

# Self-sustained etch masking: a new concept to initiate the formation of nanopatterns during ion erosion

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(Dated: July 3, 2009)

## Abstract

Materials allowing for rapid and reliable formation of nanopatterned surfaces is an important issue in many areas of science today. Self-organized pattern formation induced by ion erosion is a promising bottom-up approach. In the case of the III-V semiconductors, this method can lead to several remarkable structure types even if the formation mechanism has yet to be found. Through high resolution chemical scanning transmission electron imaging and x-ray photo emission, we show that the capacity of III-V semiconductors to pattern under ion erosion is linked to the phase diagram of these materials. We suggest an original scenario to explain the specific behavior of III-V semiconductors, where one species segregates and acts as a continuously resupplied etching shield. This new concept is at variance with the standard Bradley Harper model and opens new perspectives for bottom up patterning of compound materials.

Control of the growth and self-organization of nanostructures is a major issue in science today. Especially the growth of low-dimensional high aspect ratio structures has attracted a lot of attention due to the potential applications in electronics, nanophotonics and life science [1–4]. Significant efforts are put into the investigation of bottom-up approaches to handle the synthesis and local arrangement of nanostructures. However, a generic concept for bottom-up patterning allowing to freely choose a broad range of morphologies and materials has yet to be found. A very promising technique is based on the surface instability which can induce spontaneous nanopatterning simply by the exposure to a unfocused ion beam. In principle, the method of maskless ion patterning can treat large areas and is easily integrated into most mainstream thin film processing technologies but is hampered by a limited choice of materials and morphologies.

The first reports of ion induced nanopatterning deal with the creation of well-ordered low-amplitude ripple patterns [5]. Bradley and Harper (BH) have established that the pattern generation process is a general feature induced by the dependence of the sputtering yield on the local curvature [6] which is predicted by Sigmund’s classical sputtering theory for off-normal sputtering [7, 8]. The BH model has successfully been compared with experimental data on ripples [9, 10]. In addition, dot patterns can be obtained on monoatomic materials like Si and Ge. This can be achieved using an isotropic ion impact either by abrasion normal to the surface or by a combination of oblique ion incidence and sample rotation [11, 12]. In most cases a high ion fluence and heavy ions are mandatory. The BH type of patterns has been subject to considerable fundamental research and recently non-linear extension of the BH model successfully predicted features of dot patterns like growth saturation or hexagonal ordering [13, 14]. Nevertheless, the method has come short of applications due to the low amplitude and limited flexibility in the choice of period.

To extend the range of materials and achieve deeper structures through maskless ion patterning, several groups have proposed techniques to modify the BH mechanism by an external perturbation. In practice this is done by adding an external pollutant. Several methods to introduce the pollutant have been suggested ranging from the use of an external deposition source [15] to simultaneous co-sputtering and redeposition of the pollutant [16]. The idea that pollutants can induce pattern and especially cone formation goes back to the eighties where Rossnagle *et al.* [17] attributed the occurrence of micron sized cones on sputtered metal targets to impurities from the surroundings. Currently, many teams are

investigating how to improve these methods as they often lead to sparse and inhomogeneous patterns over a limited area.

The discovery of the formation of dense cone patterns on III-V semiconductors [18] has spurred a renewed interest for sputter-induced patterns. Surprisingly, at normal-incidence and low acceleration energies, high aspect ratio structures readily form, opening for fast and low cost formation of functional surfaces [19]. On the III-V semiconductors the pattern formation is remarkable for the rapid formation rate, the low saturation leading to high aspect ratio structures [19, 20], and the occurrence of dense patterns over large surface areas. Moreover, the growth rate is enhanced by increasing temperature [20] - opposite to the behaviour encountered on other systems [21]. In addition, off-normal sputtering leads to tilted structures [19] instead of ripples. None of these features can be accounted for by the BH model or pollutant mechanism. Clearly, there is a lack of understanding of the distinct capacity of spontaneous ion-induced pattern formation on III-V semiconductors.

