Surface Characterisation and Cathodoluminescent Response of Nanodot-Patterned GaSb Surfaces by Low Energy Ion Sputtering

Surface Characterisation and Cathodoluminescent Response of Nanodot-Patterned GaSb Surfaces by Low Energy Ion Sputtering

J. L. Plaza[1], P. Hidalgo[2] and E. Diéguez[1]

[1] Laboratorio de Crecimiento de Cristales, Departamento de Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049, Cantoblanco, Madrid, Spain

[2] Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28045, Madrid, Spain.

joseluis.plaza@uam.es

Abstract. The scope of this paper is to analyse the effect of Au and Cr impurities, diffused onto GaSb substrates on the formation of nanodots created by LEIS using Ar+ ions It is concluded that oblique incidence in rotating configuration delays the formation of the nanodots compared to previously reported normal incidence experiments. The presence of cracks induced by the sputtering process has been observed both in the Au and Cr diffused samples. Cathodoluminescence (CL) spectra obtained in irradiated samples both pure and Cr-diffused have revealed no difference between them, showing the usual three band encountered in this material (Band Gap at 798 meV, A Band at 777 meV and tail-states at 815 meV). However, a fourth band has been detected in the Au sample centered at 769 meV.

1. Introduction

In the last few years, much effort has been directed to the development of periodic nanostructures and this has become one of the main goals in the field of nanotechnology. In particular, the formation of controlled nanostructures in semiconducting materials appears to be an important issue in the future development of the next generation of optoelectronic devices. Amongst the available nanostructuring tools, electron beam lithography (EBL) is becoming an essential technique in the fabrication of controlled and periodical nanostructures, however, due to its low throughput the role of this technique is being relegated, at the present, to the fabrication of prototypes in the laboratory environment or as support technique in the industry [1]. These difficulties are stimulating a great amount of effort in order to develop parallel processing techniques to be employed in the fabrication of nanostructures. Amongst them we can mention, for example, the self assembly of semiconductor nanocrystals [2] or the Stransky-Krastanov method for the growth of semiconductor heterostructures and quantum dots [3]. It has also been recently reported that low energy ion sputtering (LEIS) at normal incidence, appears to be a very promising technique for the fabrication of nanostructures and quantum dots representing an attractive alternative to the Stranski-Krastanov method. It has been demonstrated, for example, that hexagonal arrays of uniform semiconductor quantum dots can be developed by LEIS using Ar^{+} ions [4,5]. In particular, it has been shown by Facsko et al. [6] that dot patterns can be

spontaneously formed on GaSb and InSb when surfaces of these materials are sputtered with low energy argon ions at normal incidence.

An additional advantage of this technique is that the size and the density of the dots can be controlled independently by tuning the sputtering time and the energy of the incident ions. The formation of these ordered nanostructures has been extensively studied and reviewed both for metals [7] and semiconductors [8]. The self-organization of quantum dot periodic arrays during sputtering has been attributed to an interplay between surface roughening induced by the ion sputtering and smoothing processes of the surface [4].

Gallium antimonide. (GaSb) is one of the semiconductors that is becoming very relevant in the field of optoelectronics and communications (see for example the review from Dutta et al. [10] and references therein). Very recent papers have already been published on the formation of nanostructures on this material by using low energy Argon ion sputtering, such the series of papers above mentioned by Facsko et al. [4-6], who studied the formation of hexagonal nanostructure arrays and quantum dots on GaSb. We can also mention the analysis carried out by Panning et al [9], on the *p* to *n*-type conversion on GaSb surfaces by using the same technique. However, more research needs to be focused on the LEIS technique on semiconductor materials. For example, to the best of the author's knowledge, nothing has been published on the effect of diffused dopants on the formation of nanostructures created by LEIS.

