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Investigations of the crystallization mechanism of CrSb and $CrSb_2$ multilayered films using *in-situ* X-ray diffraction and *in-situ* X-ray reflectometry

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ABSTRACT

Chromium and antimony multilayered films with variable elemental layer thickness were deposited on (1 0 0)-Si substrate cooled with liquid nitrogen. The stoichiometry of the films was adjusted to Cr:Sb=1:1 and 1:2. The *thickness* of Cr–Sb repeating units of these multifilms was varied between 11.4 and 102.5 Å. Satellite maxima in the X-ray reflectivity curves observed for films in the *as-deposited* state demonstrate an alternating stacking of the evaporated elements. The reactivity of the superlattice reactants was investigated with temperature dependent *in-situ* X-ray diffractometry and X-ray reflectometry. The crystallization temperature of CrSb depends on the double-layer thickness and is about 90 °C for a Cr:Sb ratio of 1:1 and double-layer thickness of 53.7 Å where nucleation and crystal formation occurs at the element interfaces, while for a thin double-layer thickness (11.4 Å) first interdiffusion of the elements occurs before crystallization starts, i.e., an amorphous intermediate is formed prior to crystallization of CrSb. A decomposition reaction into $CrSb_2$ occurs at about 230 °C, and up to about 575 °C, CrSb, $CrSb_2$ and amorphous Cr coexist. For the ratio Cr:Sb=1:2 and a thin double-layer thickness prior to crystallization of $CrSb_2$ nano-sized crystallites with a composition near $CrSb_2$ nucleate and grow. These crystallites are then successively transformed in long-range ordered crystals exhibiting a pronounced preferred orientation. For films with a thicker repeat unit first formation of CrSb is observed which then reacts with elemental Sb yielding crystalline $CrSb_2$. An activation energy for interdiffusion of Cr and Sb of about 1.8 eV is estimated for a film with Cr:Sb=1:1 exhibiting a double-layer thickness of about 53.7 Å and an energy for crystal growth of about 1.1 eV. For the film with the thinner double-layer thickness of 11.4 Å a lower value of the activation energy for interdiffusion is obtained. For $CrSb_2$ the energy for crystal growth is about 3.0 eV being significantly larger than for CrSb. Specific resistivity and Hall coefficient measurements were performed for crystalline CrSb and $CrSb_2$ films. The temperature-dependent resistivity measurement exhibits a metallic behavior for CrSb and semi-conducting properties for $CrSb_2$.

1. Introduction

In the Cr–Sb system only two thermodynamically stable compounds are known: hexagonal NiAs type CrSb (space group: $P6_3/mmc$) and orthorhombic marcasite type $CrSb_2$ (space group: *Pnnm*) [1–10]. CrSb is metallic [11–13] and shows antiferromagnetism with a Néel temperature around 450 °C [2,13–21]. Investigations were focused on the variation of the unit cell dimensions with temperature [6,20] or composition and homogeneity range of CrSb [22]. A structural phase transition from NiAs type to MnP type is observed above 17 GPa [23–25].

Multilayered CrSb films were prepared by evaporation of elemental Cr and Sb, and epitaxial growth was observed for a substrate temperature $T_{sub} \geq 90$ °C [26–28]. CrSb monolayers were deposited and were separated from each other by a [0 0 1]-oriented Sb buffer layer in order to decouple the anti-ferromagnetically orientated sheets to generate ferromagnetic properties. A variation of the paramagnetic Curie temperature was reported for different numbers of adjacent monolayers between the crystalline Sb buffers [27–29]. The magnetization of the CrSb monolayers is reported to be about 0.2 μB per Cr atom at 1.7 K [30].

Due to half-metallic ferromagnetic properties metastable zincblende type CrSb was investigated intensively. This phase is obtained by epitaxial growth of Cr and Sb on substrates like GaAs [31–34], (1 0 0)-NaCl [35] or (1 0 0)-KCl [36,37]. The experiments

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show ferromagnetism at room-temperature and a magnetic moment per Cr atom between 3 and 5 μ_B [33,35] which was supported by theoretical calculations [21,38].

The second thermodynamically stable compound is $CrSb_2$ [1,2,39]. The magnetic, electrical and thermoelectric properties are only known for bulk material. Magnetic measurements show an antiferromagnetic behavior with $T_N \approx 273$ K [40–44] and a magnetic moment of 1.94 μ_B/Cr [43]. $CrSb_2$ is a semi-conductor with a specific feature at the Néel temperature and another unusual behavior between 50 and 80 K due to an electronic change of the spin system [9,44–47]. The activation energy E_a for different temperature ranges are, e.g., 32.6 meV (276–310 K), 35.7 meV (60–276 K), 4.6 meV (12–60 K), and 0.9 meV (7–12 K) [45,48]. At room temperature the value for the Hall effect R_H suggests n-type behavior [48–50], while in one study a change of the dominating charge carrier type from n-type to p-type was observed at about 200 K [9]. A polymorphic form with the $CuAl_2$-type structure (space group: $I4/mcm$) was observed above 5.5 GPa [51–53].

