Atomic and electronic structures of two-dimensional layers on noble metals

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Atomic and electronic structures of two-dimensional layers on noble metals

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Cover images

Top left: LEED pattern from an As/Ag(111) surface alloy

Top right: STM image of the As/Ag(111) surface alloy

Bottom: ARPES data from a Te/Ag(111) surface alloy

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Abstract

Two-dimensional (2D) materials, in the form of a single atomic layer with a crystalline structure, are of interest for electronic applications. Such materials can be formed by a single element, e.g., by group IV or group V elements, or as a 2D surface alloy. As these materials consist of just a single atomic layer, they may have unique properties that are not present in the bulk. The (111) surfaces of the noble metals Ag and Au are important for the preparation of several 2D materials. To investigate the atomic and electronic structures, the following experimental techniques were used in this thesis: angle resolved photoelectron spectroscopy (ARPES), scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The 2D structures studied in this thesis include arsenene (an As analogue to graphene) and As/Ag(111), Sn/Au(111), and Te/Ag(111) surface alloys.

Arsenene has been thoroughly investigated theoretically for many years and several interesting properties important for next generation electronic and optoelectronic devices have been described in the literature. This thesis presents the first experimental evidence of the formation of arsenene. A clean Ag(111) surface was exposed to arsenic in an ultra-high vacuum chamber at an elevated substrate temperature (250 to 350 °C). The resulting arsenic layer was studied by LEED, STM and ARPES. Both LEED and STM data resulted in a lattice constant of the arsenic layer of 3.6 Å which is consistent with the formation of arsenene. A comparison between the experimental band structure obtained by ARPES and the theoretical band structure of arsenene based on density functional theory (DFT), further verified the formation of arsenene.

The As/Ag(111) surface alloy was prepared by exposing clean Ag(111) to arsenic followed by heating to 400 °C. This resulted in an Ag₂As surface alloy which formed by the replacement of every third Ag atom by an As atom in a periodic fashion. LEED showed a complex pattern of diffraction spots corresponding to a superposition of three domains of a reconstruction described by a $\begin{pmatrix} 14 & 0 \\ -1 & 2 \end{pmatrix}$ unit cell. STM images revealed a surface with a striped atomic structure with ridges characterized by a local $\sqrt{3} \times \sqrt{3}$ structure. ARPES data showed three alloy related bands of which one can be associated with the $\sqrt{3} \times \sqrt{3}$ structure on the ridges. This band shows a split in momentum space around the $\bar{M}$ point along the $\bar{\Gamma} \bar{K} \bar{M}$ direction of a $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone in similarity with a Ge/Ag(111) surface alloy.

Sn/Au(111) surface alloys can be prepared with different periodicities. An Au₂Sn phase characterized by a $\sqrt{3} \times \sqrt{3}$ periodicity and an Au₃Sn phase with a

2×2 periodicity are formed containing 0.33 and 0.25 monolayer of Sn, respectively. The clean Au(111) surface itself, shows a complex reconstruction, the so called herringbone structure, that can be viewed as a zig-zag pattern of stripes described by a $22 \times \sqrt{3}$ unit cell. The replacement of Au atoms by Sn results in change of the periodicity of the herringbone structure to $26 \times \sqrt{3}$ and $\approx 26 \times 2\sqrt{3}$ for the Au₂Sn and Au₃Sn surface alloys, respectively. Furthermore, the local 1×1 periodicity of clean Au(111) is replaced by a $\sqrt{3} \times \sqrt{3}$ and a 2×2 periodicity as is clear from STM images of the respective cases. ARPES data are presented for the Au₂Sn surface alloy, which reveal an electronic band structure with similarities to other striped surface alloys. In particular, the split in momentum space around the $\bar{M}$ point of a $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone is observed also for Au₂Sn.

A Te-Ag binary surface alloy can be formed by evaporating 1/3 monolayer of Te onto a clean Ag(111) surface followed by annealing. After this preparation, LEED showed sharp $\sqrt{3} \times \sqrt{3}$ diffraction spots that is evidence for a well-ordered surface layer. ARPES data revealed two distinct electronic bands that followed the $\sqrt{3} \times \sqrt{3}$ periodicity. One of these bands showed a small spin-split of the Rashba type. The experimental band structure was compared with the theoretical bands of several atomic models of Te induced structures on Ag(111). An excellent fit was obtained for a Te-Ag surface alloy with a planar honeycomb structure, with one Te and one Ag atom in the unit cell. A semiconducting electronic structure of the Te-Ag surface alloy was inferred from the ARPES data in agreement with the ≈ 0.7 eV band gap predicted by the DFT calculations.

Populärvetenskaplig sammanfattning

Tvådimensionella material, i form av ett atomlager med en kristallin struktur, är av intresse för elektroniska tillämpningar. Sådana material kan bildas av enskilda grundämnen, t ex från grupp IV eller grupp V i periodiska systemet, eller som en ytlegering. Eftersom dessa material består av bara ett enda atomlager, kan de ha unika egenskaper som inte förekommer i ett tredimensionellt material. (111)-ytorna av ädelmetallerna Ag och Au är viktiga för framställning av flera tvådimensionella material. För att undersöka atom- och elektronstrukturer används följande experimentella tekniker i denna avhandling: vinkelupplöst fotoelektronspektroskopi (ARPES), sveptunnelmikroskopi (STM) och elektrondiffraktion (LEED). De tvådimensionella strukturer som studeras i denna avhandling innefattar arsenen (ett material analogt med grafen bildat av arsenik) och följande ytlegeringar, As/Ag(111), Sn/Au(111) och Te/Ag (111).

Arsenen har undersökts grundligt teoretiskt under många år och flera intressanta egenskaper som är viktiga för nästa generations elektroniska och optoelektroniska tillämpningar har beskrivits i litteraturen. Denna avhandling presenterar de första experimentella bevisen på bildandet av arsenen. En atomärt ren Ag(111)-yta exponerades för arsenik i en vakuumkammare vid en förhöjd substrattemperatur (250 till 350 °C). Det resulterande lagret av arsenik studerades med LEED, STM och ARPES. Baserat på data från både LEED och STM kunde gitterkonstanten för arsenikskiktet bestämmas till 3,6 Å i överensstämmelse med den teoretiska gitterkonstanten för arsenen. En jämförelse mellan den experimentella bandstrukturen uppmätt med ARPES och beräknade elektronband verifierade att arsenen hade bildats.

En ytlegeringen mellan As och Ag framställdes genom att den rena Ag (111)-ytan exponerades för arsenik följt av upphettning till 400 °C. Detta resulterade i ett yttre atomlager med stökiometrin, Ag₂As. Denna ytlegering motsvarar att var tredje Ag-atom har ersatts av en As-atom på ett periodiskt sätt. LEED visade ett komplext mönster av diffraktionspunkter som visar på förekomsten av tre domäner av en rekonstruktion beskriven av en $\begin{pmatrix} 14 & 0 \\ -1 & 2 \end{pmatrix}$ -enhetscell. STM-bilder avslöjade en atomstruktur med åsar som kännetecknas av en lokal $\sqrt{3} \times \sqrt{3}$ -struktur. Tre legeringsrelaterade elektronband kunde identifieras i ARPES-data, av vilka ett kan kopplas till $\sqrt{3} \times \sqrt{3}$ -strukturen på åsarna. Detta band visar en splittring runt $\bar{M}$ -punkten längs $\bar{\Gamma} \bar{K} \bar{M}$ -riktningen av Brillouinzonen för en $\sqrt{3} \times \sqrt{3}$ -yta i likhet med Ge/Ag (111).

