Local disordering in epitaxially strained CoAl films grown on GaAs (001)

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Local disordering has been analyzed in ordered intermetallic CoAl films epitaxially grown on GaAs(001) substrates by molecular beam epitaxy. Transmission electron microscopy investigations demonstrate the appearance of the bcc phase in the CoAl epilayer, which is the disordered version of the B2 crystal lattice type. Variations in the growth temperature between 100 and 300 °C reveal that the degree of thermal disordering and the volume fraction of the disordered bcc phase increase with increasing temperature. Interface reactions were observed in the sample fabricated at 300 °C resulting in the formation of CoAs precipitates at the interface. These precipitates contribute to the plastic relaxation of the 1.2% lattice mismatch between the CoAl film and the GaAs substrate affecting the strain-induced order–disorder transition. The impact of disordering is discussed in connection to the high diffusivity of vacancies and Co atoms existing in the intermetallic alloy.


I. INTRODUCTION

Intermetallic alloys, including FeAl, CoAl, and NiAl, are of great importance since these materials have not only good strength-to-weight ratio but also excellent corrosion and oxidation resistance. These properties make them promising candidates for high-temperature and soft magnetic materials.1 In combination with semiconductor materials, they open potentialities as spin injectors or mirrors applied in novel optoelectronic or spintronic devices. Furthermore, buried intermetallic films between two III–V compound semiconductors may possibly be used in resonant tunneling diodes and metal-base transistors.2 Among these intermetallic alloys, CoAl is especially attractive for epitaxial growth due to its low lattice mismatch with respect to GaAs. As a member of 3d transition metals, Co crystallizes with Al in a stable cubic B2 structure over a wide composition range (46–58 at. % Co).3 This ordered B2 structure can be considered as two interpenetrating primitive cubic sublattices [cf. Fig. 1(a)], one occupied by Co and the other one by Al atoms. On the other hand, random occupancy of both sublattices by either Co or Al atoms introduces the transition from B2 to the basic bcc structure and, simultaneously, a change in the space group symmetry as indicated in Fig. 1(b).

The atomic ordering is closely related to the physical properties of the intermetallic alloys. For instance, the degree of ordering in Fe,Pt,Nb, bulk alloys results in substantial variations in the Curie temperature.4 Moreover, a slight atomic disordering in 3d transition metal aluminides—like FeAl or CoAl—from the equiatomic alloy to the metal rich one leads to the occurrence of local magnetic moments. This finding is explained by the formation of antisite defects, i.e., 3d transition metal atoms at Al sites, which are associated with an effective magnetic moment.5 The exact knowledge of the mechanisms of order–disorder transitions in intermetallic alloys is, therefore, a prerequisite for a more detailed understanding of their electronic and magnetic behavior.

The epitaxial growth of CoAl films on GaAs (001) substrates by molecular beam epitaxy (MBE) (Ref. 6) has been systematically studied previously together with their overgrowth with semiconductor layers.7,8 However, there were no studies about the order–disorder phenomena in these structures. It is thus the aim of the present work to investigate the local disordering in intermetallic CoAl alloys epitaxially grown on GaAs(001) substrates by applying different transmission electron microscopy (TEM) techniques. The degree of disordering found in the MBE grown films is discussed with respect to the specific growth temperature and the epitaxial strain state. Thermal and strain-induced order–disorder mechanisms are introduced and discussed depending on the practical growth conditions.

II. EXPERIMENTAL DETAILS

The CoAl thin films were deposited on GaAs (001) substrates in a two-chamber MBE system. After growing a superlattice of Al0.3Ga0.7As and GaAs and a 1.2 nm thick AlAs buffer layer, which is used intentionally to suppress interface reactions between the intermetallic alloy and the compound semiconductor, the template was transferred into the As-free metal chamber. Subsequently, a 40 nm CoAl film was deposited with a very low growth rate in the range between 0.04 and 0.0735 nm/min. Three samples were fabricated under identical MBE growth conditions except for the growth temperature, which was set to 100 °C, 200 °C, and 300 °C, respectively, in each case. In situ reflection high-energy electron diffraction patterns taken during growth are shown in Fig. 1.
indicate a following cube-on-cube epitaxial orientation relationship between the CoAl and the GaAs crystal lattices: \((001)_{\text{CoAl}}\parallel(001)_{\text{GaAs}},\ (110)_{\text{CoAl}}\parallel(110)_{\text{GaAs}}\). Based on this orientation, the natural lattice mismatch is calculated to be 1.2% along both in-plane directions.

