atom vibrations and how it effects the Debye-Waller factor. Calculations of the surface heat capacity of simple cubic solids have been carried out. The surface specific heat is proportional to T^2 at low temperatures and to the surface area of the solid [Wallis (54)].

Surface diffusion.- The diffusion of atoms along the solid surface has been studied by several experimental techniques. These include studies by field electron emission microscope, grain boundary grooving, sinusoidal profile and single scratch decay techniques. Results obtained by these different techniques disagree widely [Gjostein (55)]. Surface diffusion

studies by field emission microscopy are carried out at a lower temperature than the studies by the other techniques and, in general, yield lower activation energies and pre-exponential factors. This disagreement may partly be due to the difference in the ambient conditions in which these experiments are carried out which can markedly effect surface diffusion rates. It is also likely that the different experimental techniques measure the diffusion flux of surface atoms of different kind. The surface is heterogeneous, atoms can occupy positions of a wide range of binding energies. There are atoms adsorbed on the surface, at kinks, in ledges, and there are surface vacancies. Depending on the experimental technique the diffusion flux may include atoms in one or several of the different positions [Blakely (56)]. Studies of surface diffusion on several face-centered cubic metal surfaces (Cu, Au, Ni, Ag, Fe) showed that the activation energies increase markedly with increasing temperature. Gjostein and Winterbottom (57) have suggested that this is

due to a change in the mechanism of atomic transport at the surface. It was proposed that at low temperatures the low value of ΔE (diffusion) reflects the energy necessary to move vacancies along the surface. For this case the activation energies are roughly $\Delta E_{(diffusion)} = 0.24\ \Delta H_{(sub)}$, where $\Delta H_{(sub)}$ is the heat of sublimation for the metal. At high temperatures the dominant carriers of the surface diffusion flux are assumed to be ad-atoms with $\Delta E_{(diffusion)} = 0.54\ \Delta H_{(sub)}$.

New experimental techniques for surface diffusion studies include the use of radioactive tracers [Turnbull (58)] laser beam reflection experiments from sinusoidal surfaces [Bonzel and Gjostein (59)], and intensity measurements of diffraction spots after ion bombardment as a function of annealing temperature in low energy electron diffraction studies (6).

Vaporization kinetics.- The vaporization of surfaces, far from equilibrium is most likely controlled by a surface reaction which takes place prior to the desorption of the vaporizing species into vacuum. This is certainly the case for solids which associate or dissociate upon vaporization [Somorjai (60)]. The rate limiting surface reaction step may be charge transfer [Somorjai and Lester (61)] or the breaking away of surface atoms from kink positions at ledges [Hirth and Pound (62)] or chemical rearrangements of surface atoms at kinks (60). A review of the vaporization mechanisms of solids have been published recently (60). The vaporization mechanism of sodium chloride single crystals have been studied [J. E. Lester (63); G. A. Somorjai (64)]. It was found that the steady state evaporation rate increases by three-fold with increasing density of dislocations (10^6–10^7 cm^{-2}). It was shown that there is no equilibrium on the surface between the dominant vaporizing species, the monomer, and dimer molecules. The vaporization rates of boron [Burns

et al (65)], aluminum and gallium oxides [Burns (66)] have been monitored through the melting point. There is a discontinuous increase in the evaporation rates of the oxides as the crystal structure collapses to that of the maximum rate of vaporization which is calculated from the equilibrium vapor pressure measurements. Boron on the other hand shows no discontinuity of the vaporization rate upon melting.

Rosenblatt et al (67) have studied the temperature dependence of the evaporation rate of arsenic and antimony single crystal surfaces. The vaporization of both solids seem to be limited by a chemical association reaction which takes place at the ledges in the surface. Ward et al (68) have observed marked deviation of the distribution of effusing particles from a Knudsen cell from the cosine law at high temperatures. They show that complete thermodynamic equilibrium is seldom achieved in high temperature Knudsen experiments. The interaction between the vapor and the cell plays an important role in the establishment of solid-vapor equilibrium.