Ytlegeringar mellan Sn och Au kan skapas i det översta lagret av Au(111). En Au₂Sn-fas karakteriserad av en $\sqrt{3} \times \sqrt{3}$ -periodicitet och en Au₃Sn-fas med en

2×2 -periodicitet kan bildas med 0,33, respektive 0,25 monolager av Sn. Den rena Au(111)-ytan har en komplex rekonstruktion vilken kan liknas vid ett fiskbensmönster av band som beskrivs av en $22 \times \sqrt{3}$ -cell. Utbytet av Au-atomer mot Sn resulterar i en förändring av periodiciteten hos rekonstruktionen till $26 \times \sqrt{3}$ och $\approx 26 \times 2\sqrt{3}$ för Au_2Sn , respektive Au_3Sn . Dessutom ersätts den lokala 1×1 periodiciteten för den rena Au(111)-ytan med en $\sqrt{3} \times \sqrt{3}$, respektive en 2×2 -periodicitet, vilket framgår av STM-bilder. ARPES-data som presenteras för Au_2Sn , visar tydligt att bandstrukturen har likheter med andra ytlegeringar av samma typ. Detta gäller i synnerhet för splittringen runt $\bar{M}$ -punkten i Brillouin-zonen.

En binär, tvådimensionell, legering mellan Te och Ag kan bildas genom att förånga $1/3$ monolager av Te på en ren Ag(111)-yta följt av uppvärmning. Efter denna behandling uppvisade LEED väldefinierade diffraktionspunkter med $\sqrt{3} \times \sqrt{3}$ -periodicitet vilket är bevis för ett välordnat ytskikt. ARPES-data avslöjade två dispersiva elektronband som också följde $\sqrt{3} \times \sqrt{3}$ -periodiciteten. Ett av dessa band hade en liten spinnuppdelning. Den experimentella bandstrukturen jämfördes med de teoretiska banden av flera atommodeller av Te-inducerade strukturer på Ag(111). En utmärkt överensstämmelse erhöles för en ytlegering med en plan, grafenliknande, struktur, med en Te och en Ag-atom i enhetscellen. En halvledande elektronstruktur kunde konstateras från ARPES-data i överensstämmelse med ett beräknat bandgap på $\approx 0,7$ eV.

Dedicated to

My wife and daughter

Preface

This PhD work was performed from October 2013 till September 2019 in the Semiconductor Materials Division at the Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden.

The research was focused on the preparation and characterization of 2D atomic layers of arsenene and surface alloys of As/Ag, Sn/Au and Te/Ag on the (111) surfaces of the noble metals of Ag and Au. The experimental techniques used in this thesis were ultra-high vacuum scanning tunneling microscopy (STM) at IFM, Linköping University and angle resolved photoelectron spectroscopy (ARPES) at MAX-lab in Lund, Sweden. Both systems were equipped with low energy electron diffraction (LEED).

This thesis is composed of four introductory chapters followed by the research results in the form of five manuscripts. The first chapter is a brief description of periodicities in two dimensions. The second chapter describes the experimental techniques used in this work. The atomic and electronic structures of the (111) surfaces of the noble metals, Ag and Au, are presented in the third chapter. The fourth chapter gives summaries of the manuscripts.

List of the included papers

Paper I

Experimental evidence of monolayer arsenene: An exotic two-dimensional semiconducting material

Jalil Shah, W. Wang, H.M. Sohail and R.I.G. Uhrberg.

Manuscript

Paper II

A quasi one-dimensional structure formed by an As/Ag(111) surface alloy

Jalil Shah, W. Wang, H.M. Sohail and R.I.G. Uhrberg.

Manuscript

Paper III

Atomic and electronic structures of the Au₂Sn surface alloy on Au(111)

Jalil Shah, W. Wang and R.I.G. Uhrberg.

Manuscript

Paper IV

Atomic structure studies of two-dimensional Sn/Au surface alloys on Au(111)

Jalil Shah, W. Wang and R. I. G. Uhrberg.

Manuscript

Paper V

Formation of a Te-Ag honeycomb alloy: A novel two-dimensional material.

Jalil Shah, H.M. Hafiz, R.I.G. Uhrberg and W. Wang.

Manuscript

My contribution to the papers

Paper I and II

Responsible for the initiation of the experimental parts of the projects involving arsenic induced 2D structures. Performed LEED, ARPES and STM studies. Wrote the first version of the manuscripts. Discussed the data and worked on the finalization of the manuscripts together with the co-authors.

Paper III and IV

Performed LEED and STM studies, analyzed all experimental data and wrote the first versions of the manuscripts. Discussed the data and worked on the finalization of the manuscripts together with the co-authors.

Paper V

Responsible for the experimental part of the Te-Ag surface alloy project. Performed LEED and ARPES studies. Discussed the experimental data with the co-authors.

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Finally, I am very thankful to my wife (Saeeda Zain) and my sweet daughter (Zyna Shah) for being part of my life. It is a blessed time with both of you. I am also very thankful to my brothers and sisters.

List of abbreviations

2D	two-dimensional
BZ	Brillouin zone
SBZ	surface Brillouin zone
ML	monolayer
fcc	face centered cubic
hcp	hexagonal close packed
ARPES	angle resolved photoelectron spectroscopy
LEED	low energy electron diffraction
STM	scanning tunneling microscopy
PES	photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy
UPS	ultraviolet photoelectron spectroscopy
UHV	ultra-high vacuum
S.S	Shockley surface state
E_F	Fermi level
VB	valence band
CB	conduction band

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Introduction to the subject of the thesis

The research presented in this thesis is within the realm of material science. Different materials have been of fundamental importance for the development of human civilizations, from the stone age till the modern age. Advanced technologies have become essential parts of our daily life and they are, to a large extent, based on the discovery and development of materials with very specific properties. The information technology (IT) is one example where the design and synthetization of electronic materials have made it possible to build computers and smart phones with higher and higher performance over the years, leading to a wealth of digital applications.

Current integrated circuits used in electronic devices are to the largest extent based on silicon (Si) with different dopings to achieve the wanted properties for each application. Examples of other basic materials are galliumarsenide (GaAs) and silicon carbide (SiC). To improve the performance of an integrated circuit it is important to make the dimensions of the constituent materials smaller. As the dimensions have now reached the order of nanometers ($\text{nm}=10^{-9} \text{ m}$) one is getting close to the limits of what is physically possible. A material that is 1 nm thick may only contain 2-3 atomic layers. At such small dimensions, quantum physics phenomena play an important role and materials may exhibit properties that thicker layers lack. Reducing the size of a material to just one atomic layer in one dimension results in a truly two dimensional (2D) structure, reduction in two dimensions results in a 1D chain of atoms, and reduction in all three dimensions results in a 0D quantum dot.

The aim of the research in this thesis was to synthesize and characterize 2D materials. Research on layered materials has been going on for decades. Well studied examples are transition metal dichalcogenides such as MoS_2 , WSe_2 , MoTe_2 , and other, which are made up of weakly bonded 2D layers. Graphite is another layered material made up of 2D sheets each consisting of a single layer of carbon atoms. The successful isolation of such a layer (graphene) by A. Geim and K.