There is scant knowledge on the microscopic behavior of compound materials under ion sputtering and its impact on the pattern formation during the sputtering process. Shenoy *et al.* [22] did a theoretical investigation of the sputtering of alloys based on the BH model. They found no essential difference from the behavior of monoatomic species, except a tendency to composition modulation coupled with the ripple morphology. On the III-V semiconductors, other authors have speculated that either redeposition [23] or change of surface composition [20] may be responsible for the cone formation. Some authors have proposed an external seeding mechanism, due to initial defects or redeposition [24].

In the following paper, we investigate one of the III-V semiconductors, GaSb. Through analytical scanning transmission electron microscopy (STEM) and X-ray photo emission spectroscopy (XPS), we present a detailed study of the link between morphology and composition of the surface. It allows us to propose a clear and versatile mechanism for the pattern formation, based on phase separation instead of the BH instability. Segregation from the bulk of the material initiates the patterning process with the unique advantage over pollutants that it maintains a robust shielding effect all through the abrasion process, thereby sustaining the formation of dense high aspect ratio patterns. These findings open intriguing perspectives for the design of new materials for self-organized patterning by ion sputtering.

Nanopatterned samples were prepared in a UHV chamber with base pressure of  $10^{-9}$

mbar using commercially available GaSb(100) wafers. The sputter gas was 500 eV Ar<sup>+</sup> with a flux of 0.032 mA/s cm<sup>2</sup>. The samples were exposed to the ion beam for times up to 600 s. The angle of incidence was either normal to the sample surface, or with an oblique angle of 60° from the sample normal. The temperature of the samples was around 30°C.

The structure of the obtained pillars was scrutinized in detail. Transmission Electron Microscopy (TEM) specimens were prepared using simple mechanical cleavage and re-dispersion on a TEM carbon grid. High resolution imaging was done in TOPCON002B at 200KeV. The bright field transmission electron microscopy (BFTEM) images evidence very long structures with a spherical cap (figure 1a). The structures are covered by an amorphous layer which can be ascribed to damage by the ion beam [18]. The internal structure of the sample appears as polycrystalline even though the original substrate was a single crystal (figure 1a Insert). The structural modification of the material extended beyond the amorphous damage layer where the ion/substrate interaction is normally considered to occur. Other authors have reported that the crystalline order of the substrate is maintained through the nanostructure [18, 25]. However, these observations have been carried out on structures a few tens of nanometers deep and using a different preparation technique. Clearly, patterns obtained by oblique angle sputtering consist of inclined pillars with the tip pointing toward the incident ion beam (figure 1b). Such morphologies are in blatant contradiction with previously suggested BH models where oblique ion incidence leads to ripple formation as reported in [24].

Nanoscale chemical mapping was performed by a combination of Electron Energy Loss Spectroscopy (EELS) and Scanning TEM (STEM) High Annular Dark Field (HADF) imaging in a dedicated instrument (cold FEG STEM VG HB501). Spectrum imaging was performed by scanning the specimen with a probe of 0.7 nm in diameter and acquiring a spectrum in each point, as described in more details in [26]. Spectrum images were obtained with the O K edge, Sb M4,5 and Ga L2,3. Figures 1c and d show the morphology of the pillars along with a chemical map of the tip of a pillar, with different colors denoting the three elements Ga, O and Sb. The superficial layer is clearly oxidized. This is not very surprising as the samples were removed from the vacuum chamber to prepare the TEM specimen. Furthermore, it is in accordance with the fact that GaSb is easily oxidized by the creation of Ga<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>5</sub> [27] and the presence of an amorphous damage layer is making this reaction more favorable. The most striking information though, is that the spherical cap of the nanopillars is significantly enriched in Ga with respect to the remaining

structure (figures 1d). Clearly, the tip contains a large amount of Gallium meaning that a significant segregation has occurred. The fact that the chemical composition is different in the tip region can explain why we observe a polycrystalline structure. GaSb is stable as a crystal only in the stoichiometric form [28] and Sb has a slightly higher sputtering yield than Ga [29]. This will force a composition deviation at the beginning of the sputtering process inducing segregation into Ga and GaSb rich domains; the polycrystalline nature of the tip could be a direct consequence of this phenomenon.

