Epitaxial Growth and Magnetic Properties of NiMnAs Filmson GaAs Substrates

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(Received 26 September 2018)

Single-phase Ni0.92Mn1.08As films with strained C1b symmetry are grown on GaAs (001) substrates. In addition, a preferred epitaxial configuration of (110)-orientated Ni0.92Mn1.08As on (001)-orientated GaAs is revealed by synchrotron radiation measurement. The magnetic properties of the films are found to be significantly influenced by the growth temperature and the optimized growth temperature is determined to be ~370°C. According to the results of x-ray absorption spectroscopy, these phenomena can be attributed to the variation of the local electronic structure of the Mn atoms. Our work provides useful information for the further investigations of NiMnAs, which is a theoretically predicted half-metal.

PACS: 75.50.Cc, 75.70.Ak, 81.05.Bx, 81.15.Hi

Heusler alloys have been extensively investigated due to their rich physical connotation and potential applications. Some intriguing physical phenomena, such as helimagnetism, non-collinear magnetism, and/or the superconducting behavior have been successfully identified in this kind of alloys. In addition, the shape memory effect accompanied by the thermoelastic martensitic transformation in some Heusler alloys also renders them the ideal functional materials for practical applications. Among the numerous Heusler alloys, we notice that a series of Heusler alloys also renders them the ideal functional materials for practical applications. For instance, as the widely studied half-metallic Heusler alloy, NiMnSb has been successfully identified in this kind of alloys.

Specifically, half-Heusler alloy NiMnAs with the C1b structure was theoretically predicted to be half-metallic, with its Tc much higher than room temperature (~840 K). More importantly, as a compound isoelectronic with NiMnSb, NiMnAs has some unique features that are absent in NiMnSb: while the half-metallicity of NiMnSb was found to be sensitive to the interface of heterojunction and the expansion and/or compression of its crystal lattice, the influence of the interface and lattice distortion on NiMnAs was predicted to be relatively weaker. Furthermore, the minority spin gap of NiMnAs is larger (~0.69 eV) than that of NiMnSb, ensuring a much more robust half-metallicity against external perturbation. However, to our best knowledge, cubic NiMnAs has not been synthesized before, due to its tendency of crystallizing in the hexagonal or orthorhombic structures. For these reasons, the experimental investigations on NiMnAs with C1b structure are immensely limited, which makes the synthesis and fundamental characterizations of this material meaningful and challenging.

In this Letter, we succeed in growing high-quality Ni0.92Mn1.08As films with the strained C1b crystal structure using molecular-beam epitaxy. The Ni0.92Mn1.08As (110) plane is found to be parallel with the GaAs (001) plane. In addition, the growth temperature (Tg) dependence of the magnetic properties for the Ni0.92Mn1.08As films is systematically studied, in which an optimized growth temperature is determined to be ~370°C. For the sample grown at this optimized Tg, relatively high Tc, large saturation magnetization (Ms) and coercive field (Hc), as well as pronounced in-plane magnetic anisotropy (MA) are obtained. Based on this newly synthesized film, rich
spin-dependent physics in NiMnAs can be explored. This will facilitate further investigations of this material and its relevant devices.

![Diagram](Fig. 1. (a) Schematic diagram of layer structure of epitaxial Ni$_{0.92}$Mn$_{1.08}$As films. (b) Typical RHEED pattern of Ni$_{0.92}$Mn$_{1.08}$As film grown on the GaAs (001) substrate, in which the incident electron beam is along the GaAs [110]. The RHEED pattern of GaAs (001) with the same electron-beam incident angle with respect to the in-plane GaAs crystallographic direction is shown in the inset. (c) XRR data (black solid line) and the fitting curve (blue-dashed line) of the Ni$_{0.92}$Mn$_{1.08}$As film with the thickness of ∼30 nm. (d) EDS spectrum of the Ni$_{0.92}$Mn$_{1.08}$As film grown at 370°C.