Novoselov, was an achievement that was awarded the Nobel prize in Physics in 2010. The many intriguing and promising properties of this archetype of a 2D material have led to a boom in the research activities not only on graphene but also on other 2D materials, both existing and other conceivable ones. The obvious ones to synthesize are graphene like structures made of Si (silicene), Ge (germanene), and Sn (stanene), which belong to group IV of the periodic table in similarity to carbon. Also, 2D materials of group V elements are of interest such as phosphorene (P), arsenene (As), antimonene (Sb) and bismuthene (Bi). Ideally, one would like to prepare freestanding 2D layers to avoid interaction with a substrate that influences the intrinsic properties. This is of course extremely difficult to achieve with a material that is just one atomic layer thick. Thus, the 2D layers have to be prepared on top of some substrate that is chosen to result in the least possible interaction with the 2D layer.

This thesis presents the preparation of arsenene on Ag(111), an As/Ag(111) surface alloy, various Sn/Au(111) surface alloys, and a binary Te-Ag surface alloy on Ag(111). Atomic and electronic structures were studied by angle resolved photoelectron spectroscopy (ARPES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). The combination of these three experimental techniques provides a thorough picture of the studied materials. The experimental data are compared to theoretical electronic band structures and atomic structures.

CHAPTER 1: INTRODUCTION TO TWO-DIMENSIONAL STRUCTURES

1.1 Surface atomic structure

1.1.1 Real space lattices in two dimensions

A two-dimensional (2D) crystal can be described by a 2D lattice of mathematical points, where one or several atoms, called the basis, are associated with each lattice point. The lattice is generated by repeating unit cells that are defined by two vectors $\bar{a}_1$ and $\bar{a}_2$ as exemplified in Fig. 1.1. The parallelogram formed by $\bar{a}_1$ and $\bar{a}_2$ is called a *unit cell*. Unit cells can be defined in many ways. The ones with the smallest possible area, as the one in Fig. 1.1, are called *primitive cells*. The set of lattice points is described by translational vectors of the form

$$\bar{T} = n\bar{a}_1 + m\bar{a}_2 \quad 1.1$$

where n and m are integers which can be both positive and negative.

Figure 1.1: 2D lattice in real space with an example of a primitive cell.

Another type of primitive cell is the so-called *Wigner-Seitz cell* that can be constructed by choosing an arbitrary lattice point and then identifying the nearest neighboring lattice points. By drawing lines that are perpendicular to lines connecting the selected lattice point with its neighbors, there will be an enclosed area, as illustrated in Fig. 1.2. The cell formed in this way contains one lattice point, which is the definition of a primitive cell.

Figure 1.2: Wigner-Seitz primitive cell for a 2D lattice in real space. The solid lines have been drawn at half the distance between neighboring lattice points.

Five different lattices, so called Bravais lattices, are sufficient to describe any periodic 2D structure, see Fig. 1.3.

1. Square lattice $|\bar{a}_1| = |\bar{a}_2|, \theta = 90^\circ$
2. Rectangular lattice $|\bar{a}_1| \neq |\bar{a}_2|, \theta = 90^\circ$
3. Oblique lattice $|\bar{a}_1| \neq |\bar{a}_2|, \theta \neq 90^\circ$
4. Centered rectangular lattice $|\bar{a}_1| \neq |\bar{a}_2|, \cos \theta = |\bar{a}_1|/2|\bar{a}_2|$
5. Hexagonal lattice $|\bar{a}_1| = |\bar{a}_2|, \theta = 120^\circ$

Figure 1.3: Bravais lattices showing the five possible periodicities in two-dimensions.

The Wood notation is used to describe the periodicity of a 2D superstructure when the angle between the two basis vectors is the same as that of the substrate. In the Wood notation the ratios of the lengths of the basis vectors of the superstructure and those of the substrate are specified. Also, the relative angle of rotation between the two lattices is indicated if it differs from 0° . The Wood notation is expressed in the form of

$$(c_1/a_1 \times c_2/a_2) - R\theta \quad 1.2$$

Where c_1 and c_2 are the absolute values of the primitive vectors of the superstructure and θ is the rotation angle of the superstructure with respect to the substrate lattice.

Figure 1.4(a) shows a $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ periodicity with respect to the 1×1 hexagonal substrate. In cases when the Wood notation is not applicable, one has to use a transformation matrix to describe the relation between the basis vectors of the superstructure and those of the substrate. The relation is given by

$$\begin{pmatrix} \bar{c}_1 \\ \bar{c}_2 \end{pmatrix} = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} \begin{pmatrix} \bar{a}_1 \\ \bar{a}_2 \end{pmatrix} \quad 1.3$$

$$\Rightarrow \quad \bar{c}_1 = T_{11}\bar{a}_1 + T_{12}\bar{a}_2 \quad \text{and} \quad \bar{c}_2 = T_{21}\bar{a}_1 + T_{22}\bar{a}_2 \quad 1.4$$

Where T_{ij} is an integer.

The matrix form $\begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$ is included for the $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ periodicity in Fig. 1.4(a) and for the $\begin{pmatrix} 4 & 0 \\ 1 & 2 \end{pmatrix}$ superstructure which cannot be expressed by the Wood notation, see Fig. 1.4(b).

Figure 1.4: Examples of superstructures and the use of Wood and matrix notations. (a) $\sqrt{3} \times \sqrt{3} - R30^\circ$ and the alternative $\begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$ matrix notation. (b) A superstructure with a rectangular unit cell described by a $\begin{pmatrix} 4 & 0 \\ 1 & 2 \end{pmatrix}$ matrix. For convenience, rectangular unit cells on a hexagonal surface are often labeled based on the lengths of the two sides. This alternative notation is $4 \times \sqrt{3}$ in this case.

1.1.2 Reciprocal space lattices in two dimensions

When investigating 2D periodic structures by diffraction methods or when studying band structure of the valence electrons, which both involve wave vectors, $\bar{k}$, it is necessary to go to reciprocal space. The absolute value of the $\bar{k}$ vector is

given by $2\pi/\lambda$ where λ is a wavelength, and the dimension of $\bar{k}$ is thus 1/length. It is quite straightforward to construct a reciprocal space where the $\bar{k}$ vectors can be conveniently described. From a real space lattice defined by the primitive vectors $\bar{a}_1$ and $\bar{a}_2$, the corresponding primitive vectors in reciprocal space $\bar{b}_1$ and $\bar{b}_2$ are calculated from

$$\bar{b}_1 = 2\pi \frac{\bar{a}_2 \times \hat{n}}{|\bar{a}_1 \times \bar{a}_2|} \quad \text{and} \quad \bar{b}_2 = 2\pi \frac{\hat{n} \times \bar{a}_1}{|\bar{a}_1 \times \bar{a}_2|} \quad 1.5$$

where $\hat{n}$ is a unit vector normal to the surface. From these relations we can note some properties of the reciprocal lattice vectors.

1. Reciprocal lattice vectors lie in the same plane as the real space vectors.
2. Reciprocal lattice vectors are perpendicular to the real space vectors.
3. The dimension of a reciprocal lattice vector is 1/length.

The parallelogram formed by $\bar{b}_1$ and $\bar{b}_2$ is called a *primitive cell* in reciprocal space, shown in Fig. 1.5.

Figure 1.5: Reciprocal space lattice and primitive lattice vectors corresponding to the 2D hexagonal real space lattice in Fig. 1.1. Note that the reciprocal lattice is rotated by 90° compared the real space lattice.