RECENT STUDIES OF SURFACE CONTAMINATION

The detection and analysis of minute impurities is particularly important in surface studies where the structure of the surface and the nature of gas-solid interactions can be strongly affected by surface contaminants. The availability of ultra high purity materials and ultra high vacuum not only allowed to carry out more definitive experiments in surface science but has increased the demand for analytical tools for the detection of surface impurities in concentrations of less than a monolayer ($< 10^{15}$ cm^{-2}).

One of the most promising tools for detecting small concentrations of atoms on the surface is the analysis of electron beam excited Auger electrons from surface atoms [Tharp & Scheibner (69); Harris (69a)]. This measurement involves the energy analysis of a low energy electron beam ($1\text{-}10^4$ eV) which is back-scattered from the surface. The inelastic losses include electronic excitations within the impurity atoms at the surface. Such electronic transitions

are characteristic for a given element and can be identified. Oxygen on metal surfaces, gold, and silver on ionic single crystal surfaces have been analyzed [Weber and Peria (70)]. This technique is simple to apply it can detect amorphous layers which may be invisible by LEED in surface concentrations of less than a tenth of a monolayer.

Another type of analytical technique which also uses an electron beam is electron beam desorption. The adsorbed atoms may be ionized by the incident electrons and subsequently desorbed. This way they can be detected by a mass spectrometer [Lichtman & McQuistan (71)]. Noticeable advances have been reported in detection sensitivity when using polycrystalline surfaces [Lichtman & McQuistan (72)]. Menzel and Gomer (73) have reported very low ionization efficiencies for reactions between low energy electrons and several adsorbed atoms, however. In view of this and several other investigations of adsorbate-electron interactions it is less likely that this technique is applicable for analysis

of surface impurities on single crystals of low surface area. The fragmentation of adsorbed molecules by the incident electrons makes direct identification of the surface species by mass spectrometric analysis difficult.

High energy electrons at a grazing incident may also be used to obtain information about the impurities at the surface [Sewell and Cohen (74)]. In this case the emitted soft x-rays which are characteristic of the emitter atoms are analyzed. While the technique of electron beam excitation of impurity atoms and subsequent analysis of the inelastic loss spectra detects light impurity atoms on the surface with great sensitivity, analysis of the x-ray emission spectra after electron bombardment of surfaces should be sensitive to the presence of heavy impurity atoms [Hagstrom et al (75)].

GAS-SOLID INTERACTIONS

The Structure of Adsorbed Gas Layers on Surfaces

One of the important discoveries of low energy electron diffraction studies is that atoms adsorbed on a solid surface

can form ordered periodic structures (5). The nature of the surface structure depends on the crystal orientation, temperature, and the concentration of adsorbed gas atoms. The adsorption of oxygen, hydrogen, and carbon monoxide have been studied on a variety of metal and semiconductor surfaces. In almost every case chemisorption was accompanied by the formation of ordered surface structures. It is apparent that ordering is preferred on most surfaces over the formation of adsorbed amorphous gas layers. It has been reported [Germer (76); (19)] that a strongly exothermic surface reaction (for example, chemisorption of oxygen on nickel surfaces [Germer and MacRae (77)] can dislodge the substrate atoms from their equilibrium positions in the surface and cause a surface structural rearrangement which is commonly called "reconstruction." The reconstructed surface structure is composed of both metal and chemisorbed atoms in periodic arrays. Although changes in the diffraction pattern during chemisorption can be analyzed in several

different ways [Bauer (79)] complementary experimental evidences seem to indicate that reconstruction is the most likely interpretation of the structural changes observed during the oxidation of nickel surfaces. Reconstruction at the surface may be looked at as the precursor of oxidation reactions which proceed into the bulk via a diffusion controlled mechanism.

