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Mapping the surface reconstructions of MnSb(0001) and $(1\bar{1}01)$

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Abstract

The surface reconstruction periodicities of epitaxially grown MnSb (0001) and $(1\bar{1}01)$ have been determined under a range of beam fluxes and substrate temperatures using reflection high energy electron diffraction. A number of previously unreported surface reconstructions were observed. On MnSb(0001), reconstructions ordered from Mn rich to Sb rich are: $(2\sqrt{3}\times 2\sqrt{3})$R30°, (2×2), (1×1) and triple domain (1×4). For MnSb$(1\bar{1}01)$, distorted (4×2) and simple (1×2) surface symmetries occur. The common (0001) surface reconstructions of MnAs and MnSb are briefly reviewed and discussed.

Keywords: Reflection high energy electron diffraction (RHEED); Scanning tunnelling microscopy; Gallium arsenide; Single crystal epitaxy; Magnetic films; Metal–semiconductor magnetic hetero-structures; Single crystal surfaces

1. Introduction

In recent years, MnSb and MnAs have attracted a great deal of attention as potential materials for epitaxial hybrid spintronic devices, where, for example, ferromagnetic materials are used to inject spin polarised currents into conventional non-magnetic semiconductors. Both MnAs and MnSb exhibit room temperature ferromagnetism ($T_C^{MnSb} = 587$ K, $T_C^{MnAs} = 318$ K) and have the NiAs crystal structure, which consists of alternating Mn and Sb(As) hexagonal close packed layers with stacking order ABAC. They can readily be grown by molecular beam epitaxy (MBE) on III–V semiconductor substrates [1–9]. For the purpose of spin injection, the spin-dependent electronic structure of the interface between the injection material and the semiconductor is of profound importance [10,11]. Even for crystallographically perfect interfaces with a favourable Schottky barrier height, localised minority spin states could strongly affect spin transport, and so the detailed atomic structure of the interface must be known. For example, several surfaces and *ideal* interfaces of the related half-metallic material NiMnSb have been shown theoretically to lose half-metallicity due to the development of minority spin states which cross the Fermi level [12–14]. *Real* interfaces would normally be produced by film growth using MBE on III–V semiconductor substrates, during which a pronounced surface reconstruction is often present. This means that ideal interfaces are unlikely to be formed and the structure of the real interface depends in detail on the substrate surface structure. 'Inverse' interfaces may also be required, either to optimise the atomic structure of the interface for spin injection or for some advanced spintronic device designs, and so the surface reconstruction of the epitaxial ferromagnet is also important. There have only been a few reports of the reconstructions on the MnSb(0001), MnAs(0001) and MnAs$(1\bar{1}00)$ surfaces, the results of which are summarised in Table 1. In this paper we report several new surface reconstructions of the MnSb(0001) and MnSb$(1\bar{1}01)$ crystal faces. We also briefly review and discuss the surface crystallography and reconstruction of the (0001) surfaces of MnSb and MnAs in general terms, particularly with reference to the III–V-like structures proposed to date.

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Table 1
Epitaxial growth orientations for MnSb and MnAs on GaAs, and surface reconstructions reported in the literature

	Substrate	Reconstructions	References
MnSb(1$\bar{1}$01)	GaAs(001)	$(1\times2)^*$	
		dis$(4\times2)^*$	
MnSb(0001)	GaAs(111)B	$(2\sqrt{3}\times2\sqrt{3})$R30°*	
		(2×2)	[1,6]
		(1×1)	[15]
		td$(1\times4)^*$	
MnAs(1$\bar{1}$01)	GaAs(001)	–	[1]
MnAs(1$\bar{1}$00)	GaAs(001)	(1×2)	
		(1×1)	
		(2×1)	
		(4×1)	[2–5]
MnAs(0001)	GaAs(111)B	(2×2)	
		td(1×3)	[7,8]

Reconstructions labelled with an asterisk are new and reported in this paper.

