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Effect of disorder on the resistivity of CoFeCrAl films

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Structural and electron-transport properties of thin films of the ferrimagnetic Heusler compound CoFeCrAl have been investigated to elucidate structure-property relationships. The alloy is, ideally, a spin-gapless semiconductor, but structural disorder destroys the spin-gapless character and drastically alters the transport behavior. Two types of CoFeCrAl films were grown by magnetron sputtering deposition at 973 K, namely polycrystalline films on Si substrates and epitaxial films on MgO (001) substrates. The resistivity decreases with increasing temperature, with relatively small temperature coefficients of −0.19 $\mu\Omega\text{cm}/K$ for the polycrystalline films and −0.12 $\mu\Omega\text{cm}/K$ for the epitaxial films. The residual resistivity of the polycrystalline films deposited on Si is higher than that of the epitaxial film deposited on MgO, indicating that the polycrystalline films behave as so-called dirty metals. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Spin-gapless semiconductors (SGS), which have a semiconducting or insulating gap in one spin channel and a zero gap at the Fermi level in the other spin channel, have recently attracted much attention due to voltage-tunable spin polarization, the ability to switch between spin-polarized $n$-type and $p$-type conduction, high spin polarization at the Fermi level, and potentially high carrier mobility.1–7 The materials, which were first proposed theoretically and then verified experimentally in the form of Co-doped PbPdO$_2$ films,2 can be regarded as a combination of gapless semiconductors such as HgCdTe, HgCdSe, HgZnSe, and graphene,8,9 and half-metallic ferromagnets.10 Recently, some Heusler alloys, such as Mn$_2$CoAl, CoFeCrAl, CoFeMnSi, and CoFeMnGe have been predicted to be SGS.11 However, many Heusler alloys exhibit substantial chemical disorder, which potentially destroys spin-gapless semiconducting behavior. For example, Fe and Co exhibit a high degree of solid-solution type disorder in CoFeCrAl.4,13,14

Pronounced chemical disorder leads to dirty-metal behavior, characterized by resistivities of the order of 200 $\mu\Omega\text{cm}$ and observed, for example, in Ti-Al, Nb$_3$Sn, and Ni-Cr-Al.15–19 Spin-gapless semiconductivity and dirty-metal are difficult to distinguish experimentally, because high resistivities are also expected for SGS and because both dirty metals and SGS exhibit negative temperature coefficients of the resistivity (TCR), as contrasted to the positive TCR of ordinary metals. Ideal SGS have the infinite residual resistivity at zero temperature (‘freeze-out regime’), due to the absence of carriers at the Fermi level, but thermal excitations are very effective in creating carriers, because the gap width is zero. This causes a negative TCR. Weak chemical disorder in SGS is likely to create some carriers even at zero temperature so that the residual

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The residual resistivity is finite but large.\textsuperscript{13} The high residual resistivity of dirty metals and their negative TCR have very different origins. They are linked to the electrons’ mean free path becoming comparable to the interatomic distance so that the electrons are no longer described by well-defined $k$-vectors.\textsuperscript{19}

The unusual magnetoresistance (MR) effect, linear in magnetic field and positive,\textsuperscript{20} varies greatly among spin-gapless semiconductors and is only partially understood. MR values of 150\% are observed in Co-doped PbPdO\textsubscript{2},\textsuperscript{2,21} but much smaller values of 9\% and 0.6\% have been reported for bulk and thin film Mn\textsubscript{2}CoAl, respectively,\textsuperscript{3,7,12} and the magnetoresistance of bulk CoFeCrAl is about 1.5\%\textsuperscript{5}. The difference reflects the electronic structure of the materials: a magnetic field changes the direction of the Co spins in the doped PbPdO\textsubscript{2}, which is a very effective magnetoresistive mechanism, whereas the MR in the Heusler requires an electron transfer from the minority spin channel to the majority spin channel, which is energetically rather unfavorable.

While both SGS and dirty metals have similar resistivities and TCRs, and the magnetoresistance is not very telling, the two classes of materials can be distinguished by considering the residual resistivity as a function of the chemical disorder. Figure 1 outlines the idea. If one has samples with different degrees of chemical order, for example, due to different processing parameters or substrate, then a distinction between SGS and dirty metals may be possible. In the SGS regime, the residual resistivity decreases with increasing disorder, because the disorder creates carriers. In dirty metals, the residual resistivity increases with the disorder, because the disorder is the very origin of the resistivity.

Here we consider thin films of CoFeCrAl, a material that has been predicted to be a SGS in its fully ordered Y structure.\textsuperscript{11} In this system, the degree of order can be controlled by the choice of substrate: films deposited on MgO are much better ordered than films on Si.