Cross-sectional specimens for TEM were prepared by mechanical thinning followed by argon ion milling. A cooling system operating at liquid nitrogen temperature is adopted to avoid sample heating and to reduce the ion beam spreading, semidivergence angle, and objective aperture diameter operating at 300 kV and with a point resolution of 0.17 nm. Electron diffraction, bright-field TEM, and dark-field (DF) TEM as well as high-resolution (HR) TEM are acquired in a JEOL 3010 UHV microscope operating at 300 kV and with a point resolution of 0.17 nm. The EMS\(^{\text{TM}}\) simulation software\(^9\) is used to calculate the electron diffraction pattern and the phase contrast of the HRTEM images. Thereby, values for spherical aberration, focus spread, semidivergence angle, and objective aperture diameter are set to be 0.6 mm, 10 nm, 1.0 mrad, and 20 nm\(^{-1}\), respectively.

III. EXPERIMENTAL RESULTS

A. Determination of local disordering in CoAl films

Figure 2(a) shows a DFTEM micrograph of the CoAl/template heterostructure, which was taken with the superlattice reflection \(g_{\text{CoAl}}=[001]\). The image clearly displays dark regions in the CoAl film grown at 200 °C. Since the intensity of the superlattice reflection decreases with the extent of disordering, the dark areas directly correspond to regions of reduced order. In addition to this fact, the Al(Ga)As layers of the template appear as bright stripes because the chemical sensitive (002) reflection of zinc-blende structures is located very close to the (001) superlattice reflection of the intermetallic CoAl film, and thus both reflections are selected by the aperture.

Investigations using selected area electron diffraction (SAD) are not applicable for the detection of fluctuations based on order–disorder transitions on the nanometer scale due to the relatively large aperture sizes available in the microscope. For this reason, nanobeam diffraction is utilized adjusting an electron beam diameter of about 2 nm. The Figs. 2(b) and 2(d) show experimental nanobeam diffraction patterns of two neighboring bright and dark areas in the CoAl film [indicated by circles in Fig. 2(a)]. The clear dissimilarity between these two patterns is discernible by the existence of the (001) superlattice reflection. For further identification, kinematical diffraction simulations are performed based on the B2 and bcc structure and their corresponding results are revealed in Figs. 2(c) and 2(e), respectively. The good agreement between the experimental and simulated diffraction pattern demonstrates that B2 and bcc phases are both present in the CoAl film.

The coexistence of ordered and disordered phases in the CoAl films is furthermore demonstrated by HRTEM investigations. Figure 3(a) shows the cross-sectional lattice image of the heterosystem near the interface obtained along the [110]-zone axis of CoAl and GaAs. The experimental HRTEM micrograph has been Fourier-filtered in order to reduce the noise and improve the image contrast [Fig. 3(b)]. The interface appears laterally smooth with a structural roughness of one to two monolayers. There is no indication of plastic relaxation of the lattice mismatch, i.e., the CoAl film is coherently strained. The HRTEM contrast inside the CoAl film in Fig. 3 represents a simple interference pattern of lines running parallel to the \{110\} planes that locally turn into a rectangular point grid. The quantitative analysis of the HRTEM contrast requires image simulations, which are mainly dependent on the specimen thickness \(t\) and the objective defocus value \(\Delta f\) of the objective lens. The Figs. 4(a) and 4(b) reveal simulated thickness-defocus maps for the bcc and the ordered B2 structure in the range of \(t\) between 4 and 8 nm and \(\Delta f\) between \(-30\) and \(-80\) nm. On the basis of these maps, it is figured out that the experimentally detected simple line patterns are in good accordance with simulated lattice images of the bcc structure at \(t=6\) nm and \(\Delta f=\sim-60\) nm, while the rectangular point grid patterns agree with the B2 structure at the same sample thickness and defocus values. Actually, since the interplanar lattice spacing belonging to the (002) reflection lies beyond the point resolution of

![Image](https://via.placeholder.com/150)

**FIG. 2.** (a) (110) cross-sectional DFTEM image of the CoAl layer grown at 200 °C with \(g_{\text{CoAl}}=[001]\). The nanobeam diffraction patterns of neighboring regions [as indicated by circles in Fig. 2(a)] are shown in (b) and (d). The simulated (110) kinematical diffraction patterns of B2 (c) and bcc phase (e) of the CoAl alloy are also shown for comparison. The size of the calculated reflections corresponds to the intensity.

**FIG. 3.** Cross-sectional HRTEM image of the heterosystem along [110]-zone axis (a) and its Fourier-filtered version (b). The simulated contrasts of the B2 and bcc structures are inserted for clarification.
our 300 kV microscope, the lattice image contrast of the bcc structure only displays vertical lines, which originate from the interference between the direct beam and the (110) reflection [cf. Fig. 2(d)]. On the other hand, the presence of the (001) superlattice reflection of the B2 phase induces the visibility of lattice fringes parallel to the interface, and the HR-TEM contrast results in a rectangular point grid pattern. Consequently, the experimental contrast in the CoAl film shown in Fig. 3 is characterized by a predominating grid pattern (B2) in the region near the interface while the line pattern (bcc) is more pronounced away from the interface. This finding is in agreement with the results of the nanobeam diffraction and the dark-field imaging.