It is the scope of this paper to analyse the effect of Au impurities, diffused onto GaSb substrates on the formation of nanodots created by LEIS using Ar^+ ions. Dopant diffusion in semiconductors has been traditionally used [see for example the review by Willoughby ref [11] and references therein] in order to fabricate semiconductor diodes and other devices based on a single piece of semiconductor material with two different kind of conductivities (*p-n*). It is the possibility to create this kind of structures what has driven us to study the effect of LEIS on diffused GaSb surfaces instead of simply using intentional doping during the GaSb crystal growth process, in which case the whole material would have only one type of conductivity (*p* or *n*). It is also the aim of this work to obtain the threshold conditions from which the nanodots are formed both in pure and Au-diffused GaSb. This is why this work is presented as the results of three successive sputtering experiments, analysing the progressive changes in the surface until the nanodots are formed.

2. Experimental

In order to carry out a systematic study of the effect of LEIS on Au and Cr-diffused GaSb substrates, the analysis of three samples submitted to LEIS was thought to be necessary. In order to fulfil this requirement without introducing possible structural differences between the substrates, a single wafer from a Bridgman-grown GaSb ingot grown in our laboratory (Ga, Sb 6N) was initially taken and polished with 1 μm alumina powder. The wafer was divided into three pieces of the same size in order to prepare the three different samples. The first one, S_{ctr}, served as control sample and was exposed to the LEIS process without any other previous treatment. On the second, S_{Au}, and third S_{Cr} samples, Au and Cr respectively were thermally evaporated by using an electron gun. An Edwards auto 306 Turbo was employed for this purpose. The evaporation parameters were; evaporation time: 12 , 5min; electron beam current; 40 , 45mA, base pressure: $3.4x10^{-5}$, $3.0 \ x10^{-5}$ mbar: thicknesses of the evaporated films: 130 nm ,170 nm for Au and Cr respectively. After the evaporation process and in order to diffuse the Au and Cr into the surface of the substrate, an annealing treatment was carried out. The annealing time was 9 hr. The annealing temperature was as low as $250 \ ^0C$ in order to avoid high losses of Sb during the annealing. This process was performed under 300 ccm of nitrogen flux. After the annealing process we proceeded to remove the layers by using wet chemical etching with HCl. This acid does not damage the GaSb surfaces. The etching time was 2 hours immersing the sample in HCl heated at 60 ^0C in a hot plate inside a laminar flow fume-cupboard. Subsequently, the sample was rinsed in acetone. Finally the sputtering process was carried out on the three (pure (S_{crt}), Au-diffused (S_{Au}) and Cr-diffused GaSb (S_{Cr}) samples by using Ar^+ ions.

The samples were irradiated with low energy Ar ion in a sequence of three succesive sputtering processes in order to control the stage at which the nanodots are formed. This work is described in detail elsewere. The accelerating voltages and ion fluxes used were in the range 500-600 V and 6×10^{15}-1.5×10^{16} $cm^{-2}s^{-1}$ respectively. An ion flux of 10^{16} $cm^{-2}s^{-1}$ is considered by many authors [1-8] as the upper limit in which the conditions of the Bradley-Harper model are fulfilled [13]. The total exposure time was 38 min. This model explains the ripples and nanostructures formed during LEIS as instability of fluctuation which results from the competition between the roughening, by the sputtering depending on the local curvature and the smoothing by the surface diffusion. In all the cases, the incidence angle of the ion beam against the target was 45^0 and the target (samples) rotated at 15 rpm. The successful technique of rotating sample under oblique incidence in creating hexagonal arrangement of regular dots has already been reported by several researchers [5,13-14]. However it has been reported that both configurations lead to stable hexagonally ordered dot patterns [2-6]. The system used in our sputtering experiments was a Millatron Ion Miller from Commonwealth Scientific Corp. The resulting samples were characterized by cathodoluminiscence technique. CL-SEM measurements were performed either in a Leica 440 or a Hitachi S-2500 scanning electron microscopes. The CL measurements, were carried out at liquid nitrogen temperature by using a OL-730 TE germanium detector at 10-15 keV of electron beam energy.