The translational vectors in reciprocal space are defined as

$$\bar{G} = h\bar{b}_1 + k\bar{b}_2 \quad 1.6$$

where h and k are integers called *Miller indices* which can be both positive and negative.

Figure 1.6: (a) Sketch of the construction of the Brillouin zone in reciprocal space for the hexagonal lattice. (b) Periodic zone scheme for two SBZs including high symmetry points.

1.1.3 Surface Brillouin zone (SBZ)

The Wigner-Seitz primitive cell in reciprocal space is called Brillouin zone (BZ). For the study of electronic band structures of crystals, the BZ concept is very important. Figure 1.6(a) shows the Wigner-Seitz construction of the Brillouin zone of a 2D structure. Two SBZs are drawn one below the other corresponding to a periodic zone scheme and the two high symmetry directions $\bar{\Gamma}_1\bar{K}$ and $\bar{\Gamma}_1\bar{M}$ are shown in Fig. 1.6 (b).

1.2 Electronic band structure

1.2.1 Bulk electronic band structure

A single isolated atom has two types of electrons, i.e., the deep core electrons and the outermost valence electrons. The valence electrons are important for chemical interaction while the core electrons are much less affected by the surrounding of the atom. The orbitals associated with the outermost electrons are called valence orbitals. When a number, N , of atoms are brought together to form a crystalline solid, the wave functions corresponding to the valence orbitals start to overlap. The degenerate set of N discrete valence levels split into a set of levels with different

energy in order to accommodate all electrons without violating the Pauli exclusion principle. This set of energy levels is called an electronic band. This can be divided into occupied and unoccupied parts. A band gap may separate the occupied part (valence band) from the unoccupied part (conduction band) as is the case of semiconductors.

Because of the periodic nature of the lattice of a crystalline solid, there is an associated periodic potential. Electrons interacting with the periodic potential can be described by so called Bloch waves. The wave function describing a Bloch wave has the form

$$\Psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \quad 1.7$$

which is a product of a plane wave $e^{i\vec{k}\cdot\vec{r}}$ and a function $u_{\vec{k}}(\vec{r})$, which has the periodicity of the crystal lattice. Allowed electron energies in a crystalline solid is a function of wave vector $\vec{k}$ described by $E(\vec{k})$.

1.2.2 Surface electronic band structure

At surfaces, the periodicity is broken in the direction normal to surface plane. This condition opens up for the existence of electronic states localized to the surface that are not allowed in the three-dimensional bulk. The wave functions of surface states decay exponentially both inward, i.e., toward the bulk, and outward resulting in a confinement to the surface layer. Because of the lack of periodicity in one dimension, the band structure of surface states only depends on a two-dimensional wave vector, $\vec{k}_{\parallel}$, in the surface plane. Thus, the complete band structure is given by the relation $E(\vec{k}_{\parallel})$.

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CHAPTER 2: SURFACE ANALYTICAL TECHNIQUES

2.1 Low energy electron diffraction (LEED)

LEED is an ultra-high vacuum (UHV) technique that is widely used in material science to analyze periodic structures of surfaces [1,2]. Electrons with energy in the range of typically 20 to 200 eV are diffracted from the topmost atomic layers of the material. This energy range results in a small mean free path of the electrons and the technique is therefore well suited for the study of surfaces. LEED is particularly useful to obtain the periodicity of 2D materials.

The energy of the electrons incident on the surface is given by

$$E_{\text{kin}} = \frac{\hbar^2 k^2}{2m} \quad 2.1$$

Where

$$k = \frac{2\pi}{\lambda}$$

From these relations we get the expression for the de Broglie wavelength, λ , which is the wavelength that is associated with an electron of energy E .

$$\lambda = \hbar \pi \sqrt{\frac{2}{mE_{\text{kin}}}} \quad 2.2$$

The de Broglie wavelengths for electrons in the range 20-200 eV are $\approx 1\text{-}3 \text{ \AA}$. These wavelengths are suitable for diffraction studies since they are of the order of interatomic distances.

The diffraction condition is given by a simple expression in reciprocal space

$$\bar{k} - \bar{k}_0 = \bar{G} \quad 2.3$$

where $\bar{k}_0$ is the wave vector of the incident electrons, $\bar{k}$ is the wave vector of the diffracted electrons, and $\bar{G}$ is a reciprocal lattice vector (translational vector of the reciprocal lattice).

Figure 2.1 shows a graphical illustration of the diffraction condition according to the Ewald method. In the case of a 2D lattice, such as that of a surface, there is a 2D reciprocal lattice in the surface plane. In the third dimension, which is necessary in order to use the Ewald method, the reciprocal lattice consists of rods that are perpendicular to the surface and located at the points of the 2D reciprocal lattice.

Figure 2.1: Ewald sphere and the reciprocal lattice rods with Miller indices. The wave vector of the incident electron beam, $\bar{k}_0$, and of seven diffracted beams are shown. In the case of the $\bar{k}_{30}$ diffraction the $\bar{G}$ vector has also been included.

A reciprocal lattice rod is formed by closely spaced reciprocal lattice points that results in a continuous rod. The points where the Ewald sphere intersects the reciprocal lattice rods fulfill the diffraction condition $\bar{k} - \bar{k}_0 = \bar{G}$.

A schematic drawing of the experimental set-up of LEED is shown in Fig. 2.2. The electron gun produces a beam of monochromatic electrons with an energy $eI-VI$. The sample and the first grid are both grounded to create a field free space for the diffracted electrons. Second and third grids have a negative biased of $(-V + \Delta V)$. These two grids act as a high pass filter that prevents inelastically scattered

electrons from reaching the fluorescent screen. The fourth, grounded, grid, screens the other grids from the high positive voltage ($+HV$) applied on the fluorescent screen. This high positive voltage is necessary in order to give the electrons enough energy to produce bright light spots. In this way the diffraction pattern can be made visible on the LEED screen.

Figure 2.2: Schematic drawing of the experimental set-up of LEED. When the beams of diffracted electrons hit the fluorescent screen, they give rise to a pattern of bright spots. This LEED pattern is a direct image of the 2D reciprocal space.

2.2 Scanning tunneling microscopy (STM)

Scanning tunneling microscopy is a technique used in studies of the atomic structure of surfaces and 2D materials [3,4]. It is based on the phenomenon of quantum mechanical tunneling which allows an electron to tunnel through a potential barrier that would be impenetrable according to classical mechanics. In the case of STM, the potential barrier corresponds to the vacuum gap between a tip and a sample, where the height of the potential barrier is given by the work functions of the tip and sample material. The STM technique, developed by Gerd

Binnig and Heinrich Rohrer, was published in 1982 [5]. They were awarded the Nobel Prize in 1986 for this invention, which revolutionized the study of the atomic structure of surfaces.

The working principle of an STM is quantum mechanical tunneling between a conducting sample and a sharp metallic tip that is scanned along x and y a few Å above the surface. The tip is attached to a piezoelectric scanner which controls the movement of the tip along the x , y , and z -directions. Applying a bias voltage to either the sample or the tip will result in a tunneling current that is fed into the control electronics of the STM. A schematic STM diagram is shown in Fig. 2.3.

Figure 2.3: Schematic drawing of a scanning tunneling microscope (STM) set-up.

