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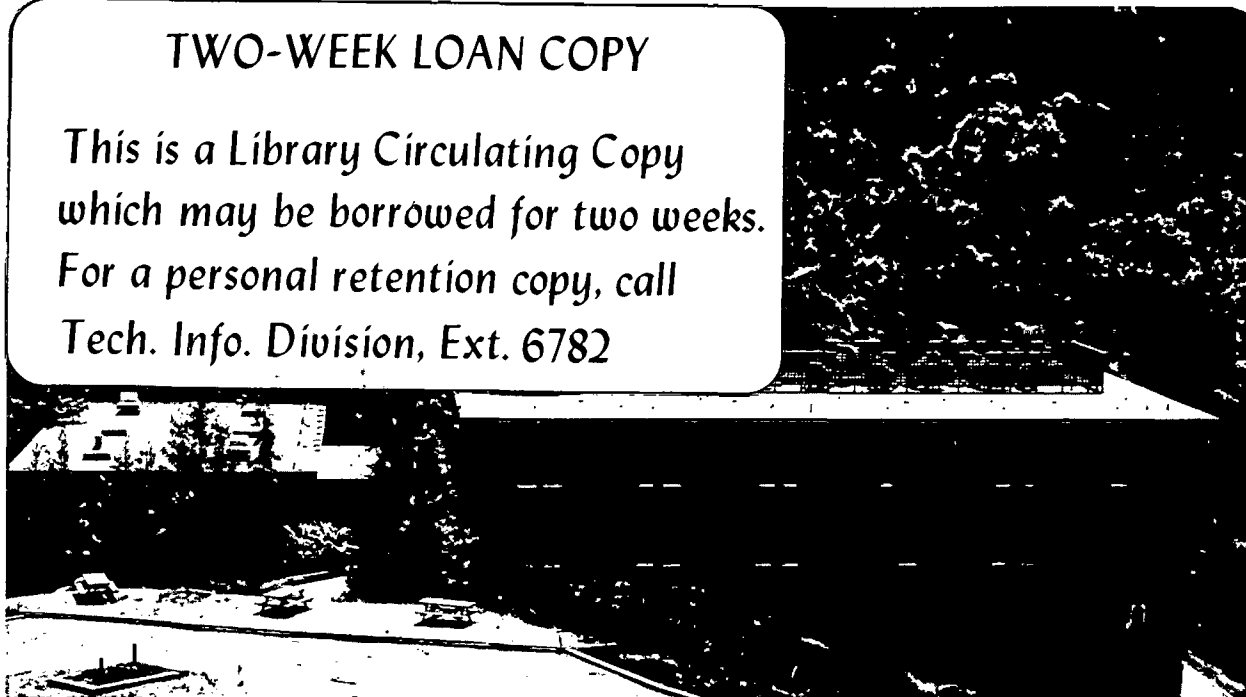
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SURFACE STRUCTURES OF METALLIC MONOLAYERS ON
METAL CRYSTAL SURFACES

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Abstract

The structures of adsorbed metals on single crystal surfaces of other metals have been reviewed and tabulated. Most of the adsorbates of over one hundred systems studied form ordered surface structures that may undergo changes as the coverage in the monolayer is increased. At low coverages the adsorbate and substrate surface structures are closely related indicating the predominance of the adsorbate-substrate interaction in determining ordering. At higher coverages there are more complex ordering characteristics. Although the relative atom sizes and magnitudes of adsorbate-substrate and substrate-substrate interactions influence the ordering in the monolayer general conclusions that have predictive value must await the availability of more experimental results on more metal adsorbate-substrate systems.

Introduction

The structure of monolayers of adsorbed gases on single crystal substrate surfaces has been the subject of intensive study over the past 15 years. Low energy electron diffraction (LEED) was utilized in most of these investigations. The diffraction pattern revealed the size and orientation of the surface unit cell and its changes as the amount of adsorbate was varied.¹

The surface structures of monolayers of metals condensed on single crystal surfaces of other metals represents a special class of adsorbates that received much less attention. This group is of considerable importance for carrying out fundamental surface studies as well as in many technological applications. The theories of crystal growth may be tested on these systems. Phase transformations (order-order, order-disorder) and the electronic structure in two dimensions can be explored. The importance of lattice mismatch and the different surface free energies of the metal substrate and adsorbate in producing the interface structure can be examined. These systems find applications in the preparation of chemically passive coatings, magnetic films, metal single crystals and chemically selective catalysts, or as electrically (electron emitters, etc.) active surface layers.

We have reviewed the surface structures of metal monolayers deposited on single crystal metal surfaces as they were determined by the techniques of low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED) and transmission electron diffraction (TED). We have listed the surface structures of nearly 100 systems that were studied along with the experimental conditions (substrate-structure, method of deposition) and techniques that were utilized to obtain these structures. Although the data base is inadequate to draw too many general conclusions certain distinct features of ordering show up and will be discussed.

It should be noted that in several of the studies reported here the cleanliness of the surface before and during the metal monolayer deposition has not been ascertained. Thus, caution should be exercised when correlating the observed surface structures with each other and with other properties of the metal monolayer. Whenever

surface structural studies were carried out in combination with other surface diagnostic studies such as Auger electron spectroscopy (AES), thermal desorption (TD) or work function change (WF) measurements, they are also indicated in the tabulation.

Results

In Table I the metal substrate-metal adsorbate systems that were studied are listed. The orientation of the metal substrate largely determines the structural properties of the monolayer, at least at low coverages. Therefore this is the key information that is provided in this Table. In Table II the structure produced by the metal monolayer or several structures that formed in some cases with increasing coverage are tabulated. The techniques of deposition are also indicated; (VD) for vapor deposition, (ID) for ion beam deposition, (S) for surface segregation from the bulk along with other complementary surface diagnostic techniques that were utilized. The techniques of investigation, LEED, RHEED, TED, AES and WF are listed along with references. The monolayer surface structures are provided using the matrix notation that gives the coefficients of the surface unit mesh vectors referenced to the surface unit cell vectors of the substrate. For those readers who are unfamiliar with this notation, the Appendix gives a more detailed explanation.

In forming ordered overlayers both the interatomic distances and the surface tensions of the metal adsorbate-substrate pairs may play important roles. Thus, we list in Table II the nearest neighbor distances and the heats of vaporization for both the metal adsorbate and the metal substrate. For metals the surface tensions σ are simply related to the heats of vaporization, ΔH_V , as

$$\sigma \text{ (ergs/mole)} = 0.15 \Delta H_V \text{ (kcal/gr.atom)}.^2$$

Some of the surface structures exist only in a finite temperature range. We have deleted this information from Table II for the sake of simplicity. The reader is referred to the original paper, referenced in the Table, for more experimental information.

