Improvement of structural, electronic, and magnetic properties of Co$_2$MnSi thin films by He$^+$-irradiation

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The influence of 30 keV He$^+$ ion irradiation on structural, electronic and magnetic properties of Co$_2$MnSi thin films with B2 order was investigated. It was found, that irradiation with light ions can improve the local chemical order. This provokes changes of the electronic structure and element-specific magnetization towards the bulk properties of the well-ordered Co$_2$MnSi Heusler compound with L2$_1$ structure.

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Half-metallic ferromagnetism, theoretically expected for the L2$_1$ ordered Co$_2$MnSi Heusler compound, in combination with a large band gap of 0.4 eV to 0.8 eV for the minority spin states and a high Curie temperature of 985 K makes this Heusler compound a very promising candidate for the modern field of spintronic devices. In recent years, great progress has been made in the fabrication of magnetic tunnel junctions (MTJ) with a single integrated Co$_2$MnSi electrode, and an exceptionally high TMR effect of 570% at 2 K has been reported for a MTJ structure with both electrodes consisting of Co$_2$MnSi. In the latter case, the spin polarization estimated by Julli`ere’s formula was reported to be 89% and 83% for the bottom and top electrode, respectively. At room temperature (RT), however, the TMR effect is largely reduced. Moreover, spin polarization, experimentally observed on single crystalline Co$_2$MnSi films at RT, remains with 12% far below the theoretically predicted 100%. Strongly supported by ab initio calculations, partial chemical disorder is assumed to be one of the possible reasons for this discrepancy.

Annealing at high temperatures, typically in the range of 400-500$^\circ$C, is a conventional way to reduce the chemical disorder in the deposited Co$_2$MnSi films. However, high temperature annealing often leads to interdiffusion and local changes of the stoichiometry in Heusler compounds. For FePt thin layers, however, it has been demonstrated that the degree of chemical order can be alternatively controlled by post-growth irradiation with He$^+$ ions. In both completely disordered and partially L1$_0$ ordered FePt films an enhancement of long range order was found after 130 keV He$^+$ ion irradiation at moderate processing temperatures. The post-growth irradiation process thus improves local order leaving the large-scale elemental distribution intact. Moreover, the initial crystallographic structure is maintained due to the absence of extended collision cascades. In view of the successful results for FePt and other binary systems, the question arises whether the light-ion irradiation technique is also applicable for the improvement of chemical order in Co$_2$MnSi, representing, as a ternary compound, a more complex system.

In this work, we investigate the effect of 30 keV He$^+$ ion irradiation on chemical order of Co$_2$MnSi thin films. The samples are exposed to different fluences of He$^+$ ions. The information about the ordering properties is obtained from X-ray diffraction (XRD), X-ray absorption and circular magnetic dichroism (XAS/XMCD), and photoemission spectroscopy at high energies (HAXPES).

A (001)-oriented Co$_2$MnSi layer of 30 nm thickness was grown on a Cr-buffered MgO(001) substrate by means of inductively coupled plasma (ICP) assisted magnetron sputtering. The chemical composition of the deposited film was nearly stoichiometric (Co: 48.9%; Mn: 24.7%; Si: 26.4%). Annealing at 350$^\circ$C followed the deposition of the Co$_2$MnSi layer. Subsequently, a 1.3 nm Al capping layer was deposited to prevent oxidation of the Co$_2$MnSi film. To ensure equal initial conditions for all irradiation experiments a single 1 in$^2$ Co$_2$MnSi sample was pre-
pared which was cut into 5×5 mm² pieces before carrying out the irradiation. The entire surface of the 5×5 mm² Co₂MnSi samples has been irradiated with 30 keV He⁺ ions at ambient temperature using a DANFYSIK low energy ion implanter. The ion fluence was varied between 10¹⁴ and 10¹⁶ ions/cm² using a beam current between 0.5 and 2.5 μA/cm².

XAS/XMCD measurements were performed at the beamline BL47XU of SPring-8 (Japan). The photon energy was fixed at 7.940 keV. The kinetic energy of the photoemitted electrons was analyzed by means of a hemispherical analyzer (Scienta R4000-12kV) with an overall energy resolution of 250 meV [10].

Results of XRD structural characterization of the as deposited Co₂MnSi film are shown in the insets of Fig. 1. The (220) equivalent reflections were observed with four-fold symmetry in the x-ray pole figure scan providing evidence of the epitaxial growth of the Co₂MnSi layer. The x-ray θ-2θ diffraction pattern exhibits clear (200) B2 superstructure reflections. Since no (111) reflections, indicative for the L₂₁ phase, were detected in the pole figure scan (not shown here), it is concluded that the fabricated film was predominantly of B2 order. The presence of a certain amount of A₂ type disorder cannot be excluded from these results.

After the ion bombardment, the (111) equivalent reflections are still absent in the pole figure scans while (220) pole figures remain similar to the one presented in the inset of Fig. 1. A detailed analysis of θ-2θ-scans recorded from irradiated samples reveals an increase of the ratio of (200) and (400) integrated intensities for the fluences of 1×10¹⁴ and 5×10¹⁴ ions/cm² (see Fig. 1). Comparing with simulated peak intensities this result clearly suggests a qualitative improvement of the B2 order in the irradiated Co₂MnSi films. A transition to the L₂₁ ordered phase, however, was not observed.