To image the topography/corrugation of a surface, the STM can be used in two modes called constant current and constant height mode, respectively. In constant current mode, the z -position of the tip is regulated by feedback electronics during scanning in order to maintain a constant current. The up and down motions of the tip during scanning trace the corrugation of the surface and these traces are used to construct an image of the surface. The advantage of this mode is that surfaces

with large corrugations can be scanned without crashing the tip. In constant height mode, the tip scans the topography of the surface while the feedback system is turned off. As the tip scans the surface there is a variation in the tunneling current which is transformed into an STM image which is related to the integrated local density of states. The advantage of this mode is that surfaces can be scanned at a high speed if they are sufficiently flat.

2.2.1 Theoretical description of STM

When a metallic tip is brought close to a metallic substrate the wavefunction of the electrons of the tip will overlap with the wavefunctions of the electrons of the substrate surface. As illustrated in Fig. 2.4(a), the wavefunction of the electron in a metal has a plane wave solution but in the vacuum barrier the wavefunction decays exponentially. At the boundaries of the barrier the wavefunction is continuous and there is probability that the electron will tunnel through the barrier. The Schrödinger equation in the barrier has the form

$$\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \psi - \phi \psi = -E \psi \quad 2.4$$

The solution is

$$\psi(d) = \psi(d=0)e^{-Kd} \quad 2.5$$

Where $K = \frac{\sqrt{2m(\phi-eV)}}{\hbar}$ is the decay constant. d is the distance between the tip and the substrate surface. ϕ is the average work-function given by $\frac{\phi_T + \phi_S}{2}$, $\hbar$ is the Planck constant (h) divided by 2π , and m and e are the mass and the elementary charge. The electron probability in the barrier is proportional to the square of the wavefunction which can be written as

$$|\psi(d)|^2 = |\psi(0)|^2 e^{-2Kd} \quad 2.6$$

Using the definition of the local density of states (LDOS)

$$\rho(z, E) = \frac{1}{\varepsilon} \sum_{E-\varepsilon}^E |\psi_n(z)|^2 \quad 2.7$$

the following expression applies when a small bias voltage is applied

$$\rho(0, E) = \frac{1}{\varepsilon} \sum_{E-\varepsilon}^E |\psi_n(0)|^2 = \frac{1}{eV} \sum_{E-eV}^E |\psi_n(0)|^2 \quad 2.8$$

Therefore, the expression for the tunneling current that flows across the barrier is proportional to the electron probability at some distance d .

$$I \propto \sum_{E_F-eV}^{E_F} |\psi(0)|^2 e^{-2Kd} \quad 2.9$$

$$I \propto \text{probability of tunneling} = \sum_{E_F-eV}^{E_F} |\psi(0)|^2 e^{-2Kd} \quad 2.10$$

$$I = eV \rho(0, E_F) e^{-2Kd} \quad 2.11$$

For a 1D vacuum barrier, the tunneling current, I , has an exponential dependence on the separation, d , between the tip and sample.

Figure 2.4: Energy and tunneling diagram. (a) Positive sample bias. (b) Negative sample bias. Here, ϕ is the average of the tip, ϕ_T , and the sample, ϕ_S , work functions.

2.3 Photoelectron spectroscopy (PES)

PES utilizes the photoelectric effect [6,7]. The kinetic energies (K.E.) of electrons emitted from a solid is measured by PES. These data are used to determine the binding energies of the electrons to get information about electronic structure. In this thesis, PES is used to study the surface electronic structure of crystalline solids. An electron with an initial energy E_i can be excited to a final energy E_f by absorbing the energy of a photon [8]. In a PES study, the energy, direction and polarization of the incident photons along with the emission direction of the emitted electrons as a function of polar and azimuthal angles are important parameters. To be emitted from the solid, the energy of the photoelectron must be sufficient to overcome the work function of the material defined by

$$\phi = E_{\text{vac}} - E_F \quad 2.12$$

From the above equation, the work function is defined as the difference between the Fermi level, E_F , and the vacuum level, E_{vac} .

The kinetic energies of the photoelectrons emitted from a sample, are measured by an electron analyzer. From this information one can determine the electron binding energies which are given by

$$E_B = h\nu - E_{\text{kin}} - \phi \quad 2.13$$

Here $h\nu$ is the photon energy, h is the Planck constant and ν is the frequency of the photon. E_B is the binding energy which is the important parameter in the PES process.

PES can be divided into two regimes according to the energy of the incident photons. These are UPS (ultraviolet photoelectron spectroscopy) and XPS (x-ray photoelectron spectroscopy) [9]. Photons in the ultraviolet region are used for studies of the valence electronic states. The main use of UPS is to determine the electronic band structure of solids and in particular the band structure of surfaces

where the energy is measured as a function of wavevector, $\bar{k}_{\parallel}$. The limitation of UPS is that only the valence electrons and a few shallow core levels can be reached.

In XPS, photons in the x-ray region are used for the study of electronic structure of solids. XPS is used for a wide range of studies but for solids the information obtained is related to the binding energy, the chemical states, the elemental composition, the electronic states and the thickness of layers grown on top of solids. Due to the higher photon energies, a wide range of core levels can be investigated from various elements. The deeper core level electrons are different from the valence electrons since these electrons are not taking part in chemical bonds and they are unique for every element.

In contrast to these conventional sources, a more versatile light source is synchrotron radiation which provides photons that are polarized, and the photon energy can be continuously tuned from ultraviolet to x-rays [10]. This facilitates the studies of the electronic structures of both the VB and core levels. A schematic diagram of the photoemission process is shown in Fig. 2.5.

Figure 2.5: Schematic diagram of the photoemission process.

Here $h\nu$ is the photon energy used to excite the electrons and E_B is the binding energy of the electron. $E_{\text{kin-v.b}}$, $E_{\text{i-v.b}}$ and $E_{\text{f-v.b}}$ are the kinetic, initial and final energies of the valence band electrons, respectively. $E_{\text{kin-c.l}}$, $E_{\text{i-c.l}}$ and $E_{\text{f-c.l}}$ are the kinetic, initial and final energies of the core level electrons, respectively.

A three-step model is sometimes used to describe the photoemission process. The excitation of the electron from the initial to the final state corresponds to the first step. The transport of the electrons to the surface is treated as a second step, during which the electrons can suffer both elastic and inelastic scattering. In the third and final step, the electrons are emitted from the sample, which is associated with an energy loss corresponding to the work function. This energy loss results in refraction of the electron wave.

2.3.1 Angle resolved photoelectron spectroscopy (ARPES)

ARPES is used to study the electronic band structure of crystalline materials [2,9]. The geometry of an ARPES experiment is shown in Fig. 2.6. Incident photons excite electrons of the material which are emitted in different directions. The kinetic energies of the emitted electrons are analyzed as a function of polar angle, θ_e , and azimuthal angle, φ . The information about the electronic band structure as a function of wavevector, k , is obtained by the following free electron relations,

$$E_{\text{kin}} = \frac{\hbar^2 k^2}{2m} \quad 2.14$$

$$\text{and} \quad k = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \quad 2.15$$

where k is the magnitude of the wavevector.

As illustrated in Fig. 2.6, the k -vectors of the photoelectrons can be divided into parallel ($\bar{k}_{\parallel}$) and perpendicular ($\bar{k}_{\perp}$) components with respect to the surface. The kinetic energy of the photoelectrons can be written as

$$E_{\text{kin}} = \frac{\hbar^2 (\bar{k}_{\parallel}^2 + \bar{k}_{\perp}^2)}{2m} \quad 2.16$$

Where

$$k_{\parallel} = |\bar{k}| \sin \theta = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \sin \theta \quad 2.17$$

$$k_{\perp} = |\bar{k}| \cos \theta = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \cos \theta \quad 2.18$$

Figure 2.6: Schematic diagram showing the geometry of an ARPES experiment.