Discussion

Most of the studies that monitor the condensation of metal adsorbates on metal crystal surfaces report the formation of ordered two dimensional structures. At low coverages the substrate periodicity determined the surface structure of the adsorbate as the two unit cells are closely related. This indicates the predominance of the adsorbate-substrate interaction in influencing the ordering.

At high coverages the metal adsorbate ordering characteristics are more complex. Often a $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ structure is observed indicating nearly identical substrate and adsorbate lattice parameters. This is the case for platinum deposited on a gold (100) surface.³⁻⁶ This may happen when the bulk interatomic distances of the two metals are quite similar. Alternatively, coincidence structures are observed if the substrate and adsorbate interatomic distances are different, for example when lead is adsorbed on the gold (100) surface.^{5,6} While mismatch in lattice parameters necessitates the formation of coincidence lattices, both adsorbate-substrate and adsorbate-adsorbate interactions may be of equal importance in this circumstance. These two types of structures are generally observed on the (100) and (110) fcc and (100) and (111) bcc surfaces.

It is often found that the observed surface structure is a combination of the structures of the pure adsorbate and pure substrate, for example rhodium adsorbed on a tungsten (110) surface.⁷ In this circumstance the adsorbate-adsorbate interaction is much stronger than the adsorbate-substrate interaction. This situation is more likely to be observed on more densely packed surfaces like the (111) fcc, the (110) bcc and the (0001) hcp surfaces.

The data listed in Table II also show that the adsorbed metal almost always forms a near monolayer on the metal substrate regardless of the relative magnitudes of the surface free energies. Simple thermodynamic arguments would predict the formation of a monolayer of adsorbate as long as its surface tension is lower than that of the substrate. In this circumstance the monolayer adsorption lowers the total surface free energy of the system. In the case of adsorbed metals with surface tensions that are higher than that of the metal substrate, the formation of three-dimensional crystallites is predicted to expose as much bare substrate surface area as possible in order to minimize the surface free energy of the system. There are some obvious violations of these simple thermodynamic concepts that lead to monolayer formation in most cases. For example, molybdenum on the nickel (111) face,⁸ platinum on the gold (100) surface,^{3,4} and copper on the

zinc (0001) crystal face⁹ all exhibit monolayer formation while the metal adsorbate surface tensions are larger than that of the metal substrates. There are clearly other strong interactions involved in the adsorption and ordering of metal monolayers that override the influence of surface forces that give rise to the surface tensions of the clean metals.

An interesting case to consider is iron deposited on a tungsten (110) surface¹⁰ that forms three-dimensional crystals. In this circumstance the formation of an adsorbed monolayer would be expected, using surface thermodynamic arguments, which does not seem to occur. In order to verify how the relative atom size, surface tension differences and the substrate surface structure influence the ordering characteristics the adsorbate and substrate should be interchanged. For example the adsorption of nickel on platinum crystal faces and the adsorption of platinum on the same crystal faces of nickel should be studied.

It would be of considerable importance to carry out thermal desorption studies wherever experimentally possible to determine the heats of desorption of the metal adsorbates from the different metal substrates. These measurements, when carried out as a function of coverage, would yield valuable insight into the energetics of metal-metal interactions at the surface. For many systems, however, the adsorbed metal would rather diffuse into the bulk of the metal substrate than desorb as the temperature of the system is increased. Work function change measurements during the adsorption of metal atoms on the metal substrate would also be of great value. These studies would indicate the direction and magnitude of the charge transfer upon adsorption that may be correlated with the ordering characteristics.

Using high Miller Index stepped and kinked metal surfaces as substrates, a great deal of additional information can be obtained about the mechanisms of ordering and metal-metal interactions.

Conclusion

Over 100 metal adsorbates have been investigated on metal crystal surfaces by the techniques of LEED, RHEED and TED. In almost every case ordered metal monolayers form. At low coverage the substrate periodicity determines

the surface structure of the adsorbate. At high coverages the surface structures are determined by a combination of factors that include the relative atomic sizes and the relative magnitudes of the adsorbate-substrate and substrate-substrate interactions. At present the data-base is too small to suggest correlations of ordering behavior that would have predictive value. A model that was proposed recently would require that the adsorbate and substrate layers have the highest possible symmetry¹¹. This area of surface science appears to hold the promise of exciting new discoveries by experimentalists and the development of new physical models by theorists. Because of their importance in studies of condensation and crystal growth and for many applications in technologies the metal adsorbate-metal substrate systems will likely be investigated with increasing frequency in the near future.

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APPENDIX

Notation of Surface Structures

LEED diffraction patterns represent the reciprocal lattice of the surface and the diffraction pattern must be converted to real space in order to obtain the surface structure. In this appendix we will show how this conversion is performed and how the surface structures are denoted. First, the relationship between the reciprocal and real lattices of the substrate will be shown, then determination of adsorbate surface structures from the LEED pattern will be discussed.

The diffraction pattern or reciprocal lattice has translational periodicity which is given by the vector \vec{T}^* which has the form $\vec{T}^* = h\vec{a}^* + k\vec{b}^*$ (1)

where h and k are integers and \vec{a}^* and \vec{b}^* are the vectors of the primitive surface reciprocal mesh. The translational periodicity of the surface in real space is given by the vector \vec{T} which has the form $\vec{T} = n\vec{a} + m\vec{b}$ (2)

where n and m are integers and \vec{a} and \vec{b} are the vectors of the primitive surface mesh. The reciprocal unit cell vectors \vec{a}^* and \vec{b}^* are related to the real space unit cell vectors \vec{a} and \vec{b} by the following equations:

$$\vec{a}^* = \frac{\vec{b} \times \vec{z}}{\vec{a} \cdot \vec{b} \times \vec{z}} \quad (3a)$$

$$\vec{b}^* = \frac{\vec{z} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{z}} \quad (3b)$$

where z is the surface normal. The relationship between the reciprocal and real space vectors is illustrated for a two-dimensional hexagonal lattice in Fig.1.

Adsorbing a gas on a surface usually results in a change in the diffraction pattern, corresponding to the appearance of a new surface mesh. This is illustrated in Fig.2 which shows a diffraction pattern of a clean Pt(111) surface and the diffraction pattern produced after the adsorption of an ordered layer of adsorbate. Fig.3 shows the unit mesh responsible for the diffraction patterns in Fig.2 superimposed on a model of the Pt(111) surface. No information concerning the location of the adsorbate within this unit mesh is indicated since this formation can only be obtained from analysis of the diffraction spot intensities.

In order to make the transition from the diffraction pattern in Fig.2 to the surface structure in Fig.3 the adsorbate surface reciprocal mesh is referenced

to the substrate reciprocal mesh. This is done by visual inspection of the diffraction pattern where the differences in spot intensities are neglected and only the positions of the diffraction beams are considered.

