

6 Summary

This thesis investigates the interplay between reduced dimensionality, electronic structure, and interface effects in ultrathin metal layers (Pb, In, Al) on a variety of substrates (Si, Cu, graphite). These layers can be grown with such a perfection that electron confinement in the direction normal to the film leads to the occurrence of quantum well states in their valence bands. These quantum well states are studied in detail, and their behaviour with film thickness, on different substrates, and other parameters of growth are used here to characterise a variety of physical properties of such nanoscale systems. The sections of the thesis deal with a determination of quantum well state energies for a large data set on different systems, the interplay between film morphology and electronic structure, and the influence of substrate electronic structure on their band shape; finally, new ground is broken by demonstrating electron localization and correlation effects, and the possibility to measure the influence of electron-phonon coupling in bulk bands.

The thesis first discusses the theoretical approach to describe quantum well states within the particle-in-a-box model; this picture is then extended to the “phase-accumulation” model in order to be able to include influences on quantum well states due to the substrate. In order to obtain more insight into the detailed electronic structure of the quantum well states in the direction parallel to the surface, density functional theory calculations on free-standing metal slabs are used. The principle of an image type electron energy analyser is discussed, and it is shown that this type of analysers provide a perfect instrument for the study of details in the band structure of quantum well states; an experimental station of this type was built up in the course of the thesis work.

Binding energies and the in-plane dispersion of quantum well states in the different metals show a good correspondence to expectations from a theoretical approach. The preparation of atomically flat layers does, however, depend on the combination of substrate and overlayer material. It is shown that the stability of certain layer thicknesses is directly related to the binding energy of the highest occupied quantum well state; layers with a lower density of states at the Fermi level are more stable. It is found that the interface conditions can influence the exact energy position of the QWS, in some cases resulting in an energetically favourable or unfavourable situation influenced by just a small change in the boundary conditions at the interface. Especially in thin lead films, the influence of energy minimization effects on the formation of “magically, marginally and critically” stable heights is found to be very strong, resulting in different stable configurations, again depending on the nature of the substrate.

The influence of the substrate and interface is studied by considering the effect that strain in the metal overlayer, induced by the substrate, can have on the quantum well states. For indium on Si(111) and Si(100), quantum well states are only observed when the overlayer is relaxed towards the body-centred tetragonal structure. It is found that the formation of discrete states in the metal overlayer in regions with a higher density of states in the substrate depends on the exact interface

lattice structure; when a commensurate lattice is formed, effective confinement only occurs within the band gap of the substrate. The transmission of electrons across the interface is studied by introducing a double quantum well consisting of Pb on an Al layer on Si(111). This double quantum well possesses an additional interface between Pb and Al, and electron transport across the interface is directly reflected by the characteristics of the quantum well states that may form. It is found that, although Pb and Al have a different lattice constant, the system forms *one* large quantum well with *one* electronic structure.

Hybridization between quantum well states and the substrate bands can have a profound influence on the electronic structure of the quantum well states, leading to an anti-crossing gap or an inverted band dispersion. This hybridization is shown to be a tool to measure the ground state of the substrate bands independently of any other assumptions. In order to obtain an adequate determination of the in-plane effective mass of quantum well states, this interaction with the substrate bands has to be incorporated. Taking such effects into account, it is found that the in-plane dispersion corresponds well with theoretical considerations and the dispersion of the bulk band that the quantum well states are derived from. However, Pb on Si(111) provides an exception to this behaviour; values for the effective mass are found in this system that are almost an order of magnitude higher than expectations. This high effective mass is attributed to electron localization and, considering the fact that the electron interaction energy is larger than the band-width of the state, also of electron correlation effects.

Quantum well states are shown to be good candidates for measurements of electron-phonon coupling in *bulk* metals, and the influence of this effect on the band structure of the quantum well states is discussed. Angle-resolved photoemission measurements on quantum well states, where the real part of the self energy can directly be obtained from the data, are shown for the first time. From this data the electron-phonon coupling parameter is determined for bulk indium, which matches to theoretical expectations.

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Zusammenfassung

In dieser Dissertation wird die Wechselwirkung zwischen Dimensionalität, elektronischer Struktur und Grenzflächeneffekten in ultradünnen Metallschichten (Pb, In, Al) auf verschiedenen Substraten (Si, Cu, Graphit) untersucht. Derartige Schichten können so perfekt erzeugt werden, daß das „Confinement“ der Elektronen in der Richtung senkrecht zur Schicht die Aufspaltung des Valenzbandes in Quantentopfniveaus zur Folge hat. Diese Quantentopfniveaus werden im Detail untersucht, und ihre Abhängigkeit von Schichtdicke, der Art des Substrates, und anderen Wachstumparametern wird benutzt, um eine Reihe von Eigenschaften derartiger Nanosysteme zu charakterisieren. Die Abschnitte der Dissertation legen eine Analyse der Energien der Quantentopf-Zustände für ein große Anzahl von Systemen vor, analysieren die Einwirkung der elektronischen Struktur auf die Morphologie des Schichtwachstums, und klären den Einfluß der Substrat-Bandstruktur auf die Dispersion der Zustände; schließlich wird der bisher noch nicht untersuchte Einfluß von Lokalisierung und Korrelation der Zustände sowie der Elektron-Phonon-Kopplung in Volumenbänden behandelt.

