Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Applied Surface Science 254 (2008) 2067–2071
applied surface science
www.elsevier.com/locate/apsusc

Age-induced oxide on cleaved surface of layered GaSe single crystals

S.I. Drapak [a,*], S.V. Gavrylyuk [a], Z.D. Kovalyuk [a], O.S. Lytvyn [b]

[a] I.M. Frantsevich Institute of Materials Science Problems, National Academy of Sciences of Ukraine, Chernivtsi Department, 5 Iryna Vilde Str., 58001 Chernivtsi, Ukraine

[b] Lashkarev Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Prospect Nauky, 03028 Kyiv, Ukraine

Received 1 August 2007; received in revised form 12 August 2007; accepted 12 August 2007
Available online 17 August 2007

Abstract

It is shown that a long-term keeping of a layered gallium monoselenide at room temperature results in formation of the intrinsic oxide at a cleaved surface of semiconductor. It is found that the chemical compositions of the intrinsic oxide at the surfaces of the intentionally undoped and doped samples of GaSe are different. The electrical properties of the GaSe-intrinsic oxide system are presented. It is established that intrinsic oxide films at the surface of GaSe are characterized by current instability with N-type current–voltage characteristic. The influence of relative humidity on changes of capacitance and surface resistivity of the intrinsic oxide is also discussed.

PACS : 68.47.Fg; 61.10.−i; 87.64.Dz; 47.55.dr; 77.84.Bw; 73.61.−r; 07.07.Df

Keywords: Gallium selenide; Intrinsic oxide; X-ray diffraction (XRD); Atomic force microscopy (AFM); Electrical properties; Humidity sensing

1. Introduction

The interest to investigations of layered GaSe is caused not only by the possibility of using this material as the basis for various optoelectronic devices [1,2] but also its promising applications for preparations of nanoparticles, including nanotubes [3], as well as in planar nanotechnologies [4,5]. Therefore, the study of aging processes in gallium selenide becomes an important problem now. It is accepted that a cleaved surface (CS) of GaSe is perfect not only from the viewpoint of geometrical structure but also in the sense of its inertness to sorption of foreign atoms from the atmosphere. Moreover, according to Ref. [6], even thermal treatment in the air at $T \leq 400\ ^{\circ}\mathrm{C}$ does not lead to formation of any new phases on the GaSe surface. Nevertheless, the electrical properties of photosensitive GaSe-based heterostructures prepared by a method eliminating interdiffusion, in some cases, cannot be explained without taking into account the presence of a thin dielectric gap at the interface [7]. Indeed, we have found that during a long-term keeping at the ambient conditions, a cleaved GaSe (0 0 0 1) surface undergoes visible changes. Namely, after 2–2.5 years the surface of the Cd- or Dy-doped samples gets covered with a thin transparent film of the intrinsic oxide (Ox). The reflection spectra of these films have interference maxima and minima in the visible spectral range. The Ox, appearing on the CS of undoped GaSe single crystals, has a form of matt coating.

In this paper we present the results of initial investigations of the electrical properties of the GaSe–Ox system, which make it evident that the intrinsic oxide layer is the reason of the current instability with N-type *I–V* characteristics. It confirms a qualitative model proposed by us to explain the properties of diodic photosensitive structures prepared on the basis of *p*-GaSe [7,8].

2. Experimental procedure

The experimental investigations were carried for both intentionally undoped and doped with Cd and Dy *p*-GaSe single crystals grown by the Bridgman method from stoichometric melts. The density of dopants in the melt did not exceed 0.05%. The resistivity of undoped *p*-GaSe is high enough, and at $T = 300$ K it ranges between 10^3 and $10^4\ \Omega$ cm ($p \sim 10^{14}$ cm^{-3}).

* Corresponding author. Tel.: +380 37 2 520050/22 36018; fax: +380 37 22 36018.
E-mail address: drapak@unicom.cv.ua (S.I. Drapak).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.08.034