In general, the formation of crystalline solids is not well understood and for a more directed synthesis and reaction planning the fundamental reaction steps must be investigated and evaluated [54]. To study the formation of crystalline solids X-ray based *in-situ* techniques are appropriate because formation of crystalline precursors or intermediates, phase transitions and transformations can be easily monitored on an appropriate time scale. A promising approach to investigate the formation of crystalline solids is based on thin film couples. The advantages of this approach were demonstrated in the past [55–77]. Several compounds reported in this context are thermodynamically not stable and can only be prepared using the thin film approach. The purpose of the present investigation is to study the formation mechanisms of CrSb and $CrSb_2$ prepared as multilayered Cr–Sb films using *in-situ* X-ray scattering techniques. Samples were prepared by layer-by-layer deposition in order to start experiments in the amorphous state and to follow the crystallization up to elevated temperatures. The crystalline films were further characterized by measuring the specific resistivity, Hall coefficient and charge carrier mobility/density.

2. Experimental details

Multilayered films of CrSb and $CrSb_2$ were deposited by thermal evaporation of single elements (Chromium: ChemPur 99.98% and Antimony: Aldrich 99.999%) in an ultra high vacuum chamber from Omicron NanoTechnology (Taunusstein, Germany) with a base pressure of $p < 1 \times 10^{-8}$ mbar on 2×2 cm (1 0 0)-Si single crystal substrates. The single layer thickness was adjusted by the shutter opening times of each evaporation cell, while Cr was heated at 1350 °C and Sb at 370 °C. The evaporation rate was determined by a quartz monitor before and after deposition and nitrogen cooling was applied to the substrate during deposition. The multilayered films consist of 20, 25 and 135 Cr–Sb double-layers with a repeating unit ranging from 11.4 to 102.5 Å and a total film thickness up to 256 nm which was determined by X-ray reflectivity (XRR) measurements of *as-deposited* films and compared with a simulation of the measured data assuming the following structure: [Si/native SiO_x/$(Cr/Sb)_m$] with $m=25$ and 135 for CrSb, and $m=20$ and 25 for $CrSb_2$ (X'Pert Reflectivity program). The chemical composition of the films was determined in a scanning electron microscope (SEM, Philips ESEM XL30 instrument) by energy dispersive X-ray spectroscopy (EDX, EDAX detector, Oxford Instruments). The acceleration voltage was set to 15 keV in order to penetrate the thin film and keep the substrate signal as low as possible. The Cr–K and Sb–L signals do not overlap neither with each other nor with the Si–K emission and were used to determine the Cr and Sb contents. The average composition was calculated using data of five measurements across each sample yielding an estimated error of about ± 2.5 at% (Table 1).

Investigation of the samples in the *as-deposited* state and crystallization of the films during heating was done by *in-situ* X-ray diffractometry (XRD) and *in-situ* XRR (instrument: PANalytical X'Pert Pro diffractometer, Cu K_α radiation, Göbel mirror at the incident beam, PIXel detector, step size=0.1° for XRD patterns). All *in-situ* measurements were carried out in a high temperature chamber (HTC, Anton Paar HTK 1200N) under Helium atmosphere. The temperature was increased in steps of 2, 5 and 25 °C, respectively, with a heating rate of 2 °C/min and held at constant temperature during the measurement.

Rietveld refinements were performed using the fundamental approach implemented in the TOPAS Academic software [78]. Refined parameters: zero point, scale factors for each phase, lattice parameters of each phase, size broadening, and background. CrSb: all atoms on special positions; $CrSb_2$: Cr on special position, Sb on site 4g with coordinates x, y, 0. The x and y coordinates were fixed during Rietveld refinements.

Temperature-dependent measurements of specific resistivity and Hall effect of CrSb and $CrSb_2$ films were performed by the van der Pauw Method [79–82] using a physical property measurement system (PPMS, Quantum Design). Copper wires with a diameter of 50 μm were connected with conductive silver onto the corners of the films. The measurements were done from 310 to 2 K and back to 310 K applying a current of 5.0 μA. The magnetic field applied perpendicular to the film surface was set to 5.0 T and kept constant for each cycle. In order to estimate the contribution of the (1 0 0)-Si substrate to the electrical data of the films the resistivity of the substrate was also measured yielding a value being 5 orders of magnitude larger than of the crystalline films. Hence, the influence of the substrate is negligible.

3. Results and discussion

Before the results of the *in-situ* experiments are discussed the crystal structures of CrSb and $CrSb_2$ should be briefly mentioned (Fig. 1). In the structure of CrSb, Cr is surrounded by 6 Sb atoms in an octahedral environment and Sb is in trigonal-prismatic coordination of six Cr atoms. Along the c-axis, $CrSb_6$ octahedra share common faces and in the a–b-plane common edges. In $CrSb_2$ the Cr atom is also in an octahedral environment which is more distorted than in CrSb due to the presence of Sb_2 dumbbells. The $CrSb_6$ octahedra share common edges along [0 0 1] and in the other directions they are corner-linked.

The results presented here were obtained on several multilayered films with Cr–Sb double-layers as repeating unit, different

Table 1
Characteristics of the multilayered films with Cr:Sb ratios of 1:1 and 1:2. Deviations of the composition and the double-layer thickness were estimated on the basis of the EDX data and the XRR curves. The thicknesses of the films were measured after deposition and before separating into four equal pieces.

Sample	Cr [at%]	Repeats	Cr/Sb layer thickness [Å]	Total thickness [Å]
21St1	50(5)	25	16.2/37.5(2)	1343(5)
21St2	54(5)	25		
21St3	53(5)	25		
33St2	53(5)	135	4.5/6.9(2)	1539(5)
25St1	33(5)	20	13.2/53.3(2)	1330(5)
25St2	35(5)	20		
25St3	35(5)	20		
20St4	33(5)	25	21.1/81.4(2)	2563(5)