



Growth and structure of Cr thin films on GaAs(001)

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Abstract

Growth of Cr thin films on GaAs(001) was carried out using molecular beam epitaxy and was investigated by in situ reflection high-energy electron diffraction (RHEED) and ex situ X-ray diffraction (XRD). The results show that there are two competing mechanisms during the growth, and the film structure strongly depends on the growth temperature. The single-crystalline Cr films with the body-centered-cubic (bcc) structure are obtained, with the epitaxial relationship of $(001)[001]_{\text{Cr}} \parallel (001)[001]_{\text{GaAs}}$ and $(001)[100]_{\text{Cr}} \parallel (001)[100]_{\text{GaAs}}$. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The 3d transition metals exist in a variety of crystallographic phases. Thin-film growth of these materials on semiconductor substrates have proven to be very important both for the potential application in spintronics and for the fundamental research in magnetism. Significant progress has been made during the last decades. The thermodynamically stable body-centered-cubic (bcc) Fe was obtained by epitaxial growth on GaAs substrate [1,2]. The bcc Co [3–5] that does not occur in nature and the face-centered-cubic (fcc) Mn [6–8] which exists only at high temperature were also obtained by epitaxial growth on GaAs substrates. In addition, the metastable fcc-Fe [9] and fcc-Co

[10] were realized, respectively, by epitaxial growth on Cu(100) and C(100). All of these have greatly increased the variety of magnetic materials by essentially making “new” materials from “old” elements.

Chromium is a bcc 3d transition metal with intriguing magnetic properties. Its lattice constant is 0.2885 nm and is perfect match to half of the GaAs lattice constant 0.565 nm (<1.9%), as shown in Fig. 1. Similar to the cases of bcc-Fe and bcc-Co on GaAs(001) [1–5], Cr should be expected to have grown epitaxially on GaAs(001) with the epitaxial relationship:

$$(001)[001]_{\text{Cr}} \parallel (001)[001]_{\text{GaAs}}$$

and

$$(001)[100]_{\text{Cr}} \parallel (001)[100]_{\text{GaAs}}. \quad (1)$$

However, the epitaxial relationship was found to be very different in experiment [11]:

$$(112)[1\bar{1}0]_{\text{Cr}} \parallel (001)[1\bar{1}0]_{\text{GaAs}}$$

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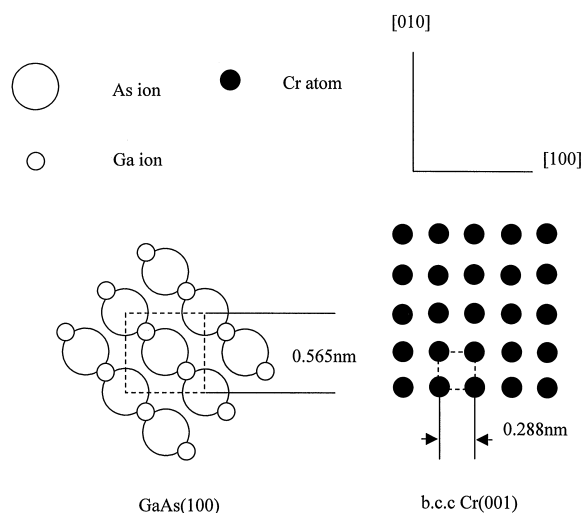


Fig. 1. Schematic view of nonreconstructed GaAs(001) and bcc-Cr(001) surfaces.

and

$$(11\ 2)[\bar{1}\ \bar{1}\ 1]_{\text{Cr}} \parallel (0\ 0\ 1)[1\ 1\ 0]_{\text{GaAs}} \quad (2)$$

in spite of the similarity of both the structure and parameter of Cr and Fe or Co. No explanations have been given why Cr behaves so differently.

