In order to characterize the interface/surface properties of polycrystalline Co$_2$MnSi Heusler alloy films, grain-size evolution with increasing annealing time has been investigated. Here, samples with nanometer-scale grains have been prepared by our specially-designed sputtering system in order to maximize the interface/surface area. Our well-controlled grains clearly show Si phase segregation. This Si phase becomes conductive near room temperature and may be responsible for the significant decrease in tunneling magnetoresistance previously reported by Wang et al., Appl. Phys. Lett. 93, 122506 (2008). © 2009 American Institute of Physics. [doi:10.1063/1.3276073]

Polycrystalline films were prepared using a HiTUS sputtering system to deposit with full control of the grain size. MgO (001) substrates were cleaned with acetone and intentionally maintained to be slightly lower than the stoichiometric value by $5 \times 10^{-5}$ Pa. The plasma was generated by an rf field at $3 \times 10^{-1}$ Pa Ar pressure and steered onto the target with a dc bias ($V_T$) ranging from $-250$ to $-990$ V, which controlled the deposition rate. This resulted in the change of the average grain size of as-deposited films. The smaller grains are expected to exhibit significant properties due to grain-boundary effects, while the larger ones exhibit properties closer to those of the bulk material. The Co$_2$MnSi films were grown at 573 K, and the film thickness maintained at 23 nm with a 2 nm thick Ru capping layer. The chemical compositions of the samples were estimated from energy dispersive x-ray spectroscopy (EDX). These films were systematically annealed at 760 K for 3 to 9 h. This is the maximum temperature we could achieve for annealing and is near the annealing temperature used in the earlier studies. After each annealing, magnetization curves were measured by using a PMC alternating gradient force magnetometer (AGFM) at RT. Grain size analysis was also carried out by transmission electron microscopy (TEM), and the crystal structures were characterized by grazing incidence X-ray diffraction (XRD).

The chemical composition of the Co$_2$MnSi Heusler alloy films were measured by EDX and the data is listed in Table I. The Co concentrations are found to decrease with increasing annealing temperature due to the saturation magnetization [empirically known to follow the Bloch formula $T^{3/2}$ (Ref. 4)]. This suggests that a small fraction of atomically disordered phases cannot be ignored in the spin-polarized electron transport at a finite temperature. The elimination of such disordered phases, especially near the barrier interface, should improve the TMR ratios further and should realize half-metallicity at RT. In this study we fabricated polycrystalline Co$_2$MnSi films with controlled grain sizes by sputtering in order to investigate the dependence of both the magnetic and structural properties on the annealing time. In particular, the surface/interface phase segregation has been studied.

### Table I. Chemical compositions of the films measured by EDX. Those for segregated phases are shown in parenthesis.

<table>
<thead>
<tr>
<th>Bias voltage [V]</th>
<th>Co [at. %]</th>
<th>Mn [at. %]</th>
<th>Si [at. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-250</td>
<td>67.48(21.03)</td>
<td>12.78(18.87)</td>
<td>19.74(60.10)</td>
</tr>
<tr>
<td>-500</td>
<td>60.19(51.36)</td>
<td>21.87(27.77)</td>
<td>17.94(20.87)</td>
</tr>
<tr>
<td>-750</td>
<td>51.39(28.27)</td>
<td>31.27(22.02)</td>
<td>17.35(49.71)</td>
</tr>
<tr>
<td>-990</td>
<td>49.39(34.96)</td>
<td>33.83(28.07)</td>
<td>16.79(36.97)</td>
</tr>
</tbody>
</table>

---

1. Electronic mail: ah566@ohm.york.ac.uk.
2. Present Address: Department of Physics, Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2AZ, England.
in these Si-poor matrices. The values are shown in parenthesis in Table I.