For the general case the relationship of adsorbate reciprocal mesh to the substrate reciprocal is given by the equations

$$\vec{a}^{*'} = m_{11}^* \vec{a}^* + m_{12}^* \vec{b}^* \quad (4a)$$

$$\vec{b}^{*'} = m_{21}^* \vec{a}^* + m_{22}^* \vec{b}^* \quad (4b)$$

where $\vec{a}^{*'}$ and $\vec{b}^{*'}$ are the vectors of the primitive adsorbate reciprocal mesh and the coefficients m_{11}^* , m_{12}^* , m_{21}^* and m_{22}^*

define the matrix $M^* = \begin{pmatrix} m_{11}^* & m_{12}^* \\ m_{21}^* & m_{22}^* \end{pmatrix}$.

In real space the adsorbate mesh is related to the substrate mesh by the equations

$$\vec{a}' = m_{11} \vec{a} + m_{12} \vec{b} \quad (5a)$$

$$\vec{b}' = m_{21} \vec{a} + m_{22} \vec{b} \quad (5b)$$

where \vec{a}' and \vec{b}' are the vectors of the primitive adsorbate mesh and the coefficients m_{11} , m_{12} , m_{21} and m_{22} define the matrix

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}.$$

The coefficients of the two matrices M and M^* are related by the following equations:

$$m_{11} = \frac{m_{22}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6a)$$

$$m_{12} = \frac{-m_{21}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6b)$$

$$m_{21} = \frac{-m_{12}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6c)$$

$$m_{22} = \frac{m_{11}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6d)$$

so that if either M or M^* is known the other may be readily calculated. In LEED experiments M^* is determined by visual inspection of the diffraction pattern and then transformed to give M which defines the surface structure in real space.

For the case of adsorption on Pt(111) visual inspection of the LEED patterns in Fig. 2 gives $M^* = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$. From employing equations (6a) through (6d) the matrix M is found to be $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$, so $\vec{a}' = 2\vec{a}$ and $\vec{b}' = 2\vec{b}$ as depicted in Fig. 3.

In addition to the matrix method of denoting surface structures another system, originally proposed by Wood (3), is also used. While the matrix notation can be applied to any system, Wood's notation can only be used when the angle between the adsorbate vectors \vec{a}' and \vec{b}' is the same as the angle between the substrate vectors \vec{a} and \vec{b} . If this condition is met, then the surface structure is labeled using the general form $(nxm)R\phi^\circ$ or $c(nxm)R\phi^\circ$, depending on whether the unit mesh is primitive or centered. In Wood's notation the adsorbate unit mesh is related to substrate unit mesh by the scale factors n and m where

$$|\vec{a}'| = n |\vec{a}| \quad (7a)$$

$$|\vec{b}'| = m |\vec{b}| \quad (7b)$$

$R\phi^\circ$ indicates a rotation of the adsorbate unit mesh by ϕ° from the substrate unit mesh. For $\phi=0$ the $R\phi^\circ$ label is omitted, so the surface structure in Fig. 3 is labeled as a (2x2). The label for the total system refers to the type of substrate, the surface structure formed by the adsorbate and the adsorbate. The platinum-adsorbate system shown in Fig. 4 would be labeled as Pt(111)- $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$ in matrix

notation and as $Pt(111)-(2 \times 2)$ in Wood's notation, Wood's notation is more commonly used and the matrix notation is usually only applied to systems where the angle between the adsorbate vectors differs from the angle between substrate vectors.

An example of an adsorbate which has a centered unit mesh is shown in Figs.4 and 5. In Fig.4 diffraction patterns from a clean Rh(100) surface and a Rh(100) surface after exposure to oxygen are shown. By visual inspection it can be seen that $M^* = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$, so using equations (6a) through (6d) yields $M = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$. M defines the primitive unit mesh of the adsorbate, which is drawn in with solid lines in Fig.5. This unit mesh is labeled as $(\sqrt{2} \times \sqrt{2})R45^\circ$ in Wood's notation. Since the centered unit mesh drawn in with dotted lines in Fig.5 also describes the adsorbate mesh, another way of labeling this structure would be $c(2 \times 2)$. The total system is labeled as $Rh(100) - \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} - 0$, $Rh(100) - (\sqrt{2} \times \sqrt{2})R45^\circ - 0$ or $Rh(100) - c(2 \times 2) - 0$. Of these three labels only the first two refer to the primitive unit mesh of the oxygen surface structure.

