ARTICLE IN PRESS
SCT-20763; No of Pages 5
Surface & Coatings Technology xxx (2015) xxx–xxx
Contents lists available at ScienceDirect
Surface & Coatings Technology
journal homepage: www.elsevier.com/locate/surfcoat

Properties of CdSb thin films obtained by RF sputtering

A.I. Savchuk [a], V.V. Strebezhev [a], G.I. Kleto [a], Y.B. Khalavka [b], I.M. Yuriychuk [a,*], P.M. Fochuk [b], V.M. Strebezhev [a]

[a] Department of Physics of Semiconductors and Nanostructures, Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine
[b] Department of Inorganic Chemistry, Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine

ARTICLE INFO

Article history:
Received 14 May 2015
Revised 14 November 2015
Accepted in revised form 3 December 2015
Available online xxxx

Keywords:
Thin film
Heterojunction
RF sputtering
CdSb
In_4Se_3

ABSTRACT

CdSb thin films have been deposited on single crystals of layered III–VI compounds In_4Se_3 and In_4Te_3 by ion–plasma RF sputtering to obtain new heterojunctions of two compounds with significant mismatch of lattice constants. Conditions of heteroepitaxy of CdSb films strongly differ at deposition on the surface of In_4Se_3 or In_4Te_3 crystals. CdSb films on In_4Se_3 substrates with crystallite size of 400–600 nm have been obtained at optimal RF power mode, that is confirmed by SEM and AFM microscopy studies. The results of electron probe microanalysis confirm compliance of films' composition with stoichiometric CdSb. For CdSb films deposited on In_4Te_3 crystal substrates a system of islands due to Stranski–Krastanov mechanism was recorded. Morphologically different forms of CdSb film growth are promising for the creation of active regions of elements for various applications. Photosensitive elements for near-infrared region with the given selective position of the photosensitivity maxima have been studied on the base of the obtained CdSb–In_4Se_3 and CdSb–In_4Te_3 film heterojunctions.

1. Introduction

CdSb, In_4Se_3 and In_4Te_3 single crystals are promising materials for the use in infrared technology, optoelectronics and sensor techniques [1–6]. These compounds are orthorhombic anisotropic semiconductors and have close bandgap values 0.48 eV (In_4Se_3) and 0.65 eV (In_4Te_3, CdSb) [7,8,4]. Optical properties and photoelecrical properties of In_4Se_3, In_4Te_3 and CdSb compounds in the infrared region are well studied [9–11]. However, to our knowledge, there are no data about obtaining and investigation of heterojunctions formed on these semiconductors.

The new thin film heterojunctions CdSb–In_4Se_3 and CdSb–In_4Te_3 can be used for the creation of photodetectors and radiation sensors, sensitive in the near infrared region. However, thin films and epitaxial layers of these compounds are relatively little studied [12–16]. Orthorhombic lattices of CdSb and chalcogenides In_4Se_3 and In_4Te_3 have considerable differences in parameters [5,3,17]. Heterojunctions with a significant mismatch in crystal lattices are actively studied recently. Such structures reveal specific mechanisms of lattice conjugation, such as pseudomorphism, Volmer–Weber or Stranski–Krastanov type, that is so-called van der Waals epitaxy which is important for nanotechnology [18].

In developing CdSb–In_4Se_3 (In_4Te_3) heterojunctions it is advisable to use In_4Se_3 and In_4Te_3 as a substrate, that follows from unique physical and chemical properties of these semiconductors. In_4Se_3 and In_4Te_3 single crystals are layered with a pronounced (100) cleavage plane [1,3,17]. Substrates for heterostructures can be produced by cleavage of these crystals in the direction of (100) plane without additional mechanical treatment. This forms a mirror cleavage surface, which is inert to moisture and chemicals [8,17,19–21]. Therefore, In_4Se_3 layered crystals and its isomorphic counterpart In_4Te_3 have advantages when used as a substrate for producing heterojunctions with low density of surface states on heteroboundary.