There is considerable experimental evidence indicating that hydrogen surface structures can easily be detected on tungsten single crystal surfaces by low energy electron diffraction [Estrup and Anderson (79)]. Thus, electron scattering from ordered arrays of hydrogen atoms is strong and unlike x-ray scattering it can be applied to verify the positions of hydrogen atoms in hydrogen containing solid surfaces.

Low energy electron diffraction studies of physical adsorption of xenon, and bromine on graphite single crystal surfaces showed that well defined surface structures formed

at low temperatures [Lander (80),(81)]. These studies seem to provide the first evidence that physical adsorption also takes place via the formation of crystalline phases even for noble gas adsorbates for which the lateral bonding is weak. The two dimensional condensation of adsorbed bromine to the liquid state could also be monitored by LEED (81).

It is apparent from the available experimental data that ordering of adsorbed atoms into surface structures of different kind is an essential part of the adsorption process. The correlation of adsorption data obtained from adsorption isotherms, field ion microscopy or work function measurements, etc., with the surface structures of adsorbed gases detected by low energy electron diffraction should greatly aid our understanding of the nature of the adsorption phenomena.

LEED studies further showed that surface structures are formed during the simultaneous adsorption (co-adsorption) of two gases which would not form in the presence of only one or the other gas component. The formation of these mixed

surface structures seem to be a general property of adsorbed gas layers on metal surfaces. Estrup and Anderson (82) showed that the simultaneous adsorption of N_2 and CO on the W (100) surface give a series of surface structures none of which can be formed by the individual gases. Similar results were obtained by the co-adsorption of O_2 and CO on the W (110) surface [May et al (83)].

The adsorption of oxygen and carbon monoxide on the (110) and (112) faces of tungsten has been studied by Germer et al. (84),(85)]. Several surface structures have been found. The adsorption of nitrogen, hydrogen and thorium on tungsten surfaces have been studied by Estrup et al (86),(87). The initial adsorption of oxygen on the (110) face of copper indicate the formation of a disordered layer which becomes ordered with increased exposure to gas (19). Ertl (88) has studied the adsorption of O_2 and N_2O on all three low index faces of copper.

The adsorption of oxygen on clean germanium surfaces [Botkin and Madix (89)], the adsorption of H_2S and H_2Se on the Ge (111) surface [Van Bommel & Meyer (90)] have been studied. The adsorption of CO and CO_2 on the Mo (110) surface [Haas et al. (91)] and the adsorption of O_2 and other gases on the Fe (011) face have been investigated [Pignoces et al. (92)]. In every case ordered surface structures have formed. Some of the structural properties of the chemisorbed structures have been reviewed by Estrup et al. (93). The thermal ordering of oxygen on nickel has been studied by Germer et al. (94).

Studies of Crystal Growth and Epitaxy on an Atomic Scale

Several investigations of the deposition of condensible vapor on single crystal substrates have been carried out using LEED. These studies gave valuable information about the initial steps of condensation, growth, and alloy formation and the experimental conditions which influence these

processes. Again, these processes take place via the formation of ordered surface structures. The symmetry and the unit cell dimensions of these structures depend on the substrate orientation, the deposition temperature and the condensing vapor flux. Moreover, the structure of the epitaxial deposit was very sensitive to the presence of chemisorbed oxygen [Taylor (95)]. Thus, condensation experiments must be performed under ultra high vacuum conditions to maintain reproducibility.

The surface structures produced by the epitaxial deposits may be divided into two groups. Those which have unit cells which are the same as that of the substrate unit cell or have lattice parameters which are integral multiples of that which characterizes the substrate, belong to the first group. These structures are superposed on the substrate unit cell [Bauer (96)]. The surface structures with unit cells which are slightly larger or smaller than the substrate unit cell belong to the second group. These may be called

coincidence surface structures. Depending on the lattice mismatch every n^{th} atom may coincide with one of the substrate atoms thereby producing a characteristic diffraction pattern [Tucker (97)].