Figure 2 shows XAS data recorded at the Co L₂,₃ edge comparing irradiated and non-irradiated samples. A satellite peak appears at 3.8 eV above the Co L₃ absorption edge. This feature has been reported for thin Co₂MnSi films by different groups [5, 20, 21]. In particular, it has been demonstrated that the intensity of the satellite directly correlates with the degree of ordering inside the Co₂MnSi layer [20]. The intensity of the Co L₃ satellite is plotted in Fig. 2(b) as a function of ion fluence. One can clearly see that at fluences of 1×10¹⁴ and 5×10¹⁴ ions/cm² the intensity of the satellite peak in-
increases with respect to the case of the non-irradiated sample [see also inset in Fig. 2(a)]. This suggests, in good agreement with the results of XRD characterization, that in this particular range of applied fluences the local order in the bulk of Co$_2$MnSi films is increased after the irradiation. For higher fluences, however, the intensity of the satellite decreases indicating an increasing level of disorder introduced by the ion bombardment beyond $5 \times 10^{14}$ ions/cm$^2$.

We determined the element-specific magnetic moments per 3d-hole of the Co$_2$MnSi films exposed to different ion fluences. The corresponding values are shown in Fig. 3. The volume magnetic moments of both Co and Mn are in good agreement with values reported in Ref. [20] for the same kind of Co$_2$MnSi samples. As a result of ion irradiation we observe an increase of the spin magnetic moments on both Co and Mn atoms up to a fluence of $5 \times 10^{14}$ ions/cm$^2$ and a subsequent decrease for higher fluences (Fig. 3(b)). This is again a strong hint of the improvement of chemical order inside the Co$_2$MnSi layer introduced by the irradiation with He$^+$ ions. The ratio of orbital and spin magnetic moments (Fig. 3(c)) shows for Co a pronounced peak at a fluence of $1 \times 10^{15}$ ions/cm$^2$ indicating a reduction of symmetry. At the Mn site the effect is less pronounced.

Assuming the number of 3d-holes for Co and Mn to be 2.4 and 4.5 per atom [2], respectively, and taking into account an additional correction factor of 1.5 for the number of Mn 3d-holes [22], which is necessary due to the mixing of two Mn $j$ levels, the saturation magnetization of the investigated Co$_2$MnSi films is calculated. The corresponding values are presented in Fig. 3(a). The saturation magnetization increases up to a fluence of $1 \times 10^{15}$ ions/cm$^2$ reaching the value of $5 \mu_B$/f.u. theoretically predicted for the well-ordered Co$_2$MnSi bulk and decreases for fluences beyond $1 \times 10^{15}$ ions/cm$^2$. This behavior is confirmed by the results of SQUID measurements (not shown here) and provides a further hint for the improvement of chemical order provoked inside the Co$_2$MnSi layer by the irradiation with He$^+$ ions.

The HAXPES valence band spectra are shown in Fig. 4 comparing the non-irradiated film and the bulk reference sample with the sample irradiated with the optimum fluence of $5 \times 10^{14}$ ions/cm$^2$. The inelastic mean free path of the 8 keV electrons is expected to be about 13 nm in AlO$_x$ and 8 nm in Co$_2$MnSi [28]. This allows for an investigation of the bulk electronic properties of Co$_2$MnSi films below the capping layer [28].

The valence band spectrum of the non-irradiated film has a wide maximum in the energy range from about 7 eV to 0 eV without distinct features. In particular, the pronounced peak of the $d$-states - being well resolved in the valence spectrum of the bulk sample - is largely smeared out. This broadening points to a high disorder in the sample. After irradiation, the valence band spectrum of the thin film resembles much closer that of the bulk material, in particular close to the Fermi energy. The peak at about 1.3 eV is due to emission from flat $d$-bands that belong to minority $t_{2g}$ states localized in the Co planes as well as highly localized Mn $d$-majority $e_g$ states [18, 24].
The similarity of the electronic structure of the irradiated sample and the bulk sample provides clear evidence on the structural improvement of the Co$_2$MnSi film after irradiation.

In conclusion, motivated by a successful application of light-ion irradiation for the improvement of chemical order in thin FePt layers, the effect of a 30 keV He$^+$ ion bombardment on structural, electronic and magnetic properties of Co$_2$MnSi thin films was investigated. The results of XRD, XMCD and HAXPES investigations demonstrate that the light-ion irradiation technique has the potential to invoke local chemical order in Co$_2$MnSi Heusler films without the need of high-temperature annealing. The presence of local chemical order in Heusler compounds is absolutely crucial for the appearance of half-metallic ferromagnetism and the desired complete spin-polarization of conduction electrons. The standard procedure of high-temperature annealing close to the melting point needed to invoke the chemical order, that is applied to bulk materials, is inhibited for the preparation of thin film multilayer structures because the interdiffusion of different layers will destroy the stoichiometric composition. Light-ion irradiation provides a formidable method to overcome this problem. Future studies will show whether a combination of mild annealing and irradiation further improves the local order. Our results also implicate that light-ion irradiation can improve local chemical order in other ordered compounds that are related to the Co$_2$MnSi Heusler compound, i.e. in other half-metallic Co$_2$YZ (Y=3d metal, Z=main group element) Heusler compounds and in Ni$_2$MnGa shape memory compounds.

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