New photosensitive heterojunctions can be produced by deposition of CdSb thin films on these substrates. However, stoichiometric CdSb thin films are difficult to obtain because they decompose when deposited in vacuum. Many research groups used an evaporation method from different sources for each component for producing CdSb and ZnSb films [14–16]. Unfortunately, this method is associated with the considerable difficulties in ensuring congruent Cd and Sb vapor flows [16]. Ion–plasma RF sputtering techniques are efficient for producing stoichiometric films of various materials [22–24]. In the present paper we propose to carry out deposition of CdSb thin films on In_4Se_3 and In_4Te_3 single crystals by ion–plasma RF sputtering in order to provide stoichiometric composition and required structure of the films.

2. Materials and methods

Peculiarities of In_4Se_3 and In_4Te_3 semiconductor crystals are in their layered structure with significant anisotropy of mechanical, electro–optical properties and high photosensitivity. In_4Se_3 and In_4Te_3 single crystals grown by the Czochralski method using the Peltier effect were used as the substrates for obtaining film heterojunctions. Single crystals were grown in [010] crystallographic direction. Concentration of carriers in n-In_4Se_3 substrates was $4 \cdot 10^{15}$ cm^{-3}, electrical conductivity — $4 \cdot 10^{-2}$ $Ohm^{-1} \cdot cm^{-1}$. Concentration of carriers in p-type conductivity In_4Te_3 crystals at room temperature was $5 \cdot 10^{15}$ cm^{-3}. Substrates of 0.4–0.6 mm thickness were obtained by cleavage of the crystals in the

* Corresponding author.

http://dx.doi.org/10.1016/j.surfcoat.2015.12.007
0257-8972/© 2015 Published by Elsevier B.V.

direction of (100) plane. The advantage of these plates is their high surface stability to external factors, chemicals, mechanical stability and strength. According to [19] such substrates are well suited for solar cell devices and for growth of nanostructured elements.

At present there is little information [16] about obtaining cadmium antimonide films. In particular, the possibility of producing CdSb layers by cathode RF sputtering has not been studied. This method, compared to the thermal evaporation in vacuum, has advantages at deposition of multicomponent alloys and compounds, because it provides stoichiometric composition of films and high adhesion to the substrate [22, 24]. The shortcoming of the method is pollution of the films by atoms from the gas phase.

In the present work cadmium antimonide thin films have been obtained by cathode RF sputtering for the first time. CdSb single crystal target in the form of 50 × 50 × 8 mm plate was placed on the flat cathode with water cooling. Concentration of carriers in undoped crystalline CdSb target was $(3–5)\cdot 10^{15}$ cm^{-3} at 77 K. The holder of the substrates was placed at a distance of 35 mm from the target surface. Working volume has been pumped to 10^{-4} Pa vacuum before sputtering. After that, the camera was supplied with argon at pressure within 3–5 Pa. The frequency of the applied RF signal was of 1.75 MHz. Parameters of sputtering process such as substrate temperature, RF-power, pressure in the chamber, distance from the target to the substrate play an important role in the formation of the structure and determine physical characteristics of the films. It is known that crystal structure is more perfect when the temperature of the substrate is increased [24]. In Table 1 we list some parameters of the processes for obtaining cadmium antimonide films at two different modes. Then in the presented paper we have studied the effect of the sputtering mode on the structural and chemical compositions, and the optical and electrical properties of CdSb films deposited on In_4Se_3 and In_4Te_3 substrates.

The structure of CdSb films obtained by two technological modes was examined by atomic force microscopy on NT-206 ATM, by scanning electron microscopy, and by X-ray microanalysis on SEM-microscope Zeiss EVO 50. Electrophysical properties of CdSb–In_4Se_3 and CdSb–In_4Te_3 film heterojunctions were studied by measuring I–V characteristics and spectral photosensitivity characteristics by standard methods.