Die Dissertation beginnt mit einer theoretischen Herangehensweise an Quantentopf-Zustände im einfachen „Teilchen-im-Potentialtopf“-Modell; dieses Bild wird zum Phasenakkumulationsmodell erweitert, damit der Einfluss des Substrats und der Grenzflächen einbezogen werden kann. Dichtefunktionaltheorieberechnungen für freistehende Metallschichten werden mit den gemessenen Ergebnissen verglichen, damit die detaillierte elektronische Struktur der Quantentopf-Zustände in der Richtung parallel zur Oberfläche im Detail verstanden werden kann. Das Prinzip der bilddarstellenden Elektronenenergieanalysatoren wird erörtert. Es wird gezeigt, dass diese Analyserentypen perfekt für eine eingehende Untersuchung der elektronischen Struktur von Quantentopf-Zustände geeignet sind; im Rahmen der experimentellen Arbeiten zur Dissertation wurde ein derartiges Meßsystem aufgebaut.

Aus den Untersuchungen geht hervor, dass es eine gute Übereinstimmung zwischen der gemessenen Energien und Dispersion der Quantentopf-Zustände und den theoretischen Vorhersagen gibt. Die Präparation von atomar flachen Schichten hängt allerdings von der Kombination von Substrat- und Schichtmaterial ab. Die Stabilität von Schichten mit einer bestimmten Anzahl von Lagen steht in direktem Zusammenhang mit der Bindungsenergie des höchsten besetzten Quantentopf-Zustands; Schichten mit einer niedrigen Zustandsdichte am Fermi-Niveau sind stabiler. Man spricht in diesem Zusammenhang auch von „magischen“ Schichtdicken. Selbst kleine Änderungen der Grenzflächeneigenschaften beeinflussen die Bindungsenergie der Quantentopf-Zustände und können zu einer energetisch bevorzugten oder benachteiligten Situation führen. Vor allem in dünnen Pb-Schichten ist der Einfluss von Energieminimierungen sehr stark, was – in Abhängigkeit von der Art des Substrates – zur Bildung unterschiedlich stabiler Konfigurationen führt.

Die Einflüsse von Substrat und Grenzfläche werden anhand der Wirkung gemessen, die eine substratinduzierte Verspannung in Metallschichten auf das Auftreten von Quantentopf-Zuständen hat. Bei Indiumschichten auf Si(111) und Si(100) werden Quantentopf-Zustände nur in Schichten mit relaxierter tetragonal-raumzentrierter Struktur beobachtet. Die Bildung diskreter Zustände in der Schicht in Energiebereichen, in denen eine höhere Zustandsdichte im Substrat vorliegt, wird durch Details der Kristallstruktur an der Grenzfläche bestimmt; bei kkommensurablen Grenzflächen erfolgt effektives „Confinement“ nur in der Bandlücke des Substrats. Die Grenzflächentransmission von Elektronen wurde mithilfe der Herstellung einer doppelten Quantentopf-Struktur von Pb auf einer Al-Schicht auf Si(111) erforscht. Dieser doppelte Quantentopf hat eine zweite Grenzfläche zwischen Pb und Al. Die Eigenschaften der Quantentopf-Zustände in diesem System weisen auf den Elektronentransport über diese Grenzfläche hin. Es wird nachgewiesen, dass das System – trotz der unterschiedlichen Gitterkonstanten von Pb und Al – die Eigenschaften von *einem* Quantentopf mit *einer* elektronischen Struktur hat.

Der Einfluss der Hybridisierung zwischen Quantentopf-Zustände und den Bändern im Substrat auf die elektronische Struktur der ersteren wird demonstriert. Die Folge ist eine „no-crossing“-Bandlücke oder eine invertierte Banddispersion. Es zeigt sich, dass diese Hybridisierung benutzt werden kann, um die Bandstruktur des Substrats im Grundzustand zu bestimmen. Diese Wechselwirkung zwischen den Bändern im Substrat und dem Quantentopf-Zustand sind zu berücksichtigen, damit eine korrekte Bestimmung der effektiven Masse erfolgen kann. Für den Großteil der Systeme stimmen die gemessenen Banddispersionen und die theoretischen Erwartungen überein. Allerdings stellt sich heraus, dass Pb auf Si(111) eine Ausnahme bildet. Die Werte der effektiven Masse in diesem System liegen um eine Größenordnung höher als erwartet. Diese hohe effektive Masse ist ein Hinweis auf Elektronenlokalisierung und Korrelationseffekte, wenn man berücksichtigt, dass die Elektronenwechselwirkungsenergie größer ist als die Bandbreite des Zustands.

Schließlich wird gezeigt, dass die Bestimmung von Elektronen-Phononen-Kopplungsparametern im Volumen von Metallen anhand der Messung von Quantentopf-Zuständen möglich ist. Der Einfluss der Elektronen-Phononen-Kopplung auf die Bandstruktur wird diskutiert. Zum ersten Mal werden winkelaufgelöste Photoelektronenspektren von Quantentopf-Zuständen gezeigt, bei denen der Realteil der Selbstenergie direkt bestimmt werden kann. Diese Daten ergeben für In einen Elektronen-Phononen-Kopplungsparameter λ von 0.9, welcher exzellent mit den theoretischen Erwartungen übereinstimmt.