In accordance with the model of Shenoy *et al.* [22] for sputtered alloys, we present experimental proof that spatial composition modulation can occur within the patterns formed by ion sputtering. However, these remarkable findings give rise to an intriguing question: is the segregation a consequence of structure formation as suggested by Shenoy *et al.*, or the cause of the peculiar capacity of GaSb to form nanostructures? A more detailed physical chemical characterization of the behavior of the composition during ion sputtering and especially at the onset of patterning is called for. Unfortunately, STEM imaging cannot be applied at the beginning of the structure formation process and the combination of a complex morphology and chemical pattern is a major challenge for all chemical surface spectroscopies. None of the currently available tools allows spatial resolution at the scale relevant for the characteristic length scale under consideration here. Inspired by the STEM analysis, which revealed the presence of a thin oxide layer surrounding the pillars, we decided to use X-ray core level photoemission (XPS) on structures where the surface was intentionally oxidized after abrasion. XPS was carried out using a XRC1000 double head X-ray source and a Phoibos 100 hemispherical analyser both from SPECS. The data collection was done using the Al line at  $28^\circ$  incidence and  $24.5^\circ$  detection angle from the sample normal. The binding energy of the  $\text{Sb}3d_{3/2}$  line is highly dependent on the local environment and an important shift of 3eV is observed depending on whether Sb is surrounded by Ga or Oxygen [27]. This allows for an unambiguous identification of Sb atoms in an oxidized state at the surface, and Sb occurring in subsurface GaSb. Figure 2 shows the evolution of the O1s,  $\text{Sb}3d_{5/2}$ ,  $\text{Sb}3d_{3/2}$ ,  $\text{Ga}2p_{3/2}$  and C1s line for three samples at different sputtering exposure. Before ion impact the presence of a double peak in the  $\text{Sb}3d_{3/2}$  line shows an important native oxidation layer on the surface as well as Sb linked to GaSb in the subsurface layer. The existence of an oxidized layer on GaSb crystals has often been under consideration because of its impact on surface preparation for epitaxial growth [27]. Upon ion exposure the surface oxide linked

to Sb disappears leaving only the line linked to the presence of Sb in the GaSb compound: The O1s line reveals a small component of oxygen at 528.5eV in the surface which can be attributed to Ga-O. This can further be confirmed by the presence of the Ga2p<sub>3/2</sub> peak which occurs at 1119 eV, and the very low quantity of carbonaceous species, as seen by the C1s line, excluding that the detection of oxygen is due to CO containing contaminants. Clearly, the absence of the Sb-O peak indicates that no Sb is present in the surface layer. Interestingly, the Sb surface component reappears upon further ion exposure, as revealed by the presence of an oxidized Sb in the Sb3d<sub>3/2</sub> line for the sample sputtered for 300 s. We note that no additional external materials were detected, which rules out deposition of extraneous species from the grid of the ion gun or the chamber. This indicates that external seeding is not at the origin of the pattern.

To follow the dynamics of both segregation and morphology, the evolution of the atomic content of Sb as a function of sputtering time and the mean height of the surface morphology were investigated (figure 3). The AFM image of the surfaces and the deduced spatial concentration and morphology are depicted in figure 4. Before sputtering, the surface is rather flat and presents a thick oxidized layer (figure 3 and 4 region 1). As the Sb content in the surface decreases (figure 3) the AFM imaging reveals a surface pattern resembling what can be observed during phase separation processes in thin films [30] and the mean roughness remains small (figure 4 region 2). The depletion of Sb provokes a segregation of Ga which can be understood from the phase diagram of GaSb where no intermediate compositions are stable [28]. This is a very characteristic feature of many III-V semiconductors. Shortly after, Sb reappears at the surface and the AFM images indicate a fast height increase of the structures, i.e. initiation of the pillar growth (figure 3 and 4 region 3). We can interpret this as a consequence of the presence of a nearly pure Gallium layer at the surface, which has formed a pattern driven by the segregation process. Recently, several authors have reported that the defect mediated diffusion of Ga in GaSb is very fast [31]. Moreover, Gallium has a fairly high surface tension [32] with respect to the one of GaSb, which can explain the rapid kinetics and dewetting nature of the segregation process. Coalescence of the droplets is prevented by the eroding action of the ion beam, which explains their homogenous size distribution. These Gallium caps are acting as a sputtering shield and induce the formation of the pillars. Clearly, the chemical inhomogeneity precedes and initiates the amplification of the morphology. This shielding mechanism can explain the specific pattern formation on

