Atomic ordering in intermetallic CoAl alloys epitaxially grown on GaAs (001)

Q Wan, R Hey and A Trampert
Paul-Drude-Institut, Hausvogteiplatz 5-7, 10117 Berlin, Germany
Email: qianwan@pdi-berlin.de

Abstract. Epitaxially grown intermetallic CoAl alloys on GaAs (001) are investigated by transmission electron microscopy (TEM). Nanobeam diffraction proves the coexistence of the ordered B2 (CsCl) structure and its disordered BCC version, which is also verified by high-resolution TEM. From dark-field imaging, it is observed that the relative volume fractions of these two phases depend on the growth condition: the lower the growth temperature, the larger the proportion of B2 phase. The mechanism is discussed with respect to the diffusivity of vacancies and Co atoms.

1. Introduction
Intermetallic alloys, including FeAl, CoAl and NiAl, are of great importance since these materials not only have good strength-to-weight ratio but also excellent corrosion and oxidation resistance, which make them good candidates for high-temperature and soft magnetic applications [1]. In combination with semiconductor heterostructures, they are able to be integrated in a number of devices, e.g. spin injectors and mirrors. Furthermore, buried intermetallic film between two III-V structures could possibly be used in resonant tunneling diodes and metal base transistors [2]. Among these intermetallics, CoAl is especially attractive for epitaxial growth due to its low lattice mismatch of 1.2% with respect to GaAs. As a member of 3d transition metals, Co is well known for the formation of a stable B2 structure with Al over a wide composition range (46-58 at. % Co) [3]. This B2 structure can be considered as two interpenetrating primitive cubic sub-lattices [cf. Fig. 1(a)], where each Co atom has eight Al atoms as nearest neighbours and vice versa. On the other hand, a complete disorder between two sub-lattices results in a reduction of crystal symmetry to BCC as shown in Fig. 1(d).

Atomic ordering is closely related to the materials’ electronic and magnetic properties. It is therefore highly desirable to achieve fully ordered structure of the film including a high quality interface to the substrate. However, overgrowth of semiconductors with metal layers is quite challenging because of the interfacial reactivity and the problem of combining polar with nonpolar crystals [4]. Here we study the microstructural properties of a CoAl layer grown on GaAs (001) substrate by molecular beam epitaxy (MBE). The atomic ordering and interface perfection were investigated by means of TEM methods.

2. Experiment
The CoAl thin films were deposited on GaAs (001) substrates by MBE. After growing a superlattice of Al_{0.3}Ga_{0.7}As and GaAs and an AlAs layer as a buffer layer, which is used to suppress the interface reaction between the metal and the substrate, the template was then transferred into the As-free metal...
chamber, where a 40 nm CoAl layer was deposited with a very low growth rate of 0.147 nm/min. The growth temperature for CoAl was varied in a range of 100-200 °C.

Cross-sectional specimens for TEM were prepared conventionally by mechanical thinning and ion beam milling. Because the metal alloy is very sensitive to the ion bombardment, a cooling system operating at liquid nitrogen temperature is adopted to reduce the damage. Selected area electron diffraction patterns (SADP), high-resolution lattice images as well as dark-field images were recorded in a JEOL 3010 UHR microscope operating at 300kV. The EMS™ software package is employed to calculate the diffraction pattern and to simulate the high-resolution TEM contrast, which is based on the Bloch wave method. The spherical aberration, the focus spread, the semi-divergence angle and the objective aperture diameter used in the simulation were assumed to be 1.0 mm, 10 nm, 1.0 mrad and 20 nm, respectively.

Figure 1. Crystal structure of the (a) B2 and (d) BCC phase and their respective simulated DP (b) and (e) along the [110] zone axis in kinematical approximation. The nano-beam DPs of neighbouring regions in the CoAl layer grown at 200 °C are also shown in (c) and (f) for comparison.

3. Results and Discussion

Electron diffraction is able to determine the crystal structure with high spatial resolution. Figures 1(b) and 1(e) represent the respective calculated electron DP of the B2 and BCC structure along the [110] zone axis in the kinematical approximation. As expected from their crystal symmetries, the DP of the B2 structure shows almost the same spot arrangement as the one of the BCC structure except for an extra (001) spot if one considers only fundamental reflections. The appearance of the reflections and their intensity are defined by their structure factor $F$. If CoAl is ordered, $F_{001}$ is a nonzero value given by $f_{Co} - f_{Al}$, where $f_{Co}$ and $f_{Al}$ are the respective atom form factors of Co and Al. However, once Co and Al are mixed up, i.e., the ordering is destroyed, $F_{001}$ equals zero given by
\( f_{(Co,Al)} - f_{(Co,Al)} \), where \( f_{(Co,Al)} \) is the average atom form factor of Co and Al. Spots like (001), which are present because of the ordering of the material, are generally called “superlattice” reflections.