3. Results and discussion

In order to get information about the thickness of the diffused Au and Cr layers, a secondary ion mass spectrum was obtained during the LEIS (see Fig.1). Only the relevant elements Au and Cr are shown in Fig. 1 as Ga and Sb remained constant throughout the process and gave no additional information. The presence in sample of Au and Cr several nm deep into the GaSb surface shown by the SIMS spectrum is a confirmation of the actual formation of Au and Cr diffusion layers. However the concentration of Au and Cr decays with depth. This is a common behaviour of impurity diffusion in semiconductors [11]. We can also extract information about the thickness of the impurity layers created during the diffusion process, according to the point where the signal reaches a flat evolution. This point indicates that the diffusion layer has been almost completely removed from the surface by the erosive effect of the sputtering process. The thickness thus obtained is about 12 nm for Au and 21 for Cr.
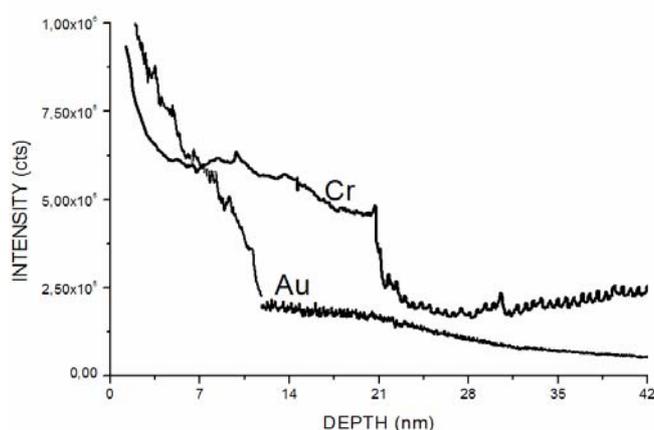

Figure 1. Secondary ion mass spectrum for Au and Cr diffused impurities.

In order to identify possible sputtering-formed nanostructures, we have performed an ultrahigh resolution SEM analysis of these samples. Some typical images obtained from this analysis are presented in Fig. 2. In these images it is observed the formation of dot hexagonal arrays at the

nanometre scale (about 50-80 nm in diameter). Fig. 2a shows an SEM image obtained from the surface of the pure sample S_{ctr} after the sputtering process. Similar images, obtained from S_{Au3} and S_{Cr} are shown in Figs. 2b and 2c respectively. It is worth noting that, apparently, the structure of the surface regarding to the geometry, arrangement and size of the nano dots, is nearly the same in all the samples. However, detailed preliminary studies on these samples based on statistical distributions obtained from Atomic Force Microscopy (AFM) images (Cr diffussion; [16], Au diffusion; to published elsewhere) have shown slight variations on the size of the dots increasing in the case of Au and decreasing in the case of Cr, compared to the pure sample. Although these effects are probably induced by the dopant diffusion, the overall effect of these dopants is small and still remains unclear wether the changes in the size of the dots would be predictible considering only the diffused atom. However, a general result drawn from the mentioned AFM analysis is that the aspect ratio of the dots remains the same both in pure and diffused samples. Therefore the dopant nature does not seem to affect to the geometry and distribution of the dots. This uncertainty in the dopant effect comes from the fact that the diffusio layer width is much lower (120 nm for Au, 20 nm for Cr) than the depth at which the nanodots start to form (40 nm). Therefore, at this depth a very low dopant concentration is expected as shown by the SIMS spectra. However the defects found on the Au surface really suggest certain lattice distortion which is developed by the ion sputtering as the deffects shown in Fig 2c. These results suggest the possibility to diffuse smaller elements or the use of non equilibrium techniques like ion implantation in order to increase the thickness of the diffusion layer and to find out whether or not there is any additional effect on the formation of quantum dots induced by the presence of impurities. Such experiments are currently under way.
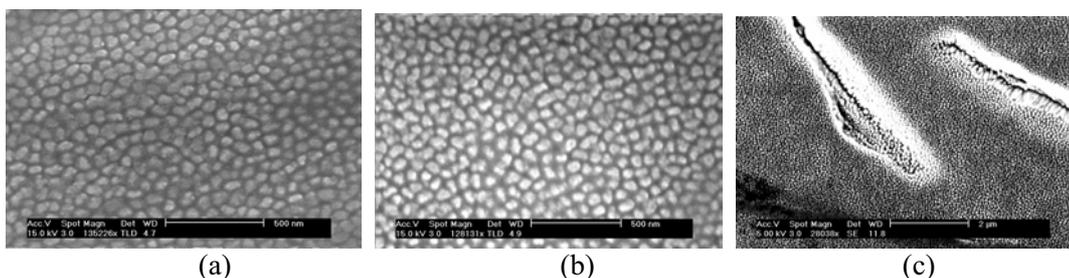