In our experiment, a series of NiMnAs films were epitaxied on GaAs (001) substrates at different temperatures, and the layer structure is schematically shown in Fig. 1(a). In detail, a 150-nm-thick undoped GaAs buffer layer was firstly grown on a GaAs (001) substrate after the desorption of the natural oxide layer at ∼580°C. Subsequently, the substrate was cooled down to room temperature and a ∼0.6-μm-thick low-temperature NiMnAs layer was deposited to eliminate the influences of interfacial reaction. Meanwhile, the sample surface was monitored using in situ reflection high-energy electron diffraction (RHEED), which presents the typical pattern of amorphous material after the deposition of the low-temperature layer. We annealed this layer until the RHEED patterns changed to streaky stripes, indicating the transition of the film to the form of crystalline. Afterwards, the NiMnAs films with a fixed thickness of ∼30 nm were grown at various temperatures (250, 300, 330, 370 and 400°C). In this growth stage, RHEED always shows streaky (1 × 2) patterns. Figure 1(b) presents the RHEED pattern of the film with the incident electron beam along the GaAs [110], suggesting a layer-by-layer growth mode and the high quality of the films. As a reference, the RHEED pattern of GaAs (001) with the same electron-beam incident angle with respect to the in-plane GaAs crystallographic direction is shown in the inset of Fig. 1(b). To prevent the NiMnAs film from being oxidized, a 3-nm-thick GaAs capping layer was finally grown. The thickness and growth rate of the NiMnAs films were calibrated by x-ray reflectivity (XRR) measurement (see the raw data and fitting curve in Fig. 1(c)), which also implies a relatively smooth interface between the NiMnAs film and the GaAs substrate. This is consistent with the observed RHEED patterns (Fig. 1(b)). In addition, energy dispersive spectrometer (EDS) was used to check the chemical composition of the films. The result of Ni:Mn~0.92:1.08 is shown in Fig. 1(d), which is a good representation of the stoichiometric NiMnAs films.

![Diagram](Fig. 2. (a) Room-temperature XRD (λ$_1$ ∼ 1.5406 Å) data of the Ni$_{0.92}$Mn$_{1.08}$As films with various growth temperatures. The curves are offset for clarity. (b) In-plane x-ray diffraction result of Ni$_{0.92}$Mn$_{1.08}$As film using the synchrotron radiation (λ$_2$ ∼ 0.6895 Å). The inset schematically shows the configuration of (110)-orientated Ni$_{0.92}$Mn$_{1.08}$As film on the (001)-orientated GaAs substrate.

We first used a laboratory x-ray diffractometer (λ$_1$ ∼ 1.5406 Å) to unveil the crystal structure of the films. Figure 2(a) illustrates the room-temperature ω-2θ diffraction results from five Ni$_{0.92}$Mn$_{1.08}$As films with different growth temperatures. For each diffraction curve, three peaks can be seen, among which the peaks at 2θ ∼ 31.6° and 2θ ∼ 66.1° correspond to the reflections of GaAs (002) and (004) crystallographic planes, respectively. The relatively weak peak between the above two peaks should be attributed to the x-ray diffraction of the Ni$_{0.92}$Mn$_{1.08}$As film, which slightly shifts with the variation of the growth temperature, implying the change of the lattice relaxation. Except for these three peaks, no other peaks can be found in the broad 2θ range, which suggests that all of the Ni$_{0.92}$Mn$_{1.08}$As films are high-quality single-crystalline films without observable second phase. Considering that the lattice constant of NiMnAs with C$_{11}$ structure is similar with GaAs,[19,23,27] and the reflection position of the film (2θ ∼ 44°) is very close to that of the GaAs (220) plane. Hence, it is reasonable to ascribe this peak to the reflection of quasi-cubic Ni$_{0.92}$Mn$_{1.08}$As (220) crystallographic plane. In other words, the configuration of (110)-orientated Ni$_{0.92}$Mn$_{1.08}$As on (001)-orientated GaAs...
probably establishes between the film and the substrate.

To confirm the above special epitaxial relationship, an experimental setup based on synchrotron radiation was utilized, in which the diffraction data were collected with the sample rotating under a grazing incident high-energy x-ray (λ_1 ~ 0.6895 Å). Figure 2(b) presents the typical result of the Ni_{0.92}Mn_{1.08}As film grown at T_g ~ 370°C, in which the sample was slowly rotated around the surface normal (characterized by angle φ) from 0° to 180°. We define φ = 0° as one of the angles corresponding to the diffraction peaks of the film (004) planes. It can be seen that one GaAs (004) diffraction peak appears at φ = 45°, which, together with the above XRD data, unambiguously verify the (quasi-)cubic structure of Ni_{0.92}Mn_{1.08}As and reveal the epitaxial configuration of (110)-oriented Ni_{0.92}Mn_{1.08}As film on (001)-oriented GaAs substrate (see the inset in Fig. 2(b)). A similar epitaxial relationship was also found between the Ni_3MnIn Heusler film and the InAs substrate regardless of the large lattice mismatch between them, which was attributed to the interaction at the heterostructure interface [28,29]. Considering that these two Mn-based Heusler alloy have similar growth conditions, such as epitaxial technique and growth temperature, it is reasonable to also ascribe the 90° rotation growth of the Ni_{0.93}Mn_{1.08}As films to the interface interaction, although the detailed mechanism needs to be further investigated.