In this work we investigated the film structures of Cr on GaAs(001) as a function of growth temperature. The results show that there are two competing growth mechanisms in the Cr thin-film growth, corresponding exactly to the foregoing-mentioned growth orientations (1) and (2), respectively. Same as the previous result [11], the film growth is indeed dominated by orientation (2), at lower growth temperatures $20^\circ\text{C} < T < 70^\circ\text{C}$. However, at higher growth temperatures $T > 130^\circ\text{C}$, the film growth turns out to be dominated by the orientation (1). At intermediate growth temperatures $70^\circ\text{C} \leq T \leq 130^\circ\text{C}$, these two domains coexist in the Cr films.

2. Experiment

The heteroepitaxial growth was carried out in an MBE growth chamber connected with the VG-ESCALAB-5 electron spectrometer system. The Te-doped GaAs(001) single-crystal wafers

were polished and treated by an ordinary device-cleaning process. The final substrate cleaning was performed by a chemical etching method using $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 5 : 1 : 1$ before loading into the MBE system and flashing to 580°C in the ultra-high vacuum chamber. For clean GaAs(001) substrates before epitaxy, 4×1 reconstruction patterns were observed by reflection high-energy electron diffraction (RHEED). The Auger electron spectra show that the surfaces are free of carbon and oxygen contamination. The background pressure in the growth chamber was 3×10^{-8} Pa. The 99.99% pure Cr pieces were charged in an Al_2O_3 crucible of a Knudsen cell. The deposition rate used in this experiment was fixed at 0.2 nm/min as measured by a quartz thickness monitor and double checked by Auger electron spectroscopy. The bcc-Cr coverage is expressed in nanometer (nm) with 1 ML (monolayer) = 0.15 nm relative to the GaAs(001) surface atomic density of 6.3×10^{14} atoms/cm².

3. Results and discussion

The growth of Cr on GaAs(001) was first investigated when the substrate was kept at room temperature. Fig. 2(a) shows a typical RHEED pattern for a clean GaAs(001) surface, with an electron beam along the GaAs[110] direction. Following the evolution of the RHEED patterns after opening the Cr source, we first find that some polycrystalline circles start to appear as the substrate spots fade away. A typical diffraction pattern at this stage is shown in Fig. 2(b). This disordering is presumably caused by the chemical reaction between Cr and GaAs at the interface, although a clear picture about the detailed interface structure is still lacking [12]. After the Cr coverage reaching beyond ~ 1.2 nm, a new diffraction pattern starts to appear and becomes dominant. Fig. 2(c) shows a typical pattern at this stage. This diffraction pattern persists as long as we continue the Cr growth. After some careful analysis of the diffraction pattern, we convince ourselves that it should be caused by the above-mentioned epitaxial orientation (2). In order to prove this, we show in Figs. 3(a) and (b) the two epitaxial relationships between the substrate and epilayer as mentioned above as (1) and (2), together