(a)   (b)   (c)

Figure 2. Ultra-high resolution SEM images from sputtered (a) pure GaSb. (c) shows a typical defect found onto the Au-diffused sputtered surfaces.

Regarding to the composition of the nanodot patterned surfaces, previous EDX analysis have revealed a Ga enrichment of the sputtered surfaces close to 5 %. This fact has also been observed by Facsko et al [2] by using Auger spectroscopy in undoped GaSb sputtered samples and it is attributed to Sb losses from the surface during the sputtering. This preferntial sputtering is still more evident in the case of the diffused surfaces where the Ga concentraton appears to be up to 25 % higher compared to the pure GaSb sample.

In order to get some idea about the luminescente response of these nanostructured surfaces by LEIS, a cathodoluminescence analysis was carried out. Regarding to the pure sample, S_{crt}, the CL panchromatic images and emisssion spectra present the same structure as the pure GaSb samples previously analysed [16]. However, it is observed a very weak luminescence compared to pure GaSb non irradiated samples. This decreasing luminescence could be related to the damage induced by the irradiation which could have induced a very high density of non-radiative defects. Typical CL images of this sample is shown in Fig. 3a where a very high grain boundary density can be observed. We can observe in Fig 3b corresponding to a Secondary electron image that there appear some defects that they only contribute to the topographic contrast in CL. In order to analyze radiative centres CL spectra were carried out and no different characteristics compared to those of the bulk material were observed. This fact is shown in a typical CL spectrum from an irradiated as-grown sample in Fig. 3c.

CL images and a characteristic spectrum of the Cr-diffused irradiated GaSb sample (S_{Cr}) are presented in Fig 4. It shows both in the CL spectrum and in the CL images, the same behavior as the previous samples (S_{crt}). This behavior has already been observed in Cr-doped bulk samples [16], where the Cr concentration was not too high. In that work, it is reported an increasing A band when the Cr concentration is low. In this case, although the expected Cr concentration is low as indicated on the SIMS spectra, a modification of the A band intensity cannot be observed compared to the native sample. However, it is observed an increment in the overall luminescence signal regarding to the pure irradiated sample. The subsequent thermal treatments could be responsible of this increasing luminescence.
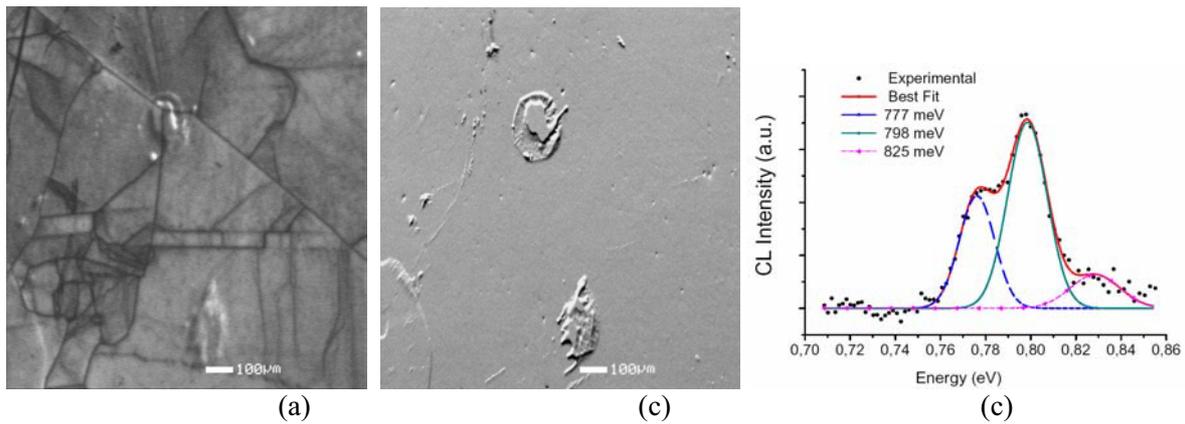

Figure 3. CL (a), SEM (b) images and CL spectra (c) from sputtered pure GaSb.