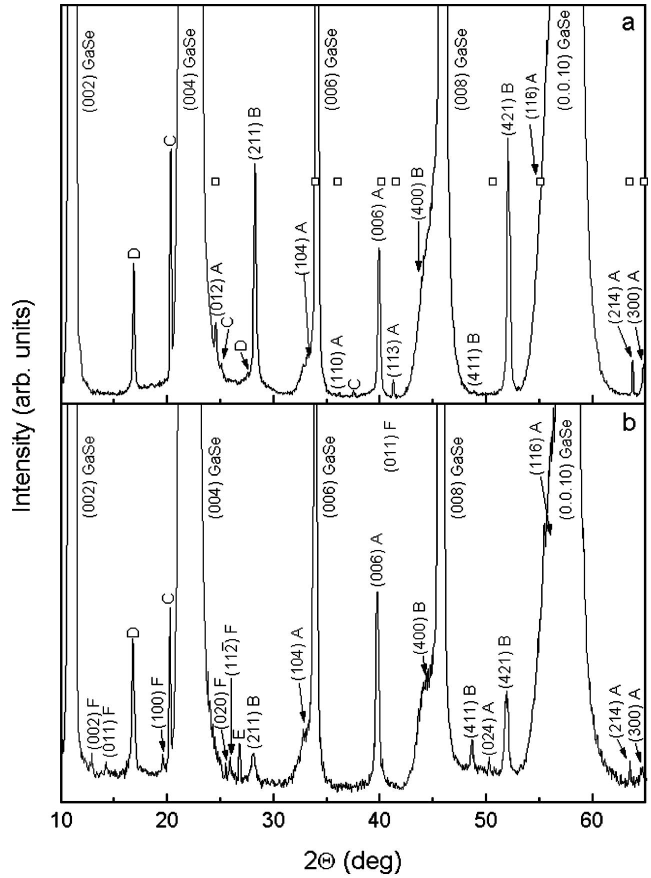

Fig. 1. XRD patterns of intrinsic oxide films grown on cleaved surfaces of GaSe single crystals: (a) doped with Cd; (b) intentionally undoped. (A) trigonal Ga_2O_3, (B) tetragonal SeO_2, (C) gallium selenate $Ga_2(SeO_4)_3$, (D) gallium selenite hydrate $Ga_2(SeO_3)_3 \cdot 6H_2O$, (E) SeO_3 and (F) monoclinic Se_2O_5. The symbols □ represent the 2θ positions of the most intense peaks of trigonal Ga_2O_3 phase [11].

Therefore, for the preparation of various optoelectronic devices it makes use of GaSe doped with Cd or Dy [1,2,7]. It makes possible to decrease the resistivity of gallium selenide and, as a result, to decrease the series resistance of photosensitive structures. The samples cleaved in the open air had the form of plane-parallel plates 1–10 mm thick. We kept them at the ambient conditions (room temperature and relative air humidity of 58 ± 10%) at least for 5 years.

The X-ray diffraction (XRD) patterns of the Ox formed on a GaSe CS were recorded by using a DRON-3 diffractometer with Cu Kα radiation (λ = 1.51418 Å). The surface morphology of the Ox was observed by an atomic force microscope (AFM) in tapping mode. The electrical properties of the Ox have been measured for both metal–oxide–semiconductor and semiconductor–oxide–semiconductor structures. To make the ohmic contacts to gallium selenide, we used the metallic indium. The In contacts to the semiconductors have been deposited onto just cleaved GaSe surfaces. Metallic indium and weakly degenerated Bi_2Te_3 (E_g = 0.17 eV; $p \approx 2 \times 10^{19}$ cm^{-3} at T = 300 K) have been used as the contact materials to the oxide films for the metal-oxide-semiconductor and semiconductor-oxide-semiconductor structures, respectively. Current–voltage (I–V) measurements were made according to the conventional method. Capacitance–voltage (C–V) characteristics, dependences of C and capacitive resistance R_C of the structures on the frequency in the range f = 100 Hz to 35 MHz were measured at room temperature by using a quality-factor meter E4-7. The thickness of the Ox films appeared at the surface of the doped GaSe samples were estimated by a laser ellipsometer LEM-2. The technique of the investigations of changes in electrical properties of a sub-gate layer of the dielectric and surface resistivity of dielectrics with relative humidity (RH) of the air is described in Refs. [9,10].

3. Results and discussion

As follows from the X-ray diffraction patterns, independently of dopant nature the Ox films appearing at the GaSe:Cd (Dy) SCs consist preferably of Ga_2O_3 with inclusions of SeO_2, $Ga_2(SeO_4)_3$, and $Ga_2(SeO_3)_3 \cdot 6H_2O$ [11] (Fig. 1a). Except for the case of above-mentioned compounds, the Ox composition of undoped GaSe samples at SCs (Fig. 1b) also includes selenium oxides SeO_3 and Se_2O_5.

The AFM images of the Ox films appearing at the GaSe and GaSe:Cd (Dy) CSs are presented in Fig. 2. As one can see, there are separate inclusions with vertical and lateral dimensions

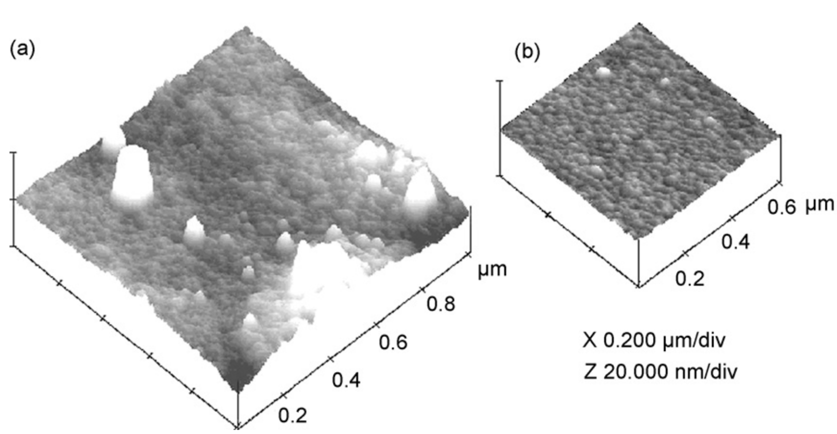

Fig. 2. AFM images of the intrinsic oxide films appeared at cleft surfaces of layered GaSe crystals due to long-term keeping under ambient conditions: (a) intentionally undoped crystal and (b) doped with Dy.