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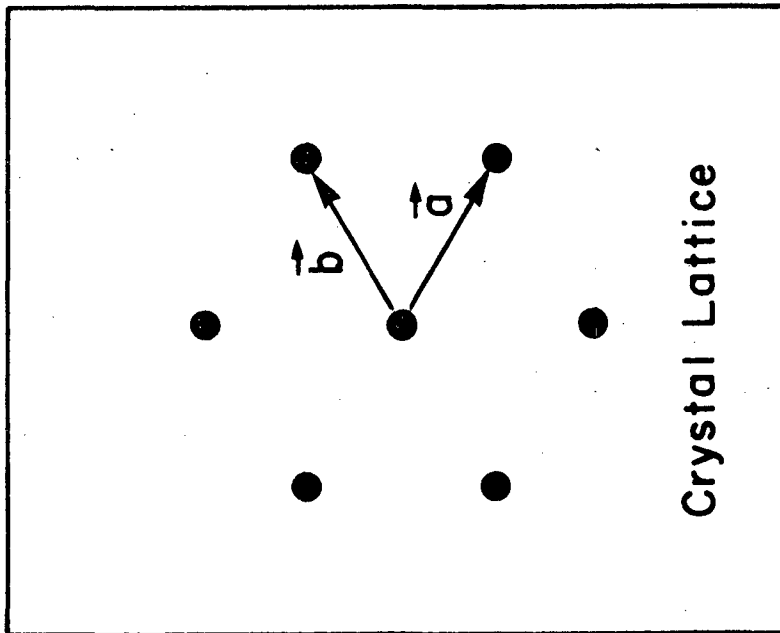
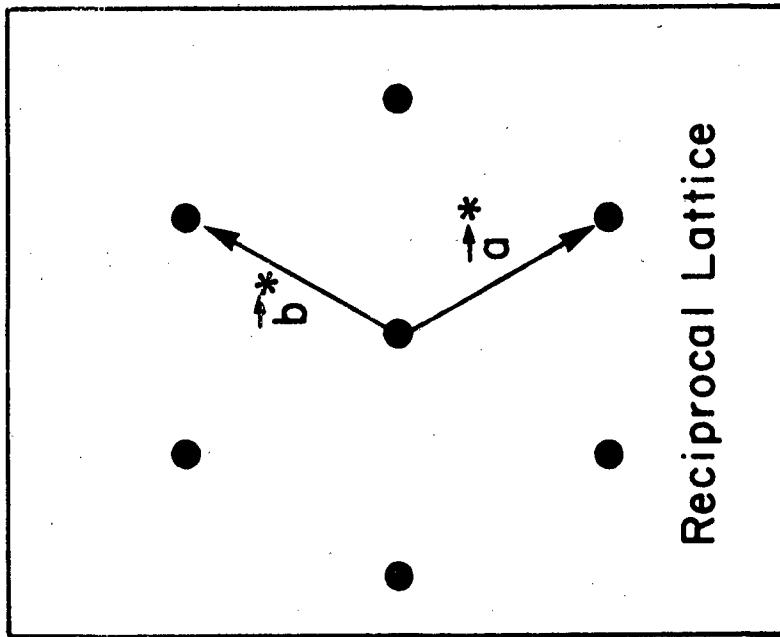
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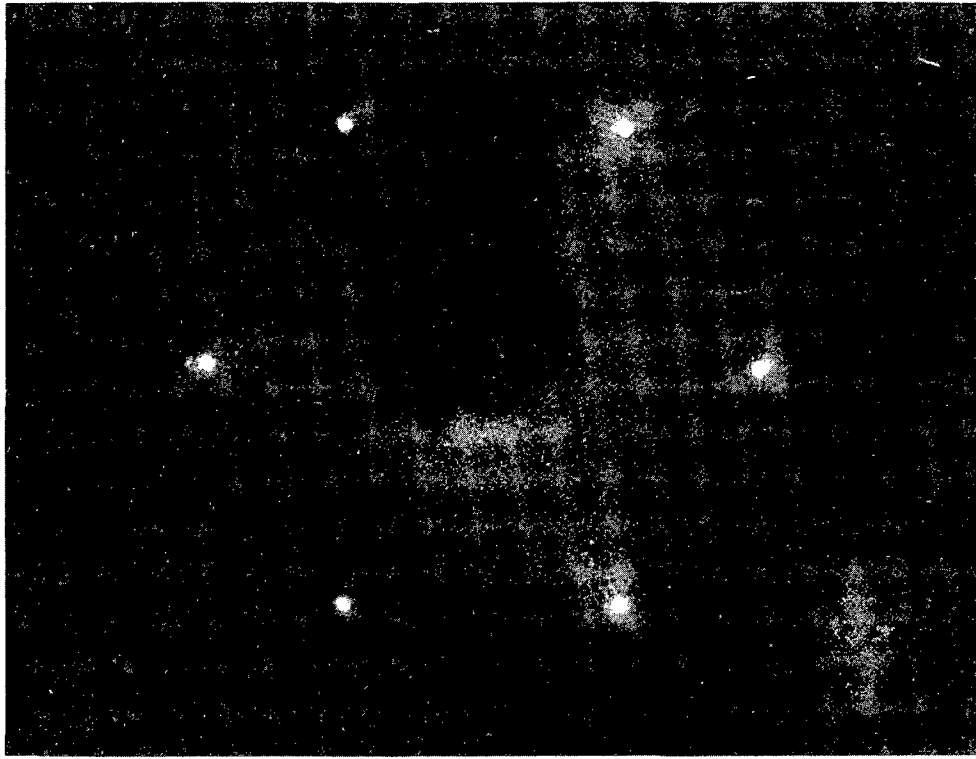
Figure Captions

- Fig. 1 Real space vectors \vec{a} and \vec{b} and reciprocal space vectors \vec{a}^* and \vec{b}^* of a two-dimensional hexagonal lattice.
- Fig. 2 LEED patterns of a clean Pt(111) surface and the same surface after exposure to a gas. In both diffraction patterns the incident electron beam energy is 68 eV.
- Fig. 3 Real space unit cells of Pt(111)-(1x1) and Pt(111)-(2x2).
- Fig. 4 LEED patterns of (a) clean Rh(100) at 74 eV and (b) oxygen covered Rh(100) at 85 eV.
- Fig. 5 Real space unit cells of the (2x2)_{R45°}-0 (solid lines) and c(2x2)-0 (dashed lines) on the Rh(100) surface.



