Surface & Coatings Technology 206 (2012) 3146–3150

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

XPS–AES study of the surface composition of GaSb single crystals irradiated with low energy Ar ions

C. Palacio [a,*], J. Olvera [b], J.L. Plaza [b], E. Diéguez [b]

[a] Departamento de Física Aplicada, Facultad de Ciencias Módulo 12, Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain
[b] Departamento de Física de Materiales, Facultad de Ciencias Módulo 4, Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain

ARTICLE INFO

Article history:
Received 6 September 2011
Accepted in revised form 30 December 2011
Available online 5 January 2012

Keywords:
Gallium antimonide
X ray photoelectron spectroscopy
Sputtering

ABSTRACT

Detailed XPS and Auger analysis has been carried out in situ during the formation of nanostructures on GaSb surfaces under low energy Ar^+ beam sputtering. A model is suggested to correlate the geometry of the formed nanostructures with the elemental Ga and Sb concentrations at the surface after the ion bombardment. This model is based on the assumption that the nanodots formed during bombardment are Ga enriched. This assumption enables the calculation of the dot surface coverage. The obtained values agree very well with the experimental ones measured by using high resolution scanning electron microscopy.

1. Introduction

In the last decades, there has been devoted a great effort in developing periodic nanostructures. In fact, this has become one of the main goals in the field of nanotechnology. In particular, the formation of controlled nanostructures in semiconductors is an important issue in the future development of the next generation of optoelectronic devices. Among the most widely used nanostructuring tools, we can quote electron beam lithography (EBL) as the key technique for the fabrication of controlled and periodical nanostructures. However, its low throughput relegates the role of this technique, at the present, to the fabrication of prototypes in the laboratory environment or as support technique in the industry [1]. These facts serve as strong stimulus for developing parallel processing techniques which can be used for the fabrication of massive production of devices at the nanoscale level. Self assembly of semiconductor nanocrystals [2] or the Stranski–Krastanov (SK) method for the growth of semiconductor heterostructures and quantum dots [3] can be mentioned as some of these promising nanofabrication methods. This last technique has recently enabled the fabrication of long-range ordered dot arrays [4–6], and fully ordered 3D quantum dot arrays [7]. Such ordered quantum dots show extremely small size dispersions [8], narrow photoluminescence peak line widths [9], and fine structure splitting and are even suitable for single photon sources [10].

A decade ago low energy ion sputtering (LEIS) has been presented [11–13], as a very promising technique for the fabrication of nanostructures and quantum dots. This technique is an attractive alternative to the SK method due to a much more simple and inexpensive experimental equipment needed compared with a sophisticated and expensive MBE-based technique like SK. A small high vacuum chamber and a standard low energy (1 to 5 kV) ion gun are enough to fabricate a rudimentary but effective LEIS system. In spite of the simplicity of the experimental LEIS system, very good results have been reported like the fabrication of hexagonal arrays of uniform semiconductor quantum dots, by using Ar^+ ions [11,12]. Facsko et al. [12,13] have demonstrated that dot patterns can be spontaneously created on GaSb and InSb when the surfaces of these materials are sputtered with low energy argon ions at normal incidence. In addition, these dots were shown to exhibit quantum confinement properties.

An additional advantage of this technique is that, by tuning the sputtering time and the energy of the incident ions, the size and the density of the dots can be independently controlled. The formation of these ordered nanostructures has been extensively studied and reviewed both for metals [14] and semiconductors [15]. The self-organization of quantum dot periodic arrays during sputtering has been attributed to the interplay between surface roughening induced by the ion sputtering and smoothing processes of the surface. These ideas are based on the Bradley–Harper model which explains the ripples and nanostructures formed during LEIS as an instability of fluctuation in the height function, which results from the competition between the roughening (induced by the sputtering which depends on the local curvature) and the smoothing (induced by the surface diffusion) of the surface [11].

Gallium antimonide (GaSb) is a relevant semiconductor in the field of optoelectronics and communications (see for example the review from Dutta et al. [16] and references therein). Very recent papers have been published on the formation of nanostructures on

* Corresponding author. Tel.: +34 914975266; fax: +34 914974949.
E-mail address: carlos.palacio@uam.es (C. Palacio).

0257-8972/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2011.12.046

this material by using LEIS, such as the series of papers abovementioned by Facsko et al. [11–13], who studied the formation of hexagonal nanostructured arrays and quantum dots on GaSb. The self-organization of quantum-dot periodic arrays during sputtering has been attributed to the interplay between surface roughening induced by the ion sputtering and smoothing processes of the surface [11]. These processes have been taken into account to develop an important mathematical model due to Bradley and Harper [17] which takes the analytical form of a linear partial differential equation which describes the surface evolution under continuous sputtering conditions. The Bradley–Harper model successfully predicts the ripple morphology and the ripple orientation as a function of the incidence angle of the ion beam. In this model the periodic structure results from the interplay between roughening mechanisms which leads to a negative surface tension, and a smoothing mechanism due to surface diffusion. The former rises from the tendency to maximize the surface during the sputtering process as a result of a higher sputtering yield in depressions than on elevations. This linear (BH) model was extended recently by higher order terms of the derivative of the height function [18,19] to provide a non linear equation, called Kuramoto–Sivashinsky (KS) equation [20] which has been successfully used by Facksco [13] in order to simulate the irradiation conditions for the formation of Ripples and dots on GaSb surface under low energy ion irradiation.