Finally, the results of the CL analysis from the Au-diffused sample (S_{Au}) are shown in Fig. 5. A different behaviour of this sample compared to that from the pure and Cr-diffused irradiated samples can be observed. These differences appear both in the images and in the spectra. The CL images present a more homogeneous behaviour than the rest of the samples. In addition the CL intensity is much higher than in the other two samples. This fact is possibly associated to a non-radiative recombination centers reduction. The lowering in the grain boundary density, observed in CL images, could be related to the thermal treatment performed in order to induce, Au diffusion, although it has to be pointed out that the same thermal treatment was developed in the case of Cr-diffused sample.
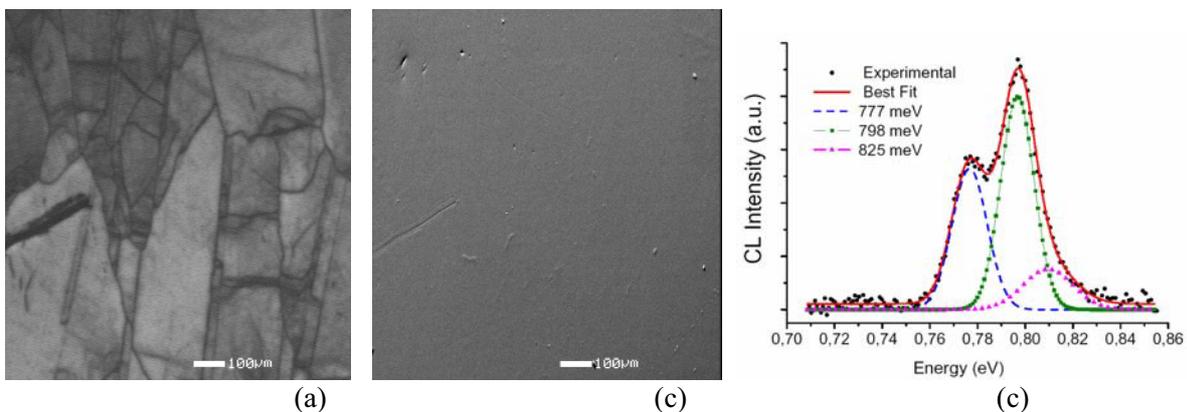

Figure 4. CL (a), SEM (b) images and CL spectra (c) from sputtered Cr-diffused GaSb.

As it has been previously mentioned, the CL spectra are also different compared to those from pure and Cr-diffused sample. We can observe the presence of three bands characteristics on pure GaSb (Band gap at 798 meV, A band at 777 meV and the tail-states band at 815 meV) and, in addition to these three bands we also observe a fourth band whose origin still remains unclear and which is related to the presence of Au. This new band is centred at 767 meV and the mechanism by which this band is formed could be the same to that in previously reported in Ru-doped GaSb samples [16].
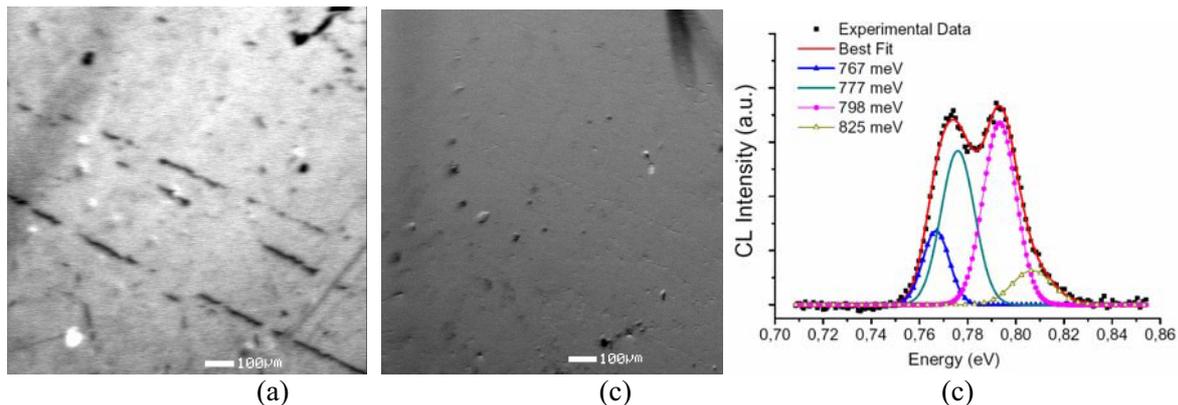