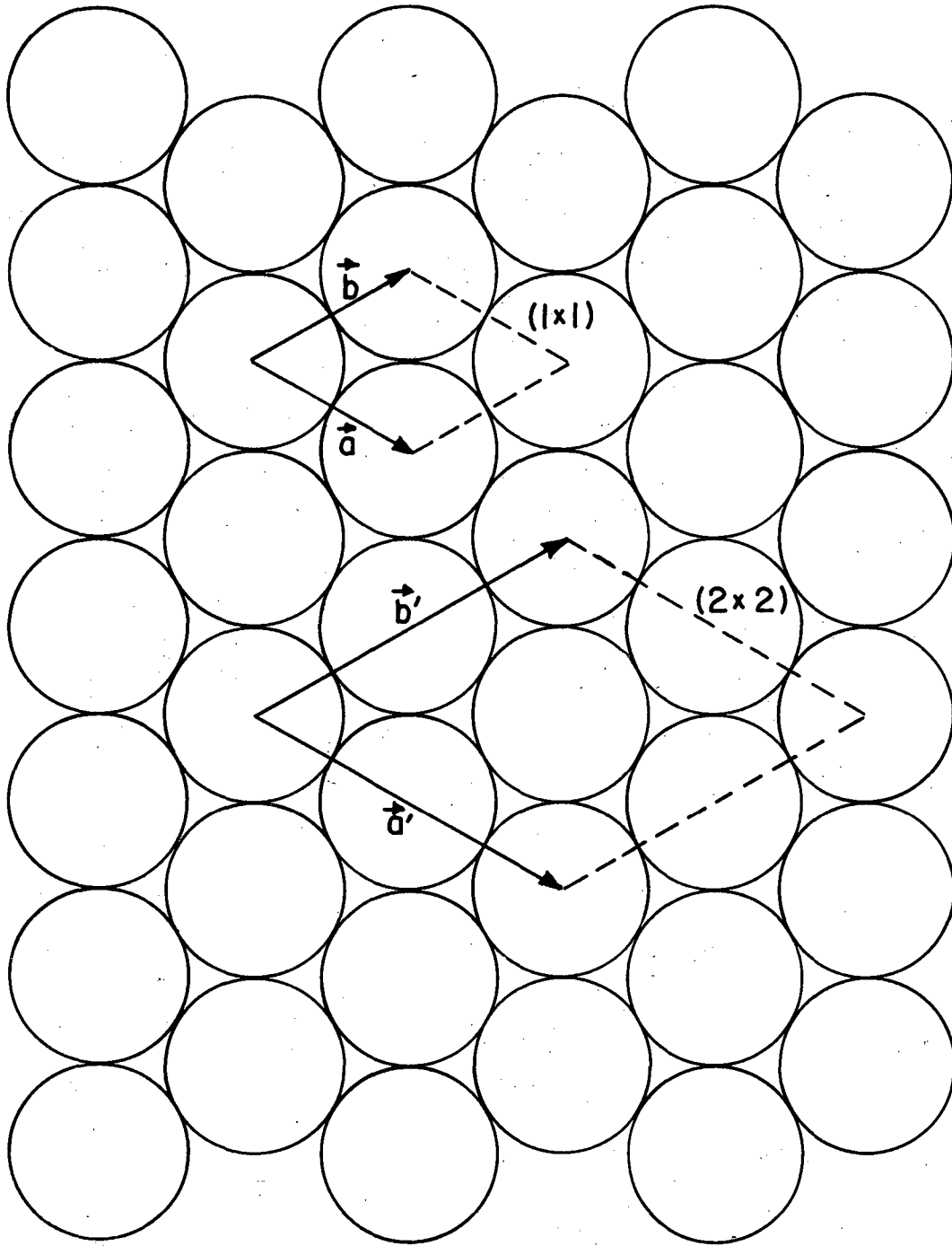
XBL 787-9590

Fig.1



XBB 7511-8226

Fig. 2



XBL7510-7551

Fig.3



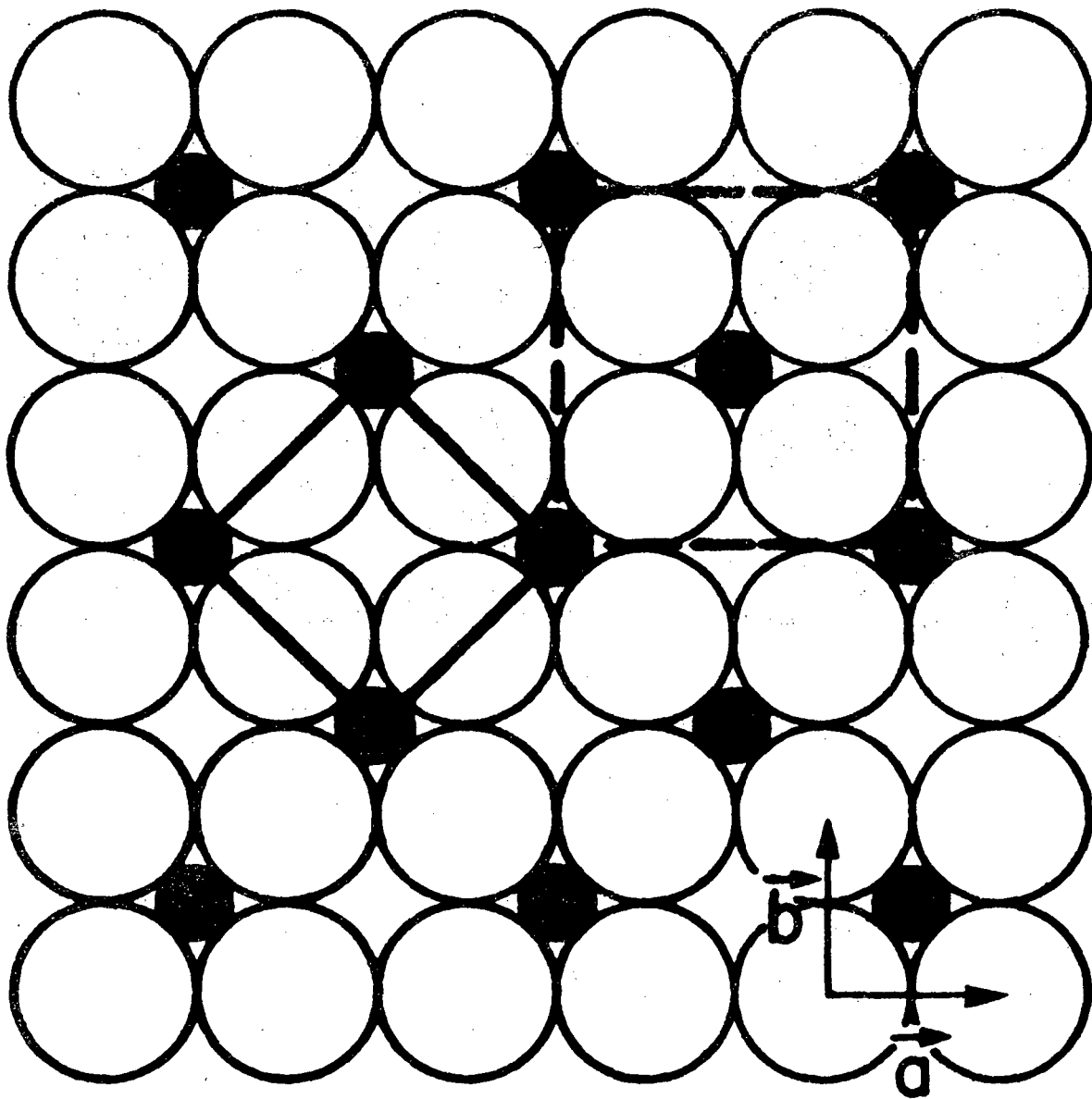
a



b

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Fig.4



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Fig.5

TABLE CAPTIONS

Table I. Metal substrate-metal adsorbate systems that were studied. The crystal structure and orientation of the substrates are indicated.

Table II. The surface structures of metal adsorbates on ordered metal crystal surfaces. The interatomic distances, heats of evaporation and the techniques of investigation are denoted.

Table I

SUBSTRATE CRYSTAL FACES

-26-

Adsorbates	fcc metals									bcc metals				hcp metals			rhombohedral metal
	Rh	Ir	Ni	Pd	Cu	Ag	Au	Al	Fe	Nb	Ta	Mo	W	Ti	Re	Zn	
Li													(110) (112)				
Na			(100) (111) (110)			(111) (110)	(100)	(100) (111)				(110)	(100) (110) (112)				
K			(100) (110)									(110)	(100)				
Rb						(111)						(110)	(100)				
Cs			(100) (110)									(110)	(100) (110)				
Be													(110)				
Mg						(111)											
Sr													(110)				
Ba			(100)										(100) (110)		(0001)		
Sc													(110)				
Y													(110)				
Zr													(100)				
Cr		(111)	(100)			(111)	(111)										
Mo			(111)														
Mn									(111)								
Fe	(100)		(100)	(100)	(100) (111)		(100) (111)	(100) (111)					(110)				(0001)
Co			(100)		(100)	(111)											
Ni				(100)	(100) (111)	(100) (111)			(111)								
Pd						(111)	(100) (111)						(110)				
Pt							(100) (111)										
Cu			(100)			(100) (111)	(111)						(100) (110)	(0001)		(0001)	
Ag			(111)	(100)	(100) (111)		(100)					(110)	(100) (110)				
Au		(111)	(111)	(100) (111)	(100) (111) (110)	(100) (111)				(100)			(100) (110)				
Zn						(111)											
Cd						(111)								(0001)			
Hg													(100)				
Al						(111)				(110)	(110)						
Tl						(111)											
Sn					(100) (111)	(111)		(100) (111)	(110)			(100)					
Pb			(100) (111)		(100)+ step (111)	(111)	(100)+ step (111)	(100) (111)					(100) (110)				
Sb						(111)							(100) (110) (112)				
Bi					(100) (111)	(111)	(100) (111) (110)										
Th										(100)		(100)					