By measuring the polar angle and the kinetic energy of the photoelectrons, the electronic band dispersion, $E_B(\bar{k}_{\parallel})$, can be mapped out in two dimensions. This band dispersion is a function of θ_e , from which $\bar{k}_{\parallel}$ can be figured out using equation 2.17 above. An example of such band dispersion data is shown in Fig. 2.7.

One important concept when it comes to the electronic properties of a material is the Fermi surface. In two-dimensions, the Fermi surface corresponds to a constant energy contour at the Fermi level mapped in the (k_x, k_y) -plane. Constant energy contours in

Figure 2.7: Electronic band dispersion obtained by ARPES from a TeAg surface alloy. The $\bar{k}_{||}$ -values were derived from equation 2.17.

general are obtained by cutting through a three-dimensional data set, $E(k_x, k_y)$, as schematically illustrated in Fig. 2.8.

Figure 2.8: Schematic illustration of a three-dimensional data set, $E(k_x, k_y)$ from ARPES. Constant energy contours are obtained by selecting the data in the (k_x, k_y) -plane at a specific energy.

In the photoemission process, $\bar{k}_{||}$ is conserved except for a possible addition of a surface reciprocal lattice vector, $\bar{G}$,

$$\bar{k}_{||, \text{outside}} = \bar{k}_{||, \text{inside}} + \bar{G} \quad 2.19$$

Due to the broken symmetry at the surface the perpendicular wavevector, $\bar{k}_\perp$, is not conserved. When the electrons are emitted from the sample, they lose energy corresponding to the workfunction, which results in a reduction of the wavevector, as described by eq. 2.20. This reduction is limited to the $\bar{k}_\perp$ component which results in a refraction of the electron wave.

$$\frac{\hbar^2 k_{\text{inside}}^2}{2m} - \phi = \frac{\hbar^2 k_{\text{outside}}^2}{2m} \quad 2.20$$

2.3.2 Core level spectroscopy

In XPS, electrons from the core levels are excited and their binding energies are measured. This technique gives information about the chemical composition, chemical state and electronic structure of solid materials. At a surface, there is a change in the chemical environment which may result in a shift of the core level binding energy. The line shape and the number of components obtained from a core level spectrum provide both chemical and structural information. Choosing a photon energy that results in a kinetic energy near the escape depth minimum makes the technique surface sensitive.

The line shape of a core level spectrum is mainly determined by chemical shifts, surface shifts, energy losses due to electron-electron interaction, phonon excitations and core hole lifetimes along with the instrumental resolution.

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CHAPTER 3: (111) SURFACES OF NOBLE METALS

The atomic positions at the surface of a crystalline material differ usually from those of an ideally truncated bulk crystal. In the simplest case, the outermost atomic layers may just be displaced perpendicular to the surface plane, which is called relaxation. If the atomic rearrangement includes both vertical and lateral displacements, that might include several layers, a reconstruction has occurred. These changes take place to minimize the energy of the surface-bulk system. For metals, which have non directional bonds, relaxation is the most common case manifested as a change in the interlayer distance between the topmost planes. The Ag(111) surface is an example of simple relaxation while Au(111) exhibits both vertical and horizontal displacements. This chapter is about the atomic and electronic structures of Ag(111) and Au(111) surfaces.

3.1 Ag(111) and Au(111) surfaces

The noble metals Ag and Au are used as substrates for the preparation of 2D surface alloys in this thesis. The outer electronic configurations of Ag($4d^{10}5s^1$) and Au($5d^{10}6s^1$) are similar, i.e., the valence shells of these elements contain one s-electron and a completely filled d-subshell. The s-electron takes part in chemical interaction through metallic bonds. (111) surfaces of these metals have a quasi 2D electron gas which is confined to a few of the topmost atomic layers. This 2D electron gas forms the so called Shockley surface state (S.S) [1] which is located in the projected gap of the bulk band structure around the $\bar{\Gamma}$ -point of the SBZ.

Figure 3.1: Model of the fcc structure. Top view of the stacking of three close packed atomic layers. Each layer corresponds to a (111) plane of the fcc structure. The illustrated stacking order defines the fcc structure.

Both Ag and Au crystals have the face centered cubic (fcc) structure. This structure is obtained by a special stacking sequence of close packed atomic layers, as illustrated in Fig. 3.1.

The stacking sequence of three successive close packed layers defines the fcc structure. The atoms of layer B are located at threefold hollow sites of layer A and the atoms of layer C occupy threefold hollow sites of layer B, i.e., the ones that result in a shift between layers A and C. This stacking sequence is repeated to form the fcc structure (ABCABC....).

3.1.1 Ag(111)

Crystalline Ag has a lattice constant of $4.09 \text{ \AA}$ when the fcc structure is described by the conventional cubic unit cell [2]. The Ag(111) surface has an interatomic distance of $2.89 \text{ \AA}$ which is the lattice constant of the surface. It is challenging to obtain nice atomically resolved images of the Ag(111) surface by STM due to the small unit cell and small corrugation.

An STM image of the clean Ag(111) surface is shown in Fig. 3.2(a). The white blobs correspond to the positions of Ag atoms. This surface is not reconstructed, and the white diamond shows the 1×1 unit cell in real space. The LEED pattern in Fig. 3.2(b) shows the structure in reciprocal space of the Ag(111) 1×1 surface. The 1×1 unit cell in reciprocal space, shown by the black diamond, is rotated by 90° compared to real space.

Figure 3.2: (a) STM image of the Ag(111) surface showing the hexagonal close packed arrangement of atoms. A 1×1 unit cell is shown by the white diamond. (b) LEED pattern of clean Ag(111) using an electron energy of 113 eV. The unit cell in reciprocal space is shown by the black diamond. (STM data was obtained by Weimin Wang)

The electronic structure information from clean Ag(111) obtained by ARPES is shown in Fig. 3.3.

Figure 3.3: (a) 1×1 SBZ with symmetry points. (b) and (c) ARPES data from clean Ag(111) along the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ lines of a 1×1 SBZ using a photon energy of 27 eV. (ARPES data were obtained by Jacek Osiecki and Roger Uhrberg)

Results from two different symmetry lines of the SBZ are included, i.e., along the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ lines, indicated in Fig. 3.3(a). The Shockley surface state (S.S) which is the signature of clean Ag(111) is indicated by the black arrows in Figs. 3.3(b) and 3.3(c). The minimum energy of the S.S is about 60 meV below the Fermi level [3,4]. Apart from the S.S, bulk emission is also present, indicated by B. These dispersive features correspond to emission from three-dimensional bulk bands. The information about this emission is essential for the interpretation of the ARPES data from the 2D surface alloys studied in this thesis.

