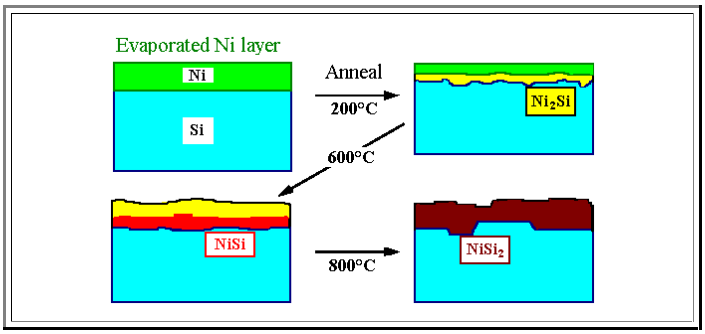
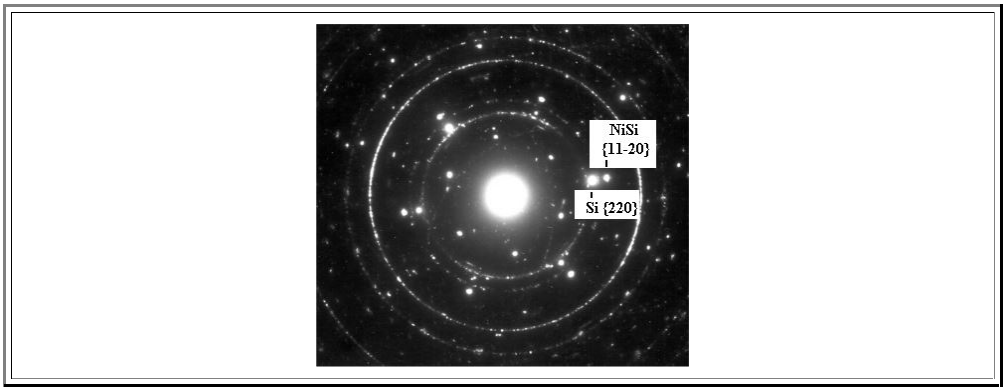
8.2 Case Studies

8.2.1 Ni Silicides

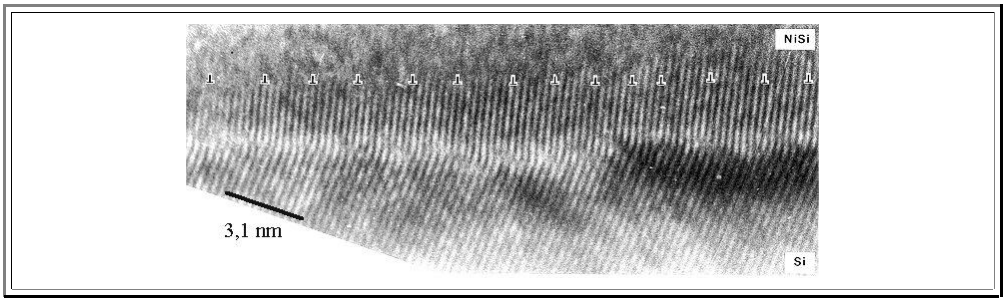
- We will look in some detail on the system **Si - silicide - metal**, where many phase boundaries can be observed. The basic experiment consists of depositing a metal (here **Ni**) on **Si** (either in a **{100}** or **{111}** orientation), and induce some reaction by heating.
  - Three different **Ni**-silicides will form consecutively:



- Altogether five different phase boundaries may be encountered, some of which are shown in the picture above:
  - **Si - Ni**,
    Si - Ni_2Si and **Ni_2Si - Ni**,
    Si - NiSi and **NiSi - Ni_2Si**,
    Si - $NiSi_2$, and **$NiSi_2$ - NiSi**.
- Major findings are:
  - The interface between **Si** and **Ni** does not really exist because immediately after the (room temperature) evaporation, a thin **Ni_2Si**-silicide layer forms between the **Si** and the **Ni**.
  - The **Ni_2Si** layer is polycrystalline; the interface between **Si** and **Ni_2Si** seems to be incoherent - i.e. if there is any structure it is not observed with "normal" **TEM**.
- The interface between **{111} Si** and **NiSi** is epitaxial, however, and thus semicoherent *against all expectations*:
  - **NiSi** is reported to crystallize in an *orthorhombic* lattice; on **{111}** Si substrates, however, a *hexagonal* lattice is observed (which can be cobtained from an orthorhombic lattice by slight adjustments of the lattice parameters).
  - The misfit is *extremely large* (ca. **15%**) and would require a distance of **0,6 nm** for **b = *a*/2<110>** misfit dislocations. Such a small spacing is usually considered to be too small to be meaningful - epitaxial relationships thus should not exist. The diffraction pattern, however, indicates a clear epitaxial relationship (with a bit of polycrystallinity as indicated by the rings):