For the detection of phase fluctuation on a nanometre scale, the conventional selected area diffraction method is not applicable because of its relatively large aperture size. We determine the local atomic ordering of the metal layer by the nanobeam diffraction method, which uses an electron beam with diameter of 2 nm. The nanobeam diffraction patterns of two neighbouring areas in the CoAl film are shown in Figs. 1(c) and 1(f), which are in agreement with the simulated DP of B2 and BCC structure. It is thus demonstrated that B2 and BCC phases are both present in the layer.

![Figure 2. Crystal structure and its corresponding simulated lattice fringes for (a) BCC phase (b) B2 phase. (c) Cross-sectional High-resolution TEM image of the hetero-system along [110]-zone axis and its Fourier-filtered version (d). The simulated patterns for B2 and BCC are shown as insets.](image)

The coexistence of both phases in the film is also demonstrated by high-resolution TEM. Figure 2(c) shows the cross-sectional lattice image of the hetero-system obtained along [110]-zone axis. The image has been Fourier filtered in order to reduce the noise and to obtain a more well-defined contrast as shown in Fig. 2(d). Besides the abrupt interface indicating no obvious interfacial reaction, a simple vertical line pattern as well as a rectangular network pattern are observed in the film. Determination of the crystal structure from a lattice fringe image requires a careful comparison between experimental and simulated images, because the contrast pattern is very sensitive to the specimen thickness (\( t \)) as well as the defocus (\( \Delta f \)) of objective lens. From a comparison of \( t-\Delta f \) maps (not shown here) with the high-resolution TEM image, it is found that the simple vertical line pattern coincides well with the simulated lattice image of BCC structure (\( t=5 \) nm, \( \Delta f=-76 \) nm), while the rectangular network pattern agrees with the B2 structure (\( t=6 \) nm, \( \Delta f=-76 \) nm), as shown in Fig. 2(a) and 2(b), respectively. Actually, since the interplanar spacing corresponding to the (002) spot is beyond the point resolution of our 300kV TEM, the lattice morphology of the BCC structure only displays the vertical lines, which originate from the interference between the direct beam and the (1-10) reflection [cf. Fig 1(f)]. The presence of the (001) spot of the B2 phase induces the visibility of lattice fringes parallel to the surface. Therefore, the observed high-resolution TEM contrast is a rectangular network pattern.

The spatial distribution of the B2 phase was analyzed by using dark-field imaging with the extra (001) as the g-vector. Figure 3(a) shows the cross-sectional TEM micrograph taken under such imaging conditions, where the bright and dark contrast in the metal layer is related to B2 and BCC phase, respectively. The fine speckle contrast confirms the coexistence of both phases. It is known from theoretical calculations that in a CoAl alloy system, the mobility of the Co atoms is quite high [5]. They can diffuse out of their original position leaving vacancies behind and occupy the available Al-type sites on the Al sub-lattice. These so-called anti-structure Co atoms cause local composition
deviations of the CoAl layer from the equiatomic stoichiometry and lead to an increase of disorder. In order to intensify the atomic ordering of the intermetallic layer, a lower growth temperature of 100 °C was adopted, suppressing the diffusion of vacancies and Co atoms. Figure 3(b) shows the corresponding cross-sectional dark-field TEM image taken under the same imaging conditions as Figure 3(a). The proportion of bright areas is larger as compared to the sample grown at 200 °C indicating a higher fraction of ordered phase.

Another remarkable characteristic observed in both dark-field images is related to the continuous dark band running parallel to the film surface. The transition region occurs at about 30 nm from the interface independent of the growth temperatures used. Although the reason for this collective disorder transformation is not clarified yet, it can be attributed to the accumulated epitaxial strain in the layers [6]. Indeed, the lattice mismatch between CoAl and GaAs amounts to 1.2%. No indication for the plastic relaxation by misfit dislocation is observed at the interfaces even though the layer thickness reaches about 40 nm. It can be therefore concluded that the existing mismatch strain plays a role in the transition and leads to disorder close to surface.

![Figure 3](image)

**Figure 3.** (110) Cross-sectional dark-field TEM image of the CoAl layer grown at (a) 200 °C and (b) 100 °C with $g = 001$. The bright contrast in the metal layer is related to the B2 structure.

4. Conclusion
In summary, the crystal structure, local ordering and its spatial distribution of CoAl grown on GaAs (001) is determined on nanometre scale. The coexistence of both BCC phase and ordered B2 phase is demonstrated. With lower growth temperature, a higher fraction of ordered phase is acquired.

Acknowledgement
The authors would like to thank M. Höricke for the sample preparation.

References
[1] Lee YP, Kim KW, Rhee JY, et al. 1999 Phys. Rev. B **59**, 546
[2] Sacks RN, Qin L, Jazwiecki M et al. 1999 J. Vac. Sci. Technol. B **17**, 1289
[3] Mayer D, Willerding B, Wandelt K et al. 1998 J. Phys.: Condens. Matter **10**, 10839
[4] Sands T et al. 1990 Mater. Sci. Rep. **5**, 99
[5] Stefanou N et al. 1987 Phys. Rev. B **35**, 2705
[6] Herman MA, Richter W, Sitter H *Epitaxy: physical principles and technical implementation* (Berlin: Springer)