Structure and magnetic properties of the Co$_2$FeAl and Co$_2$NiSi Heusler alloy films

I V Malikov$^1$, V A Berezin$^1$, L A Fomin$^1$, Yu A Perevozchikova$^2$, N S Bannikova$^2$, E I Patrakov$^2$, L I Naumova$^2$, A A Semiannikova$^2$, M A Milyaev$^2$, P S Korenistov$^2$ and V V Marchenkov$^{2,3}$

$^1$IMT RAS, Chernogolovka 142432, Russia
$^2$M.N. Mikheev Institute of Metal Physics, Ekaterinburg 620108, Russia
$^3$Ural Federal University, Ekaterinburg 620002, Russia

E-mail: fomin@iptm.ru

Abstract. The structural and magnetic properties (field dependences of the magnetization in magnetic fields of up to 6 kOe) of thin-film Co$_2$FeAl, and Co$_2$NiSi Heusler alloys grown by pulsed laser deposition on glass and a single-crystalline Al$_2$O$_3$ R-plane substrate at different growth temperatures (20, 280 and 420 °C) were studied. It was found that the stoichiometric composition of the films depends on the substrate temperature during growth and repeats the composition of the target for films grown at low temperatures. The films deposited on a single crystalline Al$_2$O$_3$ substrate have uniaxial magnetic anisotropy in the plane.

1. Introduction
The progress of modern nanoelectronics and spintronics requires the search and creation of new magnetic materials with high spin polarization of charge carriers. The corresponding materials should have high Curie temperatures $T_C$ because spintronic devices will mainly be used near the room temperature. Many of Heusler alloys, for example Co$_2$YSi and Co$_2$YAl ($Y = Ti$, V, Cr, Mn, Fe, Co, Ni) are known to be half-metallic ferromagnets [1 - 4], in which the electronic spectrum at the Fermi level $E_F$ has an energy gap for one of the spin directions and its absence for another one. Therefore 100% spin-polarization can be realized at $E_F$. For this reason, it is of interest to use these alloys in spintronics for creating instruments based on the magnetic tunneling and giant magnetoresistance effects, as a spin as spin-polarized electron injectors in structures switchable by a spin-polarized current and in magnetic transitions, where, as was shown [5], the spin nonequilibrium of conduction electrons due to injection leads to radiative electron transitions between spin subbands. Thus, it is possible to create a laser operating in the THz range at room temperature. Such device can be created using planar (film) technology. Therefore, the study of the properties of films and film structures is an important part of such researches. And epitaxy processes can provide additional benefits to such materials. In our previous papers [6, 7] the films of Fe$_2$CoAl and Co$_2$FeAl Heusler alloys grown on the R-plane sapphire substrate were studied using scanning atomic and magnetic force microscopies, supplemented with measurements of film magnetoresistance. Nonmonotonic dependences of the films’ morphological and magnetic properties on their growth temperature were obtained. The dependencies found were caused, as assumed, by the formation of some disordered phase at temperatures in some
ranges of the growth temperatures where biaxial magnetic anisotropy found. A more ordered phase was grown in the other temperature ranges, in which there was the uniaxial magnetic anisotropy.

In this paper the structural and magnetic properties (field dependences of the magnetization in magnetic fields of up to 6 kOe) of thin-film Co$_2$FeAl (CFA) and Co$_2$NiSi (CNS) Heusler alloys grown by pulsed laser deposition on glass and a single-crystal Al$_2$O$_3$ R-plane substrate at different growth temperatures (20, 280 and 420 °C) were studied. The use of these films in magnetic transitions can increase the intensity of spin-injection THz radiation when current flows through them.

2. Experimental

The Co$_2$FeAl and Co$_2$NiSi Heusler alloy films were grown by pulsed laser deposition in an ultrahigh basic vacuum $10^{-10}$ Torr on glass and a single-crystalline Al$_2$O$_3$ (-1012) R-plane substrate. Growth temperatures were 20 °C (substrate pre-annealed at 280 °C), 280 °C, and 420 °C for CFA and CNS respectively. A pulse Q-switch solid-state (AY:Nd$^{3+}$) laser with the wavelength 1.079 μm, 15 ns pulse duration, 10 Hz pulse frequency, and till 0.4 J radiation energy per pulse was used for target ablation. See [8, 9] for details. Elemental analysis was carried out by using a scanning electron microscope equipped with an EDAX X-ray microanalysis attachment. The structural analysis was performed at the Collaborative Access Center, M.N. Mikheev Institute of Metal Physics. X-ray diffraction studies were carried out at DRON-3M diffractometer using $\theta - 2\theta$ and $\omega$-scans. The thickness of the films studied by the X-ray diffraction was over 100 nm. The field dependencies of the magnetization $M(H)$ were measured at room temperature in magnetic fields of up to 6 kOe applied along normal and parallel to the film planes.