The growth of the (111) face of silicone has been studied. The growth rate was sensitive to the presence of surface structures. The periodicity corresponding to the (7 × 7) surface structure could be maintained throughout the condensation process [Jona (98)]. The epitaxy of Cr, Sn, Pb, Al, In, P, Ca, and Ba on the (111) face of silicone has been studied [Gobeli et al. (99),(1)]. Three-ordered phases with successive addition of cesium were observed to form. In the presence of the (7 × 7) surface structure no ordering of the condensed cesium could be detected. The other metals, however, formed well ordered structures on both the Si (111) and the Si (111) – (7 × 7) surfaces and showed order-disorder transitions in well defined temperature ranges [Lander & Morrison (100)].

The Cu-Ti [Schlier & Farnsworth (101)], Cu-W (95), Ni-Cu [Haque & Farnsworth (102)], Th-W [Estrup et al. (103)] systems have been studied by LEED. There was a pronounced effect on the orientation of copper on titanium and tungsten surfaces due to the presence of chemisorbed oxygen. Taylor (95) reported the appearance of a long-period superlattice "alloy" diffraction pattern when the tungsten substrate was heated after the deposition of copper. The epitaxy of metals (Au,Ag) on ionic substrates (MgO, KCl) has also been investigated (42). Haque and Farnsworth (102) reported that for the Ni-Cu (111) system at 250 volts only the atoms in the first three layers at the surface were contributing to the scattered intensity. Thus, studies of epitaxy could be useful to determine the penetration depth of the incident electron beam. The properties of sodium-covered germanium [Palmberg & Peria (104)] have been investigated. The deposition of silver on the (111) silicon surface [Spiegel (105)] and the deposition of several metals on mica [Alpress & Sanders (106)] have been studied.

Interaction of Molecular Beams with Solid Surfaces

Studies of the interaction of a beam of atoms of well-defined kinetic energy with a clean single crystal surface allow us to investigate some of the elementary steps of surface reactions. In most of these studies a velocity selected atomic or molecular beam is used [Fite & Datz (107)]. By analyzing the time of flight of the back-scattered atoms one can determine the residence time of the atom on the surface [Moran et al. (108)]. Measurements of the velocity and angular distribution of the scattered beam reveals the extent of the energy exchange and the nature of the interaction between the gas and surface atoms [Smith and Saltsburg (109)]. The extent of the energy exchange between the atomic beam and the surface may be expressed [Raff et al. (110)] in terms of an energy accommodation coefficient, $\alpha_E(\theta)$,

$$\alpha_E(\theta) = \frac{E\ (\text{incident}) - E\ (\text{final})}{E\ (\text{incident})}$$

Here E (incident) and E (final) are the energies of the

incident and reflected atomic beams. The energy accommodation coefficient can also be expressed in terms of either the temperature or the velocity of the reactive atomic beams [Thomas (111)]. Although the results ~~one~~ obtained from molecular beam experiments ~~would~~ can be exceedingly important in understanding the dynamics of surface reactions, experimental and/or theoretical work in this field is carried out only in a few laboratories. The experimental difficulties in obtaining a velocity selected molecular beam and a clean crystal surface simultaneously, are formidable. Most of the experiments have been carried out using polycrystalline surfaces [Hinchen & Malloy (112)]. Some of these surfaces have been kept "clean" by constantly depositing a fresh surface during the scattering studies [Smith and Saltsburg (113)].