We can also mention the analysis carried out by Panning et al. [21], on the *p* to *n*-type conversion on GaSb surfaces by using the same technique. However, more research is needed on the LEIS nanostructuring technique on semiconductor materials. In particular extensive research is needed in order to determine the chemical state of the surface after the ion bombardment. This subject has not been deeply studied in the existing literature and very few data are available. Facksco concluded by using Auger measurements that there is a gallium enrichment in the first 2–3 nm of sputtered GaSb surfaces [2]. However, to the best of our knowledge, no quantitative models for correlating the preferential erosion with the formation of surface nanostructures are still available. It is the scope of this paper to establish such correlation using in situ detailed XPS and Auger analysis after low energy argon ion irradiation of GaSb single crystals.

2. Experimental

A Bridgman-grown GaSb single crystal was grown in our laboratory (Ga, Sb 6N). Several wafers cut perpendicular to the growth direction <111> were lapped and polished up to 0.3 μm with alumina powder. After polishing, the samples were chemically etched in order to remove the native oxides. Since HCl-based solutions are the most effective etchant to remove native oxides on GaSb, we have used HCl: CH_3COOH (3:1) solutions combined with methanol rinsing to reduce the thickness of the residual native oxide layer up to 1.4–1.7 nm [22–25]. The relevant reactions taking place in the formation of these native oxides are: $Sb_2O_3 + 2\ GaSb \rightarrow Ga_2O_3 + 4\ Sb$ [26]. It has been shown by Raman and X-ray diffraction that these native oxides are mostly formed as β-Ga_2O_3 and Sb_2O_3 phases with a possible Sb interfacial layer in between the GaSb surface and the native oxide. Finally the sputtering process was carried out on the pure GaSb samples by using Ar^+ ions. Therefore at this level we do not expect any important effect induced by the native oxide on each subsequent sputtering process. This later statement is supported by the necessary condition of surface amorphisation as reported by Facsko et al. [11–13]. This amorphisation is created after the native oxide layer removal. For the case of 1.4-1.7 nm thick oxide layer, this process would be fast.

Both AES and XPS measurements were carried out in an ultrahigh vacuum chamber (UHV) at a base pressure better than 10^{-7} Pa analyzing in-situ the compositional changes during Ar^+ irradiation.

Auger spectra were measured in the derivative mode using a cylindrical mirror analyzer (CMA) with a nominal resolution of 0.25%. A modulation voltage of $2V_{p-p}$ was supplied to the CMA. In order to avoid electron beam effects on the analyzed surface a constant primary electron beam current density of 1×10^{-3} A/cm^2 at 3 keV primary beam energy was used. For AES the ion bombardment was carried out using Ar^+ ions at 1 and 3 keV. Due to experimental setup restrictions, the angle between the ion gun and the surface normal was 47°.

XPS spectra were measured using a hemispherical analyzer (SPECS Phoibos 100 MCD-5). The pass energy was 9 eV giving a constant resolution of 0.9 eV. The Au $4f_{7/2}$, Ag $3d_{5/2}$ and Cu $2p_{3/2}$ lines of reference samples at 84.0, 368.3 and 932.7 eV, respectively, were used to calibrate binding energies. A twin anode (Mg and Al) X-ray source was operated at a constant power of 300 W using Mg Kα radiation for the XPS measurements. For XPS the samples were bombarded using Ar^+ at 1 keV at normal incidence and a current density of 1×10^{-6} A/cm^2. In addition to that, the samples were placed in a sample stage with 4 degrees of freedom in such a way that the angle between the axis of the input lens of the analyzer and the surface normal could be varied between 0 and 70° in order to perform angle-resolved measurements. The irradiated area is close to 1×1 cm^2 which develops small and uniform roughness and induces amorphization on the GaSb surface, as deduced by "ex-situ" atomic force microscopy (AFM) measurements and therefore no important influence of the surface roughness on the ARXPS is expected.

3. Results and discussion

Fig. 1 shows (a) the Ga and the Sb concentrations and (b) the Sb intensity as a function of the take-off angle for a GaSb surface bombarded with 1 keV Ar^+ ions at normal incidence, during 270 min to

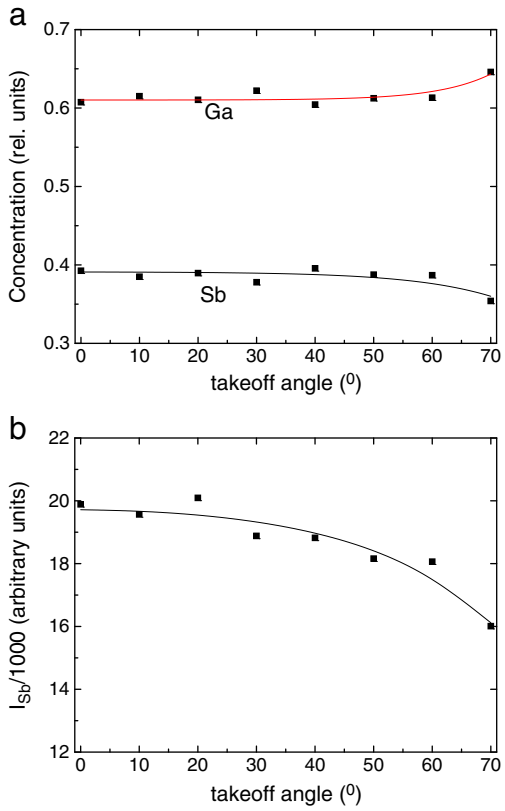

Fig. 1. (a) The Ga and the Sb concentrations (solid lines are guides to the eye) and (b) the Sb intensity as a function of the take-off angle for a GaSb surface bombarded with 1 keV Ar^+ ions at normal incidence and a dose of 1×10^{17} ions/cm^2.