Table II : Adsorption properties of metal monolayers on metal substrates. The clean substrate properties are also given for comparison. Substrates are ordered by lattice type (fcc, bcc, hcp, cubic, diamond and rhombic). The structures, nearest neighbor distances and heats of vaporization refer to the bulk material of the substrate or the adsorbate. VD, ID and S stand for vapor deposition, ion beam deposition and surface segregation, respectively. TD, WF and TED stand for thermal desorption, work function measurements and transmission electron diffraction, respectively.

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Rh	--	fcc	2.69	127	--	--	---	---	--
Rh	Fe	bcc	2.48	85	VD	(100)	TED	Fe(100) and Fe(110) Rh(100)	13
Ir	--	fcc	2.71	160	--	--	--	---	--
Ir	Cr	bcc	2.50	73	VD	(111)	LEED-AES-WF	hexagonal	14
Ir	Au	fcc	2.88	82	VD	(111)	LEED-AES-WF	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	14
Ni	--	fcc	2.49	91	--	--	---	---	--
Ni	Na	bcc	3.66	24	ID/VD	(100)	LEED-WF	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$	15/13,16-20
					ID	(111)	LEED	hexagonal	16,19,21
					ID	(110)	LEED	disordered structures, hexagonal	16,19,21
Ni	K	bcc	4.52	19	ID/VD	(100)	LEED-WF/LEED	$\begin{pmatrix} 4 & 0 \\ 0 & 2 \end{pmatrix}$ / hexagonal	15/18,22
					ID	(110)	LEED	disordered structures	16
Ni	Cs	bcc	5.23	16	ID	(100)	LEED-WF/LEED	$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$ / hexagonal	15/23
					ID	(110)	LEED	disordered structures	16
Ni	Ba	bcc	4.35	36	VD	(100)	LEED-WF	disordered overlayer	15
Ni	Cr	bcc	2.50	73	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	23
Ni	Mo	bcc	2.72	128	S	(111)	LEED	$\begin{pmatrix} 5 & 0 \\ 0 & 5 \end{pmatrix}$, $\begin{pmatrix} 4 & 0 \\ 0 & 4 \end{pmatrix}$, $\begin{pmatrix} 2 & 0 \\ 5 & 10 \end{pmatrix}$, $\begin{pmatrix} 1 & 0 \\ 5 & 10 \end{pmatrix}$	8
Ni	Fe	bcc	2.48	85	VD	(100)	TED	(110) Fe (100) Ni	13
Ni	Co	hcp	2.50	93	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	25
Ni	Cu	fcc	2.56	73	VD	(100)	RHEED-AES	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	26

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Ni	Ag	fcc	2.89	61	VD	(111)	LEED/AES	$\begin{pmatrix} 6 & 0 \\ 0 & 6 \end{pmatrix}$	27/28
Ni	Au	fcc	2.88	82	S	(111)	LEED-AES/LEED	$\begin{pmatrix} 6 & 0 \\ 0 & 6 \end{pmatrix}, \begin{pmatrix} 13 & 0 \\ 0 & 13 \end{pmatrix} / \begin{pmatrix} 6 & 0 \\ 0 & 6 \end{pmatrix}$	29/30
Ni	Pb	fcc	3.50	42	VD	(100)	LEED	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 2 & 3 \end{pmatrix}$	31
					VD	(111)	LEED	$\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}, \begin{pmatrix} 7 & 0 \\ 0 & 7 \end{pmatrix}, \begin{pmatrix} 13 & 0 \\ 0 & 13 \end{pmatrix}, \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} / \text{hexagonal}$	31/32
					VD	(110)	LEED	rotated $\pm 3^\circ$, $\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$ $\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 4 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 5 & 0 \\ 0 & 1 \end{pmatrix}$	31
Pd	--	fcc	2.75	90	--	--	---	---	--
Pd	Fe	bcc	2.48	85	VD	(100)	TED	(100) Fe (100)Pd and (110) Fe (100) Pd	13
Pd	Ni	fcc	2.49	91	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	33
Pd	Ag	fcc	2.89	61	VD	(100)	LEED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	34
Pd	Au	fcc	2.88	82	VD	(100)	LEED/TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	34/35,36
					VD	(111)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	36
Cu	--	fcc	2.56	73	--	--	---	---	--
Cu	Fe	bcc	2.48	85	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	13,37,38
					VD	(111)	LEED-AES	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	39
Cu	Co	hcp	2.50	93	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	40,41
Cu	Ni	fcc	2.49	91	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	42
					VD	(111)	LEED/RHEED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	43,44/45
Cu	Ag	fcc	2.89	61	VD	(100)	LEED	$\begin{pmatrix} 2 & 0 \\ 1 & 5 \end{pmatrix}$	34,46
					VD	(111)	LEED/RHEED, TED	$\begin{pmatrix} 8 & 0 \\ 0 & 8 \end{pmatrix} / \text{three dimensional crystals}$	46/45,47-50