Figure 4(a) shows the magnetization curves of the Co2MnSi films at RT as a function of the annealing period. All the films exhibit almost no magnetic moment at RT before annealing, which agrees with the small initial grain sizes (<2 nm). The values of the saturation magnetization saturate after around 2 h annealing for the films grown at \( V_T = -250 \) and \(-750 \) V, which agrees with the above optimized annealing condition. For the two remaining films the saturation magnetization increases monotonically. The value of the saturation magnetization is almost saturated after 5 h annealing. For these samples, the measured magnetic moment per formula unit is less than 65% of the calculated...
value from a generalized Slater–Pauling curve \( \langle 5 \mu_B/\text{f.u.} \rangle \). \(^6\)

For the Co\(_2\)MnSi film with an average grain size of 18 nm, corresponding to the sample grown at \( V = -750 \) V, the volume of the bulk Co\(_2\)MnSi matrices is calculated to be 54% of the total volume. This corresponds to a three-monolayer-thick disordered surface or interface region as previously reported for epitaxial films. \(^7\) This is also consistent with data from X-ray magnetic circular dichroism studies in similar Co-based Heusler alloy films. \(^5,8\) In addition, for our sputtering system, the packing density of similar films has been measured to be approximately 90%. \(^9\) Therefore about 49% of the saturation magnetization is expected as compared with that of an epitaxial Co\(_2\)MnSi film. Because our Heusler alloy films are not fully \( L_2_1 \) ordered, an additional decrease in the saturation magnetization is also expected. This means that the samples with small grain sizes are dominated by surface/interface properties as compared with epitaxial films. It should be noted that the purpose of this study is not to maximize the saturation magnetization with the perfect \( L_2_1 \) structure but to maximize the area of the interface/surface of Co\(_2\)MnSi polycrystalline grains. Additionally, the coercivity \( H_C \), determined from the magnetization curves measured at RT [Fig. 4(b)], decreases with increasing target bias and hence increasing grain size. The film grown at \( V_T = -990 \) V shows a coercivity of 16 Oe, which is comparable with that for a highly ordered Co\(_2\)MnSi film. \(^10\) This provides further evidence that the bulk regions of the Co\(_2\)MnSi grains are highly ordered.

These results suggest that two types of behavior exist in the films. The films with smaller grains have their magnetic behavior dominated by the grain boundaries, while those with larger grains exhibit bulk properties. In particular the structural characterization by XRD shows significant Si phase segregation, which may be responsible for the decrease in the grain sizes after about 5 h annealing as observed from the TEM analysis. Since Si phase segregation was observed at the surface of all the Co\(_2\)MnSi films with Si-poor concentrations, this may also occur in epitaxial Heusler films with much larger grains. Here Si segregated nanoparticles at the Heusler/tunnel barrier interfaces become almost insulating at low temperature where very large TMR ratios are observed. Si normally behaves as a conductor at RT, and therefore opens additional transport paths for a spin-independent tunneling current across Heusler alloy/barrier interfaces. This results in a significant decrease in TMR ratios as observed for most epitaxial tunnel junctions with Co\(_2\)MnSi (Ref. 2) and Co\(_2\)Fe(Si,Al) (Ref. 3) Heusler alloy films. Si segregation can be avoided by intentionally reducing the Si concentrations in a few monolayers near the interfaces and surfaces in such Heusler alloy films. As theoretically predicted, the \( B_2 \) disordered structure does not disrupt the half-metallicity in some cases. \(^11\) Such an interfacial treatment may maintain the half-metallicity at RT resulting in significant TMR ratios at RT.

In summary, chemical composition analysis has shown that Si phase segregation occurs at the surface of Co\(_2\)MnSi sputtered films with nanometer-scale grains after annealing and occurs for all grain sizes. Based on our detailed analysis of the grain-sizes, the annealing condition is optimum at 760 K for 6 h. Even under this condition, segregated nanoparticles with Si concentrations up to 60% are observed by EDX. Such minor phase segregation is difficult to detect by macroscopic measurements such as magnetic studies and XRD as bulk effects dominate these measurements especially for the case of epitaxial films. Our findings provide a way to improve interface properties of Heusler alloy films to achieve the half-metallicity at RT.

The authors would like to thank Professor K. O’Grady of the University of York for the use of his facilities, fruitful discussions and proof-reading the manuscript.

---