Fig. 3. (a) Temperature dependence of the magnetization for the Ni_{0.92}Mn_{1.08}As films grown at different temperatures, in which the magnetization component was measured along the GaAs [110] direction. The growth temperature dependence of the Curie temperature is summarized in the inset. (b) Magnetic hysteresis loops for the Ni_{0.92}Mn_{1.08}As films deposited at various temperatures. These hysteresis loops were measured along the GaAs [110] direction at 5 K. (c) Growth temperature dependence of the coercive field and saturation magnetization extrapolated from (b). (d) Normalized magnetic hysteresis loops for the Ni_{0.92}Mn_{1.08}As film with T_g ~ 370°C at 5 K, in which the applied magnetic field is along the GaAs [110] (black), [110] (red) and [001] (blue) directions, respectively.

![Fig. 4. Room-temperature (a) Mn 2p, and (b) Ni 2p XAS spectra of the Ni_{0.92}Mn_{1.08}As films with various growth temperatures. The curves are offset for clarity.](image)

The Quantum Design superconducting quantum interference device (SQUID) magnetometer was utilized to characterize the basic magnetic properties of the Ni_{0.92}Mn_{1.08}As films. Figure 3(a) shows the temperature dependence of the magnetization for the Ni_{0.92}Mn_{1.08}As films grown at different temperatures, in which the magnetization component projected to GaAs [110] direction was measured. It can be seen that T_C is significantly affected by the growth temperature and varies from 45 K to 295 K, among which the highest T_C is obtained at T_g ~ 370°C (see the inset in Fig. 3(a)). Note that all of the T_C values are much smaller than that predicted by the theoretical work (~840 K) [18,19]. These lower T_C values are possibly attributed to the fact that the synthetic Ni_{0.92}Mn_{1.08}As films undergo the lattice distortion due to the strain between the film and the substrate. Meanwhile, the theoretical models predicting T_C of NiMnAs may need to be further improved [18,19]. In addition, we also find that the curves with the growth temperature higher than 250°C all exhibit a hump within a large temperature range, which may be induced by the spin reorientation transition (SRT) effect. A similar phenomenon was observed in (Mn_{1−x}Ni_x)_{65}Ga_{35}, in which the SRT effect was suggested to be resulting from the presence of a temperature-sensitive helical spin structure [30]. Figure 3(b) presents the magnetic hysteresis loops (~3 T–3 T) for the previously-mentioned five samples at 5 K, in which the external magnetic field was applied along the GaAs [110] direction. It can be seen that the in-plane ferromagnetic behavior featuring a relatively rectangular loop appears in the samples with T_g higher than 300°C, and the most pronounced in-plane magnetic anisotropy arises at T_g ~ 370°C. The values of $H_C$ and $M_s$ are extrapolated from these loops, which are summarized in Fig. 3(c). Evidently, the largest $H_C$ and $M_s$ are also obtained at $T_g$ ~ 370°C, as indicated by the
dashed ellipse. Therefore, the optimized growth temperature associated with the largest values of $T_C$, $H_c$, $M_s$ and the most pronounced MA is determined to be $\sim 370^\circ C$. To further clarify the magnetic anisotropy of these samples, magnetic hysteresis loops with the external magnetic field along the GaAs [110], [110] and [001] directions were measured at 5 K, in which the Ni$_{0.92}$Mn$_{1.08}$As sample grown at $T_s \sim 370^\circ C$ was selected as a representative (see Fig. 3(d)). As we can see, compared with the out-of-plane direction, a four-fold in-plane magnetic anisotropy is dominant in our sample. Deeper insights of the $T_s$-dependent magnetic properties are critical because they can effectively tailor the magnetism of Ni$_{0.92}$Mn$_{1.08}$As, which motivates us to unravel its microscopic origin.

