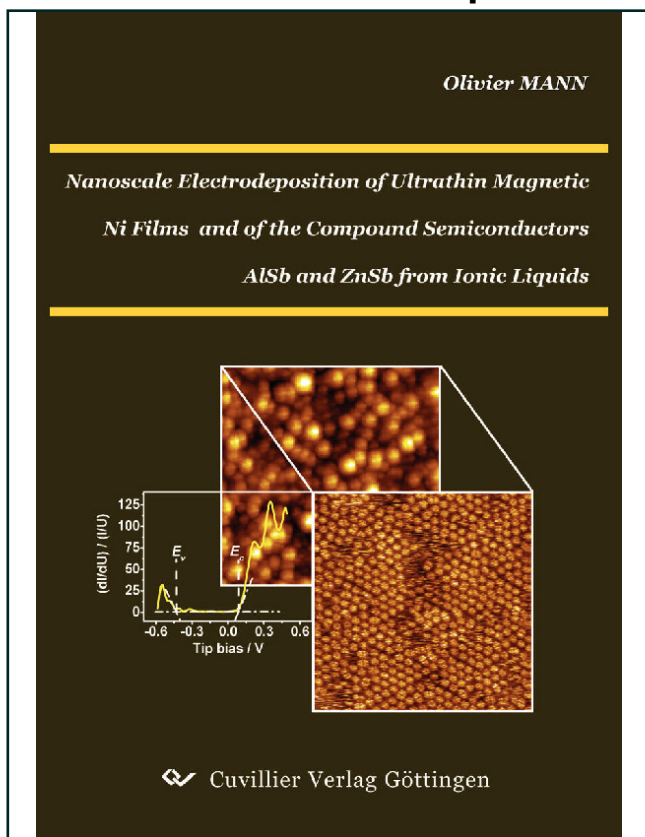




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Nanoscale Electrodeposition of Ultrathin Magnetic Ni Films and of the Compound Semiconductors AISb and ZnSb from Ionic Liquids



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Chapter 1

Introduction

The interest in nanomaterials, their fabrication and characterization, has increased tremendously in recent years. This has several reasons. One is nanotechnology which generally is considered as the key technology of this century. Taking, as an example, computer industry and the development of microelectronic devices, it is now widely recognized that miniaturization of conventional transistor cannot continue much longer following Moore's law [1]. Consequently, new materials and processes on the nanometer scale are searched for. The same applies for new magnetic storage devices with an increased storage capacity. There are many more applications of nanoscience where interdisciplinary research in physics, chemistry, materials science or bioscience will be necessary.

From a more fundamental point of view, new phenomena on the nanometer scale are especially exciting, see also [2]. These include: size-dependence of the electronic properties of nanometer sized clusters, magnetism in low dimensional ultrathin films, self-assembling of nanostructure, molecular electronics and designed complex materials, and finally, development of new tools to characterize nanostructures like the scanning probe microscope (SPM). In general, objects on the nanometer scale are dominated by their surface states and by interfacial interactions. Therefore, surface and interfacial investigations are basic for the understanding of nanoparticles and structures.

Numerous techniques are used to fabricate these nanostructures among which the vapor and electrochemical deposition methods play an important role. However, molecular beam epitaxy and similar vacuum deposition techniques [3, 4, 5, 6] require

the use of expensive equipment and, moreover, the deposition process is difficult to control. On the other hand, electrochemical methods like electrochemical deposition and in-situ scanning tunneling microscopy, have proved their versatility and efficiency in the last decade [7, 8, 9, 10, 11, 12]. There are several reasons which show this. For instance, the electrochemical deposition along its economical side is more convenient than the growth in vacuum since it can be controlled more easily through different parameters such as deposition potential, current density, temperature, and concentration of metal ions. This technique was first developed for applications with aqueous electrolytes where Cu [10, 11, 12], Ni [13, 14, 15], Co [16, 17, 18]... were successfully electrodeposited. However, the evolution of hydrogen can strongly influence the deposition process as for instance in Ni or Zn [19] deposition. For this reason a new generation of electrolytes was used: the ionic liquids. These latter possess several outstanding properties such as low vapor pressure, good solubility of metal salts and good ionic conductivity, and, last but not least, large electrochemical windows (up to 6 V) which make them good candidates for electrolytes. Thus, the extension of this technique of electrodeposition to ionic liquid electrolytes enables new materials to be electrodeposited such as transition metals or compound semiconductors. As a matter of fact, numerous pure elements such as Ti [20], Ge [21] Al, can only be electrodeposited from the ionic liquid electrolyte with the necessary large electrochemical window. In the case of transition metals like Ni, Co, Fe [22, 23, 24] ionic liquid electrolytes have the advantage that no H_2 evolution interferes with growth and nucleation of the nanostructures.

In this work, the electrocrystallization of metals and compound semiconductors at the Au(111)/ionic liquid interface is studied. Two main objectives are outlined as follows. First, the two- and three-dimensional electrocrystallization of nickel on Au(111) is studied where emphasis is given to a special morphology of the Ni deposits exhibiting a specific magnetic interaction. Secondly, the electrodeposition of antimony from Al- and Zn-based ionic liquid at room and elevated temperature, respectively, are studied by in situ STM and electrochemical methods.

The thesis is presented as follows: After a brief introduction, the second chapter deals with the theoretical and basic backgrounds of each method used in this study. Then, the experimental setup as well as the data analysis procedure are presented in chapter 3. The experimental results of the electrodeposition of Ni are presented

and discussed in chapter 4. The deposition of Sb from an Al-based IL at room temperature and from a Zn-based IL at elevated temperature are set out in chapter 5 and chapter 6, respectively, together with the results of AlSb and ZnSb electrocrystallization. Emphasis is given to the formation and the electronic properties of the respective compound semiconductor, $\text{Al}_x\text{Sb}_{1-x}$ and $\text{Zn}_x\text{Sb}_{1-x}$ along with a qualitative discussion of doping of the stoichiometric compound semiconductor by varying the deposition potential. Finally, chapter 7 presents a brief discussion of this work.

