Characterization of Thin Film CuCr$_2$Se$_4$ Synthesized by A Modulated Elemental Reactant Deposition

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For several decades, spinel-structured compounds of chemical formula MCr$_2$Se$_4$ (M = first row transition metal) have been of interest for their exceptional intrinsic magnetic properties [1-3]. As opposed to the traditional ferrite spinels, which tend towards ferrimagnetism, these materials typically demonstrate ferromagnetism in addition to magneto-optical and ferroelectric behaviors. An example of particular interest is the compound CuCr$_2$Se$_4$, both because of its high Curie temperature and for the changes in magnetization the material undergoes during electromagnetic stimulation. Studies have also suggested that the magnetic properties of these materials are affected by the bulk morphology of the material, with the Curie temperature for nanocrystalline materials differing from those of polycrystalline and thin film materials [3,4]. This work details the XRD, EPMA, and TEM characterization of a CuCr$_2$Se$_4$ thin film synthesized using a novel single step synthetic method, elucidating a number of previously unexplained aspects of CuCr$_2$Se$_4$ thin films.

Thin films were deposited by evaporating elemental Cu, Cr, and Se in stoichiometric proportion on wafers of {001} silicon. Films were annealed at 600°C for 1 hour in a nitrogen atmosphere. Samples were initially analyzed using X-ray reflectivity and diffraction. Samples were then cross sectioned and prepared for TEM analysis using the small angle cleavage technique (SACT) [5]. High-resolution (HR) TEM imaging was performed at 300 kV operating voltage with a Philips CM300FEG TEM (C$_s$ = 1.2 mm) using a 10.8 mrad objective aperture semi-angle. Thin-film composition was measured by electron microprobe analysis (EPMA) using a Cameca SX-100 microprobe running Probe for Windows and StrataGem data postprocessing.

The films were found by X-ray diffraction analysis to be single phase and highly textured, as shown in Figure 1. Rocking curves suggest that the film has a preferred growth orientation with the <111> planes parallel to the substrate. EPMA analysis verified the composition of CuCr$_2$Se$_4$, as shown in Table 1. HRTEM analysis yielded a lattice image consistent with the spinel structure as shown in Figure 2.

References
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FIG. 1. X-ray diffraction pattern for the thin film CuCr$_2$Se$_4$ showing an absence of all reflections except the 222 and 444, suggesting a highly textured film.

FIG. 2. HRTEM micrograph and (inset) optical diffractogram of the CuCr$_2$Se$_4$ thin film viewed along the [110] zone axis.

TABLE 1. EPMA data for CuCr$_2$Se$_4$ annealed at 600°C for 1 hour.

<table>
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<tr>
<th>Annealing</th>
<th>Cu</th>
<th>Cr</th>
<th>Se</th>
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<tbody>
<tr>
<td>wt%</td>
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<td>21.1</td>
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