B. Influence of growth temperature

Generally, MBE is often used as a growth technique that is far away from thermodynamic equilibrium because surface diffusion processes are kinetically restricted. The growth kinetics determines the amount of incorporated point defects during MBE and thus affects the formation of disordering. Specific variations in the growth temperature should therefore open the possibilities to investigate the effect of order–disorder transitions and their results on the microstructure. Accordingly, samples grown at different temperature are observed by dark-field imaging using the (001) superlattice reflection under near two-beam condition. The micrographs provide information about the degree of disordering as well as the spatial distribution between ordered and disordered phases. The Figs. 5(a)–5(c) present a series of cross-sectional (001) DFTEM micrographs of CoAl layers grown at 100, 200, and 300 °C. As explained, the bright and dark contrast inside the CoAl film corresponds to the B2 and bcc structure, respectively. The sample grown at 100 °C has the largest fraction of ordered phase as indicated by a continuous bright band running parallel to the interface. When the growth temperature is increased to 200 °C [cf. Fig. 5(b)], the degree of ordering diminishes as recognizable in the interruptions of the bright band by many dark spots resulting in a more specklelike contrast. For both specimens, the area near the surface is highly disordered. The coarsening of the speckle contrast in the CoAl film grown at 300 °C [Fig. 5(c)] demonstrates a further increase in disordering compared to the sample grown at 200 °C. Surprisingly, no continuous dark band is observed near the surface region in this sample. On the other hand, an unusual array of periodic dark contrast is detected near the interface crossing the AIAs layer as indicated by arrows in Fig. 5(c). The HRTEM image of such an area [Fig. 5(d)] reveals a trapezoid shaped domain with side facets parallel to the [111] planes of AIAs and GaAs. The area of those domains extends from the CoAl film into the AIAs and GaAs buffer layer indicating the initiation of interface reaction when the growth temperature reaches 300 °C. The HRTEM contrast inside the domain appears distorted compared to the ambient AIAs and GaAs suggesting the onset of a precipitate formation. Based on the results of the three samples, it can be deduced that the degree of disordering is smallest in the film grown at 100 °C and increases with increasing temperature as expected for the thermal induced order–disorder transitions.

C. Influence of strain relaxation

The thickness of the epitaxial CoAl film is beyond the critical layer thickness for plastic relaxation that is calculated based on the Matthews–Blakeslee model. However, there is...
no indication for plastic relaxation by misfit dislocations at the interfaces for samples grown at 100 and 200 °C. The pseudomorphical growth of CoAl is demonstrated by the superposition of the in-plane (110)CoAl and (220)Al(Ga)As reflections in the selected area diffraction pattern shown in Fig. 6(a). Accordingly, the splitting between the out-of-plane (004)Al(Ga)As and (002)CoAl reflections is detected that originates from the tetragonal distortion of the cubic CoAl lattice. Due to the lattice mismatch of 1.2% and the given film thickness of about 35 nm, strain energy is accumulated in the intermetallic film that should give rise to a stress-driven order–disorder phase transition. In fact, a continuous dark band is observed at around 30 nm away from the interface in the DFTEM of the samples grown at 100 and 200 °C [Figs. 5(a) and 5(b)]. When the growth temperature is increased to 300 °C, the lattice mismatch strain is partly relieved by a nearly periodic array of coherent precipitates along the interface generated as a consequence of the strong Co diffusion. This plastic relaxation process is clearly denoted by the separation of the in-plane (110)CoAl and (220)Al(Ga)As reflections as shown in Fig. 6(b). That means that due to the epitaxial strain relief, there is no sufficient driving force for the order–disorder transition and, therefore, the corresponding dark band of a disordered phase along the surface region is not observed in the 300 °C sample [Fig. 5(c)].