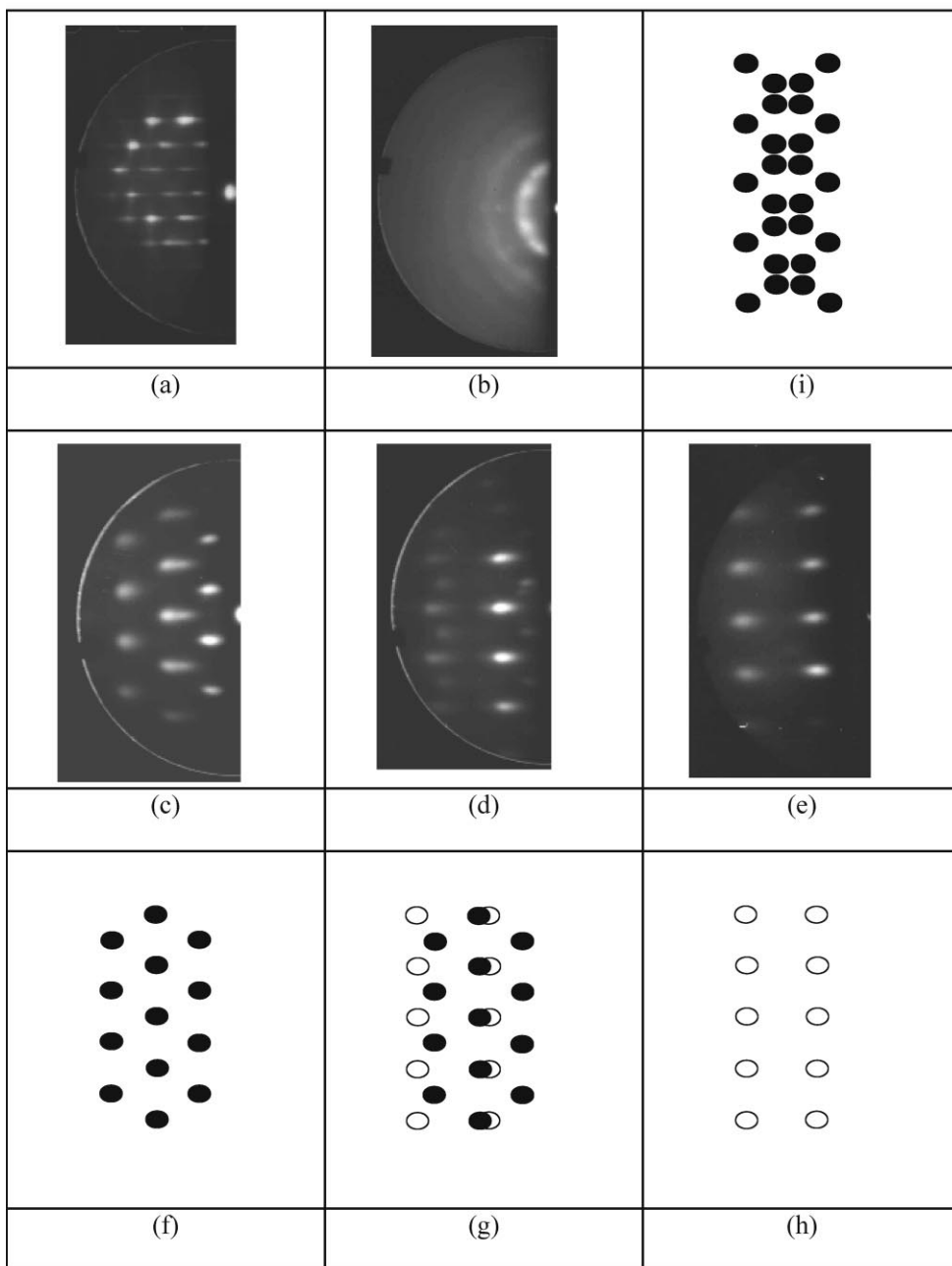


Fig. 2. RHEED patterns for different thin films grown on the GaAs(001) substrate at different temperatures, taken with the incident electron beam along the substrate $[1\ 1\ 0]$ direction: (a) clean GaAs(001); (b) 1.0 nm, 25°C; (c) 5.0 nm, 25°C; (d) 1.6 nm, 100°C; (e) 4.0 nm, 160°C; (f)–(i) calculated diffraction patterns explained in the text.

with the corresponding Miller indices. Based on the symmetry consideration, there are in principle two types of structures marked as (I) and (II). According

to types (I) and (II) in Fig. 3(b), we then calculated the RHEED diffraction patterns as shown in Figs. 2(f) and (i), respectively. Comparing them to the