Chapter 2

Theoretical Background

In order to get informations on the early stage of crystallization of metals and semiconductor scanning probe microscopy (SPM) and electrochemical methods were used. Thus, morphological changes occurring at the working electrode during the electrodeposition can be observed in-situ. Moreover scanning tunneling spectroscopy methods allow to get a qualitative insight into the electronic properties of the deposits.

In the following chapter the theoretical background of the experimental methods will be presented in order to get a better understanding of their application.

2.1 Scanning tunneling microscopy (STM)

The STM is known as a powerful tool used to image the surface density of electrons of conducting samples where the high spatial resolution correlated to structural and electronic properties represent two of its most obvious advantages. As a matter of fact the use of this method has increased exponentially since its invention by Binnig and Rohrer in 1982 [25, 26, 27]. A general view of the physics involved in the mechanism will be presented in this section.

2.1.1 Tunnel effect

In order to understand the mechanism of STM it is of interest to introduce the concept of the tunnel effect. Let us consider the case of an incident particle upon a barrier with a potential energy larger than the kinetic energy of the particle. Considering a classical (macroscopic) approach the only possibility for the particle of energy E

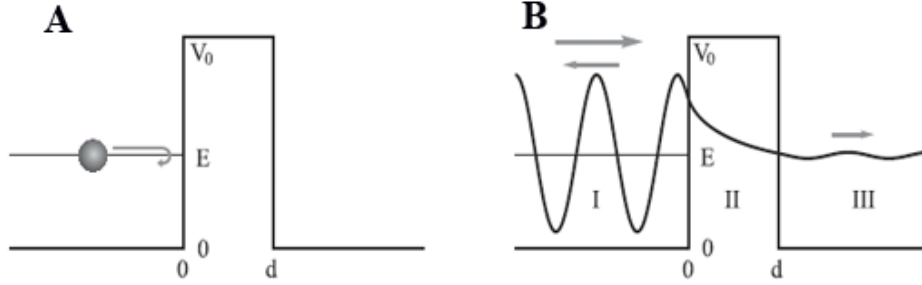


Figure 2.1: One-dimensional tunnel effect. (A) In classical mechanics an electron is reflected by the potential barrier V_0 when its energy $E < V_0$. (B) In quantum mechanics the electron is described by its wave function where the probability to traverse the barrier is non-zero.

to overcome the potential barrier V_0 is given by $E > V_0$, otherwise it is reflected as presented in Figure 2.1A. However on the atomic scale the problem has to be solved in terms of quantum mechanics. As a matter of fact, the probability of an electron to tunnel through the barrier is non-zero independently of its kinetic energy (even if $E < V_0$). This latter is sketched in Figure 2.1B for an electron of energy E , mass m , and a potential of height V_0 and width d . In quantum mechanics the properties of a system are defined in terms of a wave function, ψ , obtained by solving the time-dependent Schrödinger equation given by:

$$i\frac{\partial}{\partial t}\psi(\vec{x}, t) = \hat{H}\psi(\vec{x}, t) \quad (2.1)$$

where \hat{H} is defined as the Hamiltonian of the system. Its expression has a kinetic energy contribution $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ and a potential energy contribution $V(\vec{x})$. This latter one fulfills the conditions of each region as follows:

$$\begin{aligned} \mathbf{V} &= \mathbf{0} \text{ in region I, where } x < 0 \\ \mathbf{V} &= \mathbf{V}_0 \text{ in region II, where } 0 \leq x \leq d \\ \mathbf{V} &= \mathbf{0} \text{ in region III, where } x > 0. \end{aligned}$$

To simplify the calculation the time-dependent Schrödinger equation is simplified by considering a one-dimensional tunneling barrier with a potential independent of time. Thus, Eq. 2.1 can be written as

$$\left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E \psi(x) \quad (2.2)$$

According to the boundary conditions given above three solutions to this equation are of interest:

Region I:

$$\psi_x(x) = A \exp(ikx) + B \exp(-ikx), \quad \text{for } x < 0 \quad (2.3)$$

Region II:

$$\psi_x(x) = C \exp(\kappa x) + B \exp(-\kappa x), \quad \text{for } 0 \leq x \leq d \quad (2.4)$$

Region III:

$$\psi_x(x) = C S(E) \exp(ik(x-d)), \quad \text{for } x > d \quad (2.5)$$

where $k = \frac{\sqrt{2mE}}{\hbar}$ and $\kappa = \frac{\sqrt{2m(V-E)}}{\hbar}$. A more detailed presentation is given in the literature [28]. $S(E)$ is defined as the tunneling matrix element and gives the probability of a particle present at the left side of the junction to tunnel from the left side of a barrier through the right side. Therefore, the wave functions given above and their first derivatives must be continuous. These boundary conditions applied to Eq. 2.3-2.5 yield a 4 equations system for five parameters. Fixing one parameter, for instance the amplitude of the incoming electron wave A to 1 gives the following expression for $S(E)$ for $E < V$:

$$S(E) = \frac{2i\hbar^2 k \kappa}{2i\hbar^2 k \kappa \cosh(\kappa d) + (\hbar^2 k^2 - \hbar^2 \kappa^2) \sinh(\kappa d)} \quad (2.6)$$

However the tunneling barrier is composed of a transmission and a reflection coefficient where only the transmissivity can be detected in the case of a tunneling current leading to