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Cu	Au	fcc	2.88	82	VD	(100)	LEED	$(\frac{1}{1} \frac{1}{1}), (\frac{2}{1} \frac{0}{7})$	34,51
						(111)	LEED-AES/RHEED	$(\frac{2}{2} \frac{3}{3} \frac{2}{3}), (\frac{2}{0} \frac{0}{2})$, three dim. crystals	52/47,53
						(110)	LEED-AES	$(\frac{1}{1} \frac{0}{2}), (\frac{1}{0} \frac{0}{2}), (\frac{2}{0} \frac{0}{2})$, complex structures	52
Cu	Sn	diam	2.81	70	S	(100)	LEED-AES	$(\frac{2}{0} \frac{0}{2})$	54
						(111)	LEED-AES	$(\frac{1}{1} \frac{1}{2})$	54
Cu	Pb	fcc	3.50	42	VD	(100)	LEED/LEED-AES-TD/TED	$(\frac{2}{2} \frac{2}{2}), (\frac{1}{2} \frac{1}{3})$	55/56-58/59
						(111)	LEED/LEED-AES-TD	$(\frac{4}{0} \frac{0}{4})$	55/58
						(110)	LEED/LEED-AES	$(\frac{1}{1} \frac{1}{1}), (\frac{5}{0} \frac{0}{1}), (\frac{1}{1} \frac{1}{1}), (\frac{4}{0} \frac{0}{1}), (\frac{5}{0} \frac{0}{1})$	55/56
						(711)	LEED-AES/LEED-AES-TD	$(\frac{4}{0} \frac{0}{1})$	56/58
						(511)	LEED-AES	$(\frac{4}{0} \frac{0}{1})$	56
						(311)	LEED-AES	$(\frac{3}{2} \frac{1}{1}), (\frac{4}{0} \frac{0}{2})$	58
Cu	Bi	rhomb	3.07	43	VD	(100)	LEED/LEED-AES	$(\frac{2}{0} \frac{0}{2}), (\frac{1}{1} \frac{1}{1}), (\frac{1}{4} \frac{1}{5}), (\frac{5}{4} \frac{4}{5})$	60/57
						(111)	LEED	$(\frac{1}{1} \frac{1}{2}), (\frac{2}{0} \frac{1}{2}), (\frac{2}{1} \frac{3}{2})$	61
						---	---	---	---
Ag	--	fcc	2.89	61	--	--	---	---	--
Ag	Na	bcc	3.66	24	VD	(111)	LEED-AES-TD	$(\frac{1}{0} \frac{0}{1})$	62
						(110)	LEED-AES-TD	$(\frac{1}{0} \frac{0}{1})$	63
Ag	Rb	bcc	4.84	18	VD	(111)	LEED-AES-TD	$(\frac{1}{0} \frac{0}{1})$	64
Ag	Mg	hcp	3.20	32	VD	(111)	TED	disordered overlayer	65
Ag	Cr	bcc	2.50	73	VD	(111)	TED	disordered overlayer	65
Ag	Co	hcp	2.50	93	VD	(111)	TED	disordered overlayer	65

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Ag	Ni	fcc	2.49	91	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	66
					VD	(111)	TED/RHEED	hexagonal overlayer	65/67
Ag	Pd	fcc	2.75	90	VD	(111)	TED	disordered overlayer	65
Ag	Cu	fcc	2.56	73	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	66
					VD	(111)	RHEED-TED	hexagonal overlayer	68-70
Ag	Au	fcc	2.88	82	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	35
					VD	(111)	LEED-AES/TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	65,71/72
Ag	Zn	hcp	2.66	27	VD	(111)	TED	no condensation	65
Ag	Cd	hcp	2.98	24	VD	(111)	TED	no condensation	65
Ag	Al	fcc	2.86	68	VD	(111)	TED	disordered overlayer	65
Ag	Tl	hcp	3.46	39	VD	(111)	TED	hexagonal overlayer	65
Ag	Sn	diam	2.81	70	VD	(111)	TED	disordered overlayer	65
Ag	Pb	fcc	3.50	42	VD	(111)	TED	hexagonal overlayer	65,73
Ag	Sb	rhomb	2.91	47	VD	(111)	TED	disordered overlayer	65
Ag	Bi	rhomb	3.07	43	VD	(111)	TED	disordered overlayer	65
Au	--	fcc	2.88	82	--	--	---	---	--
Au	Na	bcc	3.66	24	VD	(100)	LEED	series of structures, hexagonal	74
Au	Cr	bcc	2.50	73	VD	(111)	LEED-AES-WF	hexagonal	75
Au	Fe	bcc	2.48	85	VD	(100)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	76-78
					VD	(111)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	76,78-80
Au	Pd	fcc	2.75	90	VD	(100)	LEED/TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	34/81
					VD	(111)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	36,82

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Au	Pt	fcc	2.77	122	VD	(100)	LEED-AES/TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	3/4
						(111)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	83
Au	Cu	fcc	2.56	73	VD	(100)	LEED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	34
						(111)	RHEED	extra lines	84,85
Au	Ag	fcc	2.89	61	VD	(100)	LEED/TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	34,39,86/87
						(111)	LEED-AES	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	71
Au	Pb	fcc	3.50	42	VD	(100)	LEED-AES	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 3 & 4 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$	5,6
						(111)	LEED-AES	hexagonal rotated $\pm 5^\circ$	6,88
						(110)	LEED-AES	$\begin{pmatrix} 1 & 0 \\ 0 & 3 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 7 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 7 & 0 \\ 0 & 3 \end{pmatrix}, \begin{pmatrix} 4 & 0 \\ 0 & 4 \end{pmatrix}$	6,88
						(11,1,1)	LEED-AES	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$	6
						(911)	LEED-AES	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$	6
						(711)	LEED-AES	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$	6
						(511)	LEED-AES	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$	6
						(311)	LEED-AES	$\begin{pmatrix} 5 & 0 \\ 0 & 3 \end{pmatrix}$	89
						(320)	LEED-AES	$\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$	89
						(210)	LEED-AES	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	90
Au	Bi	rhomb	3.07	43	VD	(100)	LEED	$\begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}$	91
						(111)	LEED	$\begin{pmatrix} 10 & 10 \\ 10 & 20 \end{pmatrix}$	91
						(110)	LEED	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}$	91
Al	--	fcc	2.86	68	--	--	---	---	--
Al	Na	bcc	3.66	24	ID	(100)	LEED-AES-WF	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 4 \end{pmatrix}$	92-94
						(111)	LEED-AES-WF	$\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}$	93
Al	Mn	cubic	2.24	54	VD	(111)	LEED-AES	$\begin{pmatrix} 6 & 0 \\ 1 & 2 \end{pmatrix}$, hexagonal rotated $\pm 9^\circ$	95

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Al	Fe	bcc	2.48	85	VD	(100)	TED	poor epitaxy	13
Al	Ni	fcc	2.49	91	VD	(111)	TED	$\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$	96
Al	Sn	diam	2.81	70	VD	(100)	LEED-AES	$\begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$	97
					VD	(111)	LEED-AES	hexagonal rotated $\pm 9^\circ$	98
Al	Pb	fcc	3.50	42	VD	(100)	LEED-AES	$\begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}$	97
					VD	(111)	LEED-AES	hexagonal rotated $\pm 9^\circ$	98
Nb	--	bcc	2.86	172	--	--	---	---	--
Nb	Sn	diam	2.81	70	VD	(110)	LEED	disordered structures, $\begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}$	99
Ta	--	bcc	2.86	180	--	--	---	---	--
Ta	Au	fcc	2.88	82	VD	(100)	LEED	split $\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$	100
Ta	Al	fcc	2.86	68	VD	(110)	LEED	hexagonal, square	101
Ta	Th	fcc	3.60	137	VD	(100)	LEED-WF	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	102
Mo	--	bcc	2.72	128	--	--	---	---	--
Mo	Na	bcc	3.66	24	ID	(110)	LEED-AES	no ordered structure	103
Mo	K	bcc	4.52	19	ID	(110)	LEED-AES	hexagonal	103
Mo	Rb	bcc	4.84	18	ID	(110)	LEED-AES/AES	hexagonal	103/104
Mo	Cs	bcc	5.23	16	ID	(110)	LEED-AES	hexagonal	103
Mo	Ag	fcc	2.89	61	VD	(100)	SEM-AES/LEED-AES	(100) Ag (100) Mo and (011) Ag (001) Mo	105-106
Mo	Al	fcc	2.86	68	VD	(110)	LEED-AES	hexagonal	107
Mo	Sn	rhomb	2.81	70	VD	(100)	LEED-AES	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$	108