Generally, the macroscopic magnetic properties of one material (such as $T_C$, $M_s$ and $P$) are closely associated with its electronic band structure (as described by the density of states DOS, band splitting induced by the exchange interaction, and position of Fermi energy $E_F$). These electronic band structure parameters are affected by the local electronic structures of the atoms, which can be detected by the x-ray absorption spectroscopy (XAS). Taking the advantages of the intense and tunable x-ray beams of synchrotron radiation, XAS characteristic spectra of Mn and Ni elements were obtained. Figure 4(a) shows the room-temperature Mn 2p XAS spectra of the Ni$_{0.92}$Mn$_{1.08}$As films with various growth temperatures, in which the energy of the x-ray beams was continuously changed. In the whole energy range we scanned, there are two types of XAS line shape; i.e., the shoulder structure (for the sample grown at $T_s \sim 250^\circ C$) and the multiplet structure (for the samples grown at $T_s \sim 300, 330, 370$ and $400^\circ C$), respectively. The drastic differences among the XAS results suggest the evolution of the local electronic structure of the Mn atoms, which may further affect the magnetic properties of the Ni$_{0.92}$Mn$_{1.08}$As films. In detail, the shoulder structure without apparent multiplets reflects the initial metallic Mn $L$-edge shape, and can be identified in the Mn-based metallic systems, such as MnSb and pure Mn metal. With the increase of the itinerancy of the Mn 3d electrons, the spectrum will usually be broadened. As for the multiplet structure, it probably indicates the covalent bonding of the Mn and As atoms, according to the analyses of the XAS spectra in NiMnSb. Additionally, this structure is predicted to be associated with the Mn 3d$^5$ ground state configuration, as suggested by the theoretical calculation for Mn 2p XAS spectra. To determine the role of the growth temperature in the local electronic structure of the Ni atoms, the measurement of Ni 2p XAS spectra for the above set of Ni$_{0.92}$Mn$_{1.08}$As films was also carried out, as shown in Fig. 4(b). It is evident that the corresponding XAS line shapes are almost unchanged, indicating that the variation of the growth temperature has no observable influence on the local electronic structure of the Ni atoms, which is in sharply contrary to the Mn 2p XAS spectra. Correspondingly, it can be deduced that the magnetism in the Ni$_{0.92}$Mn$_{1.08}$As films is mainly contributed by the Mn atoms, which is analogous to NiMnSb. Essentially, the local electronic structures of the Mn atoms, including the occupation of the 3d-electron orbital and the splitting of the 3d-electron energy level, are related to their coordination conditions. With the variation of the growth temperature, the chemical ordering of the Ni$_{0.92}$Mn$_{1.08}$As films will be changed, which further influences the coordination conditions of the Mn atoms. Accordingly, the electronic structures of the Mn 3d electrons will also vary with the growth temperature. Meanwhile, the DOS, the splitting of the energy band, and the location of $E_F$ in the Ni$_{0.92}$Mn$_{1.08}$As films are changed with the variation of the Mn 3d electronic structure. Considering the correlation between the macroscopic magnetism and the electronic band structure of the films, $T_C$, $P$ and $M_s$ of the Ni$_{0.92}$Mn$_{1.08}$As films will change correspondingly. In summary, the growth temperature dependence of the magnetic properties in Ni$_{0.92}$Mn$_{1.08}$As is related to the local electronic structure of the Mn atoms, while it is independent of the Ni atoms.

In conclusion, we have successfully synthesized the single-phase Ni$_{0.92}$Mn$_{1.08}$As films with strained $C_{44}$ symmetry. A preferred epitaxial relationship of Ni$_{0.92}$Mn$_{1.08}$As (110)/GaAs (001) has been revealed, regardless of the large lattice mismatch for this configuration. In addition, the growth temperature is found to have a remarkable effect on the magnetic properties of the Ni$_{0.92}$Mn$_{1.08}$As films, which can be attributed to the variation of the local electronic structure of the Mn atoms, as verified by the XAS measurements. Our work is fundamental for the further study of NiMnAs. A perspective of the high-performance spin-based devices based on this material is expected soon.