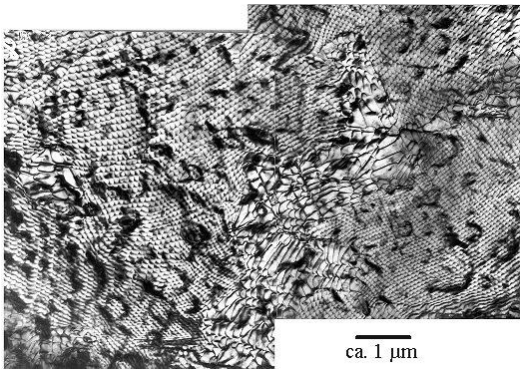
  - While no structure can be seen in conventional **TEM**, high-resolution **TEM** shows pronounced misfit dislocations relieving some of the stress at a spacing of about **1,6 nm**. This is one of the densest misfit dislocation networks ever observed. The ending lattice planes are indicated by the edge dislocation symbol somewhat above the actual interface plane.



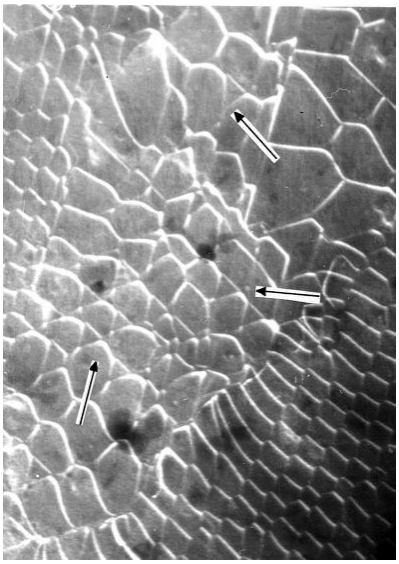
- The most interesting phase is **$NiSi_2$**; it is the final product after sufficient annealing at **800 °C**.
  - **$NiSi_2$** crystallizes in the cubic **CaF_2** - structure with a lattice constant that is only **0,3%** smaller than that of **Si**.
  - We thus can expect an epitaxial relationship with a misfit dislocation network at a spacing

$$p = b \cdot \frac{b}{(a_e - a_m)/a_m} = \frac{b}{0{,}003}$$

  - With a_{Si} **= 0,54 nm** and ***b* = *a*/2<110> = 0,382 nm** we would expect a network with a spacing of about **130 nm**.
  - What we see for an interface on a **{111}** plane looks like this:



  - This looks rather interesting. We seem to have a simple hexagonal network of dislocations, but we see some additional features: "Blackish" areas and an island with rather coarser structures embedded in a sea of something with a possible hexagonal symmetry.
- The reasons for these complications are two peculiarities of this interface, which can also be found in similar systems; in particular in the **Si - $CoSi_2$** interface.
  - *First*, it "likes" to be on **{111}**-planes. This leads to heavy facetting if the **Ni** layer is deposited on a **Si {100}** plane, but also to some facetting on **{111}**. This can be seen best in cross-section; an example is given in the illustration. We must expect that the accommodation of steps will introduce irregularities into the network.
  - *Second*, the interface is mostly *not* in a **Σ = 1** relation, i.e. with a direct continuation of the lattices, but in a **Σ = 3** relation. This means that the **$NiSi_2$** is *twinned* with respect to the substrate. An overview picture is shown in the link. This somewhat surprising result can be obtained from a careful contrast analysis of the network with micrographs taken at higher magnifications. The network then looks like this:



- Shown is one of the "islands" in a sea of regular hexagonal dislocations. Its structure looks somewhat familiar: The arrows point to extended stacking fault knots as in the case of the small angle twist grain boundary on **{111}** in **Si**.
- But in contrast to the network in the small angle twist boundary, all dislocations now are *edge dislocations*; as expected for misfit dislocations. The distance is also what would be expected for a almost fully relaxed layer of **$NiSi_2$**.

The question is, of course, why this mix of **$\Sigma = 1$** and **$\Sigma = 3$** relations? As in the case of the low angle twist boundary encountered before, nobody knows for sure. Obviously, the energy balance is rather similar for the two cases.

- Very similar interfaces have been observed in the case of **Si - $CoSi_2$** interfaces, which, except for a slightly larger misfit, have essentially the same geometry.

Despite the structural similarity to the small angle grain boundaries, the phase boundaries add new features and open questions. To get more insights, we will now discuss the case of the interface between (cubic) **Si** and (hex.) **Pd_2Si**.