3. Results and discussion

The results on the X-ray microanalysis are shown in the Tables 1 and 2. Small amount of target drops is seen on film surfaces. They are not affecting on average composition. However, the presence of droplets allows one to compare the stoichiometric composition of the target and the accuracy of transfer and preservation of the composition of the target in the film. It can be clearly seen that for CFA films at low temperatures of 20 °C and 280 °C, the composition of the target corresponds quite well to the composition of the film. At a higher temperature of 420 °C, the film has an approximate composition of Co$_{2.21}$Fe$_{1.27}$Al$_{0.52}$, i.e. a significant aluminum deficiency is observed in the film. This means that such a temperature, taking into account the not too high melting point of aluminum, creates conditions for the re-evaporation of high-energy particles after laser evaporation and is excessive for the correct accommodation of aluminum atoms in the lattice of the Heusler alloy. For the CNS alloy, there is no such problem at all three temperatures studied, since the boiling and melting temperatures of all three components included in the alloy are close and the elemental composition of the target is transferred from the film quite well.

Results of the X-ray diffraction studies show that there is only one peak in XRD patterns obtained for Co$_2$FeAl films grown on a glass substrate at 20 °C and at 280 °C. It was identified as (220) of L2$_1$ structure. The texture investigation demonstrates the $<220>$ texture. The full width at half maximum of the rocking curve ($\omega$-scan) was 6 degs and 18 degs for the Co$_2$FeAl films grown at 20 °C and 280 °C respectively. Diffraction patterns of CNS films grown on the sapphire substrate show peaks only from the sapphire. This result can be due to the tilted epitaxy of the film when the main reflex is tilted a few degrees from the normal to the film surface. It is not related to the vicinal surface of the substrate but is a specific result of stress relaxation in the growing epitaxial film. The phenomenon is very characteristic of the R-plane of the sapphire [10]. Film thicknesses of CNS grown at 20 °C and at 280 °C are 36.6 nm and 64 nm, correspondingly.

The field dependencies of sample magnetization are shown in figure 1. It is seen that hard axis and easy axis have differences in films grown at higher temperatures. It means that films CFA and CNS become anisotropic at 280 °C and 420 °C, correspondingly. At that time the CFA and CNS films grown at 20 °C and also CNS films grown at 280 °C are seem to be magnetically isotropic. The shape of the field dependencies is similar to that found in the paper [11]. The values of the coercive fields $H_c$
obtained from the field dependences of the magnetization of the samples are presented in Table 3. It can be seen from the table that with the growth temperature increase, the coercive field for the CFA alloy grown on glass decreases. At the same time, the dependence of the coercive field on the growth temperature for CNS films is nonmonotonic. Small values of the coercive field for textured CFA films grown at 280 °C and 420 °C indicate a small number of defects in these films despite a change in the composition of films grown at 420 °C.

**Table 1.** The element analysis of Co₂FeAl films grown at different temperatures.

| Temperature | Average composition | Target drop |
|-------------|----------------------|-------------|
| 20°C        | Co₁.₈₉Fe₀.₉₄Al₁.₁₇   | Co₁.₉₃Fe₁.₀₅Al₁.₀₂ |
|             |                      | Co₂.₂₁Fe₁.₂₇Al₀.₅₂ |
| 280°C       | Co₁.₈₂Fe₀.₈₀Al₁.₃₈   | Co₂.₀₄Fe₁.₀₃Al₀.₉₃ |
|             |                      | Co₂FeAl       |
| 420°C       |                      |              |