3.1.2 Au(111)

The fcc structure of crystalline Au has a lattice constant of 4.08 Å and an interatomic distance in the (111)-plane of 2.89 Å [2]. As mentioned in the beginning of this chapter, the Au(111) surface undergoes a structural modification resulting in the so called herringbone reconstruction where the surface atoms are more densely packed than in the bulk [5]. In this type of reconstruction, the surface layer is compressively strained in a $\langle -110 \rangle$ direction by 4% [6]. This uniaxial compression results from the presence of extra gold atoms in the topmost layer. The resulting periodicity can be described by a rectangular unit cell of the size $22a \times \sqrt{3}a$, where a is the lattice constant of the unreconstructed (111) surface. Within the unit cell, there are two types of domains. One corresponds to an uncompressed fcc stacking and the other to a compressed hcp stacking of the surface layer [7-9]. The periodicity of the hcp and fcc stackings results in the $22a$ dimension of the unit cell. The boundaries between hcp and fcc stackings are called ridges and can be imaged by STM. A particular feature of the ridges is the frequent changes of direction by 60° resulting in a herringbone appearance.

Figure 3.4: (a) Atomically resolved STM image of the herringbone reconstruction of Au(111) [7] (Image size $5 \times 5 \text{ nm}^2$). (b) A $50 \times 50 \text{ nm}^2$ STM image showing the herringbone pattern formed by the ridges separating fcc and hcp stacking. (c) LEED image of the herringbone reconstruction of Au(111) obtained at an electron energy of 127 eV. The 1×1 unit cell in reciprocal space corresponding to an unreconstructed surface is shown by the black diamond. The diffraction spots surrounding each 1×1 spot originate from the reconstruction. ((a) and (b) are reproduced from J. Chem. Phys. 143, 014704 (2015) with the permission of AIP Publishing and the corresponding author Holly Walen, <https://doi.org/10.1063/1.4922929> [7]. The LEED images was obtained by Weimin Wang)

The herringbone reconstruction can be imaged by the STM, where the ridges and elbows appear as bright features while the hcp and fcc regions are darker [7]. In the theoretical literature, it is shown that the contrast originates from the topography of the herringbone reconstruction and not from electronic effects. The

electronic states are uniform across the hcp and fcc regions and the measured height profile in STM images is mostly due to the physical perturbation of the surface.

Figure 3.5: (a) and (b) ARPES data from clean Au(111), with the herringbone reconstruction, displayed along the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ lines of a 1×1 SBZ. The photon energy was 26 eV. (Data were obtained by Weimin Wang)

The Shockley surface state (S.S) of the Au(111) surface is split into two branches due to spin-orbit coupling [10]. This was first observed by LaShell *et al.* using ARPES [3]. The split results in a separation between the two branches along the momentum axis by $\sim 0.02 \text{ \AA}^{-1}$. Fig. 3.5 shows the S.S located around $\bar{\Gamma}$. The split of the S.S is not resolved in Fig. 3.5 and appears as a broadening of the band in these wide range ARPES data. The bottom of the surface state band is located at $\sim 0.5 \text{ eV}$ which is in good agreement with the theoretical and experimental values in the literature [11-13]. Also, the bulk emission, B, from the s,p valence band and the emission from the 5d-bands can be observed in Fig. 3.5.

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CHAPTER 4: SUMMARIES OF THE PAPERS

The subjects of the papers are within the realm of two-dimensional (2D) materials and their potentially large importance for future applications. The interest in 2D materials increased dramatically as a consequence of the discovery of graphene which is a single layer of carbon atoms arranged in a honeycomb structure [1]. This 2D material has several unique physical properties, amongst which the electronic properties in particular gave rise to hope for significant improvements when used in electronic applications. However, this anticipated development has been severely hampered by the lack of a band gap in graphene. Other 2D materials recently studied, such as silicene, germanene and stanene, also suffer from the absence of a suitable band gap [2]. The hope has turned to other graphene like 2D materials of which the group V atoms are of special interest since theory predicts substantial band gaps of more than 2 eV in some cases [3]. Up to the point of writing this summary, there are experimental reports on 2D layers of phosphorus [4,5], antimony [6] and bismuth [7]. Phosphorene has mainly been prepared by exfoliation, which produces small flakes which impairs the usefulness of this 2D material. The studies of antimonene and bismuthene report planar honeycomb structures grown on Ag(111) and SiC(0001), respectively, which are in contrast to the theoretically predicted buckled honeycomb structures of the freestanding form of these materials. The atomic and electronic structures of arsenene, a graphene like material made of As, a group V element, is discussed in **paper I**. This paper presents the first successful preparation of single layer buckled arsenene.

Surface alloys belong to another group of 2D materials that are of great interest. In this thesis, a certain type of surface alloy has been studied. A one atomic layer thick alloy can be formed by replacing some of the surface atoms of a substrate by atoms of another element in a well-ordered way. Ag(111) is an important substrate for

these studies on which 1/3 monolayer of Ge [8,9], Sn [10], Pb [11], Sb [12] , and Bi [13], all form 2D surface alloys by replacing Ag atoms. In the case of Sn, Pb, Sb, and Bi, the surface alloys exhibit a well-ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity. The surface alloys formed by Sb, Pb, and, in particular, by Bi, have been of importance for the study of the Rashba type of spin split of surface electronic bands. The Ge/Ag(111) surface alloy differs from the other ones when it comes to details of both the atomic and electronic structures. In this thesis, the investigations of the substitutional surface alloys have been extended to include also As/Ag(111) (**paper II**) as well as various Sn/Au(111) surface alloys (**papers III and IV**)

As an extension of the family of mono atomic honeycomb structures it is of interest to investigate binary honeycomb structures. The combination of two elements results in large number of conceivable honeycomb structures. **Paper V** in this thesis presents an experimental and theoretical study of a 2D Te-Ag layer on Ag(111) exhibiting a honeycomb structure.

Paper I: Experimental evidence of monolayer arsenene: An exotic two-dimensional semiconducting material

In this paper, evidence of the successful formation of monolayer arsenene on Ag(111) is presented. This conclusion is derived from low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and angle resolved photoelectron spectroscopy (ARPES) data in combination with density functional theory (DFT) calculations of the atomic and electronic structures. A buckled honeycomb structure is formed which fits nicely with the structure predicted by theory for freestanding monolayer arsenene. LEED and STM data result in a lattice constant of 3.6 Å which is in the middle of the theoretically predicted range of 3.54 to 3.64 Å. Further support for the formation of buckled arsenene comes from the excellent agreement between the three experimentally determined electronic bands and those obtained by theoretical band structure calculations.

Our report on arsenene synthetization should open up for extensive explorations of this promising material for next generation electronic and optoelectronic devices. Theoretical investigations in the literature predict high electron mobility, large band gaps, band gap tuning by strain, formation of topological phases, quantum spin Hall effect at room temperature, and superconductivity amongst others [14-28]. Furthermore, arsenene has been identified as a promising 2D material for field effect transistors (FET) in a theoretical study [29].

Paper II: A quasi one-dimensional structure formed by an As/Ag(111) surface alloy

When arsenene is heated to 400 °C, a complex periodic structure with a $\sqrt{3} \times \sqrt{3}$ like appearance is formed. An examination of the structure by LEED at room temperature reveals 6 satellite spots around each 1×1 spot. There are also 6 spots forming a triangle centered at $\sqrt{3} \times \sqrt{3}$ positions. These LEED observations imply that the surface has a striped structure with three differently oriented domains. By comparing to simulated LEED patterns one can conclude that the striped structure has a unit cell that is described by a $\begin{pmatrix} 14 & 0 \\ -1 & 2 \end{pmatrix}$ matrix. STM images revealed the presence of ridges with three different orientations. Atomically resolved STM images show a basic $\sqrt{3} \times \sqrt{3}$ and a long range $\begin{pmatrix} 14 & 0 \\ -1 & 2 \end{pmatrix}$ periodicity formed by two types of troughs separating the ridges. The local atomic structure on the ridges shows one atomic feature per $\sqrt{3} \times \sqrt{3}$ cell, which is consistent with the formation of an Ag₂As surface alloy.