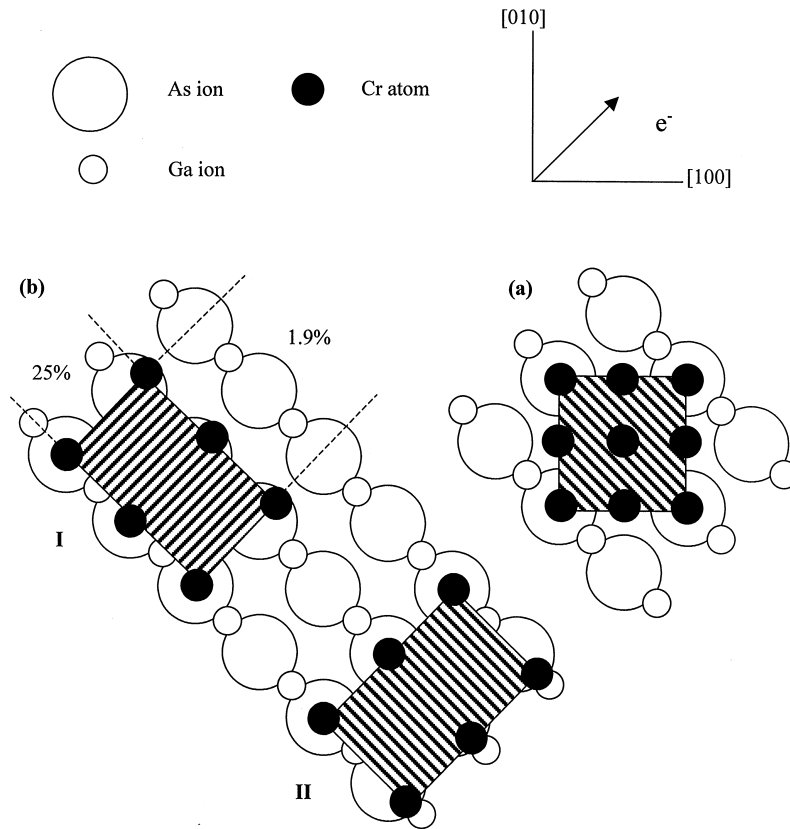


Fig. 3. Epitaxial relationships between Cr and GaAs: (a) $(001)[001]_{\text{Cr}} \parallel (001)[001]_{\text{GaAs}}$ and $(001)[100]_{\text{Cr}} \parallel (001)[100]_{\text{GaAs}}$; (b) shadow I - $(112)[1\bar{1}0]_{\text{Cr}} \parallel (001)[1\bar{1}0]_{\text{GaAs}}$ and $(112)[\bar{1}\bar{1}1]_{\text{Cr}} \parallel (001)[110]_{\text{GaAs}}$, shadow II - $(112)[110]_{\text{Cr}} \parallel (001)[110]_{\text{GaAs}}$ and $(112)[\bar{1}\bar{1}1]_{\text{Cr}} \parallel (001)[1\bar{1}0]_{\text{GaAs}}$.

experimental pattern in Fig. 2(c), it is immediately recognized that only type (I) structure exists in the Cr film. In order to confirm the epitaxial relationship (2), the X-ray diffraction was further carried out for a sample of 19 nm Cr on GaAs(001). The result is shown in Fig. 4(a), where a peak at $2\theta = 82.0^\circ$ is clearly seen besides the GaAs substrate contributions. This peak gives to $d_2 = 0.1174$ nm which agrees very well to the bcc Cr(112).

The growth of Cr on GaAs(001) was then investigated when the substrate was kept at a high-temperature range ($130^\circ\text{C} < T < 160^\circ\text{C}$). Similar to the room-temperature case as in Fig. 2(b), a ring-like pattern was observed in the first stage of Cr growth (< 1.4 nm). Then a new rectangle pattern starts to appear and becomes dominant, as shown in Fig. 2(e). This diffraction pattern persists until we

stop the growth (> 20 nm). From the previous work [3–5], it is realized that the Cr growth is with the above-mentioned epitaxial orientation (1). With the help of Fig. 3(a), we calculated the corresponding diffraction pattern as shown in Fig. 2(h). Obviously, a perfect agreement between the experiment and calculation is reached and therefore, epitaxial relationship (1) is unambiguously demonstrated. To confirm this conclusion again, the X-ray diffraction was carried out for a sample of 20 nm Cr on GaAs(001). The result is shown in Fig. 4(b), where a peak at $2\theta = 64.6^\circ$ is clearly seen besides the GaAs substrate contributions. This peak corresponds to $d_1 = 0.1441$ nm that fits exactly to the bcc-Cr(002).