IV. DISCUSSION

The compositional disorder in CoAl and some other B2-type intermetallics is dominated by the so-called triple-defect mechanism. Initially, vacancy pairs \( \text{V}_{\text{Al}}-\text{V}_{\text{Co}} \) are generated in crystals to conserve the stoichiometry. Such pairs have small binding energy and can easily dissociate in two single vacancies. Since an Al vacancy possesses a relative high formation energy, it is energetically favorable to exchange its position with one of its Co neighbors forming a Co vacancy, \( \text{V}_{\text{Co}} \), and an antisite defect, \( \text{Co}_{\text{Al}} \). The new defect pair, \( \text{V}_{\text{Co}}-\text{Co}_{\text{Al}} \), has again low binding energy and easily dissociates into two single point defects. By this chain transformation, \( \text{V}_{\text{Al}}-\text{V}_{\text{Co}} \) turns into a dissociated triple defect, two \( \text{V}_{\text{Co}}+\text{Co}_{\text{Al}} \), which preserves the basic lattice structure, i.e., the lattice constant, however, changes the crystal symmetry from ordered B2 to disordered bcc, as schematically shown in Fig. 7. With increasing temperature, the equilibrium concentrations of vacancies and antisites involved in the triple defect become higher and, accordingly, the fraction of disordered bcc phase in the alloy will be accumulated. Furthermore, the Co atoms are very active in the CoAl system. They may diffuse out of their original lattice sites leaving vacancies behind, and occupy the available Al sites or stop in interstitial positions, which introduces local disordering. Such disordering increases with increasing temperature because of the higher diffusivity of Co atoms. During MBE growth, these disordering effects are even more pronounced because the growth of our CoAl films is far away from thermodynamic equilibrium. Consequently, a smaller degree of disordered phase is observed in our experiment for the sample grown at lower temperature.

Provided that there are deviations from stoichiometry, another disorder mechanism is also feasible. Since Co vacancies \( (\text{V}_{\text{Co}}) \) and \( \text{Co}_{\text{Al}} \) antisites are the most stable point defects, an excess of Co atoms is accommodated by the generation of remaining \( \text{Co}_{\text{Al}} \), whereas an excess of Al is accommodated by the generation of remaining \( \text{V}_{\text{Co}} \). These so-called constitutional point defects lead to the modification of the lattice symmetry. However, the quantitative investigation of the chemical composition and point defect density is beyond the scope of the current work.

In order to find the main diffusing species in the system, a compositional and structural analysis needs to be performed in order to identify the interfacial reaction products in the sample grown at 300 °C [Fig. 5(d)], which is, however, complicated by the small size of the precipitates. Therefore, the sample was in situ annealed at 500 °C inside the MBE system for half an hour to intensify the interfacial reaction. Figure 8(a) shows the HR TEM micrograph of the interface in the annealed sample along the \([1\bar{1}0]_{\text{GaAs}}\) zone axis. The reaction is obviously progressed compared to the as-grown case as indicated by the quasitrapezoid shaped precipitate, which is characterized by a HRTEM contrast that is different to that of the CoAl B2 structure or the Al(Ga)As zinc-blende structure, respectively. The corresponding selected area diffraction pattern along the \([1\bar{1}0]_{\text{CoAl}}\) direction is presented in Fig. 8(b). Besides the reflections from the B2 type CoAl, an additional rectangular pattern is detected that belongs to the precipitate. A careful comparison with diffraction patterns from different possible compounds along various zone axes reveals that the arrangement of the additional spots agrees well with the diffraction pattern of the CoAs compound along the \([010]\)-direction, whose simulated version is shown in Fig. 8(c). The crystallographic structure of CoAs corresponds to an orthorhombic unit cell which has the space group Pnma and the lattice parameters \( a=0.5286\) nm, \( b=0.5350\) nm, and \( c=1.0674\) nm. The linescan from the HRTEM pattern of \([200]_{\text{GaAs}}\) zone axis reveals that the split between (110)CoAl and (220)Al(Ga)As in (b) is revealed by an intensity linescan.

FIG. 6. (Color online) Selected area electron diffraction patterns of CoAl/ template heterostructure grown at (a) 100 °C and (b) 300 °C with the electron beam along [1T0] zone axis. Notice that the split between (110)CoAl and (220)Al(Ga)As in (b) is revealed by an intensity linescan.

FIG. 7. Schematic illustration of the triple-defect mechanism in the CoAl alloy (Refs. 10 and 11).
to the AlAs and GaAs crystal lattices, because the diffusion along these close packed planes is most rapid due to their lowest diffusion activation energy. The size of the domain is limited by the diffusion length of Co atoms. When the as-grown sample is further annealed, an increased number of Co atoms are able to reach the interface to the precipitate resulting in its coarsening and the formation of a shape that corresponds to a minimal interfacial energy.

V. CONCLUSION

We have investigated the local disordering in the CoAl films on GaAs (001) fabricated at variable growth temperatures during MBE. The disordering in the epitaxial layers is induced partially by the epitaxial strain and partially by the diffusion of point defects, including vacancies and Co atoms. The strain-induced disordering diminishes with the initiation of the plastic relaxation, which is realized by the formation of a nearly periodic array of interfacial precipitates. The diffusion-induced disordering is less intense at lower growth temperature, due to the lower diffusivity and smaller concentrations of vacancies and Co antisite defects.

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