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Zinc-blende ferromagnetic CrSb film on KCl (100) substrates

Shandong Li^{a,*}, Zongjun Tian^b, Jianglin Fang^c, Jenq-Gong Duh^d, Kai-Xin Liu^d, Zhigao Huang^a, Yinhui Huang^b, Youwei Du^e

^a Department of Physics, Fujian Normal University, Fuzhou 350007, China

^b College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

^c Centre for Materials Analysis, Nanjing University, Nanjing 210093, China

^d Department of Materials Science and Engineering, National Tsing Hua Universtiy, Hsinchu, Taiwan

^e National Laboratory of Solid State Microstructure, Nanjing University, Nanjing 210093, China

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1. Introduction

In the last two decades, spintronics has become one of fast developing research branches. Spintronic devices, originating from the discovery of giant magnetoresistance in 1988 and the subsequent development of spin valve, tunneling magnetoresistance, as well as spin injection into metals, can be understood by assuming that any current of spins is carried by two 'types' of carriers, i.e. spin-up and spin-down [1–11]. The rapid advancement of magnetoelectronics and spintronics in recent years has given a strong boost in the search for novel half-metallic ferromagnets. These are spin polarized materials, which exhibit the property of having a metallic density of electron states for the one spin direction (usually majority spin), while there is a band gap around the Fermi level, E_F , for the states of the opposite spin. This half-metallic property (the name coined by de Groot and collaborators makes the one

ABSTRACT

CrSb film was deposited on KCl (100) substrates by magnetron sputtering. Strong ferromagnetism was observed in the CrSb film, which can be attributed to the CrSb phase with ferromagnetic zinc-blended structure. The investigated ZB-CrSb film about 5 nm in thickness is sufficiently thicker to be investigated the half-metallic nature of ZB-CrSb and to be practically applied in spintronics devices.

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spin channel conducting, while the other is insulating (or semiconducting) [12], so that, in the ideal case, half-metals can conduct a current which is 100% spin polarized.

In 2000, Akinaga and collaborators reported growth of a few monolayers of ferromagentic CrAs in the metastable ZB phase with magnetic moment 3 $\mu_{\rm B}/f.u.$ and Cuire temperature higher than 400 K for the first time [13]. This findings initiated a strong activity, because several merits were derived: the half-metallic property, coherent growth on a semiconductor, and T_c higher than room temperature. The activity was extended beyond ZB-CrAs, encompassing a variety of tetrahedrally bonded transition metal compounds (TBTMC) with sp atoms of the IV, V and VI groups of the periodic table. However, ZB-TBTMC phases are substantially higher in total energy than the corresponding ground state phases. Thus, it is difficult to fabricate ZB-structured thick films. Although the ferromagnetic ZB-TBTMC mono- or multilaver films have been successfully grown on GaAs, AlGaSb, and GaSb substrates by MBE, the thickness of only few molecular layers was achieved, which is too thin to be used in practice [14-18]. Thus, it is desirable to fabricate thicker and stable ZB-TBTMC films for the application and understanding their half-metallic nature. The effort to fabricate the



^{*} Corresponding author. Fax: +86 591 83486160. E-mail address: dylsd007@yahoo.com.cn (S. Li).

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thicker ZB–TBTMC films has been carried out. Recently, Deng et al. enhanced the thickness of ZB-CrSb films from 1 to 9 monolayer (ML) (\sim 3 nm) by MBE using (In, Ga)As buffer layers [17]. Moreover, nanodots and ultrathin multilayer ZB–TBTMCs have been achieved experimentally by molecular beam epitaxy (MBE) growth on III–V semiconductors [19–23]. In our previous work, nanocrystalline ferromagnetic ZB-CrSb particles was prepared by pulse laser deposition and rapidly annealing [24]. In this paper, KCI (100) substrates were used to deposit the CrSb thick film, and a room-temperature ferromagnetic CrSb film with ZB structure was obtained by magnetron sputtering.

2. Experiment

KCl (100) substrates were cleaved from a single crystal KCl bar. The cleaved substrates were immediately put into the vacuum chamber. The fresh KCl surface with roughness in the atomic scale was used as the film growth plane. CrSb films were co-deposited at 250 °C for 60 s under powers of 20 W for Cr target and 10 W for Sb. The base pressure was less than 1.0×10^{-5} Pa, and the working pressure was 0.5 Pa at Ar floating rate of 20 sccm. The nominal thickness of the CrSb films was 5.0 nm, deduced from deposition rate of 5 nm/min.

The magnetic properties of the films were measured by a superconducting quantum interference device (SQUID) magnetometer from 5 to 350 K and a paramagnetic resonance (PMR) spectrometer at room temperature. The microstructure and composition of the films were characterized by high resolution transmission electron microscope (HRTEM), atomic force microscope (AFM) and field emission electron probe microanalyzer (FE–EPMA).

3. Results and discussion

The hysteresis loops at various temperatures and the M-T curve for a 5 mm × 5 mm sample with the film plane along the magnetic field direction were measured by SQUID. Fig. 1 shows the magnetic properties of CrSb films. The diamagnetic contribution of KCl was subtracted from the total hysteresis loops. As illustrated in Fig. 1(a), the CrSb film exhibits strong ferromagnetic properties with saturation magnetization (M_S) up to 530 emu/cm³ at 5 K. Even at 300 K, M_S is as high as 410 emu/cm³. Fig. 1(b) reveals that the strong ferromagnetic property of the films maintains over room temperature. These facts demonstrate that a strong room-temperature ferromagnetic property is achieved for the CrSb film deposited on KCl (100) substrates.