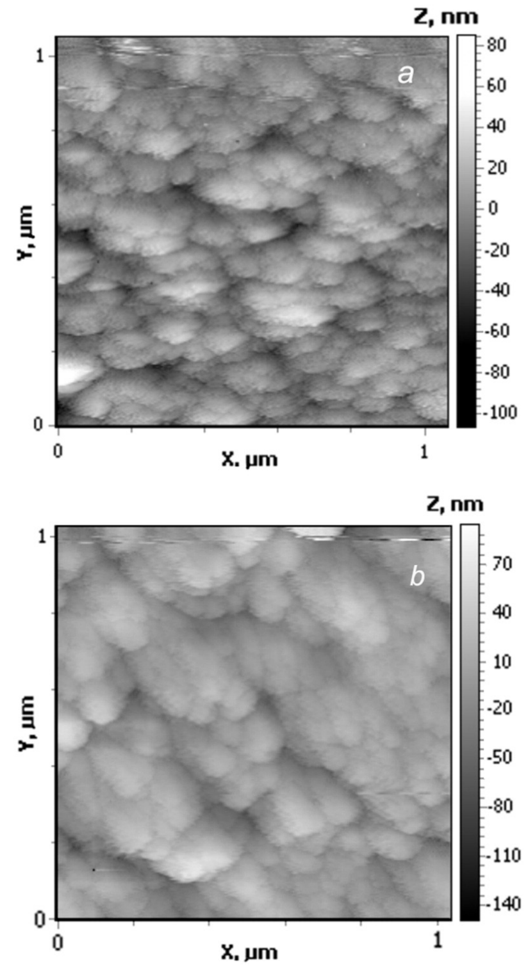

Fig. 1. AFM images of CdSb film deposited by RF cathode sputtering at mode 1 on In_4Se_3 single crystal substrate (a) and on In_4Te_3 single crystal substrate (b).

3. Results and discussion

CdSb films deposited at mode 1 on a substrate with temperature 70 °C and deposition rate of 1.9 Å/s had fine crystalline structure. The thickness of these films was of 0.7–0.9 µm. The measurements of films' thickness were carried out using multibeam interferometry with sodium light source of 0.592 µm wavelength. The presence of small 40–70 nm grains in the film was recorded by AFM both on In_4Se_3 and In_4Te_3 substrates (Fig. 1a, b). A continuous CdSb film was formed on both types of substrate. The grains on In_4Te_3 substrate are slightly larger and have partly dominant orientation. Change of experimental conditions strongly affects the films' growth shape. A significant increase in the size of CdSb film crystallites on In_4Se_3 substrates up to 400–600 nm was reached at RF power of 25 W which provided the substrate temperature of 150 °C and deposition rate of 4.1 Å/s.

As follows from AFM film profiles and their 3D-images, a continuous CdSb film was formed on the (100) surface of In_4Se_3 crystal (Fig. 2). The morphology of the film is characterized by uniform in size and shape grain areas, but there are also local differently oriented areas with significant dispersion of grain size. This diversity is caused by the interaction processes of condensed particles and change of their shape, structure and phase state at the growth process. Studies of CdSb films in the scanning electron microscope showed that the characteristic feature of the morphology was also a formation of spherical 0.3–0.6 µm islands that can be explained by an inhomogeneity of the temperature field at RF sputtering in the direction of substrate plane (Fig. 3). A complicated structure of the film crystallites was also recorded. The crystallites consist of nano-sized (50–70 nm) grains which are formed due to coalescence at initial stages of film growth. A significant influence of deviations from CdSb film stoichiometry on their specific resistivity, carrier concentrations and mobility has been mentioned in literature [14–16]. Our results of electron probe studies confirm compliance of films' chemical composition with stoichiometric CdSb (Table 2). Metastable Cd_3Sb_2 and Cd_4Sb_3 phases of Cd–Sb system [5,25] were not found in films obtained by cathode RF sputtering. As follows, RF sputtering allows one to overcome technical difficulties related to strongly different partial vapor pressures of Cd and Sb components, and obtain stoichiometric CdSb films with large grains. Such films are preferable for the use in photovoltaic cells, because the total area of grain boundaries decreased. The processes of carrier recombination and loss of nonequilibrium carriers take place on grain boundaries. Potential barriers on the interfaces between grains affect the carrier scattering processes as well as transport and kinetic properties of films.

Table 1
Parameters of two different modes for growth of CdSb films.

Deposition mode	RF-power (W)	Substrate temperature (°C)	Film deposition rate (Å/s)
1	10	70	1.9
2	25	150	4.1

The growth of the system of CdSb islands due to the Stranski–Krastanov mechanism was identified on the films deposited at mode 2 on In_4Te_3 crystal substrates at 150 °C (Fig. 4). Interaction between islands leads to the formation of ring island cells on the surface of the film. The islands were of micron size and were not quantum islands at this growth stage. Study of the films by SEM microscopy showed that