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
W	--	bcc	2.74	185	--	--	---	---	--
W	Li	bcc	3.02	32	VD	(110)	LEED-WF	$(\frac{1}{2} 5)$, $(\frac{2}{0} 2)$, $(\frac{1}{1} 1)$	109-111
					VD	(112)	LEED-WF	$(\frac{4}{0} 0)$, $(\frac{3}{0} 0)$, $(\frac{2}{0} 0)$, incoherent, $(\frac{1}{0} 0)$	110,112
W	Na	bcc	3.66	24	VD	(100)	RHEED-TD	$(\frac{1}{1} 1)$	113
					VD	(110)	LEED-WF	$(\frac{1}{2} 5)$, $(\frac{2}{0} 2)$, $(\frac{1}{1} 1)$, $(\frac{1}{0} 8)$, $(\frac{1}{0} 5)$, hexagonal	7
					ID	(112)	LEED	$(\frac{2}{0} 0)$, compressed $(\frac{2}{0} 1)$	114
W	K	bcc	4.52	19	VD	(100)	RHEED	$(\frac{1}{1} 1)$	115
W	Rb	bcc	4.84	18	ID	(100)	LEED-AES	$(\frac{1}{1} 1)$, $(\frac{2}{0} 2)$, hexagonal	116
W	Cs	bcc	5.23	16	ID-VD	(100)	LEED-AES/ LEED-WF	$(\frac{1}{1} 1)$, $(\frac{2}{0} 2)$, split $(\frac{2}{0} 2)$ / $(\frac{2}{0} 2)$, $(\frac{1}{1} 1)$, hexagonal	117,118/119
					VD	(110)	LEED/LEED-AES	disordered hexagonal, hexagonal	120,121/117
W	Be	hcp	2.22	74	VD	(110)	LEED	$(\frac{1}{0} 0)$, $(\frac{1}{0} 1)$, $(\frac{9}{1} 0)$	122
W	Sr	fcc	4.30	34	VD	(110)	LEED-WF	$(\frac{3}{2} 3)$, $(\frac{2}{0} 2)$, $(\frac{2}{1} 6)$, $(\frac{1}{0} 3)$, hexagonal	123
W	Ba	bcc	4.35	36	VD	(100)	LEED-WF	$(\frac{2}{8} 0)$, split $(\frac{1}{2} 1)$, $(\frac{1}{2} 1)$, $(\frac{1}{1} 1)$	124
					VD	(110)	LEED-WF	disordered hexagonal, hexagonal, $(\frac{2}{0} 2)$, $(\frac{2}{0} 2)$, $(\frac{3}{1} 3)$, hexagonal compact	125
W	Sc	hcp	3.25	81	VD	(110)	LEED-WF	$(\frac{1}{0} 3)$, $(\frac{2}{0} 8)$	126
W	Y	hcp	3.55	93	VD	(110)	LEED-WF	hexagonal	127,128
W	Zr	hcp	3.17	122	VD	(100)	LEED-RHEED	$(\frac{1}{0} 0)$, $(\frac{2}{1} 0)$	129
W	Fe	bcc	2.48	85	VD	(110)	LEED	three dimensional crystals	10
W	Pd	fcc	2.75	90	VD	(110)	LEED-AES	$(\frac{1}{0} 3)$, hexagonal	130
W	Cu	fcc	2.56	73	VD	(100)	LEED-AES-TD	$(\frac{2}{0} 2)$, $(\frac{1}{1} 1)$	131

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
					VD	(110)	LEED/LEED-AES WF-TD	hexagonal structures	132/131,133
W	Ag	fcc	2.89	61	VD	(100)	LEED-AES-WF-TD	$\begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	134
					VD	(110)	LEED-AES-WF-TD	hexagonal structures	134/135
W	Au	fcc	2.88	82	VD	(100)	LEED-AES-WF-TD	$\begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	134
					VD	(110)	LEED-AES-WF-TD	hexagonal structures	134,136
W	Hg	rhomb	3.01	14	VD	(100)	LEED-AES	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	137
W	Pb	fcc	3.50	42	VD	(100)	LEED/LEED-AES-WF-TD	disordered $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$, split $\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 2 & 2 \end{pmatrix}$, hexagonal/ $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	138/139
					VD	(110)	LEED-AES-WF-TD	split $\begin{pmatrix} 3 & 0 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 3 & 0 \\ 1 & 1 \end{pmatrix}$	139,140
W	Sb	rhomb	2.91	47	VD	(100)	RHEED	$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	141,142
					VD	(110)	RHEED/LEED-WF	$\begin{pmatrix} 1 & 1 \\ 0 & 4 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 3 & 0 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 4 & 0 \\ 1 & 1 \end{pmatrix}$	141/143
					VD	(112)	RHEED	$\begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	141
W	Th	fcc	3.60	137	VD	(100)	LEED/LEED-AES-WF	$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 2 & 0 \\ 1 & 3 \end{pmatrix}$, hexagonal	144-146/ 147,148
Ti	--	hcp	2.89	106	--	--	---	---	--
Ti	Cu	fcc	2.56	73	VD	(0001)	LEED	extra spots	149
Ti	Cd	hcp	2.98	24	VD	(0001)	LEED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	150

Substrate metal	Adsorbed metal	Structure	Nearest neighbor distance	Heat of vaporization (kcal/g.atom)	Deposition technique	Substrate orientation	Technique of investigation	Surface structures observed	References
Re	--	hcp	2.74	152	--	--	---	---	--
Re	Ba	bcc	4.35	36	VD	(0001)	LEED-WF	$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$, hexagonal	151
Zn	--	hcp	2.66	27	--	--	---	---	--
Zn	Cu	fcc	2.56	73	VD	(0001)	LEED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	9
Sb	--	rhomb	2.91	62	--	--	---	---	--
Sb	Fe	bcc	2.48	85	VD	(0001)	TED	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	152

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