Experimental studies of molecular beam scattering.- Much of the recent experimental results and recent developments of the theory of molecular beam scattering have been

Published in the Proc. Symposia on Rarefied Gas Dynamics (Academic Press) and in the recent Proc. Fundamentals of Gas-Surface Interactions (Academic Press, 1967). The experiments indicates that part of the molecular beam which strikes the solid surface at the specified angle of incidence is re-emitted in a lobular pattern which also shows a sharp maximum (110). The angle of reflection of this maximum is related in a reproducible way to the angle of incidence, and to the temperatures of the surface and of the incident molecular beam. The appearance of the lobe distribution instead of a single maximum is also related to surface roughness [Healy (114)]. The two limiting cases of beam scattering mechanisms are (1) diffraction and (2) diffuse scattering (109). Diffraction of He and H_2 has been detected from alkali-halide surfaces by several investigators [Crews (115); (109)]. Due to the mass and energy dependence of the de Broglie wavelength [$\lambda = (h^2/2mE)^{1/2}$] diffraction is expected to be more important in the scattering of lighter atoms with thermal velocities. The dominance of elastic

scattering indicates, of course, the absence of energy exchange between the surface atoms and the beam. Diffraction effects were conspicously absent in studies of H_2 and He scattering from silver [Saltsburg et al. (116)]. Although this result may be due to surface contamination it is likely that the difference in the phonon spectra of metal and ionic crystals is partly responsible for the presence or absence of diffraction.

Diffuse scattering is characterized by a scattered beam distribution which varies as the cosine of the angle between the scattering direction and the surface normal. Any scattering process in which the incident molecular beam resides on the surface for a long time with respect to the time of a single elastic collision may lead to partial or total equilibration and diffuse scattering. Contaminated or amorphous surfaces frequently give rise to diffuse scattering of the molecular beam (108). In fact, the irreproducibility of experiments which were carried out prior to the advent of

high vacuum technology can be traced to underfined scattering surface properties (109).

In most molecular beam scattering experiments the scattered beam has a spatial distribution which is a result of a dynamical interaction with the surface. This, in general, cannot be described by the superposition of diffraction and diffuse scattering but it is determined by the interaction potential and lattice dynamics of the surface atoms. In the following statements we shall summarize the main features of the scattering processes which were derived from many experiments.

(a) The spatial distribution of scattered particles tend to be more specular (angles of incidence and scattering are equal) for clean surfaces and more diffuse in the presence of adsorbed gases or for roughened surfaces. The accommodation coefficient is small for nonreactive beams (~ 0.01 - 0.3) for clean surfaces but approaches unity for contaminated surfaces (110).

(b) The spatial distribution of the scattered beam is

strongly dependent on the angle of incidence and varies from one gas to another for scattering from a given solid surface.

(c) The maximum of the scattered beam shifts toward the surface normal as the surface temperature increases or as the energy of the incident beam decreases {with some notable exceptions [Saltsburg & Smith (117)]}. Thus, as the attractive interaction between the beam and the surface increases the scattering becomes more diffuse. Recent experiments include scattering of H_2, He, A, Xe from Au, Ag, Ni, Pt, LiF, and NaCl surfaces [Hurlbut (118); Datz et al. (119); Smith & Fite (120)]. Saltsburg and Smith (117) have studied the scattering of CH_4 and NH_3 from Au and Ag surfaces. The spatial distributions of scattered He, H_2, and D_2 beams from (111) face of Ag have been determined (116).

The thermal accommodation coefficients of gases on different surfaces have been studied by a variety of techniques (111). The accommodation coefficient of noble gases on

tungsten have been determined by Menzel & Kouptsides (121). The accommodation coefficients of these gases on tantalum and ~~germa~~ germanium surfaces have also been studied [Kostoff et al. (122)].

There is an absence of reported data on reactive scattering studies which should certainly aid in understanding the nature of the energy transfer in chemical surface reactions. There is no experimental information available on the scattering of molecular beams from liquid surfaces. When such ~~Such~~ study is ~~when~~ compared with the scattering process from the solid surface could give information about the role of the lattice vibration spectrum in the interaction. It should be noted that many of the experimental uncertainties in scattering studies could be removed by using one face of a single crystal instead of polycrystalline surfaces.