Photoemission spectra of the As 3d core level show a single spin-split component with an asymmetry indicating that the Ag₂As alloyed layer has a metallic electronic structure. ARPES data reveal three electronic bands. Of particular interest is the split of one of the bands at the $\bar{M}$ -point, i.e., the band labeled S₂ splits into two bands S₂₊ and S₂₋. Such a split was also observed in the case of the Ag₂Ge surface alloy, which also has a striped structure [8,9].

Paper III: Atomic and electronic structures of the Au₂Sn surface alloy on Au(111)

This paper reports the atomic and electronic structures of 1/3 ML of Sn alloyed with Au in the surface layer of Au(111). The resulting Au₂Sn surface alloy has a striped phase with a $\sqrt{3} \times \sqrt{3}$ periodicity locally.

From LEED and STM, it was concluded that Au₂Sn shows a striped phase with a herringbone type of reconstruction described by a $26 \times \sqrt{3}$ unit cell. The distances between stripes are larger than for the $22 \times \sqrt{3}$ reconstruction of clean Au(111). The prevailing atomic model for the herringbone reconstruction of clean Au(111) has 23 Au atoms squeezed into a distance corresponding to 22 second layer atoms located at bulk positions [30]. In analogy, we suggest that 27 alloy atoms (Au and Sn) occupy a distance equivalent to that of 26 second layer atoms. This is supported by the size of the unit cell as determined from the alloy layer by STM. Our finding is different from the study by M. Maniraj et al. [31] where it was suggested that the periodicity of the clean Au(111) surface remained after the formation of the Au₂Sn surface alloy. As the herringbone structure corresponds to a compressed layer it imposes a slight distortion of the $\sqrt{3} \times \sqrt{3}$ unit cell.

Three two-dimensional electronic bands originating from Au₂Sn were identified by ARPES and their dispersions were mapped along symmetry lines of a $\sqrt{3} \times \sqrt{3}$ SBZ. A comparison with a theoretical band structure based on a simple $\sqrt{3} \times \sqrt{3}$ model [31] was performed. An overall agreement was found for the dispersions of all three bands, and a theoretically predicted spin-split was supported by our experimental data. One of the bands shows a split into two branches in similarity to the Ag₂Ge and Ag₂As surface alloys. This type of splitting is related to the striped structure of these surfaces and could not be reproduced by the simple model in the theoretical study.

Paper IV: Atomic structure studies of two-dimensional Sn/Au surface alloys on Au(111)

In this paper, different phases of Sn/Au surface alloys are investigated using LEED and STM techniques. The stoichiometry of Sn/Au surface alloys on Au(111) depends on the amount of Sn deposited on the surface. Each such alloy has a different 2D periodicity. The coverage range of 0.25 to 2 ML of Sn is investigated. When 0.6 ML of Sn or more is used then LEED shows a complex 12-fold pattern. There are both " 1×1 " and " 2×2 " diffraction spots following an apparent 12-fold symmetry. Other diffraction spots are also observed which generate hexagonal patterns rotated by $+15^\circ$ and -15° , respectively, compared to the hexagonal pattern formed by the 1×1 spots of clean Au(111).

The lattice constant corresponding to the $+15^\circ$ and -15° hexagonal LEED patterns is $\approx 4.1 \text{ \AA}$ which suggests the presence of two domains of a AuSn hexagonal alloy with an in plane lattice constant of $\approx 4.3 \text{ \AA}$ [32]. The STM data reveals that the surface has islands of various size and thickness but no atomically resolved images could be obtained.

Annealing the sample, with the 12-fold LEED pattern, at 200°C for 10 minutes, changed it to a $\begin{pmatrix} 13 & 0 \\ -1 & 2 \end{pmatrix} / (13 \times \sqrt{3})$ SnAu surface alloy. The LEED pattern from this surface is characterized by 1×1 spots surrounded by 6 satellite spots in similarity with clean Au(111). Centered at $\sqrt{3} \times \sqrt{3}$ positions, there are 6 diffraction spots forming a triangle. Additional features of the LEED pattern are rows of closely spaced diffraction spots between 1×1 spots and $\sqrt{3} \times \sqrt{3}$ positions. All these characteristics point at a striped structure of the surface superimposed on a basic $\sqrt{3} \times \sqrt{3}$ periodicity. Comparison between the experimental LEED pattern and the simulated LEED pattern for a $\begin{pmatrix} 13 & 0 \\ -1 & 2 \end{pmatrix}$ periodicity gives an excellent match. STM images show that the $\begin{pmatrix} 13 & 0 \\ -1 & 2 \end{pmatrix} / (13 \times \sqrt{3})$ surface alloy is free from islands. Equidistant stripes are observed by STM, which are separated by nearly $44.9 \text{ \AA}$.

This separation translates into an estimated $\approx 13.4 \times$ periodicity which is consistent with the $13 \times$ periodicity derived from LEED.

When the $\begin{pmatrix} 13 & 0 \\ -1 & 2 \end{pmatrix} / (13 \times \sqrt{3})$ phase of the SnAu surface alloy was annealed at nearly 260 °C for 10 minutes, it changed to a $\sqrt{3} \times \sqrt{3} / (26 \times \sqrt{3})$ phase. LEED data show that this Au₂Sn surface alloy has a $\sqrt{3} \times \sqrt{3}$ R30° periodicity with the typical characteristics of a striped phase. The combination of LEED and STM data resulted in a $26 \times$ periodicity of the striped structure. Thus, the Au₂Sn surface alloy is described by a $26 \times \sqrt{3}$ unit cell which differs from the $22 \times \sqrt{3}$ unit cell of the herringbone structure of clean Au(111). Atomically resolved images show that the distance between the atomic features correspond to a $\sqrt{3} \times \sqrt{3}$ unit cell.

Annealing of the Au₂Sn surface alloy at 400 °C for 10 minutes, results in Au₃Sn with a $2 \times 2 / (26 \times 2\sqrt{3})$ structure. The LEED pattern corresponds to a " 2×2 " striped phase. This phase has not been reported in the literature. STM data verify the striped structure with a local 2×2 unit cell. A single atomic feature is observed by STM per 2×2 unit cell, which implies an Sn coverage of 0.25 ML for this surface.

Paper V: Formation of a Te-Ag honeycomb alloy: A new type of two-dimensional material

In this paper, the investigations of the Ag(111) based surface alloys have been extended to involve also a group VI atom. No results for Te, the group VI neighbor to Sb, have been reported so far. Evidence is presented for the successful formation of a new type of 2D material. The combination of Ag and Te atoms forms a binary surface alloy on top of Ag(111). The 2D structure corresponds to a flat honeycomb layer with one Ag and one Te atom in the unit cell. Electronically, the 2D alloy is semiconducting with a band gap of approximately 0.7 eV. Further, a small Rashba type of spin split is observed in one of the valence bands. The conclusions in the paper are derived from LEED and ARPES data in combination with DFT calculations of the atomic and electronic structures. The close agreement between

the experimental band structure obtained by ARPES and the theoretical bands provides strong evidence for the formation of the binary honeycomb layer. Our report on the formation of a graphene-like structure formed by a binary surface alloy opens up for extensive explorations of various alloys for possible applications in next generation electronic and optoelectronic devices.

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