II. EXPERIMENTAL METHODS

A magnetron sputtering system with a base pressure of about $3 \times 10^{-8}$ Torr was used to deposit CoFeCrAl thin films onto atomically flat C-cut MgO (001) and Si substrates. The samples were co-deposited from Co, Fe, Cr and Al targets under optimized deposition conditions. A stoichiometry very close to CoFeCrAl is achieved at 973 K and DC powers of 40 W and 42 W for Al and Fe targets, and RF powers of 69 W and 33 W for Cr and Co targets, respectively. Ar pressure is $2 \times 10^{-3}$ Torr. Lower deposition temperatures yield polycrystalline CoFeCrAl films on MgO, whereas temperatures above 600 K do not affect the film growth on Si. The crystal structure and the epitaxy of the films were investigated by in-plane and out-of-plane XRD diffraction, and by pole-figure experiments using

![FIG. 1. Residual resistivity as a function of disorder (schematic). "MgO" and "Si" refer to CoFeCrAl films on MgO and Si substrates, respectively.](image-url)
a Rigaku SmartLab Diffractometer with Cu Kα radiation (wavelength 1.54 Å). Electron diffraction using the energy-dispersive X-ray spectroscopy (EDX) in the FEI Nova NanoSEM450 scanning electron microscope (SEM) yields a stoichiometry of Co$_{25.5}$Fe$_{24.6}$Cr$_{24.5}$Al$_{25.4}$, close to the ideal equiatomic composition. The thickness of the films, as determined by a Bruker Dimension Icon® Atomic Force Microscope, is about 100 nm, but to produce milled samples of CoFeCrAl on Si for Rietveld analysis, we have also deposited thicker films (about 1000 nm). The electron-transport properties were measured using a Quantum Design Physical Property measurement system (PPMS).

III. RESULTS AND DISCUSSION

In this section we compare structural and transport properties of highly ordered CoFeCrAl, deposited on MgO, and less well ordered CoFeCrAl, deposited on Si.

A. Structural comparison of CoFeCrAl on MgO and Si

Figure 2 shows the out-of-plane XRD patterns. First, the films grown on Si are polycrystalline but textured, with a preferential (220) orientation. This orientation is inferred from the strong (220) peak and the absence of (200) and (400) peaks in Fig. 2(b). Second, the films grown on the MgO substrate exhibit an epitaxial growth of the (001) type, as evidenced by the exclusively presence of only the (002) and (004) peaks in Fig. 2(b).

Due to the epitaxial character of the films, the degree of Heusler (L2$_1$ or Y) order cannot be judged from Fig. 2. This question is important, because CoFeCrAl is likely to exhibit various degrees of A2 (bcc), B2 (CsCl), and L21 (normal cubic Heusler) disorder.\(^4\)\(^5\)\(^13\) These types of disorder affect and potentially destroy SGS behavior and, in the case of A2 disorder, even halfmetallicity.\(^13\) To establish Heusler order, it is necessary to trace XRD peaks such as the (111) peak, and this peak has indeed been found after milling the films.

The respective degrees of Cr-Al B2 order (A2 disorder) and L2$_1$ order (B2 disorder) can be calculated from the long-range order parameters

\[
S_{B2}^2 = \frac{I_{200} \cdot I_{400}^f}{I_{400} \cdot I_{200}^f}
\]

(1)

and

\[
\left(\frac{S_{L21}}{2} (3 - S_{B2})\right)^2 = \frac{I_{111} \cdot I_{220}^f}{I_{220} \cdot I_{111}^f}
\]

(2)

where $I_{hkl}$ and $I_{hkl}^f$ are the experimental diffraction intensity for the (hkl) plane and its reference intensity calculated for fully ordered alloys.\(^22\) In our MgO samples, $S_{L21}$ and $S_{B2}$ are both almost 88% with errors of the order of 5%. These numbers indicate a substantial degree of Heusler order, but also some degree (12 %) of A2 (bcc) disorder.

FIG. 2. Out-of-plane XRD patterns of CoFeCrAl on (a) on Si and (b) on MgO (001).
To investigate the structure of CoFeCrAl on Si, we have used Rietveld analysis of a film ground into powder. Figure 3 shows the room-temperature x-ray diffraction pattern. The weak peaks in the pattern marked with star sign are from silicon impurity, where the silicon particles were scraped off from the substrate surface with the sample. The CoFeCrAl pattern contains the fundamental bcc peaks and the (100) super-lattice peak, which indicates that the films exhibit B2-type structural disorder. Lattice constant and density of B2-type polycrystalline CoFeCrAl film deduced from the Rietveld analysis of XRD pattern are 2.875 Å and 6.971 g/cm³, respectively.