**Table 2.** The elemental analysis of Co₂NiSi films grown at different temperatures.

| Temperature | Average composition | Target drop |
|-------------|----------------------|-------------|
| 20°C        | Co₁.₇₇Ni₀.₉₈Si₁.₄    | Co₁.₇₈Ni₀.₉₃Si₁.₃₉ |
|             | Co₁.₈₈Ni₀.₈₄Si₁.₂₈ is averaged with drops | Co₁.₈₄Ni₀.₈₂Si₁.₃₃ is averaged without drops |
|             | Co₂Ni₀.₉₉Si₁.₀₉ is averaged without drops | |
| 280°C       | Co₁.₇₇Ni₀.₉₈Si₁.₂₅   | Co₁.₆₆Ni₀.₉₄Si₁.₄₆ |
|             |                      |              |
| 420°C       | Co₁.₇₁Ni₀.₉₉Si₁.₁     | Co₁.₉₁Ni₀.₉₉Si₁.₁ |
Figure 1. Field dependencies of magnetization.

Table 3. The coercive fields of Co\textsubscript{2}FeAl and Co\textsubscript{2}NiSi films.

| Sample          | $H_C$, Oe | Sample          | $H_C$, Oe |
|-----------------|-----------|-----------------|-----------|
| Co\textsubscript{2}FeAl, 20°C | 157       | Co\textsubscript{2}NiSi, 20°C | 520       |
| Co\textsubscript{2}FeAl, 280°C | 17        | Co\textsubscript{2}NiSi, 280°C | 253       |
| Co\textsubscript{2}FeAl, 420°C | 14        | Co\textsubscript{2}NiSi, 420°C | 1438/816  |
The value of $H_c$ for CFA films decreases with increasing temperature from 157 Oe at 20 °C to 14 Oe at 420 °C. This means that the number of defects in the film decreases and the crystal structure of the alloy becomes more perfect. For CNS films, the situation is completely different. The relatively large value of $H_c$ for films grown at room temperature with an increase in the growth temperature initially decreases more than twice, and for a film grown at 420 °C it increases sharply and becomes substantially anisotropic. Large values of the coercive field for CNS films grown at 420 °C are possibly associated with the precipitation of a new nanophase during growth at high temperature [12].

4. Conclusion
The structural and magnetic properties of thin-film Co$_2$FeAl, and Co$_2$NiSi Heusler alloys grown by pulsed laser deposition on glass and a single-crystalline Al$_2$O$_3$ R-plane substrate at different growth temperatures (20, 280 and 420 °C) were studied. It was found that the stoichiometric composition of the films depends on the substrate temperature during growth and repeats the composition of the target for films grown at low temperatures. The films become magnetically anisotropic at high growth temperatures and have relatively low coercive field (except Co$_2$NiSi grown at 420 °C). Apparently, the use of these films in magnetic transitions can increase the intensity of spin-injection THz radiation when current flows through them.

Acknowledgements
This work was partly supported by the state assignment of Minobrmauki of Russia (themes “Spin” No. AAAA-A18-118020290104-2), RFBR grants (Nos. 18-32-00686 and 18-02-00739) and the Government of the Russian Federation (state contract No. 02.A03.21.0006).

References
[1] Irkhin V Y and Katsnelson M I 1994 Physics Uspekhi 37 659
[2] Katsnelson M I, Irkhin V Yu, Chioncel L et al. 2008 Rev. Mod. Phys. 80 315
[3] Marchenkov V V, Kourov N I and Irkhin V Yu 2018 Phys. Met. Metallog. 119 64
[4] Schneider H et al. 2007 J. Phys. D: Appl. Phys. 40, 1548
[5] Korenivski V et al. 2013 Europhys. Lett. 104 p. 27011
[6] Malikov I V, Fomin L A, Berezin V A et al. 2019 Ferroelectrics 541 79
[7] Malikov I V, Fomin L A, Berezin V A 2020 Ferroelectrics, 559 150
[8] Malikov I V, Mikhailov G M 1997 J. Appl. Phys. 82 5555
[9] Mikhailov G M, Malikov I V, Chernykh A V and Petrashev V T 1996 Phys. Solid State 38 1754
[10] Tricker D M and Stobbs W M 1995 Philos. Mag. A 71 1051
[11] Husain S, Barwal V, Kumar A et al. 2019 J. Magn. Magn. Mater. 486 165258
[12] Chai Y W and Kimura Y 2012 Appl. Phys. Lett. 100 033114