The growth of Cr on GaAs(001) was further investigated when the substrate was kept at intermediate temperature range ($70^\circ\text{C} < T < 130^\circ\text{C}$).

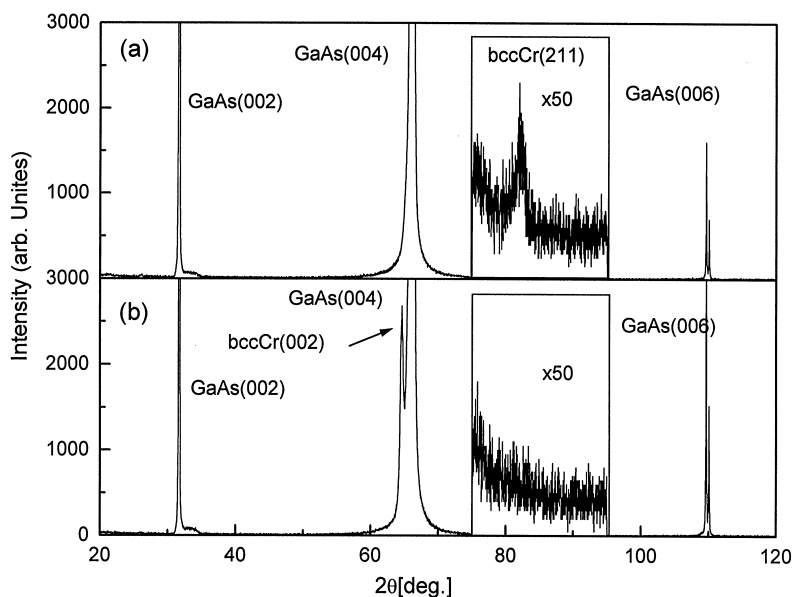


Fig. 4. X-ray diffraction spectra for (a) 19 nm Cr grown at room temperature, (b) 20 nm Cr grown at 160°C.

Similar to the low- and high-temperature cases in Fig. 2(b), a ring-like pattern was observed in the first stage for the Cr coverage < 1.3 nm. Then a diffraction pattern, as shown in Fig. 2(d), appears and persists until we stop the growth (> 20 nm). It is obvious that such a pattern is actually a mixture of Figs. 2(c) and (e), which indicates that the two domains with orientations (1) and (2) coexist in the Cr films. The calculated corresponding diffraction pattern shown in Fig. 2(g) agrees with the experiment perfectly.

It is demonstrated from the above results that there are two competing growth mechanisms for Cr on GaAs(001). The Cr film structure grown on GaAs(001) strongly depends on the growth temperature. However, there are still some puzzled questions that remain unsolved. Firstly, it is difficult to understand from the lattice-match point of view why the bcc-Cr(112) can epitaxially be grown on GaAs(001), while the lattice mismatch between the substrate and epilayer along the $[110]$ direction reaches as high as 25%. Secondly, it is hard to believe from the symmetry point of view why only type (I) structure instead of both type (I) and (II) exists in the epitaxial relationship (2). The reasons behind this are presumably correlated to the ques-

tions regarding the roles played by the interface in the problem or the apparent roles played by the chemisorption of Cr on GaAs. These certainly need to be addressed in the future with some more appropriate experimental techniques. We believe that a clear picture of interface structure will be helpful to understand these puzzles as well as the two competing growth mechanisms and their temperature dependence.

4. Conclusions

In summary, the growth of Cr thin films on GaAs(001) was carried out using molecular beam epitaxy. Two competing mechanisms in the Cr film growth are found and their temperature dependence is explored. We have reported for the first time the epitaxial growth of single crystalline bcc-Cr films on GaAs(001) and the epitaxial relationship of $[001]_{\text{Cr}} \parallel [001]_{\text{GaAs}}$ and $[100]_{\text{Cr}} \parallel [100]_{\text{GaAs}}$.

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