2. Experimental details

This work was carried out in a compact MBE chamber which contains shuttered Mn and Sb effusion cells (the latter having no thermal cracking stage), a retractable beam flux ionization gauge and an electron gun and phosphor screen for reflection high energy electron diffraction (RHEED). In an adjoining chamber is an ion gun for surface preparation and a fast sample entry system, plus a scanning tunnelling microscope (Omicron STM-1 with electronics and software from Nanograph Systems, UK). The MBE sample heater is calibrated to the melting points of In and InSb and uses two thermocouples to measure the temperature. Samples are mounted on stainless steel sample plates using In solder.

MnSb(0001) and (1$\bar{1}$01) over-layers were grown by molecular beam epitaxy on GaAs(111)B and (001) substrates (Wafer Technology Ltd., UK) respectively. Substrates were prepared ex situ by rinsing in acetone, propanol and de-ionized water to remove dust and debris. The samples were then blown dry with nitrogen and placed in the fast entry chamber. Once inside the MBE system, the samples were cleaned by annealing at 400 °C for 1 h, followed by argon ion bombarding at grazing incidence for 10 min and finally annealed at 475 °C for a further 30 min.

MnSb over-layers of thickness ~200 nm were grown at 425 °C, under Sb and Mn fluxes with directly measured beam equivalent pressures of 8×10^{-7} mbar and 1×10^{-7} mbar, respectively. The growth rate under these conditions (determined directly by epilayer thickness measurements) was 6 nm min^{-1}. Following growth, the samples were annealed at the growth temperature for several hours. The combined background pressure of Mn, Sb and residual gases in the MBE chamber during annealing with the effusion cells at standby temperature was better than 1×10^{-9} mbar. Apart from the very first stages of epitaxy, where spotty RHEED patterns appeared, sharp diffraction streaks were observed throughout the growth.

3. Epitaxial growth and orientation

The growth orientations of MnSb under these growth conditions were determined by RHEED integer order steak spacing measurements to be MnSb(0001) on GaAs(111)B, and MnSb(1$\bar{1}$01) on GaAs(001). The initial stage of growth of MnSb(0001) was monitored by scanning tunnelling microscopy (STM) and careful measurements of the spacing of RHEED features, and found to proceed by nucleation and then coalescence of strain-relaxed, flat-topped 3 D islands. After deposition of an epilayer thickness of around 10 nm, the islands have coalesced and the surfaces consist of large (>100 nm) atomically flat terraces, separated predominantly by monolayer (c/2) and bilayer (c) steps and step bunches. Sometimes incomplete layer coverage is observed, with smooth areas of MnSb several microns across separated by trenches. The identity of the epilayer as ferromagnetic MnSb was confirmed by X-ray diffraction and magnetic measurements, which indicated a magnetic moment of $3.5\mu_B$ per Mn atom and Curie temperature in excess of 400 K. The growth conditions used are reasonably optimal with respect to the surface morphology: in particular, significant deviation in the Sb to Mn flux ratio results in the development of large scale surface roughness or severely incomplete layer growth.

The MnSb(0001) and (1$\bar{1}$01) crystal orientations are illustrated in Fig. 1. Assuming an ideal bulk termination, both surfaces have four possible structures, two terminated by Mn atoms and two by Sb. For (0001) all four surfaces are simple, being just the ABAC-ordered close packed layers of the bulk. Each has a hexagonal primitive unit mesh with three dangling bonds per atom whose directions vary. By contrast, all four terminations of the MnSb(1$\bar{1}$01) surface are oblique, highly corrugated and have many distinct dangling bond directions. The terminations labelled Mn2 and Sb2 appear less favourable as a result of their higher dangling bond densities (7 rather than 5 dangling bonds per primitive mesh), although the complex nature of this surface implies that strong deviations from the ideally bulk terminated structure are likely.

4. MnSb(0001) surfaces

Surface reconstructions on the MnSb(0001) surface have been described using the Wood notation [16]. An $(n\times m)$Rθ reconstruction denotes a reconstructed unit mesh of $n\times$ in [2$\bar{1}\bar{1}$0] and $m\times$ in [11$\bar{2}$0] directions, and rotated by an angle θ. This follows the convention for III–V (111) surface reconstructions. The notation *td*$(n\times m)$ (triple domain) has been used here to represent a RHEED pattern showing three identical domains of $(n\times m)$ rotated by 120° from one another. RHEED patterns are labelled with the sample azimuth (not electron beam direction) at which they were observed.