References

[1] Felser C, Wollmann L, Chadov S, Fecher G H and Parkin S S P 2015 *APL Mater.* 3 041518
[2] Palmstrøm C J 2016 *Prog. Cryst. Growth Charact. Mater.* 62 371
[3] Galanakis I, Dederichs P H and Papanikolaou N 2002 *Phys. Rev. B* 66 134428
[4] Plant J S 1979 *J. Phys. F* 9 545
[5] Meshcheriaкова O, Chadov S, Nayak A K, Rüüker U K, Kübler J, André G, Tsurin A A, Kies J, Hausdorf S, Kalache A, Schnelle W, Nicklas M and Felser C 2014 *Phys. Rev. Lett.* 113 087203
[6] Dönni A, Fischer P, Fauth P, Confort P, Aoki Y, Sugawara H and Sato H 1999 *Physica B* 259 705
[7] Kierstead H A, Dunlap B D, Malik S K, Umarji A M and Shenoy G K 1985 *Phys. Rev. B* 32 135
[8] Stanley H B, Lynn J W, Shelton R N and Klavins P 1987 *J. Appl. Phys.* 61 3371
[9] Liu Z H, Zhang M, Cui Y T, Zhou Y Q, Wang W H, Wu G H, Zhang X X and Xiao G 2003 *Appl. Phys. Lett.* 82 424
[10] Liu G D, Chen J L, Liu Z H, Dai X F, Wu G H, Zhang B and Zhang X X 2005 Appl. Phys. Lett. 87 262504
[11] Sutou Y, Imano Y, Koeda N, Onori T, Kainuma R, Ishida K and Okawa K 2004 Appl. Phys. Lett. 85 4358
[12] Borca C N, Komesu T, Jeong H K, Dowben P A, Ristoiu D, Hordequin C, Nozières J P, Pierre J, Stadler S and Izidera Y U 2001 Phys. Rev. B 64 052409
[13] Tanaka C T, Nowak J and Moodera J S 1997 J. Appl. Phys. 81 5515
[14] Tanaka C T, Nowak J and Moodera J S 1999 J. Appl. Phys. 86 6239
[15] Datta S and Das B 1990 Appl. Phys. Lett. 56 665
[16] Caballero J A, Park Y D, Childress J R, Bass J, Chiang W C, Reilly A C, Pratt W P and Petroff F 1998 J. Vac. Sci. Technol. A 16 1801
[17] Hordequin C, Nozières J P and Pierre J 1998 J. Magn. Magn. Mater. 183 225
[18] Dinh V A, Sato K and Katayama-Yoshida H 2008 J. Phys. Soc. Jpn. 77 014705
[19] Dinh V A, Sato K and Katayama-Yoshida H 2010 AIP Conf. Proc. 1199 441
[20] Ristoiu D, Nozières J P, Borca C N, Komesu T, Jeong H K and Dowben P A 2000 Europhys. Lett. 49 624
[21] Ristoiu D, Nozières J P, Borca C N, Borca B and Dowben P A 2000 Appl. Phys. Lett. 76 2340
[22] Komesu T, Borca C N, Jeong H K, Dowben P A, Ristoiu D, Nozières J P, Stadler S and Izidera Y U 2000 Phys. Lett. A 273 245
[23] Sivakumar C 2016 PhD Dissertation (Tuscaloosa: The University of Alabama)
[24] Li G N and Jin Y J 2009 Chin. Phys. Lett. 26 107101
[25] Shin T, Park M C, Park Y, Rothberg G M, Harbison J P and Tanaka M 1997 Appl. Phys. Lett. 70 258
[26] Fjellvåg H, Kjekshus A, Andersen A F and Zieba A 1986 J. Magn. Magn. Mater. 61 61
[27] Wu Y F, Wu B, Wei Z Y, Zhou Z Y, Zhao C F, Xiong Y P, Tou S S, Yang S J, Zhou B Y and Shao Y Q 2014 Intermetallics 53 26
[28] Zolotaryov A, Voll, A, Heyn C, Novikov D, Stryganyuk G, Kornowski A, Vossmeyer T, Albrecht O, Ceric E and Hansen W 2009 J. Cryst. Growth 311 2397
[29] Bohse S, Zolotaryov A, Voll, A, Landgraf B, Albrecht O, Bastjan M, Vossmeyer T, Görß D, Heyn C and Hansen W 2012 J. Cryst. Growth 338 91
[30] Shiraiishi H, Niida H, Iguchi Y, Mitsudo S, Motokawa M, Ohayama K, Miki H, Onodera H, Hori T and Kanematsu K 1999 J. Magn. Magn. Mater. 196 660
[31] Sicot M, Turban P, Andreieu S, Tagliaferri A, De N C, Brookes N B, Bertran F and Fortuna F 2006 J. Magn. Magn. Mater. 303 54
[32] Kimura A, Suga S, Imada S, Muro T, Shishidou T, Park S Y, Miyahara T, Kaneko T and Kanomata T 1996 J. Electron Spectros. Relat. Phenom. 78 287
[33] Kimura A, Suga S, Shishidou T, Imada S, Muro T, Park S Y, Miyahara T, Kaneko T and Kanomata T 1997 Phys. Rev. B 56 6021
[34] Thole B T, Cowan R D, Sawatzky G A, Fink J and Fuggle J C 1985 Phys. Rev. B 31 6856
[35] Webster P J and munkkari R M 1984 J. Magn. Magn. Mater. 42 300