(a)   (c)   (c)

Figure 5. CL (a), SEM (b) images and CL spectra (c) from sputtered Au-diffused GaSb.

4. Concluding remarks

In conclusion, we have analysed the effect of Au and Cr diffused impurities on the structure and Cathodoluminescent response of GaSb surfaces patterned with nanodots by using low energy argon ion sputtering. The formation of dot hexagonal arrays at the nanometre scale was confirmed both by atomic force and ultrahigh resolution secondary electron microscopies both in pure GaSb and Au, Cr diffused GaSb samples. Although the thickness (12 nm for Au and about 21 for Cr) of diffused layers resulted to be smaller than the nanodot formation threshold (about 40 nm), the impurities proved to have the remarkable following effects in the formation of cracks which has been remarkably observed in the Au diffused samples. From the compositional point of view Ga enrichment at the surface has been found more pronounced in the case of diffused samples. The cathodoluminescent response of the Au diffused sample shows a new band close to 767 meV not observed in the pure and Cr-diffused sample.

References

[1] Tseng A A, Chen K, Chen C D, Ma K J 2003 IEEE *Trans. Electron. Pack. Man.* 26 141.
[2] Facsko S, Bobek T, Kurz H, Dekorsy T, Kyrsta S, Cremer R 2002 *Appl. Phys. Lett.* 80 130.
[3] Shchukin V A, Bimberg D 1999 *Rev. Mod. Phys.* 71 1125.
[4] Facsko S, Kurz H, and Dekorsy T 2001 *Phys. Rev. B* 63 165329
[5] Facsko S, Dekorsy T, Koerdt C, Trappe C, Kurz H, Vogt A, Hartnagel H L 1999 *Science* 285 1551.
[6] Facsko S, Bobek T, Dekorsy T, Kurz H 2001 *Phys. Stat. Sol.* (b) 224 537.
[7] Valbusa V, Boragno C, Buatier de Mongeot F 2002 *J. Phys.; Cond Mat.* 14 8153.
[8] Carter G 2001 *J. Phys. D; Appl. Phys.* 34 R1.
[9] Panin G N, Dutta P S, Piqueras J, Dieguez E 1995 *Appl. Phys. Lett.* 67 3584.

[10] Dutta P S, Bhat H L, Kumar V 1997 *J. Appl. Phys* 81 5821.

[11] Willoughby A F 1978 *Rep. Prog. Phys.* 4 1665.

[12] Frost F, Schindler A, Bigl F 2000 *Phys. Rev. Lett.* 85 4116.

[13] Bradley R M, Harper J M E 1988 *J. Vac. Sci. Technol. A* 6 2390.

[14] Makeev M A and Barabasi A L 1997 *Appl. Phys. Lett.* 71 2800.

[15] Plaza J L, Ruiz C M, Capote B, and Diéguez E 2006 *Surf. Coat Tech.* in press

[16] Hidalgo P, Méndez B, Dutta P S, Piqueras J and Diéguez E 1998 *Phys. Rev. B* 57 6479.