

Chapter 8

Conclusion and Outlook

When this project was started, it was not known how adsorbed Mn atoms behave and react on the most common and technologically important semiconductor, *i.e.* Si surfaces. All previous information about Mn/Si heterostructures was limited to just a few experimental reports about the growth mode of Mn on Si(111) [15, 18–20]. The scope of this work consists of the comprehensive study of the morphology and the (epitaxial-)growth mode of manganese and some Mn-silicide heterostructures on the two most practical Si surfaces (*i.e.* Si(001) and Si(111)). The goal was to understand the thermodynamic and structural stability as well as magnetic behavior of the Mn/Si system. Since the quality of the metal-semiconductor interface is crucial for practical applications, one has to know about the growth mechanism of films as well as the magnetic properties and spin polarization of the surface and interface.

In order to explore the suitability and character of the films and their interface, we perform all-electron calculations in the density-functional theory framework (Sec. 2.3) which is a powerful practical tool to study the properties of materials. The calculations were based on the generalized gradient approximation (GGA-PBE) to the exchange correlation functional (Sec. 2.4) and the full-potential augmented plane wave (FP-APW+lo) method (Sec. 2.5.1 & 2.5.2) as implemented in the WIEN2k computer package (Sec. 2.8).

The third chapter represents an important contribution towards understanding bulk properties (such as the cohesive energy, bulk stability, Mn-Si interactions and magnetic properties) of some of the Mn_xSi_y compounds which could be grown on Si surfaces. We perform systematic studies of the stability of different structures of bulk Mn-mono-silicide. We find that the CsCl structure has a cohesive energy only 0.25 eV per formula unit lower than that of the natural phase, the B20 structure, but is clearly more stable than the WC, NiAs or NaCl crystal structure.

Since surface diffusion and morphology of growth are directly related to the substrate, we studied surface reconstructions and thermodynamic stability of bare Si(001) and (111) surfaces (Chap. 5). The calculations on surface diffusion were done on the (2×2) surface reconstruction and the film growth is based on a (1×1) surface supercell.

The energetic stability, electronic and magnetic properties of different configurations of a Mn adatom on the Si substrate for low coverage (up to 1 ML) have been obtained as an early stage of epitaxial growth. We found that the most stable site is a second layer interstitial site, where the Mn atom is located beneath the Si surface dimers on Si(001), and a second layer hollow site on Si(111) (Sec. 5.3 & 7.2).

In a comprehensive calculation, we mapped out the potential energy surface (PES) for diffusion of a Mn adatom on Si(001) (Sec. 5.5). From the PES, we conclude that the energy barrier for the Mn atom to go to sub-surface interstitial site is 0.3 eV. From the calculated potential-energy surface for the Mn adatom *on* the surface, it was found that the energy barrier for on-surface diffusion is 0.55 eV which is higher than the diffusion barrier for penetration to a sub-surface site.

A large number of calculations were performed to predict the morphology and stability of ultra-thin films of Mn/Si up to 3 ML (Chap. 6 & 7). We find that for ultrathin film growth of Mn on the Si substrate, the manganese-silicon multilayers with 1:1 stoichiometry (MnSi) are more stable than a pure Mn film.

Since the rather complex natural MnSi (B20 structure) appears to be incompatible with Si(001), we introduced the epitaxial formation of a novel structure which does not exist in bulk form. As a starting point, we compare various crystal structures of Mn-mono-silicide (CsCl, WC, NiAs, NaCl). The CsCl (B2) structure is found to be the most stable structure after the natural B20 structure. Films with B2 structure can be superior to natural monosilicides because of their good lattice match (within $\sim +2\%$) with Si(001). The B2 structure yields smaller strain than the B20 structure (with lattice mismatch of 3%) on the substrate.

In Section 7.4 we compare films of the B2 structure of Mn-mono-silicide on both Si(001) and Si(111) substrates. The film formation of the B2 structure on both substrates is thermodynamically stable with respect to bulk Mn. The B2 film on Si(111) is more stable than the equivalent film on Si(001), and their stability with film thickness increases monotonously.

Although the film with the proposed B2 structure has similar structure and lattice constant with the Si substrate, it is metastable against island formation of silicon-rich compounds.

The CsCl-like films show a layered magnetic structure with strong ferromagnetic

coupling between the Mn atoms of each layer, and also sizable magnetic moments of $\sim 2 \mu_B$ in the interface and surface layer. The B2 films on Si(111) show slightly larger magnetic moments than the films on Si(001); hence the Si(111) substrate is preferable for the preparation of magnetic films. The ferromagnetic coupling between the spin moment of Mn atoms is more favorable than antiferromagnetic coupling in this film structure in both surfaces. The calculated spin polarization of this structure at both (001) and (111) surfaces is about 30%. Hence we suggest that MnSi/Si heterostructures can be used for injection of a spin-polarized current from the metal into the semiconductor.

We find that on Si(111) the most stable Mn-mono-silicide has an atomic structure similar to the bulk B20 structure and shows a $(\sqrt{3} \times \sqrt{3}) R30^\circ$ reconstruction at the surface, in agreement with experiment. Therefore, we judge that films with B20 structure of MnSi are the most interesting ones for possible spintronics applications (among the monosilicides studied here), and Si(111) is the preferred substrate for their growth.

Elaborate work was done to simulate an enormous number of configurations to gain insight into the formation of nanostructures of Mn-silicides on the Si substrate, but there are still some open questions about properties, shape, structure and size of these nanostructures. Beyond our thermodynamic approach, by using our DFT results and kinetic Monte Carlo, one could study the diffusion and nucleation processes to understand how the nanostructures form. The research in this thesis gave an idea about the possibility of applying Mn to fabricate magnetic metal-semiconductor heterostructures.

★ ★ ★ ★