most III-V semiconductors as they present similar phase diagram. The rapid creation of deep structures can be attributed to segregation induced shielding instead of surface instability described in the BH model. This process is actually close to the way patterns are normally transferred through standard lithography and etching [33]. However, the major difference is that the Gallium droplets are resupplied through continuous segregation from the material during sputtering, maintaining the shield throughout the etching process. This accounts for the low saturation rate leading to the very deep and dense patterns observed on III-V semiconductors.

The proposed mechanism is summarized in figure 5. The difference of yield between Ga and Sb creates a Ga rich surface region. Due to the phase diagram, Gallium segregates and makes droplets which act as a sputtering mask. As the cones grow, the mask is continuously resupplied by the segregation process. This is an original mechanism which does not involve the seeding of an exterior material because the material itself is at the origin of the mask and even maintains it. The segregation process does not depend on the incidence of the ion beam and this can explain the formation of tilted pillars, which appears to be unique to these materials. The suggested explanation is independent of crystalline orientation and in agreement with the fact that the patterning capacity of GaSb seems to be universal, whatever the structure of the material and the incidence of the ion-beam.

Through an investigation of GaSb we have given clear evidence that the nano patterning of the compound III-V semiconductors can be attributed to the specific phase diagram of these materials and not to the classical Bradley Harper mechanism normally evoked. As a consequence, Ga tends to segregate at the surface while Sb is preferentially removed by the ion beam. This initiates the pattern formation process where Ga droplets act as a transfer mask, leading to a dense pattern of nanopillars. This new concept of bottom-up nanopatterning opens a new challenging perspective for designing self-structuring materials beyond the III-V semiconductors. An adequate choice of sputtering conditions linked to the phase diagram can allow many other composite materials to be patterned leading to new systems and properties.

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**Figure 1: Image and structural analysis of GaSb nanocones.**

**a**, BF TEM images of the pillars, insert: zoom on the top of a pillar. **b**, SEM cross section images of a surface sputtered with a incidence angle of 60°. **c**, STEM HADF images of the pillars. **d**, EELS spectrum imaging of a tip. Ga is represented in blue, Sb in red and O in green.

**Figure 2: XPS spectra for different exposure time.**

XPS spectra of a surface sputtered for 0, 30, and 300s. The different spectra are normalized by the gallium area and shifted vertically for clarity.

**Figure 3: Evolution of the concentration and morphology of the surface with sputtering time.**

*XPS estimation of the time evolution of the quantity of Sb linked to O (surface) or Ga (subsurface) divided by the quantity of Ga. The average height of the structures measured with AFM is also given. The surface morphology is separated into three regions (see figure 4).*

**Figure 4: AFM images of samples at different sputtering exposure and sketch of the deduced spatial composition and morphology.**

*Region 1, the surface is flat with a native oxide layer. Region 2, the surface is rich in Ga. The segregated domains develop a pattern but well-formed dots are not distinguished. Region 3, dots with a gallium cap are formed and Sb is present at the side walls.*

**Figure 5: Sketch of the proposed patterning mechanism.**

*Open arrow: erosion by the ion beam, with the length of the arrow proportional to the abrasion speed. Dark arrow: surface diffusion. The gallium shielding cap is resupplied via diffusion in the Ga rich surface region initiated by the difference in the sputtering yields of Ga and Sb.*