The above XRD analysis and the peak widths in Fig. 2 indicate that the films on MgO are much better ordered than the films on Si. This finding is further supported by pole-plot analysis. Figures 4(a) and 4(b) show the pole-figure plots for the \{111\} and \{220\} planes relative to the (100) plane of MgO, respectively. These plots confirm the high degree of epitaxial crystallinity of the film deposited on MgO and establish the orientation relationship between the crystallographic axes in the film plane. The pole-plot intensities have maxima at two angles, namely 0° and at 45°, and both exhibit 4-fold symmetry, providing clear evidence that the CoFeCrAl films grown on MgO are single-crystalline with cubic crystal structure. Moreover, the azimuthal angles mean that MgO [100] and CoFeCrAl [220] are parallel and that CoFeCrAl [100] is rotated by 45° away from MgO [100]. This situation is similar to the epitaxial growth of Fe film on MgO, where the rotation of the over layer unit cell by 45° favors epitaxial growth. The lattice parameter of CoFeCrAl, about 5.74 Å, is 1.36 times that of MgO (4.21 Å) and close to the “ideal” ratio \(\sqrt{2} = 1.41\). The experimental ratio indicates that the lattice spacing \(d_{110}\) (MgO) corresponds to \(a_{100}\) (CoFeCrAl), with a small in-plane strain of about 3.6%.

B. Resistivity measurements

Figure 5 (a) shows the temperature dependence \(\rho(T)\) of the longitudinal resistivity in zero magnetic field. The films are moderately conducting, with room-temperature (RT) resistivities of 150 µΩcm (MgO) and 210 µΩcm (Si). The respective residual resistivities are 187 µΩcm (MgO) and 268 µΩcm (Si). The value of 187 µΩcm for CoFeCrAl epitaxial film grown on MgO is substantially lower than those measured in more highly disordered bulk CoFeCrAl, namely 810 µΩcm (RT) and 930 µΩcm (residual), and compare well with the room temperature resistivity of MBE-grown Mn₂CoAl films (280 µΩcm). The order of magnitude of the CoFeCrAl resistivity is consistent with both SGS and dirty-metal resistivity, but the comparison of the two substrates suggests the CoFeCrAl film on Si substrate is highly disordered and falls into dirty-metal regime, as shown in Fig. 1.

Based on the above structural evidence, the films deposited on MgO are clearly the more ordered one, both chemically and from the viewpoint of crystalline texture. In Fig. 1, they are therefore on the left of the Si films and structurally closer to an ideal SGS. Concerning transport, experiment (Fig. 5) shows that the resistivity of CoFeCrAl on MgO is lower than that of CoFeCrAl on Si.

![FIG. 3. XRD pattern and Rietveld analysis of powder sample prepared by grinding the 1000-nm-thick film.](image-url)
FIG. 4. Pole-figure plots of CoFeCrAl deposited on MgO (001): (a) $\phi$ scan for (220) diffraction ($2\theta = 44.56^\circ$) and (b) $\phi$ scan for (111) diffraction ($2\theta = 26.9^\circ$).

FIG. 5. Temperature dependence of the longitudinal zero-field resistivity of CoFeCrAl on the two substrates.

terms of Fig. 1, the reduced resistivity is consistent with two scenarios, enclosed by the dashed box. While the film on Si lies on the dirty-metal branch of the curve, the MgO film may be dirty metal or an SGS.

Note that the resistivity of the film decreases almost linearly with increasing temperature, but the temperature coefficients of the resistivity are very small, $-0.12 \mu\Omega\text{cm}/\text{K}$ for epitaxial films (MgO) and $-0.19 \mu\Omega\text{cm}/\text{K}$ for polycrystalline films (Si). By comparison, the temperature coefficients in bulk CoFeCrAl$^{13}$ and bulk Mn$_2$COAl$^{14}$ are $-0.50 \mu\Omega\text{cm}/\text{K}$ and $-0.14 \mu\Omega\text{cm}/\text{K}$, respectively. The $\rho(T)$ curves measured in a magnetic field of 70 kOe for films grown on both types of substrates are
almost identical to those zero field $\rho(T)$ curves, which indicates very small longitudinal magnetoresistance, that is, $MR = (\rho_{xx}^T - \rho_{xx}^0) / \rho_{xx}^0 \times 100\% \leq 0.5\%$. This magnetoresistance is comparable to the magnetoresistance of 0.6\% in thin-film Mn$_2$CoAl$_3$ and to that of 1.5\% in CoFeCrAl.

IV. CONCLUSIONS

In summary, magnetron sputtering was used to deposit CoFeCrAl films onto MgO and Si. The films exhibit different degrees of structural order: the MgO substrate yields well-ordered epitaxial films, whereas the films deposited on Si are highly disordered and polycrystalline. The resistivity was measured as a function of temperature and the residual resistivity was analyzed as a function of disorder. The films on Si have the higher residual resistivity, which indicates dirty-metal behavior, whereas the behavior of the films on MgO is consistent with both dirty-metal and spin-gapless semiconducting behavior.

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