Theory of Molecular Beam Scattering.- The model which has been most successful in predicting many of the properties of the scattered molecular beam is the hard sphere (110)

and independent oscillator lattice model. The hard sphere model developed by Goodman (123) and Goodman and Wachman (124) considers the interaction of a gas atom (hard sphere) with one or several lattice atoms always assumed initially at rest. The collision cross section for a given beam velocity is determined using a Lennard-Jones potential. The model predicts realistic spatial distributions (re-emission lobes) and energy accommodation coefficients. It is applicable only when the surface temperature is low compared to the beam temperature. Following Goodman, Logan, and Stickney (125), presented a simplified hard-cube model which predicts correctly the variation of the spatial distribution with surface temperature. Thus, the restriction of a stationary lattice (a surface temperature of 0°K) which was a condition in all previous calcuations has been successfully removed.

The independent oscillator lattice model has been developed by Oman, Bogan, and Li (126) considers the interaction of a gas atom with symmetrically placed mass points

which are connected by harmonic springs to each other and to a fixed site. Again a Lennard-Jones interaction potential is used. Assuming a classical motion for all particles the energy accommodation coefficients have been calculated as a function of angle of incidence, particle mass and lattice force constants. An extension of these calculations was published by Raff, Lorenzen, and McCoy (110) who have removed the 0°K surface temperature restriction and have computed spatial distributions as well. Their calculations are in fair agreement with many of the experimental observations.

In addition to these classical models several quantum interaction models have been developed. These have been reviewed by Trilling (127). Although none of these models give satisfactory explanation of all of the experimental observations, it seems certain that a judicious synthesis of these models will provide a better physical picture for the interaction of molecular beams with surfaces.

SURFACE REACTIONS

Photodecomposition of Solids

Photodecomposition is a chemical surface reaction which requires the presence of both free charge carriers and trapping atomic centers in the surface. The complex over-all reaction may be divided into separate reaction steps, (1) the creation of free carriers (electrons or holes) in excess of their equilibrium concentration by illumination. (2) trapping of charge carriers at surface sites, (3) surface and/or bulk diffusion of atoms or vacancies away from the lattice sites where the charge trapping occurred. This step is responsible for the growth of the precipitated metal particles, and (4) the removal of some of the reaction products from the solid surface.

The condition for the occurrence of photodecomposition seem to be that the diffusion step (Step 3) should be rapid enough to induce particle growth during the trapping lifetime of the free carriers. If diffusion is too slow charge

recombination will take place before the photodecomposition could occur. Thus, it is apparent that due to the exponential temperature dependence of the surface diffusion rates photodecomposition reactions which may not take place at room temperature at any appreciable rate may proceed rapidly at elevated temperatures.

Most of the photodecompositon studies have been carried out with silver halides. The mechanism of their photoreaction is discussed in several recent papers [Mees & Jones (128)].

The photodecomposition of lead-halides have also been studied [Kaldor and Somorjai (129)]. The photoreaction of $PbCl_2$ is controlled by the rate of charge transfer at chloride ion vacancy sites. Unlike for pure silver halides the threshhold energy for photodecomposition is less than the energy at the absorption edge. Similar mechanism seems to be operative for PbJ_2. The chief difference seems to be that the diffusing species are Cl in $PbCl_2$ and Pb in PbJ_2.

CdS also undergo photodecomposition in the presence of an oxidizing atmosphere at elevated temperatures (> 250°C) [Somorjai (130)]. It is apparent that the diffusion rate of cadmium is too slow at room temperature for the photoreaction to occur. The oxidizing atmosphere over the solid surface is necessary to aid the removal of sulfur atoms in the form of sulfur oxides.

The photodecomposition of α-lead-azide, PbN_6 was also investigated [Verneker & Forsyth (131)]. The decomposition rate was a linear function of the light intensity. A two step mechanism ~~is~~ was proposed. Initially electron traps (vacancies, impurities) present in the crystal give rise to a high rate of photodecomposition. During the photoreaction these traps aggregate and are eliminated. The reaction rate decreases and the steady state decomposition rate is controlled by the interaction of photoionized lead cations with the azide anions.