The PMR of the CrSb film with dimension of 4 mm × 8 mm was measured using X-band microwave frequency of 9.7 GHz in the magnetic field ranges from 0 to 10 kOe. The angles (θ) between magnetic field direction and film normal direction are varied from 0 to 90°. Fig. 2 shows the strongest PMR spectrum including the ferromagnetic resonance (FMR) peaks with $\theta = 0^\circ$. As illustrated, a broad FMR peak at 2239 Oe with resonance linewidth of 164 Oe was observed, which can be attributed to the ferromagnetic CrSb film. The PMR spectrum of CrSb film verifies the room-temperature ferromagnetic property of CrSb, which agrees with the SQUID results.

To investigate the origin of ferromagnetism in CrSb films, line scanning by FE–EPMA was carried out for each sample to detect the composition distribution in the film. Each sample was scanned with at least two trace lines. FE–EPMA results, listed in Table 1, reveal that the atomic ratio of Cr and Sb is very close to 1:1, suggesting the composition of the films is CrSb. The surface of KCl substrates and deposited films were scanned by AFM. A very smooth surface with average roughness less than 0.6 nm was present in the substrates and films, and no aggregated particle was observed.



Fig. 1. (a) The hysteresis loops of the CrSb film at 5 and 300 K, respectively; (b) the M-T cure of the film from 5 to 350 K in the magnetic field of 2 kOe.



Fig. 2. The differential PMR spectrum of CrSb film at $\theta = 0^{\circ}$.

Table 1

Compositions of the CrSb film at various test positions.

Position number	Composition (at.%)	
	Cr	Sb
1	49.84	50.16
2	49.79	50.21
3	50.32	49.68
4	50.07	49.93
5	49.99	50.01
6	49.68	50.32
7	51.06	48.94
8	50.22	49.78
9	50.03	49.97
10	49.65	50.35

Fig. 3 shows HRTEM image and electron diffraction spectra (EDS) of the CrSb film. It can be seen that the CrSb film is composed



Fig. 3. The HRTEM image and EDS (insert) of the CrSb film.

of nanocrystallites with a crystal size about 10 nm. From the EDS circles, the *d*-spacings of 2.09 and 1.48 Å are calculated, which may be assigned to the zinc-blende CrSb (220) and (400), respectively. Although there are no ZB-CrSb X-ray diffraction (XRD) JCPDS cards at this moment, XRD pattern can be calculated based on the ZB structure. According to the report by Galanakis et al. [15], the lattice constant of ZB-CrSb is 5.92 Å, thus, the *d*-spacings of ZB-CrSb (220) and (400) should be at 2.093 and 1.480 Å, respectively, which are well consistent with the EDS result. On the other hand, no *d*-spacings of KCl and other Cr–Sb compounds, such as, hexagonal NiAs-type CrSb (NA-CrSb), CrSb₂, Cr_{0.1}Sb_{0.9}, etc., are near these two values. Based on the analysis above, two circles can be assigned as (220) and (400) of ZB-CrSb, respectively. The HRTEM and EDS results reveal that a pure ZB-CrSb phase was formed in the CrSb film deposited on KCl substrates.

ZB-CrSb is a robust ferromagnetic half-metal in theory [25,26]. The microstructure analysis above demonstrates that the strong ferromagnetic properties of CrSb film are attributed to the ZB-CrSb. The real M_S of ZB-CrSb is not reported up to now. However, the strong ferromagnetic coupling in ZB-CrSb with 3 μ_B per formula unit was predicted by theoretical calculation [25,26]. With the lattice constant of a = 5.92 Å for ZB-CrSb, the theoretical M_s of ZB-CrSb is estimated as 536 emu/cm³, analogy to the calculation method reported by Akinaga et al. [13]. If taking the M_S at 5 K as the saturation magnetization of ferromagnetic CrSb, the film thickness of ZB-CrSb phase of about 5 nm is relatively thicker compared with the ones reported up to now.

As for the formation of relatively thicker ZB-CrSb films, it can be attributed to the good lattice matching between KCl and ZB-CrSb. If using a good lattice matching buffer layer, e.g. (In, Ga) as a buffer layer, the critical thickness of ZB-CrSb can be increased from 1 to 3 nm [16,17]. For the films grown on a GaAs substrate, the critical thickness of ZB-CrAs thicker than that of ZB-CrSb can also be attributed to that the lattice mismatch between ZB-CrAs and GaAs is smaller than that between ZB-CrSb and GaAs [13,17,27]. The KCl substrate has (h00) a cleavage face with surface plainness in an atomic scale, which is especially suitable for the epitaxial growth of materials with a face-centered cubic structure. A small lattice mismatch of 0.05 between KCl substrate (a = 6.260 Å) and ZB-CrSb (a = 5.92 Å) is estimated in ZB-CrSb/KCl (100) systems. This favorable lattice matching gives rise to a relatively thicker film thickness of ZB-CrSb on the KCl (100) substrates.

4. Conculsions

Room temperature ferromagnetism in CrSb film is attributed to the ferromagnetic ZB-CrSb. Relatively thicker ZB-CrSb films with a critical thickness of about 5 nm were achieved by deposition on the KCl (100) substrates.

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