Low energy electron diffraction studies of photodecomposition have not yet been carried out, as yet although diffraction patterns from silver bromide single crystal surfaces could readily be obtained.

Space Charge Limited Surface Reactions

In many surface reactions charge transfer (electron or hole) between the adsorbed gas and the solid surface is one of the important reaction steps. Charge transfer is relatively uninhibited on most metal surfaces where every surface atom may donate a conduction electron to the absorbate. Thus, when adsorption of a charged monolayer of gas takes place on a metal surface the resultant space charge layer extends to only a few atomic layers into the solid. This thin space charge region does not, in general, prevent the further migration of free carriers from the bulk to the surface. Charge transfer during the adsorption of gases on semiconductor or insulator surfaces, however, has a profound influence on the charge distribution in the solid

deep below the surface. For these solids less than one atom out of 10^6 may donate on electron (hole) to the adsorbed gas atoms [Many et al (132)]. Therefore, in order to absorb a monolayer of charged atoms (for example, $O_2 \rightarrow 2O^-$) electrons (holes) have to be transferred to the surface from atoms deep in the solid, i.e., the space charge layer may extend $\geq 10^{-4}$ cm into the bulk [Spenke (133)]. The electrical properties of thin (10^{-3} cm) insulating crystals are very sensitive to charge transfer processes at the surface [Hauffe and Engell (134)]. Electronic surface states of different types in semiconductors strongly interact with adsorbed gases. The properties of surface states have been recently reviewed by Many et al (132). For semiconductor surfaces a potential barrier builds up in the space charge region before the adsorption of a charged monolayer is completed which prevents further electron transfer from the bulk to the surface. Once this barrier is established the rate of charge transfer controlled surface reactions depends on the rate of electron

transfer over this potential barrier [Somorjai & Høering (135)]. Since the height of the barrier is proportional to the concentration of transferred electrons or to the concentration of ionized donor atoms, the rate of electron transfer to the surface obeys the equation

$$- dn/dt = k \exp(bn)$$

where n is the electron concentration and k and b are constants at a given temperature. The integrated rate equation has the form, $Bn = \log t + c$, where B and c are constants. This is the well known Elovich equation [Elovich et al (136)]. Kinetics of many adsorption [Melnick (137)] and oxidation (134) reactions follow this rate expression. Several other mechanisms have also been proposed to account for the exponential concentration dependence of the rate [Landberg (138)]. The rates of several catalytic surface reactions on semiconductor surfaces were found to be altered greatly by changing the free carrier concentration in the surface at a given temperature [Yaschenko et al (139)]. This may be carried out by

doping or illumination. The space charge limited adsorption and photodesorption of oxygen on CdS and CdSe surfaces have been investigated [Mark (140); Somorjai (141)]. The heats of adsorption of different gases were found to increase linearly with the electron concentration at the ZnO surface [Levy & Steinberg (142)]. Adsorbed gases may be desorbed from germanium surfaces by applying an electric field at the solid surface (139).

Oxidation Studies on Single Crystal Surfaces

The oxidation of several low index faces of nickel single crystals, the formation of nickel oxides have been studied using low energy electron diffraction [Germer et al (143); MacRae (144)]. LEED study of chromium surfaces shows the formation of a strongly bound amorphous oxide layer which is the probable reason for the corrosion resistance of the metal surface [Hague & Farnsworth (145)]. The oxidation of silicone [Landeer & Morrison (146)], germanium (89), platinum [Tucker (147)], molybdenum (46), tungsten [Chang (148)],

copper (88), and iron (47) single crystals have been studied. The oxidation of CO on palladium surfaces have been investigated ~~via~~ by monitoring the isotope exchange [Park (148)].

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